CLETHODIM (187)

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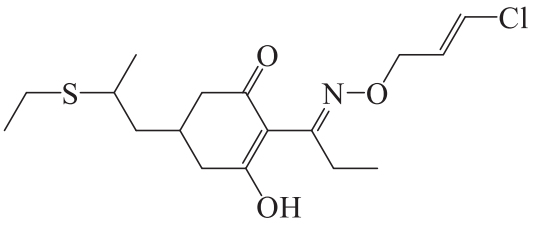
EXPLANATION

Clethodim is a fatty acid synthesis inhibitor herbicide, used for post-emergence control of annual and perennial grasses in a wide range of broad-leaved crops, including field crops (such as soya beans, cotton, flax, sunflowers, alfalfa, peanuts, oilseed rape, sugar beet, tobacco, and potatoes), vegetable crops, trees and vines. It was evaluated by the JMPR in 1994 (T, R), 1997 (R), 1999 (R) and 2002 (R). It was scheduled at the Fiftieth Session of the CCPR (2018) for periodic evaluation by the 2019 JMPR.

The Meeting received information on physical and chemical properties, animal and plant metabolism, rotational crop studies, environmental fate, analytical methods, GAP information, storage stability, processing and residue trial data on apple, pear, cherry, peach, plum, blueberry, cranberry, strawberry, cabbage, broccoli, cucumber, lettuce, pea, bean, carrot, artichoke, rape and hops.

IDENTITY

Common name	Clethodim
Chemical name	
IUPAC:	(5*RS*)-2-{(1*EZ*)-1-[(2*E*)-3-chloroallyloxyimino]propyl}-5-[(2*RS*)-2-(ethylthio)propyl]-3-hydroxycyclohex-2-en-1-one
CAS:	2-[1-[[[(2*E*)-3-chloro-2-propen-1-yl]oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one
CAS Registry No:	99129-21-2
CIPAC No:	508
Synonyms:	RE 45601
Structural formula:	
Molecular formula:	$C_{17}H_{26}ClNO_3S$
Molecular weight:	359.92

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Table 1 Physical and chemical properties of the pure active ingredient

Property	Test material purity	Results	Reference
Appearance (colour, physical state, odour)	98.3%	Green/Yellow / Liquid / Slightly sweet	Lezberg, 2003 03J0007b
Vapour pressure	98.3%	1.35×10^{-8} Pa at 25 °C The Grain estimation method	Lezberg, 2003 03J0007b
			Mak, 2003 PML 2003-C148
	93%	2.1×10^{-6} Pa at 20 °C	Franke, 2006 20050645.01

Property	Test material purity	Results	Reference
		4.9×10^{-6} Pa at 25 °C Effusion method: vapour pressure balance	
Melting point	98.3%	-80 °C (freezing temperature) Differential Scanning Calorimetry (DSC) method	Lezberg, 2003 03J0007b
			Mak, 2003 PML 2003-C148
Boiling point	93%	Approximately 110 °C (Decomposition temperature) DSC method	Franke, 2006 20050645.01
	98.5%	133 °C (Decomposition temperature) DSC method	Butler, 2009 2699/0001
Octanol/water partition coefficient	99.0%	log Pow = >4.08 at pH 5 4.14 at pH 7 4.22 at pH 9 Shake Flask method	Ashworth *et al.*, 1988 8828545
Solubility in water	99.0%	0.0181 g/L at pH 3.7 0.0718 g/L at pH 4.9 0.479 g/L at pH 5.8 1.74 g/L at 6.5 5.40 g/L at 7.0 12.4 g/L at 7.6 14.8 g/L at 7.7 HPLC method (25 °C)	Ashworth *et al.*, 1988 8828545
	98.3%	0.0530 g/L at pH 4 5.45 g/L at pH 7 58.9 g/L at pH 9 30.0 g/L at pH 10 Shake Flask method (20 °C)	Baldwin, 2003 03J0007c Weissenfeld, 2006 A46034
Solubility in organic solvents	Unspecified	950 g/L in acetone 931 g/L in hexane 934 g/L in ethyl acetate 907 g/L in dimethylformamide Shake Flask method (25 °C)	Ashworth *et al.*, 1988 8828545
	93%	244 g/L in methanol 246 g/L in 1,2-dichloroethane 247 g/L in xylene HPLC method (25 °C)	Baldwin, 2003 03J0006c
Relative density	98.3%	1.16 g/mL at 25 °C	Lezberg, 2003 03J0007b
Hydrolysis	[Propyl-1-^{14}C]-clethodim Specific activity: 56 mCi/mM, radio-purity: 98%	DT_{50} = 28 days at pH 5 DT_{50} = 300 days at pH 7 DT_{50} = 310 days at pH 9 at 25 °C	Pack, 1988 MEF-0013/8703899
	[Allyl-2-^{14}C]-clethodim Specific activity: 40.3 mCi/mM, radio-purity: 98%	DT_{50} = 54 days at pH 5 DT_{50} = 499 days at pH 7 at 25 °C	
Photolysis	[Ring-4,6-^{14}C]-clethodim Specific activity: 56 mCi/mM, radio-purity: > 97.9%	Degradation half-lives in irradiated solutions of 1.5, 6.4 and 9.3 days for pH 5, 7 and 9, respectively; corresponding effective photolysis half-lives of 1.7, 6.8 and 9.6 days. Enhanced rate of photolysis in sensitized irradiated solutions (1% acetone), with	Chen, 1988 MEF-0024

Property	Test material purity	Results	Reference
		effective photolysis half-lives of 0.94, 1.2 and 0.52 days.	
	[Allyl-2-^{14}C]-clethodim Specific activity: 40.3 mCi/mM, radiopurity: > 97.9%	Degradation half-lives in irradiated solutions 1.4, 4.1 and 5.4 days for pH 5, 7 and 9, respectively; corresponding effective photolysis half-lives of 1.5, 4.1 and 6.0 days. Enhanced rate of photolysis in sensitized irradiated solutions (1% acetone), with effective photolysis half-lives of 0.20, 0.61 and 0.33 days.	Chen, 1989 MEF-0025
Dissociation constant	98.5%	pKa = 4.47 at 20 °C Titration method	Ashworth *et al.*, 1988 8828545

Technical material

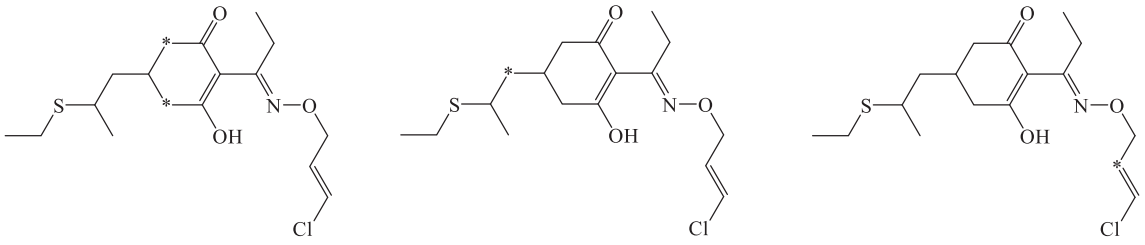
Table 2 Physical and chemical properties of the technical material

Property	Results	Reference
Appearance (color, physical state, odor)	Amber / Viscous liquid / No c haracteristic odor	Ashworth *et al.*, 1988 8828545
Density	1.14 g/cm^3 at 20 °C	
Melting range	Liquid at ambient temperature	
Stability	DT_{50} = 8.4 months at 20 °C DT_{50} = 1.2 months at 38 °C DT_{50} = 0.7 months at 50 °C	
Minimum Purity	930 g/kg	FAO Specification 2017

Formulations: Emulsifiable concentrate (EC): 116 g/L, 120 g/L, 240 g/L and 360 g/L

METABOLISM AND ENVIRONMENTAL FATE

The metabolism of clethodim has been investigated in plants and animals. The fate and behaviour of clethodim in plants, animals and the environment was investigated using the [^{14}C] labelled test materials shown in Figure 1.

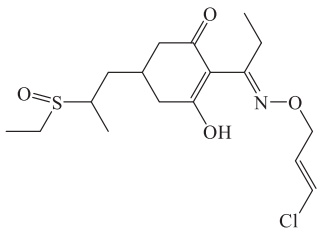
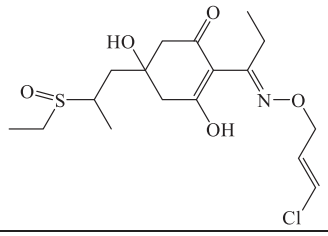
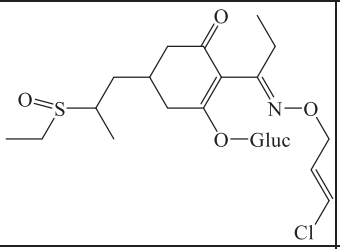
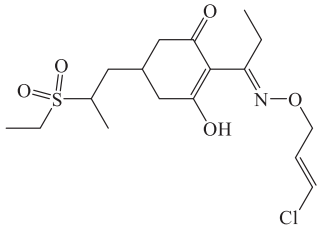
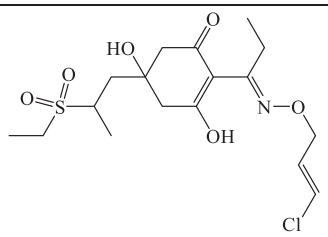
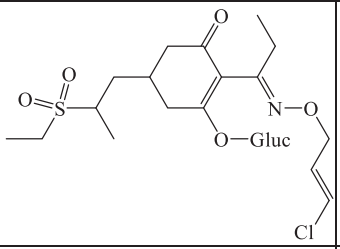
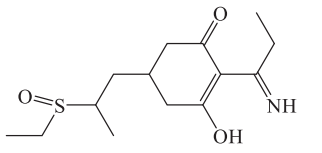


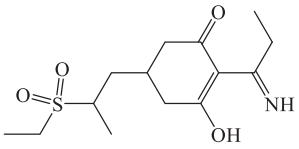
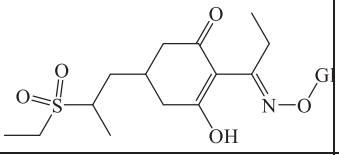
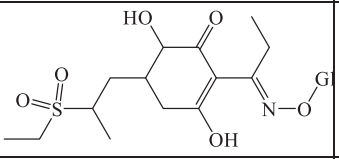
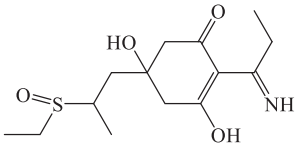
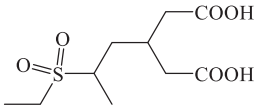
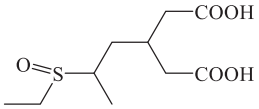
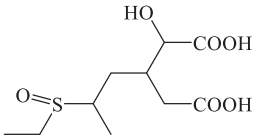
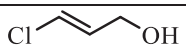
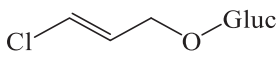
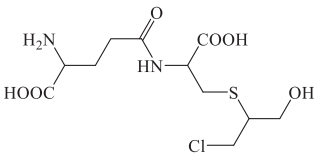
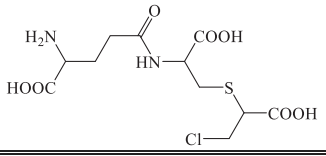
[Ring-4,6-^{14}C]-clethodim [Propyl-1-^{14}C]-clethodim [Allyl-2-^{14}C]-clethodim

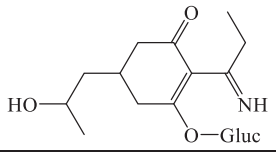
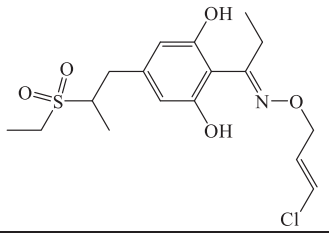
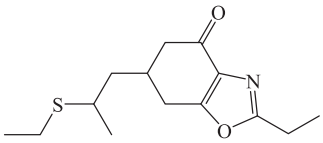
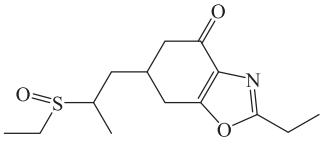
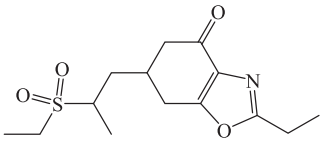
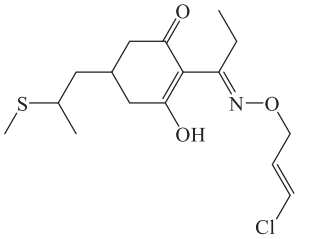
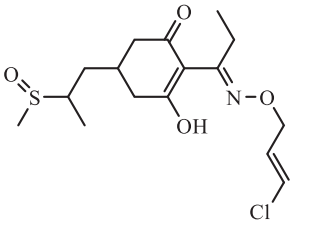
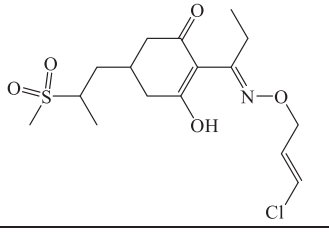
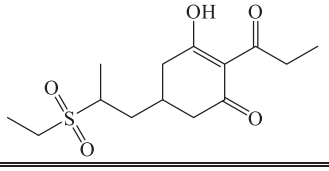
Figure 1 [^{14}C]-Labelled test materials used in plants, animals metabolism studies, and the environmental fate studies

The chemical structures of the major degradation compounds from the metabolism of clethodim are provided below.

Table 3 Chemical structures of the major degradation compounds from the metabolism of clethodim

Compound name		Structure	Found in metabolism studies
Clethodim sulfoxide	2-((E)-1-((((E)-3-chloroallyl)oxy) imino)propyl)-5-(2-(ethylsulfinyl) propyl)-3-hydroxycyclohex-2-en-1-one MW: 375.9		Plants Rat Livestock Soil
5-hydroxy sulfoxide	2-((E)-1-((((E)-3-chloroallyl)oxy) imino)propyl)-5-(2-(ethylsulfinyl) propyl)-3,5-dihydroxycyclohex-2- en-1-one MW: 391.9		Plants Rat
Clethodim sulfoxide glucoside	Clethodim sulfoxide glucoside MW: 538.1		Plants
Clethodim sulfone	2-((E)-1-((((E)-3-chloroallyl)oxy) imino)propyl)-5-(2-(ethylsulfonyl) propyl)-3-hydroxycyclohex-2-en-1-one MW: 391.9		Plants Rat Livestock Soil
5-hydroxy sulfone	2-((E)-1-((((E)-3-chloroallyl)oxy) imino)propyl)-5-(2-(ethylsulfonyl) propyl)-3,5-dihydroxycyclohex-2- en-1-one MW: 407.9		Plants Rat
Clethodim sulfone glucoside	Clethodim sulfone glucoside MW: 554.1		Plants
Clethodim imine sulfoxide M21R	5-(2-(ethylsulfinyl)propyl)-3- hydroxy-2-(1-iminopropyl) cyclohex-2-en-1-one MW: 285.4		Plants Rat Livestock

Compound name		Structure	Found in metabolism studies
Clethodim imine sulfone M23R M24R	5-(2-(ethylsulfonyl)propyl)-3- hydroxy-2-(1-iminopropyl) cyclohex-2-en-1-one MW: 301.4		Plants Livestock
M20R	Clethodim imine sulfone glucoside MW: 479.5		Plants (spinach)
M20R	Hydroxy clethodim imine sulfone glucoside MW: 495.5		Plants (spinach)
5-Hydroxy imine sulfoxide M22R	5-(2-(ethylsulfinyl)propyl)-3,5- dihydroxy-2-(1-iminopropyl) cyclohex-2-en-1-one MW: 301.4		Plants (carrot)
M18R	3-[(2-ethylsulfonyl) propyl]- pentanedioic acid MW: 266.3		Plants
M17R	3-[(2-ethylsulfinyl) propyl]- pentanedioic acid MW: 250.3		Plants
M15R	Hydroxy 3-[(2-ethylsulfinyl) propyl]-pentanedioic acid MW: 266.3		Plants
	3-Chloroallyl alcohol MW: 92.5		Water
M15A	3-Chloroallyl alcohol glucoside MW: 254.7		Plants
M19A	2-(Glutamyl-cysteinyl)-3- chloropropanol MW: 342.8		Plants (spinach)
M22A	2-(glutamyl-cysteinyl)-3- chloroacrylic acid MW: 356.8		Plants (carrot)

Compound name		Structure	Found in metabolism studies
M19R	3-hydroxy-5-(2-hydroxypropyl)-2- (1-iminopropyl)cyclohex-2-en-1- one glucose conjugate MW: 387.4		Plants (carrot)
Aromatic sulfone	(*E*)-1-(4-(2-(ethylsulfonyl)propyl)- 2,6-dihydroxyphenyl)propan-1-one O-((*E*)-3-chloroallyl) oxime MW: 389.9		Plants Rat
Clethodim oxazole	2-ethyl-6-(2-(ethylthio)propyl)-6,7-dihydrobenzo[*d*]oxazol-4(*5H*)-one MW: 267.4		Soil Water High temperature hydrolysis
Clethodim oxazole sulfoxide	2-ethyl-6-(2-(ethylsulfinyl)propyl)-6,7-dihydrobenzo[*d*]oxazol-4(*5H*)- one MW: 283.4		Rat Soil High temperature hydrolysis
Clethodim oxazole sulfone	2-ethyl-6-(2-(ethylsulfonyl)propyl)-6,7-dihydrobenzo[*d*]oxazol-4(*5H*)- one MW: 299.4		Rat Soil High temperature hydrolysis
S-methyl	2-((*E*)-1-((((*E*)-3-chloroallyl)oxy) imino)propyl)-3-hydroxy-5-(2- (methylthio)propyl)cyclohex-2-en-1-one MW: 345.9		Livestock (goat)
S-methyl sulfoxide	2-((*E*)-1-((((*E*)-3-chloroallyl)oxy) imino)propyl)-3-hydroxy-5-(2- (methylsulfinyl)propyl)cyclohex-2-en-1-one MW: 361.9		Livestock (goat)
S-methyl sulfone	2-((*E*)-1-((((*E*)-3-chloroallyl)oxy) imino)propyl)-3-hydroxy-5-(2- (methylsulfonyl)propyl)cyclohex-2-en-1-one MW: 377.9		Rat
Clethodim trione sulfoxide	5-[2-(ethylsulfonyl)propyl]-3- hydroxy-2-(1-oxopropyl)-2-cyclohexen-1-one MW: 302.4		Rat High temperature hydrolysis

PLANT METABOLISM

Plant metabolism studies were performed on spinach, soya bean, carrot and cotton with [Ring-4,6-^{14}C] and [Allyl-2-^{14}C]-clethodim. Metabolites were identified using multiple chromatographic systems and authentic standards.

Spinach

A Nature of the Residue Study in spinach (*Spinacea oleracea)* was performed with [Ring-4,6-^{14}C] - clethodim and [Allyl-2-^{14}C]-clethodim (Dohn, 2010:1809W-1). Spinach plants were grown outdoors in test plots that consisted of wooden boxes (each with an area of one square meter) located above ground level and filled with a sandy loam soil to a depth of 15 cm. [^{14}C]-clethodim was formulated as a 240 g/L suspension concentrate in water and applied once by spraying onto the leaves of the spinach plants 28 days before harvest of mature spinach. The plants were treated at a target rate of 0.50 kg ai/ha, twice the maximum recommended field rate of 0.25 kg ai/ha.

Spinach foliage was harvested 14 (immature) and 28 days (mature) after test substance application. The spinach leaves were frozen after harvest, and maintained in the frozen state throughout the study. Intact spinach samples were homogenized to a fine powder and the total radioactive residues (TRR) in the plant tissues were measured by combustion analysis.

The radioactive residues in all samples were characterized by extraction with acetonitrile:water (1:1, v/v), acetonitrile and acetonitrile:0.2N HCl (1:1, v/v) followed by chromatographic techniques (reverse phase high performance liquid chromatography (HPLC), normal phase thin layer chromatography (TLC), and high performance liquid chromatography – mass spectrometry (HPLC-MS)). Unextracted residues were quantified by combustion analysis of the PES.

Additional extractions were performed on all treated matrices. The remaining portions of each PES sample were extracted with acetonitrile/0.2N NH_4OH (1:1, v/v) on a wrist action shaker at ambient temperature for 45 minutes, 1N HCl at 87 °C for 4 hours and 24% KOH at ambient temperature on a wrist action shaker, overnight and the amounts of radioactivity in the solvent extracts and the PES were measured.

The TRRs in the treated foliage measured by the extraction procedure were 3.35-6.85 mg eq/kg. The residues is immature leaves were greater than residues in mature crops. The percent TRR characterized and/or identified in foliage ranged from 67.3-89.0%.

Clethodim was not detected in either immature or mature foliage samples. Clethodim sulfoxide and clethodim sulfone were present in both immature and mature foliage (clethodim sulfone not detected in the mature leaf sample treated with the ring label). The sub-totals concentrations of clethodim sulfoxide and clethodim sulfone were 0.210-0.381 mg eq/kg in immature foliage, and 0.119-0.172 mg eq/kg in mature foliage. These subtotals represented 3.1-7.4% TRR.

Ring-opened metabolites accounted for a significant portion of the TRR in the [Ring-4,6-^{14}C]-clethodim treated foliage. These metabolites were M15R, M17R and M18R. These compounds were collectively present at 3.82 mg eq/kg (55.8% TRR) in the immature leaves and 2.05 mg eq/kg (61.2% TRR) in the mature leaves. Other metabolites that had lost the allyl portion of the molecule included clethodim imine sulfoxide (M21) and the corresponding sulfone (M23R). Collectively, these metabolites were present at 1.41 mg eq/kg (20.6% TRR) in immature leaves and 0.251 mg eq/kg (7.5% TRR) in the mature leaves.

Two unique metabolites from [Allyl-2-^{14}C] were detected in foliage. One was M15A (chloroallyl alcohol glucoside: 1.09 mg eq/kg, 21.1% TRR in immature foliage and 0.785 mg eq/kg 22.7% TRR in mature leaves). In addition, M19A (2-(glutamyl-cysteinyl)-3-chloropropanol) was present at 0.352 mg eq/kg and 0.327 mg eq/kg in immature and mature leaves, respectively.

Table 4 Summary of radioactive residues in spinach following applications of ^{14}C-clethodim

Components		Immature (14 DAT)				Mature (28 DAT)			
		[Ring-4,6-^{14}C]		[Allyl-2-^{14}C]		[Ring-4,6-^{14}C]		[Allyl-2-^{14}C]	
		mg/kg eq	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
Extract with Acetonitrile/water[a]		6.37	92.9	4.17	80.9	3.08	91.9	2.83	81.8
	Clethodim	*ND*	-	*ND*	-	*ND*	-	*ND*	-
	Clethodim sulfoxide	*0.191*	*2.8*	*0.350*	*6.8*	*0.119*	*3.6*	*0.162*	*4.7*
	Clethodim sulfone	*0.019*	*0.3*	*0.031*	*0.6*	*ND*	-	*0.010*	*0.3*
M21R	*Clethodim imine sulfoxide*	*0.979*	*14.3*	-	-	*ND*	-	-	-
M23R	*Clethodim imine sulfone*	*0.430*	*6.3*	-	-	*0.251*	*7.5*	-	-
M15R	*Hydroxy 3-[(2-ethylsulfinyl) propyl] pentanedioic acid*	*0.875*	*12.8*	-	-	*0.476*	*14.2*	-	-
M15A	*3-chloroallyl alcohol glucoside*	-	-	*1.09*	*21.2*	-	-	*0.785*	*22.7*
M17R	*3-[(2-ethylsulfinyl) propyl] pentanedioic acid*	*2.28*	*33.3*	-	-	*1.16*	*34.6*	-	-
M18R	*3-[(2-ethylsulfonyl) propyl] pentanedioic acid*	*0.663*	*9.7*	-	-	*0.418*	*12.5*	-	-
M19A	*2-(glutamyl-cysteinyl)-3-chloropropanol*	-	-	*0.352*	*6.8*	-	-	*0.327*	*9.5*
M20R	*Glucoside of imine sulfone and Hydroxy imine sulfone*	*ND*	-	-	-	*0.308*	*9.2*	-	-
M3R		*0.04*	*0.6*	-	-	*0.055*	*1.6*	-	-
M3/4A		-	-	*0.903*	*17.5*	-	-	*0.726*	*21.0*
M10R		*0.089*	*1.3*	-	-	*0.017*	*0.5*	-	-
M10A		-	-	*0.098*	*1.9*	-	-	*ND*	-
M17A		-	-	*ND*	-	-	-	*0.066*	*1.9*
M18A		-	-	*0.114*	*2.2*	-	-	*ND*	-
M20A		-	-	*0.112*	*2.2*	-	-	*ND*	-
M25R		*0.212*	*3.1*	-	-	*0.087*	*2.7*	-	-
M25A		-	-	*0.196*	*3.8*	-	-	*0.099*	*2.9*
M26R		*0.108*	*1.6*	-	-	*0.053*	*1.6*	-	-
M26A		-	-	*ND*	-	-	-	*0.103*	*3.0*
M27R		*0.096*	*1.4*	-	-	*0.045*	*1.3*	-	-
M27A		-	-	*0.203*	*3.9*	-	-	*ND*	-
M32R		*0.093*	*1.4*	-	-	*0.024*	*0.7*	-	-
M32A		-	-	*0.064*	*1.2*	-	-	*0.046*	*1.3*
	Others	*0.290*	*4.0*	*0.657*	*12.8*	*0.067*	*1.9*	*0.504*	*14.5*
Acetonitrile/NH_4OH		0.086	1.3	0.101	2.0	0.061	1.8	0.061	1.8
1N HCl reflex		0.216	3.2	0.473	9.2	0.087	2.6	0.307	8.9
24% KOH difestion		0.146	2.1	0.306	5.9	0.110	3.3	0.176	5.1
Unextracted		0.034	0.5	0.108	2.1	0.014	0.4	0.074	2.1
TRR		6.85	100	5.16	100	3.35	100	3.46	100

[a] Extraction with acetonitrile:water (1:1, v/v), acetonitrile and acetonitrile:0.2N HCl (1:1,v/v)

ND – not detected; DAT – days after treatment; TRR – total radioactive residues

The chloroallyl moiety of clethodim was also metabolized to a polar species (referred to as M3/4A) present at 17.5-21.0% TRR. The polar region seen in the HPLC chromatograms, representing M3/4A, was isolated by HPLC fraction collection. The isolated fractions were concentrated and reanalysed by a TLC system suitable for separation of polar materials. TLC analysis of the polar region for the immature spinach extract showed that it comprised multiple components, being integrated to show at least twelve regions. The M3/4A was determined to be multi-component with no individual component representing greater than 0.018 mg eq/kg (3.6% TRR).

Clethodim is extensively metabolized in spinach and does not accumulate in foliage. Ring-opened metabolites were a significant part of identified residues in mature leaves (>10% TRR): M15R (0.476 mg eq/kg, 14.2% TRR), M15A (0.785 mg eq/kg, 22.7% TRR), M17R (1.16 mg eq/kg, 34.6% TRR), M18R (0.418 mg eq/kg, 12.5% TRR).

Soya bean, carrot and cotton

Plant metabolism of [Ring-4,6-^{14}C]-clethodim and [Allyl-2-^{14}C]-clethodim was studied on soya bean, carrot and cotton plants. Plants were treated twice at a 14-day interval with 0.28 kg ai/ha as a post-emergence foliar spray and were harvested at maturity with a PHI of 20 to 70 days (Chen, 1988: MEF-0004, MEF-0005).

Sixteen soya bean plants (cv. Hakucho Early), sixteen carrot plants (cv. Long Imperator) and six cotton plants (Acala SJ-2) were treated with ^{14}C-clethodim. The first treatment was applied when soya bean plants were at the 6-8 leaf stage, carrot leaves were 10-15 cm long and cotton plants were at the 8-12 leaf stage. Plants were sprayed with ^{14}C-clethodim in methanol (approximately 1-10 mL for each plant depending on the size of the plant) using a hand sprayer in a closed chamber.

Plants were grown to maturity in sandy soil (free of pathogens) in 4.5 or 9 L pots in the greenhouse. The greenhouse temperature was regulated between 18 °C to 29 °C and watering was done two or three times daily. The crops were harvested at 30 (soya bean), 20 (carrot) and 70 (cotton) days after the last treatment (DAT). At harvest, plants were separated by hand into leaves, stems, roots, pods, seeds, fibre and shell samples. All samples were stored in the freezer (at -20 °C), processed and extracted within 2 weeks after harvest.

The total radioactive residues (TRR) in the samples were determined by combustion and liquid scintillation counting (LSC) analysis. All samples of harvested plants were homogenized with dry ice in a blender. Homogenized samples were extracted twice with acetone, twice with methanol, twice with methanol-water (1:1, v/v), and twice with acidic methanol (0.2 N HCl in methanol). Soya bean seeds and cotton seeds were extracted twice with hexane prior to the solvent extraction sequence described above. The extracts were analysed by TLC (acetone fraction and combined fractions containing methanol; quantification by LSC of spots scraped off the plate) and HPLC (acetone fraction only) for characterisation and identification (by co-chromatography with reference standards). Radioactivity in unextracted residues was determined by combustion/LSC.

Polar and/or conjugated metabolites were isolated by preparative TLC and treated with cellulase, ß-glucuronidase or a mixture of macerozyme R-10, driselase, cellulase R-10 and pectolyase Y-23 in 2 mL of 0.1 M acetate buffer pH 4.6 (25 °C for 4 h). Released aglycons were extracted with dichloromethane at pH 1, followed by HPLC and TLC analysis. Polar and/or conjugated metabolites were also hydrolysed in 1N HCl or 1N NaOH (100 °C for 1-2 h). Released aglycons were extracted with diethyl ether:ethanol (3:1; v/v) at pH 1, followed by TLC and HPLC analysis.

The unextracted residue of cotton seed ([Ring-4,6-^{14}C] and [Allyl-2-^{14}C]-clethodim), soya bean leaves, carrot roots and cotton leaves ([Allyl-2-^{14}C]-clethodim) were treated with 1N HCl (100 °C for 2 h), followed by 20% NaOH hydrolysis (100 °C for 24 h). Both acid and base hydrolysates were saturated with ammonium sulfate then extracted with dichloromethane. Radioactivity in the residue was determined by combustion/LSC.

[Ring-4,6-^{14}C]-clethodim

Soya bean

TRRs in soya bean were 28 mg eq/kg for leaves, 0.89 mg eq/kg for stems, 0.45 mg eq/kg for roots, 1.8 mg eq/kg for pods and 3.9 mg eq/kg for seeds. All samples except the roots were further investigated. The total extracted residues were 89-99% TRR. Unextracted residues were 1.5-11% TRR (0.058-2.5 mg eq/kg).

Only the extracts of leaves and beans were subjected to TLC and HPLC analysis. No parent was detected in any of the plant parts. Major metabolites (>10% TRR) were clethodim sulfoxide (32% TRR, 1.2 mg eq/kg in seeds), imine sulfoxide (14% TRR, 3.9 mg eq/kg in leaves), 5-OH sulfone (11% TRR, 0.41 mg eq/kg in seeds) and conjugates of clethodim sulfoxide (25% TRR, 6.9 mg eq/kg in leaves). Other metabolites that were identified in leaves and seeds were clethodim sulfone, imine sulfone, 5-OH sulfoxide, aromatic sulfone and conjugates of clethodim sulfone (all < 10% TRR but ≥ 0.05 mg eq/kg). An unknown metabolite coded A was detected in leaves (5.3% TRR, 1.5 mg eq/kg).

Up to 10 metabolites, together ≤ 18% TRR (≤ 5.1 mg eq/kg), remained unidentified but were characterised as polar. Nine further metabolites were distinguished which remained unidentified together making up ≤ 7.7% TRR (≤ 2.2 mg eq/kg).

Metabolite A was not identified but (1) could not be converted to DME (dimethyl ester sulfone) or DME-OH (dimethyl ester hydroxy sulfone), (2) does not contain the chloroallyloxy moiety and (3) does most likely not contain the intact ethylthio (propyl) moiety. Metabolite A is assumed to be the result of further degradation of identified metabolites leading to complete fragmentation of the molecule.

Carrot

TRRs in carrot were 22 mg eq/kg for leaves and 0.40 mg eq/kg for roots. Both leaves and roots were further investigated. The total extracted residues were 95–96% TRR. Unextracted residues were 3.7–5.3% TRR (0.015–1.2 mg eq/kg).

The parent was only detected in the roots (0.8% TRR, 0.003 mg eq/kg). Metabolites exceeding 10% TRR were clethodim sulfoxide (16% TRR, 3.50 mg eq/kg in leaves and 29% TRR, 0.11 mg eq/kg in roots) and imine sulfoxide (22.1% TRR, 4.93 mg eq/kg in leaves). Other metabolites that were identified in leaves and roots were clethodim sulfone, 5-OH sulfoxide, 5-OH sulfone, aromatic sulfone and conjugates of clethodim sulfoxide and clethodim sulfone. Each of these was < 10% TRR. In both roots and leaves an unknown metabolite A was detected (3.9–4.8% TRR, 0.019–0.88 mg eq/kg). Up to 13 metabolites, together ≤ 2 7% TRR (≤ 6.0 mg eq/kg), remained unidentified but were characterised as polar. Nine further metabolites remained unidentified together ≤ 8.2% TRR (≤ 1.5 mg eq/kg).

Cotton

TRRs in cotton were 14 mg eq/kg for leaves, 0.66 mg eq/kg for stems, 1.36 mg eq/kg for shell, 0.056 mg eq/kg for fiber, 0.068 mg eq/kg for seeds and 0.10 mg eq/kg for roots. All samples except the roots were further investigated. Total extracted residues were 54-95% TRR. Unextracted residues were 4.6-46 % TRR (0.024-0.62 mg eq/kg).

Only the extracts of leaves and seeds were subjected to TLC and HPLC analysis. Only imine sulfoxide exceeded 10% TRR (18% TRR, 2.4 mg eq/kg in leaves). Other identified metabolites were clethodim sulfone, imine sulfone, 5-OH sulfoxide, 5-OH sulfone, aromatic sulfone and conjugates of clethodim sulfoxide and clethodim sulfone (all <10% TRR, but > 0.05 mg eq/kg in leaves). An unknown metabolite A was detected (9.6% TRR, 1.3 mg eq/kg). Up to 10 metabolites, together ≤ 32% TRR (≤ 4.3 mg eq/kg), remained unidentified but were characterised as polar. Up to 9 further metabolites remained unidentified together ≤ 22% TRR (≤ 2.9 mg eq/kg).

The majority of the released ^{14}C was very polar and was assumed to represent small ^{14}C fragments incorporated into plant constituents.

Table 5 Extractability and distribution of radioactivity following two applications of [Ring-4,6-^{14}C]-clethodim at 280 g ai/ha

Plant Part	TRR	Extracted										Unextracted	
		Hexane		Acetone		Methanol		Methanol/Water		Methanol (acidic)			
	mg eq/kg	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Soya bean													
Leaves	28	–	–	18	65	2.4	8.7	3.4	12	1.4	4.9	2.5	8.9
Stems	0.89	–	–	0.60	67	0.12	14	0.078	8.8	0.018	2.0	0.073	8.2
Roots	0.45	–	–	–	–	–	–	–	–	–	–	–	–
Pods	1.8	–	–	1.1	59	0.18	9.6	0.29	16	0.086	4.7	0.20	11
Seeds	3.9	0.058	1.5	3.4	89	0.18	4.7	0.12	3.2	–	–	0.058	1.5
Carrot													
Leaves	22	–	–	15	66	2.1	9.6	3.3	15	0.98	4.4	1.2	5.3
Roots	0.40	–	–	0.33	83	0.036	9.1	0.018	4.6	–	–	0.015	3.7

Plant Part	TRR	Extracted										Unextracted	
		Hexane		Acetone		Methanol		Methanol/Water		Methanol (acidic)			
	mg eq/kg	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Cotton													
Leaves	14	–	–	5.1	38	2.0	15	4.8	36	0.97	7.2	0.62	4.6
Stems	0.66	–	–	0.39	59	0.10	16	0.064	10	0.019	2.9	0.085	13
Shell	1.4	–	–	0.62	46	0.25	18	0.24	17	0.14	10	0.11	8.3
Fiber	0.056	–	–	0.02	3.5	0.008	14	0.016	28	0.007	12	0.024	42
Seeds	0.068	0.003	3.7	0.005	7.1	0.010	15	0.016	23	0.003	4.9	0.031	46
Roots	0.10	–	–	–	–	–	–	–	–	–	–	–	–

Table 6 Identification of radioactivity in plant extracts after two applications of [Ring-4,6- ^{14}C]-clethodim at 0.28 kg ai/ha

Components	Soya Bean				Carrot				Cotton			
	Leaves		Seeds		Leaves		Roots		Leaves		Seeds	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Extract	25	91	3.8	99	21	95	0.38	97	13	96	0.037	54
Clethodim	–	–	–	–	–	–	*0.003*	*0.8*	–	–	–	–
Clethodim sulfoxide	*1.7*	*5.9*	*1.2*	*32*	*3.5*	*16*	*0.11*	*29*	*0.55*	*4.1*	*0.003*	*4.3*
Clethodim sulfone	*0.25*	*0.9*	*0.18*	*4.6*	*0.13*	*0.6*	*0.014*	*3.4*	*0.054*	*0.4*	*0.002*	*2.8*
Imine sulfoxide	*3.9*	*14*	*0.30*	*7.8*	*4.9*	*22*	*0.040*	*9.9*	*2.4*	*18*	*0.004*	*6.0*
Imine sulfone	*2.4*	*8.7*	*0.31*	*8.1*	*1.3*	*5.9*	*0.034*	*8.6*	*0.55*	*4.1*	*0.002*	*2.3*
5-OH sulfoxide		*< 0.1*	*0.28*	*7.1*	*0.36*	*1.6*	*0.026*	*6.4*	*0.19*	*1.4*	*< 0.001*	*0.6*
5-OH sulfone	*0.86*	*3.1*	*0.41*	*11*	*0.42*	*1.9*	*0.030*	*7.6*	*0.054*	*0.4*	*0.001*	*1.6*
Aromatic sulfone	*0.14*	*0.5*	*0.058*	*1.5*	*0.067*	*0.3*	*0.006*	*1.4*	*0.068*	*0.5*	–	–
Metabolite A	*1.5*	*5.3*	–	–	*0.88*	*3.9*	*0.019*	*4.8*	*1.3*	*9.6*	–	–
Others	*2.2*[a]	*7.7*	*0.27*[a]	*7.0*	*1.5*[a)]	*6.9*	*0.03*[a)]	*8.2*	*2.9*[a]	*22*	*0.005*[e]	*6.6*
Clethodim sulfoxide conj.	*6.9*	*25*	*0.33*	*8.5*	*1.9*	*8.5*	*0.024*	*5.9*	*0.37*	*2.7*	–	–
Clethodim sulfone conj.	*0.56*	*2.0*	*0.050*	*1.3*	*0.11*	*0.5*	*0.002*	*0.5*	*0.18*	*1.3*	–	–
Polar and/or other conj.	*5.1*[b]	*18*	*0.38*[c]	*9.9*	*6.0*[d]	*27*	*0.041*[e]	*10*	*4.3*[b]	*32*	*0.020*[f]	*30*
Unextracted	2.5	8.9	0.058	1.5	1.2	5.3	0.015	3.7	0.62	4.6	0.032	46
1 N HCl soluble	Not performed										*0.009*[g]	*13*
20% NaOH											*0.009*[h]	*13*
Remaining residue											*0.014*	*20*
TRR	28	100	3.9	100	22	100	0.40	100	13.5	100	0.068	100

[a] Consists of at least 9 metabolites

[b] Consists of at least 10 metabolites

[c] Consists of at least 4 metabolites

[d] Consists of at least 13 metabolites

[e] Consists of at least 5 metabolites

[f] Contained too low radioactivity for further characterization

[g] 4% TRR was extracted with dichloromethane.

[h] 0.8% TRR was extracted with dichloromethane.

No clethodim was detected in any of the plant parts except in carrot roots (0.8% TRR, 0.003 mg eq/kg) indicating extensive metabolism of clethodim. Major metabolites (>10% TRR) were clethodim sulfoxide (in carrot leaves, carrot roots and soya beans), imine sulfoxide (in soya bean leaves, in carrot leaves and in cotton leaves), 5-OH sulfone (in soya beans) and conjugates of clethodim sulfoxide (in soya bean leaves). Other identified metabolites are clethodim sulfone, imine sulfone, 5-OH sulfoxide and aromatic sulfone. An unknown metabolite A was detected in all plant parts except soya bean beans and cotton seeds. These other identified metabolites and the unknown metabolite A exceeded 0.05 mg eq/kg, except 5-OH sulfone and metabolite A in carrot roots and all metabolites in cotton seeds (< 0.05 mg eq/kg). Unidentified fractions were characterised as either

organosoluble or polar. For all plant parts, unextracted residues (including acid and base hydrolysis) were <25% TRR.

[Allyl-2-^{14}C]-clethodim

Soya bean

TRRs in soya bean were 18 mg eq/kg for leaves, 0.83 mg eq/kg for stems, 0.58 mg eq/kg for roots, 1.6 mg eq/kg for pods and 4.3 mg eq/kg for beans. All samples except the roots were further investigated. Total extracted residues were 70–91% TRR. Unextracted residues were 8.9–30% TRR (0.25–2.1 mg eq/kg).

No parent was detected in any of the plant parts. Metabolites exceeding 10% TRR in soya bean leaves were conjugates of clethodim sulfoxide (27% TRR, 4.7 mg eq/kg) and conjugates of clethodim sulfone (12% TRR, 2.2 mg eq/kg). In soya bean seeds clethodim sulfoxide (32% TRR, 1.3 mg eq/kg), 5-OH sulfone (10% TRR, 0.43 mg eq/kg) and conjugates of clethodim sulfoxide (12% TRR, 0.49 mg eq/kg) were ≥ 10% TRR. Other metabolites that were identified in leaves and seeds were clethodim sulfone, 5-OH sulfoxide and aromatic sulfone (all < 10% TRR, but > 0.05 mg eq/kg).

Nine metabolites remained unidentified, together making up ≤ 20% TRR (≤ 1.4 mg eq/kg). Up to 10 further metabolites remained unidentified but were characterised as polar, together making up ≤ 31% TRR (≤ 5.5 mg eq/kg). Upon acid and base hydrolysis of the solid residue of the soya bean leaves, 10.8% TRR was released. The majority of the released ^{14}C was very polar and was assumed to represent small ^{14}C fragments incorporated into plant constituents.

Carrot

TRRs in carrot were 9.2 mg eq/kg for leaves and 0.62 mg eq/kg for roots. Both samples were further investigated. Total extracted residues were 88–91% TRR. Unextracted residues were 9.3–12% TRR (0.074–0.86 mg eq/kg).

The parent was only detected in the roots (1.1% TRR, 0.007 mg eq/kg). Metabolites exceeding 10% TRR in carrot leaves were clethodim sulfoxide (11% TRR, 0.97 mg eq/kg) and an unknown metabolite C (13% TRR, 1.2 mg eq/kg). In the roots, clethodim sulfoxide (34% TRR, 0.21 mg eq/kg) and 5-OH sulfone (10% TRR, 0.063 mg eq/kg) were ≥ 10% TRR. Other metabolites that were detected in roots and leaves were clethodim sulfone, 5-OH sulfoxide, aromatic sulfone, conjugates of clethodim sulfoxide and clethodim sulfone and an unknown metabolite B (in leaves only) (all < 10% TRR, but > 0.05 mg eq/kg, except aromatic sulfone in carrot roots (< 0.05 mg eq/kg)). Based on the molecular weights of metabolites B and C and the fact that the chlorine atom is missing, it was assumed that the allyloxy moiety of clethodim had been incorporated into plant constituents.

Nine metabolites remained unidentified, together making up ≤ 18% TRR (≤ 1.7 mg eq/kg). A further 13 metabolites remained unidentified but were characterised as polar, together making up ≤ 32% TRR (≤ 2.9 mg eq/kg). Upon acid and base hydrolysis of the solid residue of the carrots, 11.4% TRR was released. The majority of the released ^{14}C was very polar and was assumed to represent small ^{14}C fragments incorporated into plant constituents.

Cotton

TRRs in cotton were 6.7 mg eq/kg for leaves, 0.77 mg eq/kg for stems, 0.47 mg eq/kg for shell, 0.22 mg eq/kg for fiber, 0.22 mg eq/kg for seeds and 0.20 mg eq/kg for roots. All samples except the roots were further investigated. Total extracted residues were 28–78% TRR. Unextracted residues were 13–72% TRR (0.10–0.83 mg eq/kg).

No parent was detected in any of the plant parts. The only metabolites ≥10% TRR in cotton leaves were conjugates of clethodim sulfoxide (10% TRR, 0.67 mg eq/kg). Other metabolites that

were detected in the leaves were clethodim sulfoxide, clethodim sulfone, 5-OH sulfoxide, 5-OH sulfone, aromatic sulfone and conjugates of clethodim sulfone (all < 10% TRR, but > 0.05 mg eq/kg).

No metabolites exceeding 10% TRR or 0.01 mg eq/kg were detected in cotton seeds. Up to 9 metabolites remained unidentified, together making up ≤ 7.3% TRR (≤ 0.49 mg eq/kg). A further 10 metabolites remained unidentified but were characterised as polar, together making up ≤ 56% TRR (≤ 3.8 mg eq/kg). Upon acid and base hydrolysis of the solid residue of the cotton leaves and seeds, 9.7–42% TRR was released. The majority of the released ^{14}C was very polar and was assumed to represent small ^{14}C fragments incorporated into plant constituents.

Table 7 Extractability and distribution of radioactivity following two applications of [allyl-2-^{14}C]-clethodim at 280 g ai/ha

Plant Part	TRR	Extracted										Unextracted	
		Hexane		Acetone		Methanol		Methanol/Water		Methanol (acidic)			
	mg eq/kg	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Soya bean													
Leaves	18	–	–	11	62	1.5	8.4	1.9	11	1.2	6.8	2.1	12
Stems	0.83	–	–	0.35	42	0.081	9.7	0.11	13	0.046	5.6	0.25	30
Roots	0.58	–	–	–	–	–	–	–	–	–	–	–	–
Pods	1.6	–	–	0.72	46	0.11	7.3	0.23	15	0.12	7.6	0.38	24
Seeds	4.3	0.11	2.5	3.4	79	0.20	4.7	0.17	4.1	0.021	0.5	0.38	8.9
Carrot													
Leaves	9.2	–	–	5.4	58	0.93	10	1.5	16	0.56	6.1	0.86	9.3
Roots	0.62	–	–	0.41	66	0.058	9.4	0.066	11	0.014	2.2	0.074	12
Cotton													
Leaves	6.7	–	–	2.1	31	0.62	9.3	2.0	31	1.1	16	0.83	13
Stems	0.77	–	–	0.30	39	0.096	13	0.12	16	0.043	5.6	0.21	27
Shell	0.47	–	–	0.11	24	0.069	15	0.13	27	0.058	12	0.10	22
Fiber	0.22	–	–	0.004	1.8	0.019	8.6	0.026	12	0.014	6.3	0.16	72
Seeds	0.22	0.019	8.5	0.015	7.0	0.019	8.5	0.025	11	0.008	3.8	0.13	61
Roots	0.20	–	–	–	–	–	–	–	–	–	–	–	–

Table 8 Identification of radioactivity in plant extracts after two applications of [Allyl-2-^{14}C] - clethodim at 280 g ai/ha

	Soya Beans				Carrot				Cotton			
	Leaves		Seeds		Leaves		Roots		Leaves		Seeds	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Extracted	15	88	3.9	91	8.3	91	0.55	88	5.8	88	0.086	39
Clethodim	–	–	–	–	–	–	*0.007*	*1.1*	–	–	–	–
Clethodim sulfoxide	*0.79*	*4.5*	*1.3*	*32*	*0.97*	*11*	*0.21*	*34*	*0.35*	*5.3*	*0.007*	*3.1*
Clethodim sulfone	*0.16*	*0.9*	*0.22*	*5.1*	*0.17*	*1.8*	*0.029*	*4.6*	*0.12*	*1.8*	*0.001*	*0.4*
5-OH sulfoxide	*0.25*	*1.4*	*0.17*	*4.0*	*0.09*	*1.0*	*0.045*	*7.3*	*0.07*	*1.1*	*0.001*	*0.4*
5-OH sulfone	*0.39*	*2.2*	*0.43*	*10*	*0.16*	*1.7*	*0.063*	*10*	*0.04*	*0.6*	*0.001*	*0.6*
Aromatic sulfone	*0.07*	*0.4*	*0.081*	*1.9*	*0.06*	*0.6*	*0.005*	*0.8*	*0.03*	*0.4*	–	–
Others	*1.4*[a]	*8.0*	*0.86*[a]	*20*	*1.7*	*18*	*0.027*[a]	*4.3*	*0.49*[a]	*7.3*	*0.012*[e]	*5.6*
Clethodim sulfoxide conj.	*4.7*	*27*	*0.49*	*12*	*0.27*	*2.9*	*0.052*	*8.3*	*0.67*	*10*	–	–
Clethodim sulfone conj.	*2.2*	*12*	*0.11*	*2.5*	*0.40*	*4.3*	*0.027*	*4.3*	*0.33*	*5.0*	–	–
Metabolite B	–	–	–	–	*0.46*	*5.0*	–	–	–	–	–	–
Metabolite C	–	–	–	–	*1.2*	*13*	–	–	–	–	–	–
Polar and/or other conj.	*5.5*[b]	*31*	*0.18*[c]	*4.3*	*2.9*[d]	*32*	*0.083*[e]	*13*	*3.8*[b]	*56*	*0.064*[f]	*29*
Unextracted	2.1	12	0.38	8.9	0.86	9.3	0.074	12	0.81	12	0.13	61
1 N HCl soluble	*1.1*[g]	*6.5*	–	–	–	–	*0.047*[i]	*7.6*	*0.37*	*5.5*	*0.053*[j]	*24*
20% NaOH	*0.75*[h]	*4.3*	–	–	–	–	*0.024*[h]	*3.8*	*0.28*[h]	*4.2*	*0.040*[h]	*18*
Remaining residue	*0.24*	*1.4*	–	–	–	–	*0.015*	*0.5*	*0.17*	*2.5*	*0.041*	*19*
TRR	18	100	4.3	100	9.2	100	0.62	100	6.7	100	0.22	100

[a] Consists of at least 9 metabolites

[b] Consists of at least 10 metabolites

[c] Consists of at least 4 metabolites

[d] Consists of at least 13 metabolites

[e] Consists of at least 5 metabolites

[f] Contained too low radioactivity for further characterization

[g] 2.7% TRR was extracted with dichloromethane.

[h] ≤0.2% TRR was extracted with dichloromethane.

[i] 2.8% TRR was extracted with dichloromethane.

[j] 11% TRR was extracted with dichloromethane.

No clethodim was detected in any of the matrices except in carrot roots (1.1% TRR, 0.007 mg eq/kg). Major metabolites (≥10% TRR) were clethodim sulfoxide (in soya bean beans, in carrot leaves and in carrot roots), 5-OH sulfone (in soya bean beans and in carrot roots), clethodim sulfoxide conjugates (in soya bean leaves, in soya beans and in cotton leaves), clethodim sulfone conjugates (in soya bean leaves) and an unknown metabolite coded C (in carrot leaves). Other metabolites that were detected were clethodim sulfone, 5-OH sulfoxide, aromatic sulfone and an unknown metabolite B. All identified metabolites exceeded 0.05 mg eq/kg, except aromatic sulfone in carrot roots and all metabolites in cotton seed (< 0.01 mg eq/kg). Unidentified fractions were characterized as either organosoluble or polar. Unknown metabolites B and C were only detected in carrot leaves; they were probably formed by incorporation of the allyloxy moiety of clethodim into plant constituents. For all plant parts, unextracted residues (including acid and base hydrolysis) were < 25% TRR.

Carrot

A nature of the residue study in carrot (*Daucus carota*) was performed with [Ring-4,6-^{14}C] -clethodim and [Allyl-2-^{14}C]-clethodim (Dohn, 2009:1808W-1). Carrots were grown outdoors in test plots that consisted of wooden boxes (each with an area of one square meter) located above ground level and filled with a sandy loam soil to a depth of 23 cm. [^{14}C]-Clethodim was formulated as a 240 g/L suspension concentrate in water and applied once by spraying onto the leaves of the carrot plants 56 days before harvest of the mature carrots. The plants were treated at a target rate of 0.60 kg ai/ha, twice the maximum recommended field rate of 0.30 kg ai/ha.

Carrot roots and foliage were harvested 21 and 56 days after test substance application. The carrot roots were rinsed with water after harvest to remove soil. The carrot leaves and roots were then frozen, and maintained in the frozen state throughout the study. Intact carrot samples were homogenized to a fine powder in the presence of dry ice using homogenization equipment fitted with stainless steel blades. The total radioactive residues (TRR) in the carrot tissues were measured by combustion analysis.

The radioactive residues in all samples were characterized by extraction with acetonitrile:water (1:1, v/v), acetonitrile, and acetonitrile:0.2N HCl (1:1, v/v) and identified by chromatographic techniques (reverse phase HPLC, normal phase TLC, and HPLC-MS). Further extractions using acid/base hydrolysis were also employed. Unextracted residues were quantified by combustion analysis of the post-extracted solids (PES).

PES from all samples except for the mature carrot root [Ring-4,6-^{14}C] labelled was additionally extracted with acetonitrile/0.2N NH_4OH on a wrist action shaker at ambient temperature for 45 minutes; 0.05M EDTA in 0.05M sodium acetate buffer, pH 4.90 at 70 °C overnight, 1N HCl at 87 °C for 4 hours and 24% KOH at ambient temperature on a wrist action shaker, overnight. The 24% KOH extracts from both immature and mature roots were subjected to liquid/liquid extraction with dichloromethane under basic and acidic conditions.

A portion of the combined acetonitrile/water extracts (~100 mL) from the immature carrot foliage was reduced by rotary evaporation. The flask was rinsed with hexane. The concentrated extract and hexane rinse were combined and partitioned in an 8 mL vial. The hexane phase had only

3% of radioactivity and was discarded. The aqueous phase was concentrated and injected in two consecutive HPLC runs. The column eluent was analysed by LSC.

Isolated radioactive metabolites were further purified using HPLC. The column eluent was analysed by LSC. In some cases several radiolabelled peaks were detected. The predominant radioactive peak was subjected to LC-MS.

In carrot foliage, clethodim was detected at very small concentrations in immature foliage (0.004–0.005 mg eq/kg) but was not detected in mature foliage. Clethodim sulfoxide and clethodim sulfone were found in all foliage samples. Furthermore, M17R, M18R and M19R were significant in mature foliage samples.

In carrot roots, clethodim was detected at very small concentrations. Clethodim sulfoxide and clethodim sulfone were present in significant amounts (0.029–0.032 mg eq/kg, 18–24% TRR and 0.011–0.013 mg eq/kg, 7.0–9.9% TRR) in mature roots. The other most abundant components observed were M17R with the [Ring-4,6-^{14}C] label (0.11 mg eq/kg, 13% TRR), M3A with the [Allyl-2-^{14}C] label (0.081 mg eq/kg, 11% TRR) and M18R with the [Ring-4,6-^{14}C] label (0.072 mg eq/kg, 8.8% TRR). The absolute concentration of M3A, M17R and M18R had decreased to 0.02 mg/kg in mature carrots. The structures of the pentane dioic acid metabolites M15R, M17R and M18R were confirmed by GC-MS/MS. Clethodim is extensively metabolized and not detected or in low amounts in mature crops at levels of 0–1.1% TRR.

Table 9 Summary of radioactive residues in carrot following applications of ^{14}C-clethodim

Components		Foliage							
		Immature (21 DAT)				Mature (56 DAT)			
		[Ring-4,6-^{14}C]		[Allyl-2-^{14}C]		[Ring-4,6-^{14}C]		[Allyl-2-^{14}C]	
		mg/kg eq	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
Extract with Acetonitrile/water[a]		5.10	89.3	3.15	80.9	0.730	86.7	0.601	79.9
	Clethodim	*0.004*	*< 0.1*	*0.005*	*0.1*	*ND*	-	*ND*	-
	Clethodim sulfoxide	*0.663*	*11.8*	*0.757*	*19.4*	*0.095*	*11.3*	*0.164*	*21.7*
	Clethodim sulfone	*0.180*	*3.2*	*0.234*	*6.1*	*0.040*	*4.8*	*0.046*	*6.0*
M22R	*Imine sulfoxide & Hydroxy imine sulfoxide*	*0.710*	*12.6*	-	-	*ND*	-	-	-
M24R	*Imine sulfone*	*0.369*	*6.5*	-	-	*0.062*	*7.4*	-	-
M15R	*Hydroxy 3-[(2-ethylsulfinyl) propyl] pentanedioic acid*	*0.594*	*10.5*	-	-	*0.030*	*3.6*	-	-
M15A	*3-chloroallyl alcohol glucoside*	-	-	*0.185*	*4.8*	-	-	*0.027*	*3.6*
M17R	*3-[(2-ethylsulfinyl) propyl] pentanedioic acid*	*0.519*	*9.2*	-	-	*0.075*	*8.9*	-	-
M18R	*3-[(2-ethylsulfonyl) propyl] pentanedioic acid*	*0.410*	*7.3*	-	-	*0.068*	*8.1*	-	-
M19R	*Glucose conjugate*	*0.633*	*11.2*	-	-	*0.119*	*14.1*	-	-
M22A	*2-(glutamyl-cysteinyl)-3-chloroacrylic acid*	-	-	*0.282*	*7.3*	-	-	*0.055*	*7.3*
M26	*Clethodim sulfoxide glucoside*	*0.360*	*6.4*	*0.385*	*9.9*	*0.078*	*9.3*	*0.111*	*14.6*
M3R		*0.024*	*0.4*	-	-	*0.003*	*0.4*	-	-
M3A		-	-	*0.124*	*3.2*	-	-	*0.006*	*0.8*
M18A		-	-	*0.024*	*0.6*	-	-	*ND*	-
M19A		-	-	*0.177*	*4.6*	-	-	*0.034*	*4.5*
M24A		-	-	*0.075*	*1.9*	-	-	*0.043*	*5.7*
M27		*0.133*	*2.4*	*0.225*	*5.8*	*0.026*	*3.1*	*0.053*	*7.0*
	Others	*0.502*	*7.8*	*0.672*	*17.2*	*0.134*	*15.7*	*0.062*	*8.7*
Acetonitrile/NH_4OH		0.109	1.9	0.105	2.7	0.016	1.9	0.014	1.9
Na-acetate (EDTA), pH 4.9		0.085	1.5	0.081	2.1	0.011	1.3	0.011	1.5
1N HCl reflex		0.101	1.8	0.157	4.0	0.013	1.5	0.024	3.2
24% KOH difestion		0.276	4.8	0.319	8.2	0.063	7.5	0.081	10.8
24% KOH digestion on filter paper		0.004	0.1	0.001	< 0.1	0.001	0.1	0.004	0.5
Unextracted		0.038	0.7	0.080	2.1	0.008	1.0	0.017	2.3
TRR		5.71	100	3.89	100	0.842	100	0.752	100

Components		Root							
		Immature (21 DAT)				Mature (56 DAT)			
		[Ring-4,6-^{14}C]		[Allyl-2-^{14}C]		[Ring-4,6-^{14}C]		[Allyl-2-^{14}C]	
		mg/kg eq	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
Extract with Acetonitrile/water[a]		0.726	89.0	0.578	78.4	0.145	90.8	0.108	82.5
	Clethodim	*0.002*	*0.2*	*0.001*	*0.1*	*ND*	-	*ND*	-
	Clethodim sulfoxide	*0.132*	*16.2*	*0.163*	*22.1*	*0.029*	*18.4*	*0.032*	*24.4*
	Clethodim sulfone	*0.051*	*6.3*	*0.057*	*7.7*	*0.011*	*7.0*	*0.013*	*9.9*
M15R	*Hydroxy 3-[(2-ethylsulfinyl) propyl] pentanedioic acid*	*0.063*	*7.7*	-	-	*0.019*	*12.0*	-	-
M15A	*3-chloroallyl alcohol glucoside*	-	-	*0.048*	*6.5*	-	-	*0.004*	*3.1*
M17R	*3-[(2-ethylsulfinyl) propyl] pentanedioic acid*	*0.107*	*13.1*	-	-	*0.022*	*13.9*	-	-
M18R	*3-[(2-ethylsulfonyl) propyl] pentanedioic acid*	*0.072*	*8.8*	-	-	*0.020*	*12.7*	-	-
M3R		*0.020*	*2.5*	-	-	*0.006*	*3.8*	-	-
M3A		-	-	*0.081*	*11.0*	-	-	*0.020*	*15.3*
M17A		-	-	*0.007*	*0.9*	-	-	*0.008*	*6.1*
M27		*0.026*	*3.2*	*0.025*	*3.4*	*0.010*	*6.3*	*0.003*	*2.3*
	Others	*0.253*	*31.0*	*0.196*	*26.7*	*0.028*	*16.7*	*0.028*	*21.4*
Acetonitrile/NH_4OH		0.020	2.5	0.027	3.7	These extractions not performed on this sample		0.002	1.5
Na-acetate (EDTA), pH 4.9		0.012	1.5	0.021	2.8			ND	< 0.1
1N HCl reflex		0.016	2.0	0.036	4.9			0.005	3.8
24% KOH difestion		0.027	3.3	0.053	7.2			0.013	9.9
24% KOH digestion on filter paper		0.001	0.1	0.003	0.4			0.001	0.8
Unextracted		0.013	1.6	0.020	2.7	0.013	8.2	0.003	2.3
TRR		0.815	100	0.738	100	0.158	100	0.131	100

[a] Extraction with acetonitrile:water (1:1, v/v), acetonitrile and acetonitrile:0.2N HCl (1:1,v/v)

An unidentified metabolite (or combination of metabolites), designated M3A in carrot was detected in samples that had been treated with [Allyl-2-^{14}C] labelled clethodim. This component in the HPLC analyses was very early running, being poorly retained on the column, and thus it was not clear if this represented a single or multiple metabolites. The isolated fractions were concentrated and reanalysed by a TLC system suitable for separation of polar materials (Caine, 2012: TM/11/002). Based upon the TLC analysis of the isolated polar region, the original M3A can be seen to be multi-component with no individual component being greater than 0.018 mg eq/kg (2.4% TRR).

Clethodim is extensively metabolized in carrot plants and does not accumulate in carrot root or the foliage. The majority of the metabolites were characterized and identified. The identification of cyclohexene ring opened metabolites, with structures proposed for M15R, M17R and M18R in the study performed outdoors was different from the study performed in a greenhouse. These metabolites are postulated to be formed as a result of photolysis of the already known clethodim imine metabolites.

Summary of plant metabolism

Metabolism of clethodim was investigated in three crop groups: root and tuber vegetables (carrot), oilseed/pulses (cotton and soya bean) and leafy vegetables (spinach). It was observed that no single pathway is expected to be exclusive for a crop group.

In all three groups clethodim is extensively metabolized and not detected or in low amounts in mature crops. The one major metabolic pathway, observed in all groups, is sulfoxidation to clethodim sulfoxide followed by further oxidation to clethodim sulfone. Clethodim sulfoxide and clethodim sulfone conjugates were also identified as major or minor metabolites in all crops. Another pathway is elimination of the chloroallyl moiety, leading to the formation of clethodim imine and 3-chlorolally metabolites, including 3-chloroalcohol glucoside (M15A).

The studies in carrot and spinach performed outdoors suggest that the clethodim ring can be opened by a photolysis reaction (also from imine metabolites) to form pentanedioic acids. Metabolites M15R, M17R and M18R belong to the pentanedioic acids.

In the indoor metabolism studies in carrot, cotton and soya bean (1987/1988), no ring-opened metabolites M15R, M17R and M18R were identified. It is suggested that these metabolites are formed as a result of a photolytic reaction, while these studies were performed indoors, where access to light can be a limitation. However, since clethodim imine metabolites were detected in these studies, cleavage of the chloroallyl group must have occurred and potentially, metabolites M15R, M17R and M18R could have been formed.

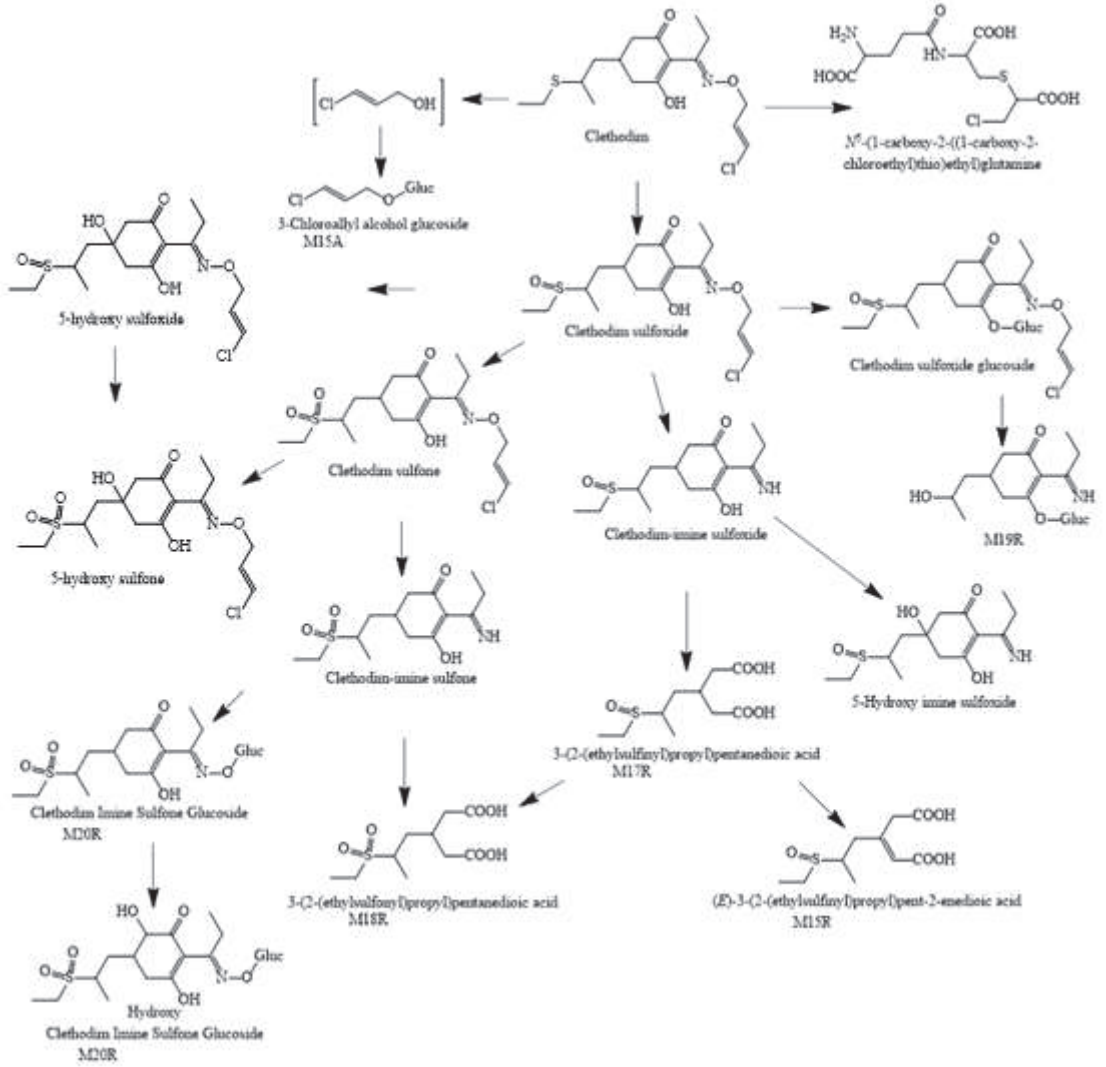


Figure 2 Metabolic Pathway of Clethodim in Plants

ENVIRONMENTAL FATE IN SOIL

The Meeting received information on degradation in aerobic soil, soil photolysis and dissipation studies. Because clethodim is intended for use as herbicide for weeds in crops, soil degradation (aerobic), soil photolysis and field dissipation studies relevant to the current evaluations were reported below (FAO Manual Third edition, 2016).

Degradation in aerobic soil

Study 1

The aerobic soil metabolism of [Propyl-1-^{14}C]-clethodim was studied in a sandy loam soil (Pack, 1988: MEF-0014). [Propyl-1-^{14}C]-clethodim was added in acetone to 50 g dry weight soil portions at a rate of 10.5 mg/kg. Treated soil was incubated in the dark at 25 °C for up to 380 days. The initial soil moisture content was adjusted to 75% of field capacity. Aerobic conditions were maintained by passing humidified air through the incubation flasks. CO_2 and volatiles were trapped in 2-ethanolamine/2-methoxyethanol and pseudocumene, respectively.

Test soil No.	6073-48
Origin location	Greenville, MS, USA
Texture	Sandy loam
% Sand	70
% Silt	17
% Clay	13
pH	7.1
Organic matter (%)	1.0
Cation exchange capacity	7.5
Maximum water-holding capacity (%)	75
Microbial biomass (mg C/100 g soil) Initial: Final:	 Not determined Not determined

Duplicate samples were analysed on days 0, 1, 3, 7, 14, 30, 61, 91, 124, 183, 275 and 380 post treatment. Samples were extracted four times with MeOH (during first extraction unlabelled clethodim was added to prevent oxidation) and two times with an aqueous $CaSO_4$ solution. Radioactivity in the combined MeOH extract, the combined aqueous extract and liquid traps was determined by LSC. Radioactivity in post-extraction solids was determined by combustion/LSC. MeOH extracts were concentrated prior to TLC (normal phase) and HPLC (reversed phase) analysis. Aqueous $CaSO_4$ extracts were not further analysed.

Table 10 Distribution of radioactivity after incubation of soil treated with [Propyl-1-^{14}C]-clethodim

Days of Incubation	% Applied Radioactivity							
	Clethodim	Clethodim Sulfoxide	Clethodim Sulfone	Clethodim Oxazole	Clethodim Oxazole Sulfoxide	Clethodim Oxazole Sulfone	Clethodim Imine Sulfoxide	Unknowns[a]
0	100	ND	ND	ND	ND	ND	ND	ND
1	77	16	ND	1.3	ND	ND	ND	ND
3	46	40	0.4	2.1	ND	ND	ND	ND
7	10	63	1.5	1.7	1.7	ND	0.6	2.1
14	2.8	57	3.7	0.5	3.1	ND	1.1	2.4
30	0.9	36	9.1	ND	5.0	1.5	1.1	3.5
61	0.2	15	11	ND	4.2	2.5	0.7	4.5
91	ND	2.2	4.4	ND	6.0	6.6	0.5	3.3
124	0.2	0.3	2.3	ND	5.3	7.5	0.2	3.5
183	ND	0.1	0.5	ND	4.8	9.4	ND	2.3
275	ND	ND	0.4	ND	3.6	9.5	ND	1.9
380	ND	ND	0.3	ND	3.0	10	ND	1.8

[a] Up to 9 different metabolites, all ≤ 2.7% AR

ND: Not detected

Table 11 Estimated DT_{50} and DT_{90} for the aerobic degradation of clethodim in sandy loam soil

	Clethodim	Clethodim sulfoxide	Clethodim sulfone	Clethodim oxazole sulfoxide
DT_{50} (d)	2.5	18	28	288
DT_{90} (d)	8.4	60	93	956
order (r^2)	first (0.997)	first (0.954)	first (0.996)	first (0.987)

Clethodim degraded in a sandy loam soil with a half-life of 2.5 days at 25 °C. Degradation was described by first order kinetics (r^2 0.997). CO_2 and bound residues accounted for 55 and 16% AR after 380 days. Clethodim sulfoxide was the most significant soil metabolite with a maximum of 63% AR after 7 days and DT_{50} of 18 days. Other significant soil metabolites were clethodim sulfone (maximum 11% AR at day 61 and a DT_{50} of 28 days), clethodim oxazole sulfoxide (maximum 6.0% AR after 91 days and a DT_{50} of 288 days) and clethodim oxazole sulfone (maximum 10% AR at day 380, no half-life determined). Other identified minor metabolites were clethodim oxazole and clethodim imine sulfoxide. Remaining unknown residues were ≤ 2.7% AR.

Study 2

The aerobic soil metabolism of clethodim was studied using [Ring-4,6-^{14}C]-clethodim and [Allyl-2-^{14}C]-clethodim in a sandy loam soil (Pack, 1990: MEF-0015/0016). [Ring-4,6-^{14}C]-clethodim was added in acetone to 50 g dry weight soil portions at a rate of 10.2 mg/kg. [Allyl-2-^{14}C]-clethodim was added in ethanol to 50 g dry weight soil portions at a rate of 10.0 mg/kg. Treated soil was incubated under aerobic conditions in the dark at 25 °C for up to 125 days. The soil moisture content was adjusted to 75% of field capacity and maintained throughout the incubation period. CO_2 and volatiles were trapped in NaOH and polyurethane foam plugs, respectively. Microbial activity (plate count) was checked prior to treatment and found acceptable.

Test soil No.	8149-34
Origin location	Greenville, MS, USA
Texture	Sandy loam
% Sand	56
% Silt	32
% Clay	12
pH	7.5
Organic matter (%)	0.9
Cation exchange capacity	8.1
Maximum water-holding capacity (%)	75
Microbial biomass Initial: Final:	 Viable (Determined by plate count) Not determined

Duplicate samples were analysed on days 0, 1, 3, 7, 14, 30, 60-62, 94-99 and 121-125 post treatment. Samples were extracted four times with MeOH (during the first extraction unlabelled clethodim was added to prevent oxidation) and three times with an aqueous $CaSO_4$ solution. Polyurethane foam plugs were three times extracted with MeOH. Radioactivity in the combined MeOH extract, the combined aqueous extract and liquid traps was determined by LSC. Radioactivity in post-extraction solids was determined by combustion/LSC. MeOH extracts were concentrated prior to TLC (normal phase) and HPLC (reversed phase) analysis. Aqueous $CaSO_4$ extracts were analysed by HPLC only.

Table 12 Distribution of radioactivity after incubation of soil treated with [Ring-4,6-^{14}C]-clethodim

Days of Incubation	% Applied Radioactivity						
	Clethodim	Clethodim Sulfoxide	Clethodim Sulfone	Clethodim Oxazole Sulfoxide	Clethodim Oxazole Sulfone	Clethodim Imine Sulfoxide	Unknowns[a]
0	89	11	ND	ND	ND	ND	0.1

Days of Incubation	% Applied Radioactivity						
	Clethodim	Clethodim Sulfoxide	Clethodim Sulfone	Clethodim Oxazole Sulfoxide	Clethodim Oxazole Sulfone	Clethodim Imine Sulfoxide	Unknowns[a]
1	50	39	2.3	1.1	ND	0.5	3.6
3	17	57	4.0	3.1	0.3	1.5	6.2
7	1.4	65	7.9	4.4	1.8	1.4	3.0
14	1.8	46	11	3.8	2.5	1.6	4.9
30	0.5	24	15	5.2	3.3	1.1	5.4
60	0.4	8.7	8.0	4.0	4.4	1.2	11
94	0.5	2.3	7.9	4.8	6.8	0.5	5.1
121	0.2	0.6	5.4	4.0	8.6	1.2	3.5

[a] Up to 10 different metabolites, all ≤ 6% AR

ND: Not detected

Table 13 Distribution of radioactivity after incubation of soil treated with [Allyl-2-^{14}C]-clethodim

Days of Incubation	% Applied Radioactivity						
	Clethodim	Clethodim Sulfoxide	Clethodim Sulfone	Clethodim Oxazole Sulfoxide	Clethodim Oxazole Sulfone	Clethodim Imine Sulfoxide	Unknowns [a]
0	94	5.3	n.d.	n.d.	n.d.	n.d.	0.5
1	60	38	n.d.	n.d.	n.d.	n.d.	0.9
3	10	73	4.7	n.d.	n.d.	n.d.	4.3
7	1.6	65	8.9	n.d.	n.d.	n.d.	8.3
14	0.8	47	12	n.d.	n.d.	n.d.	11
30	0.8	27	16	n.d.	n.d.	n.d.	12
62	0.5	7.2	12	n.d.	n.d.	n.d.	8.7
99	0.4	2.6	8.7	n.d.	n.d.	n.d.	6.3
125	0.1	0.9	4.6	n.d.	n.d.	n.d.	6.5

[a] Up to 10 different metabolites, all ≤ 6.2% AR-one unknown exceeded 5% AR at two consecutive time points

ND: Not detected

Table 14 Estimated DT_{50} and DT_{90} for the aerobic degradation of clethodim in sandy loam soil

	[Ring-4,6-^{14}C]-clethodim			[Allyl-2-^{14}C]-clethodim		
	Clethodim	Clethodim Sulfoxide	Clethodim Sulfone	Clethodim	Clethodim Sulfoxide	Clethodim Sulfone
DT_{50} (d)	1.2	18	70	1.2	19	56
DT_{90} (d)	4.1	61	232	4.0	65	185
order (r^2)	1st (0.999)	1st (0.999)	1st (0.867)	1st (0.987)	1st (0.994)	1st (0.934)

Clethodim degraded in a sandy loam soil with a half-life of 1.2 days at 25 °C. Degradation was described by first order kinetics (r^2 0.987-0.999). CO_2 and bound residues accounted for 57/45% AR (ring/allyl label) and 13/29% AR (ring/allyl label) after 121-125 days, respectively. Clethodim sulfoxide was the most significant soil metabolite with a maximum of 73% AR (allyl label, at 3 days, DT_{50} 19 days) and 65% AR (ring label, at 7 days, DT_{50} 18 days). Other significant soil metabolites were clethodim sulfone (maximum 15/16% AR at day 30/30, DT_{50} 56/70 days) and clethodim oxazole sulfone (maximum 8.6% AR at day 121, no half-life determined). Identified minor metabolites were clethodim oxazole sulfoxide and clethodim imine sulfoxide. Remaining unknowns were ≤ 6.2% AR. One of the unknowns exceeded 5% AR (maximum 6.2% AR) at two consecutive time points (allyl label day 14/30). The half-life of the unknown was estimated between 30 and 64 days.

Study 3

The degradation of clethodim was studied in three different standard soils obtained from the Landwirtschaftlichen Untersuchungs- und Forschungsanstalt (LUFA) (Heintze, 2003: 20031101/01-CABJ). [Ring-4,6-^{14}C]-clethodim was added in acetone to 50 g dry weight soil portions at a rate of 0.38 mg/kg. Treated soil was incubated under aerobic conditions in the dark at 20 °C for up to 120 days. The soil moisture content was adjusted to 45% of the maximum water holding capacity (MWHC) and maintained throughout the incubation period. CO_2 and volatiles were trapped in soda lime pellets and Tenax adsorbent, respectively. Microbial activity (short-term respiration) was checked prior to treatment and after 30 and 119 days in treated and untreated soil and found to be acceptable.

Test soil No.	BBA 2.3	BBA 3A	BBA 6S
Texture	Loamy sand	Sandy loam	Clayey loam
% Sand	55.8	42.9	22.3
% Silt	34.8	38.6	34.6
% Clay	9.4	18.5	43.1
pH	5.66	7.31	7.04
Organic matter (%)	0.86	2.42	1.75
Cation exchange capacity (mval/100 g)	8.9	18.5	22.0
Maximum water-holding capacity (%)	36.3	51.1	43.7
Microbial biomass (mg C/100 g)	24.5	44.7	29.5

The first soil extract (acetonitrile/water (1:1; v/v) at pH 5) was separated into an organic (ACN) and an aqueous phase. The organic phase was concentrated prior to TLC analysis (reversed and normal phase systems). The aqueous phase and further soil extracts (acetonitrile/water; acetone) were not subjected to chromatographic analysis.

Clethodim was identified and quantified based on reversed phase TLC only (co-chromatography with reference standard). Two regions on reversed phase TLC containing all metabolites were scraped off the plate, extracted overnight with acetone and subjected to normal phase TLC for identification and quantification of metabolites by co-chromatography with unlabelled reference standards.

Table 15 Distribution of radioactivity after incubation of soil treated with [Ring-4,6-^{14}C]-clethodim

Days of Incubation	% Applied Radioactivity					
	Extracts		Unextracted residues	CO_2	Volatiles	Mass Balance
	Organic	Aqueous				
BBA 2.3						
0.1	81.4	21.7	4.4	—	—	108
1	66.4	27.2	8.8	ND	ND	102
3	57.5	19.6	15.9	1.0	ND	94.0
7	44.5	15.1	14.3	1.9	ND	75.8
14	30.0	8.9	18.0	41.6	ND	98.4
21	22.6	6.0	17.5	45.7	ND	91.8
30	16.0	5.1	20.1	55.5	ND	96.6
59	11.2	2.4	20.1	66.8	ND	101
90	7.6	3.1	15.6	74.5	ND	101
104	6.5	2.7	14.3	77.8	ND	101
120	5.9	2.5	17.9	78.5	ND	105
BBA 3A						
0.1	75.8	25.6	10.4	—	—	112
1	72.1	22.9	9.5	ND	ND	104
3	65.6	15.6	11.9	4.7	ND	97.8
7	49.2	13.3	17.4	24.0	ND	104
14	33.8	11.3	20.2	40.5	ND	106
21	16.8	8.1	22.8	46.2	ND	93.8
30	8.2	5.2	24.3	57.7	ND	95.4
59	4.0	4.5	24.9	70.3	ND	104
90	3.1	3.7	18.7	70.9	ND	96.3
104	3.0	3.6	22.8	76.5	ND	106

Days of Incubation	% Applied Radioactivity					
	Extracts		Unextracted residues	CO_2	Volatiles	Mass Balance
	Organic	Aqueous				
120	2.8	3.5	23.4	81.1	ND	111
BBA 6S						
0.1	101	5.6	5.0	—	—	112
1	96.8	4.8	6.7	ND	ND	108
3	85.8	7.1	10.3	0.4	ND	104
7	67.6	9.4	14.0	9.4	ND	100
14	49.6	6.0	17.6	23.6	ND	96.7
21	51.4	6.4	18.1	28.8	ND	105
30	38.0	6.1	19.5	38.0	ND	102
59	15.3	5.2	24.5	49.9	ND	94.8
90	10.1	5.1	25.2	59.5	ND	99.8
104	7.3	5.3	25.8	61.8	ND	100
120	7.8	4.9	24.0	65.8	ND	102

ND: Not detected

Table 16 Quantities of clethodim and metabolites after incubation of soils treated with [Ring-4,6-^{14}C] -clethodim

Days of Incubation	% Applied Radioactivity									
	Clethodim	Clethodim sulfoxide	Clethodim sulfone	Clethodim oxazole	Clethodim oxazole sulfoxide	Clethodim oxazole sulfone	Clethodim imine	Clethodim imine sulfoxide	Clethodim imine sulfone	Origin
BBA 2.3										
0.1	3.7	57.3	1.7	1.1	5.7	1.1	0.6	3.2	3.7	3.6
1	1.0	43.8	1.4	0.3	6.4	1.0	0.3	4.0	3.8	4.5
3	0.8	30.2	2.1	0.3	6.7	2.6	0.2	3.1	6.3	5.4
7	0.7	20.7	3.5	0.2	5.9	2.2	0.2	2.8	3.7	4.8
14	0.4	12.3	4.0	0.1	3.8	3.9	0.1	1.9	3.1	0.6
21	0.7	5.3	4.3	0.3	2.0	3.9	0.2	1.7	2.9	1.6
30	0.6	2.6	1.4	0.3	1.9	4.4	0.2	0.9	2.9	1.0
59	0.6	1.8	1.0	0.2	1.1	2.7	0.1	0.5	2.4	1.0
90	0.5	1.4	0.5	0.2	0.6	2.2	0.1	0.4	1.8	0.2
104	0.4	1.3	0.5	0.2	0.6	1.5	0.1	0.3	1.8	0.3
120	0.6	1.1	0.4	0.2	0.6	1.1	0.1	0.2	0.6	0.2
BBA 3A										
0.1	16.8	42.3	0.9	1.1	4.9	1.7	0.6	1.9	3.6	2.3
1	3.9	47.5	1.3	0.5	9.4	0.8	0.4	3.1	3.5	1.9
3	0.6	38.6	2.6	0.2	13.0	1.1	0.2	4.4	1.2	3.9
7	0.5	19.8	10.4	0.2	7.0	4.2	0.2	3.1	2.6	1.6
14	0.4	5.6	14.4	0.2	2.3	6.1	0.2	0.8	3.1	1.1
21	0.3	1.5	8.1	0.1	0.4	2.2	0.1	0.4	3.6	0.3
30	0.4	2.7	2.5	0.1	0.2	0.3	0.1	0.2	1.7	0.2
59	0.3	0.5	0.3	0.2	0.1	0.1	0.1	0.1	2.6	0.1
90	0.3	0.4	0.3	0.1	0.2	0.1	ND	0.1	1.7	ND
104	0.3	0.5	0.3	0.1	0.2	0.2	0.1	0.1	1.4	0.1
120	0.4	0.3	0.3	0.1	0.1	0.8	0.1	0.1	0.6	0.1
BBA 6S										
0.1	38.0	46.2	0.6	5.9	3.8	0.2	1.3	1.4	1.0	3.2
1	24.9	40.5	0.9	5.2	10.3	1.3	1.2	2.9	6.7	3.0
3	5.5	52.0	1.9	0.7	12.1	0.5	0.3	5.2	1.0	6.9
7	0.8	36.8	4.6	0.4	15.7	3.0	0.1	3.3	1.2	1.9
14	1.0	16.1	15.9	0.3	4.6	5.8	0.3	2.7	2.3	1.0
21	1.2	19.7	16.3	0.2	5.0	3.1	0.3	2.3	2.5	0.9
30	0.9	10.3	14.4	0.1	2.6	4.1	0.3	1.5	2.9	0.8
59	0.4	1.6	4.3	0.3	0.8	3.5	0.3	0.4	2.9	1.1
90	0.6	1.3	2.6	0.2	0.5	2.1	0.1	0.3	2.2	0.4
104	0.6	1.0	1.2	0.2	0.5	1.4	0.1	0.2	2.1	0.3
120	0.9	0.9	1.2	0.3	0.5	1.8	0.1	0.2	1.7	0.4

ND: Not detected

Clethodim degraded with a half-life of < 0.1 day in a loamy sand soil (BBA 2.3), in a sandy loam soil (BBA 3A) and in a clayey loam soil (BBA 6S). CO_2 and bound residues accounted for 78.5, 81.1 and 65.8% AR and 17.9, 23.4 and 24.0% AR after 120 days in BBA 2.3, BBA 3A and BBA 6S soils, respectively. Clethodim sulfoxide was the largest soil metabolite with a maximum of 57.3% AR (BBA 2.3, 0.1 day), 47.5% AR (BBA 3A, 1 day) and 52.0% AR (BBA 6S, 3 days). Other significant soil metabolites were clethodim sulfone (maximum 4.3, 14.4 and 16.3% AR at day 21, 14 and 21 BBA 2.3/3A/6S), clethodim oxazole (maximum 1.1, 1.1 and 5.9% AR at day 0.1) and clethodim oxazole sulfoxide (maximum 6.7, 13.0 and 15.7% AR at day 3, 3 and 7). Other identified, non-significant metabolites were clethodim oxazole sulfone, clethodim imine, clethodim imine sulfoxide and clethodim imine sulfone. The aqueous fraction, which was not analysed, contained maximum 27.2, 25.6 and 9.4% AR at day 1, 0.1 and 7).

Study 4

The mineralization of clethodim was studied in two soils (da Silva, 1994: E.1.1. 137/93). A mixture of [Allyl-2-^{14}C]-clethodim and unlabelled clethodim was added to 50 g air-dry soil portions at a rate of 1 and 10 mg/kg. Treated soils were incubated under aerobic conditions at 24 °C in the dark for up to 28 days. The soil moisture content was adjusted to 60% of field capacity and maintained throughout the incubation period. Microbial activity (respiration) was checked prior to treatment and at the end of the incubation period in treated soil and found acceptable.

Test soil	Latossolo Vermelho Escuro (LE)	Areia Quartzosa (AQ)
Texture	Clay	Sand
% Sand	9.0	94.0
% Silt	13.0	2.0
% Clay	78.0	4.0
pH	5.00	4.50
Organic matter (%)	5.1	0.9
Cation exchange capacity (meq/100 cm^3)	12.70	2.10
Maximum water-holding capacity (%)	60	60
Microbial biomass	Viable	Viable

CO_2 evolution was measured (four replicates) on 7, 14, 21 and 28 days post treatment. Evolved $^{14}CO_2$ was trapped in NaOH solutions and determined by LSC.

Table 17 $^{14}CO_2$ evolution from two soils treated with [Allyl-2-^{14}C] clethodim incubated at 24 °C under aerobic conditions

Days of Incubation	$^{14}CO_2$ (% applied, Mean of four replicates)			
	LE		AQ	
	1 mg/kg	10 mg/kg	1 mg/kg	10 mg/kg
7	38.7	35.7	28.3	16.6
14	10.1	10.9	12.1	20.6
21	4.76	4.89	7.71	7.84
28	2.47	1.74	3.42	1.71
Total	56.0	53.2	51.5	46.8

$^{14}CO_2$ evolved was 53.2–56.0% of applied radioactivity in the LE soil and 46.8–51.5% of applied radioactivity in the AQ soil. No significant difference between soils and treatment was observed (at 28 days). The results indicate that the chloroallyloxyimino group of clethodim is completely mineralized in soil.

Study 5

The degradation route and rate of clethodim was investigated in three soils under aerobic conditions (Mamouni, 2006: A00426). Two different labels [Ring-4,6-^{14}C] and [Allyl-2-^{14}C] of the test item were used.

The freshly collected soils were first passed through a 2 mm sieve and equilibrated to the test conditions for about three weeks. Thereafter, the test item was applied to 100 g soil samples at a concentration of about 0.4 mg/kg dry soil. This rate is based on an application rate of 0.40 kg ai/ha, assuming an even distribution of the test item in the top 10 cm soil layer and a soil bulk density of 1.0 g/cm^3. The treated soil samples were incubated at a moisture content of about 40% MWC (between pF 2 and pF 2.5) and at a temperature of 20 ± 2 °C in the dark under continuous ventilation with moistened air. The exiting air was passed through a trapping system consisting of flasks containing ethylene glycol and aqueous sodium hydroxide for trapping organic volatiles and $^{14}CO_2$, respectively. Prior to treatment and at the end of the study, the microbial biomass was determined by the substrate induced respiration method. The results showed that the soils were viable during the study.

Duplicate soil samples were taken immediately after treatment (day 0) and after 5 hours, 1, 7, 11, 14, 28, 60 and 119 days of incubation for the samples treated with [Allyl-2-^{14}C]-clethodim. Single samples were taken immediately after treatment (day 0) and after 2, 7, 14, 23, 40 and 57 days of incubation for the samples treated with [Ring-4,6-^{14}C]-clethodim.

The samples were submitted to solvent extractions using acetonitrile/water (4:1; v/v) up to three times each for about 30 minutes by shaking at about 250 rpm followed by Soxhlet extraction using the same solvent mixture. The combined and concentrated extracts were then analysed by HPLC and 2D-TLC to determine the amounts of test item and degradation products. A total balance of radioactivity, the nature of extracted radioactivity and pattern of metabolites were established for each sampling interval.

Test soil	Montesquieu, France	Mechthildshausen, Germany	Speyer 2.2, Germany
Batch no.	06/05	07/05	F222305
pH ($CaCl_2$)	7.3	6.8	5.7
Organic carbon (g/100g soil)	2.2	1.4	2.3
CEC (meq/100 g soil)	21.0	4.8	11.0
Carbonate (% $CaCO_3$)	8.1	< 0.1	NA
Total nitrogen (%)	0.3	0.1	NA
Particle size analyses (USDA, mm):			
Soil type (USDA)	Clay loam	Loam	Loamy sand
< 0.002 (clay) %	38.4	15.0	7.9
0.002-0.05 (silt) %	37.1	37.1	14.6
> 0.05 (sand) %	24.5	24.5	77.5
Max. water holding capacity MWC; (g/100 g soil)			
at pF 1.0	65.5	40.9	56.0
at pF 2.0	40.5	26.0	17.4
at pF 2.5	31.6	20.2	12.9
40% MWC (g/100 g soil)	26.2	16.4	22.4
Biomass (mg micr. Carbon/100 g dry soil)			
Start of incubation	57.8	15.6	21.7
End of incubation	41.6	7.0	11.6

The total mean recoveries for the samples treated with [Allyl-2-^{14}C]-clethodim were 97.5–97.6% of the applied radioactivity for soils, during the study. The mean amount of total extracted radioactivity decreased continuously from 97.1–98.9% immediately after treatment to 2.0–7.6% on day 119 of incubation for soils. Soxhlet extraction released a maximum individual amount of 8.2%. The amount of unextracted radioactivity increased continuously, reaching peak values of 45.0–53.3% of the applied radioactivity in soils, after 119 days. Mineralisation to $^{14}CO_2$ was significant and increased continuously until the end of the incubation, reaching at least mean levels of 33.8–45.4% of

the applied radioactivity for soils. Other volatile products never exceeded 0.3% during the incubation period.

For the samples treated with [Ring-4,6-^{14}C]-clethodim, total mean recoveries of radioactivity were 97.4–98.7% of the applied radioactivity for soils, during the study. The amount of total extracted radioactivity decreased continuously. After 57 days of incubation, 7.1–19.4% of the applied radioactivity was extracted from soils. A maximum amount of 4.4% of the applied radioactivity was extractable from the soil using subsequent Soxhlet extraction. Unextracted radioactivity increased to maximum values of 19.3–27.6%, on day 57. The mineralisation of [Ring-4,6-^{14}C]-clethodim was very high in all three soils and increased continuously, with radioactive carbon dioxide reaching levels of 57.0–63.6% of the applied radioactivity, within the 57-day incubation period.

^{14}C-clethodim disappeared very rapidly from soil, from levels of between 87.5% and 99.0% of the applied radioactivity at the first sampling interval (about 1.5 hours after application) to below 3% of the applied radioactivity in soils by day 14. Clethodim was degraded to numerous radioactive fractions. Five metabolites were characterized as clethodim sulfone (M1, M4), clethodim sulfoxide (M2, M3, M5, M6), clethodim imine sulfoxide (M14, M15), clethodim oxazole sulfoxide (M16, M21) and clethodim oxazole sulfone (M28, M29).

Clethodim sulfoxide was the major degradate in all three soils, reaching maximum amounts of 53.8–72.0% of the applied radioactivity in the samples treated with [Allyl-2-^{14}C] and [Ring-4,6-^{14}C]- clethodim, respectively. Thereafter, it steadily degraded representing less than 7.6% in soils after about 60 days of incubation.

The second most important degradate in all three soils was clethodim sulfone. Present in significant quantities from day 7 onwards, it reached maximum amounts of 11.9–33.3% of the applied radioactivity in the samples treated with allyl-labelled and ring-labelled clethodim, respectively. Thereafter, it continuously decreased to levels below 4.7% in all three soils by day 60.

Clethodim oxazole sulfone was the third significant radioactive fraction but not exceeding 8% of the applied radioactivity. This metabolite was significant only in Speyer 2.2 (Germany) soil reaching a plateau value ranging from 6.6 to 7.5% of the applied radioactivity from day 14 to day 57 of incubation.

Analysis of the samples treated with the [Allyl-2-^{14}C]-clethodim by LC/MS showed that the metabolite clethodim oxazole sulfone never reached the maximum of 5.6% in Speyer 2.2 (Germany) on day 60 and decreased to 0.9% of the initial applied amount on day 119 of incubation. In soils of Montesquieu (France) and Mechthildshausen (Germany), it never exceeded 5% of the applied amount. Furthermore, the samples were also analysed for the metabolites clethodim imine sulfoxide and clethodim oxazole sulfoxide which never exceeded 5% within the incubation period.

All other degradates were either transient or did not exceed 5% of applied radioactivity at two consecutive sampling intervals.

The DT_{50}, DT_{75} and DT_{90} values of clethodim and its major metabolites clethodim-sulfoxide and clethodim-sulfone, based on simple first-order kinetics were calculated and are summarized in the tables below.

Table 18 Degradation rate (days) of clethodim and its metabolites

Soil		Clethodim			Clethodim sulfoxide			Clethodim sulfone		
		DT_{50}	DT_{75}	DT_{90}	DT_{50}	DT_{75}	DT_{90}	DT_{50}	DT_{75}	DT_{90}
Montesquieu, France	Allyl	0.3	0.6	1.0	3.2	6.4	10.5	16.0	32.1	53.3
	Ring	0.3	0.6	1.0	3.8	7.5	12.5	13.0	26.1	43.3
	Mean	0.3	0.6	1.0	3.5	6.9	11.5	14.5	29.1	48.3
Mechthildshausen, Germany	Allyl	0.4	0.8	1.4	7.1	14.1	23.5	24.5	49.1	81.5
	Ring	0.5	0.9	1.5	4.6	9.2	15.3	19.8	39.6	65.8
	Mean	0.4	0.9	1.5	5.8	11.7	19.4	22.2	44.3	73.7
Speyer 2.2, Germany	Allyl	0.4	0.8	1.4	3.7	7.5	12.4	4.6	9.1	15.2
	Ring	0.7	1.4	2.4	3.3	6.6	11.0	9.4	18.9	31.3
	Mean	0.6	1.1	1.9	3.5	7.1	11.7	7.0	14.0	23.3

The main degradation pathway of clethodim in soil proceeds via oxidation of the thio group to the main metabolite clethodim sulfoxide, followed by oxidation to form clethodim sulfone and microbial hydrolysis to the imine and cyclisation to the oxazole. These compounds were further degraded leading to numerous transient fractions. These products are then biodegraded mainly to carbon dioxide and unextracted residues.

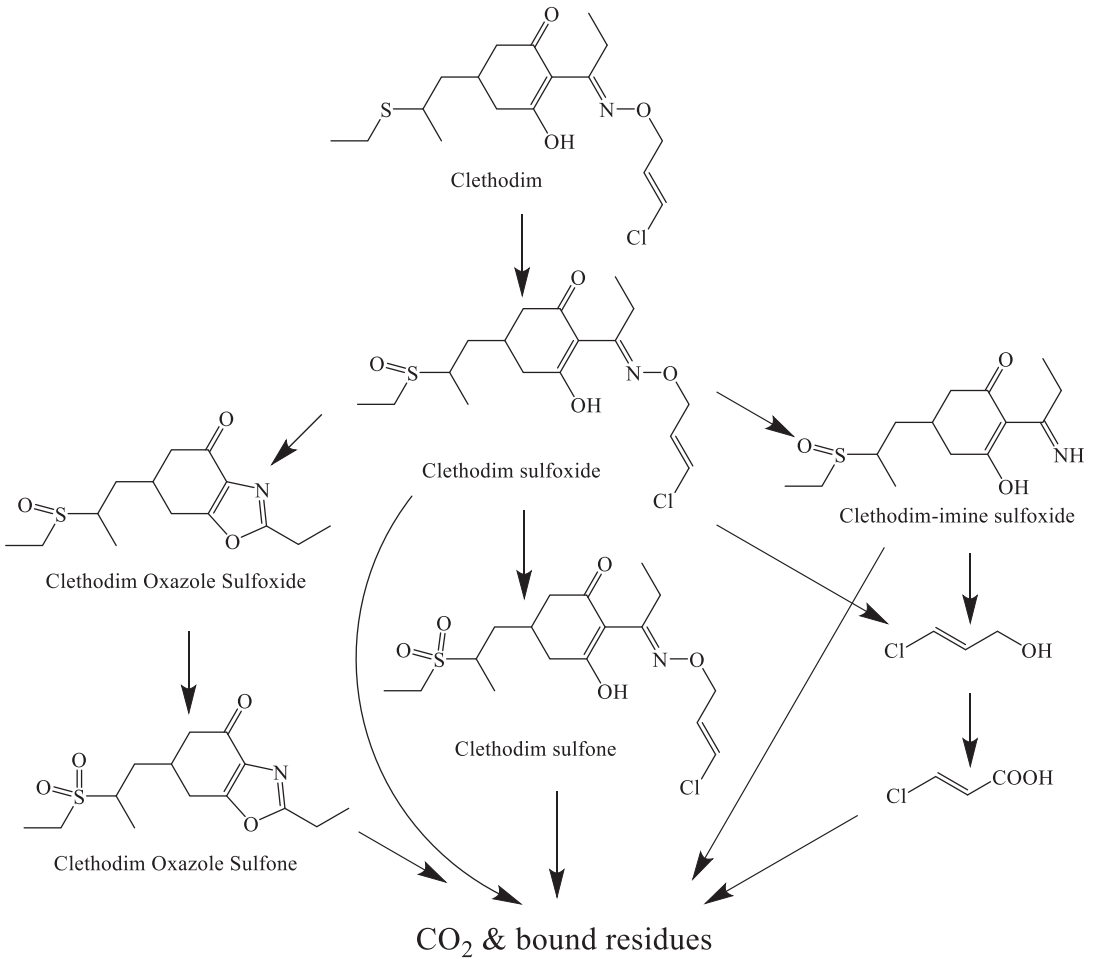


Figure 4 Metabolic Pathway of Clethodim in aerobic soil

Soil photolysis

Study 1

A photolysis study on sandy loam soil surface was conducted with [Ring-4,6-^{14}C]-clethodim at a rate of 0.28 kg ai/ha (Chen, 1988: MEF-0022). [Ring-4,6-^{14}C] clethodim was added in buffer solution (pH 6.5) to the surface of 50 g dry weight sandy loam soil portions (81.1 cm^2 in borosilicate glass containers) at a rate of 4.5 mg/kg. Treated soil was irradiated outdoors by natural sunlight (37°N, experiment 1: 30 Nov-7 Dec, experiment 2: 7-14 Dec). Light intensity was measured (twice a day) in the blue, red and far-red regions and was ~8, ~5 and ~6 µW/cm^2, respectively. Dark controls were included. The initial soil moisture content was adjusted to 75% of field capacity. CO_2 and volatiles were trapped in NaOH and xylene traps, respectively. Soil temperature was monitored throughout the irradiation period and was 11–18 °C (experiment 1) and 2–17 °C (experiment 2).

Test soil No.	6073-48
Location	Greenville, MS, USA
Texture	Sandy loam

Test soil No.	6073-48
Location	Greenville, MS, USA
% Sand	70
% Silt	17
% Clay	13
pH	7.1
Organic matter (%)	1.0
Cation Exchange Capacity (meq/100 g)	7.5
Moisture content	75% of field capacity (10.1% w/w)
Microbial biomass (start) Microbial biomass (end)	not determined not determined

Duplicate samples were analysed on days 0, 1, 2, 3, 4 and 7 post treatment. Samples were extracted four times with MeOH and two times with water. Radioactivity in the combined MeOH extract, the combined aqueous extract and liquid traps was determined by LSC. Radioactivity in post-extraction solids was determined by combustion/LSC. MeOH extracts were concentrated prior to HPLC-RAM (reversed phase), HPLC- MS/MS (reversed phase) and TLC (normal phase) analysis. Aqueous extracts were only analysed by HPLC-RAM. Compound identification was by co-chromatography with unlabelled reference standards. Clethodim sulfoxide was confirmed by HPLC-MS/MS.

Total recovery in irradiated soil ranged from 90 to 106% AR (exp 1) and from 79 to 98% AR (exp 2). The amount of MeOH-extracts in irradiated soil decreased to 78% AR (exp 1) and 62% AR (exp 2) at day 7. Unextracted residues in irradiated soil gradually increased to a maximum of 6.2 (exp 1) and 7.0% AR (exp 2) at day 7. Amounts of $^{14}CO_2$ were small: maximum 4.2% (exp 1) and 3.3% AR (exp 2). No radioactivity was detected in the xylene traps (volatiles). The results for the dark soils were similar to the results for the irradiated soil.

In irradiated soil, clethodim degraded to 3.1% (exp 1) and 5.0% (exp 2) at day 7. Clethodim sulfoxide was the most important soil metabolite in irradiated samples: maximum 74% (exp 1) and 63% AR (exp 2). Other soil metabolites in irradiated soil were all ≤ 2.6% AR (exp 1 and 2). The results for the dark soil were similar to the results for the irradiated soil. All metabolites observed in irradiated soil were also present in the dark soil.

The half-life of clethodim in irradiated soil was 1.53–1.82 days. The half-life of clethodim in dark soil was 1.87–1.96 days.

Study 2

The photodegradation of [Allyl-2-^{14}C] and [Ring-4,6-^{14}C]-clethodim on the soil surface was investigated under artificial sunlight (Mamouni, 2006: A00437). The test items were separately applied onto a thin layer of 2 mm of a clay loam soil on glass dishes. The actual concentrations applied were 44 µg (allyl-label) or 56 µg (ring-label) per 12.5 cm^2 soil sample, corresponding to approximately the maximum rate of 0.384 kg ai/ha.

Test soil (Origin) Batch no.	Montesquieu, France 06/05
Soil type (USDA) pH ($CaCl_2$) Organic carbon (g/100g soil) Cation Exchange Capacity (meq/100 g soil) Carbonate (% $CaCO_3$) Total nitrogen (%)	Clay loam 7.3 2.2 21.0 8.1 0.3
Particle size analyses (USDA, mm): < 0.002 (clay) % 0.002-0.05 (silt) % > 0.05 (sand) %	 38.4 37.1 24.5

Test soil (Origin) Batch no.	Montesquieu, France 06/05
Max. water holding capacity MWC; (g/100 g soil) at pF 1.0 at pF 2.0 at pF 2.5	 65.5 40.5 31.6
40% MWC (g/100 g soil)	26.2

Simulated sunlight from a "Suntest" apparatus equipped with a xenon lamp, with filters to remove wavelengths below 290 nm and having a mean intensity of 44.3 W/m^2 within the visual light spectrum (300 nm to 400 nm), was used for the study. This light intensity was in the same range as the intensity of natural daylight with vertical incidence under temperate climates measured in the spring with the same spectrophotometer, 47.5°N latitude (49.0 W/m^2). The 15 days suntest irradiation corresponded to about 37 days of midsummer sunlight at a latitude of 50°N and 36 days at latitudes 30-40°N. The mean temperature during the study was 20 ± 1 °C. Moistened air was sucked through the tank and any volatile products formed were trapped. The soil moisture was maintained at 75% field capacity (1/3 bar) throughout the study. Control samples were treated in the same way as the irradiated samples, with the exception that they were kept in the dark during the exposure period.

Duplicate irradiated and control soil samples were taken at various time intervals during the 15-day irradiation/incubation period. All samples were extracted with acetonitrile/water (4:1; v/v) up to three times, each for about 30 min. The extracts were then analysed by LSC, concentrated using different techniques and submitted to HPLC analysis using several different analytical methods. Selected samples were additionally analysed by TLC for confirmation of the HPLC results. The residual radioactivity in the extracted soil samples was determined by combustion.

The mean recoveries of radioactivity were 99.6 ± 3.0% and 96.0 ± 7.3% of the applied radioactivity (AR) for the samples treated with ^{14}C-ring and ^{14}C-allyl labelled clethodim, respectively. The corresponding values for the dark control samples were 102.0 ± 1.5% and 100.3 ± 3.5% AR. Mean extracted radioactivity in the irradiated samples steadily decreased to represent 24.0% and 26.1% AR at the end of the irradiation period (day 15).

For ^{4}C-ring clethodim, the amount of unextracted radioactivity was very high, reaching a peak value of 70.5% of the applied radioactivity on day 15. However mineralisation to $^{14}CO_2$ was low, not exceeding a maximum of 2.7% AR throughout the study. Other radioactive volatile substances did not account for more than 0.1% AR.

For ^{14}C-allyl clethodim, the mean amount of unextracted radioactivity and radioactivity evolved as$^{14}CO_2$ was high, reaching 31.1% and 40.0% AR on day 15 of irradiation, respectively. Other radioactive volatile substances did not account for more than 0.2% AR.

[Ring-4,6-^{14}C]-clethodim rapidly disappeared from the irradiated samples with just 32.2% AR remaining after 4 hours of irradiation. On day 3 it was no longer detected. At least eight photodegradates were formed of which the major one was characterised as clethodim sulfoxide. Clethodim sulfoxide accounted for a maximum value of 53.7% AR on day 1. Besides clethodim sulfoxide, two additional significant degradates, M(R)9 and M(R)10, were formed. Shown by HPLC and/or TLC to be multi-component fractions, M(R)9 and M(R)10 reached a plateau of about 8% AR and 7% AR during the study. These fractions contained numerous components of which none individually represented more than 3.9% AR for M(R)10 and 3.7% AR for M(R)9. Other fractions detected were minor: clethodim imine sulfoxide (max. 5.3% AR, day 3), Clethodim oxazole sulfoxide (max. 2.5% AR, day 10), Clethodim sulfone (max. 0.7% AR, day 1) and non-characterised fractions < 1.6% AR.

[Ring-4,6-^{14}C]-clethodim was also steadily degraded in the dark control samples, decreasing to levels of 58.7% to 3.2% AR on days 1 and 15, respectively. Similarly to the irradiated samples, the major degradate formed was Clethodim sulfoxide, reaching a maximum of 88.1% AR on day 10. On day 15, it had slightly declined to 81.1% AR. Two other minor fractions, Clethodim imine sulfoxide

and Clethodim oxazole sulfoxide were also formed, however they did not exceed maximum mean values of 2.1% AR and 3.3% AR throughout the study.

Table 19 Pattern of degradation products in the irradiated/dark control samples treated with [Ring-4,6-^{14}C]-clethodim (% of applied radioactivity)

	Irradiation time in days						
	0	0.17	1	3	7	10	15
Irradiated							
Extract	99.3	93.0	74.6	48.5	24.0	25.7	24.0
Clethodim	*92.2*	*32.2*	*6.9*	*ND*	*1.1*	*0.4*	*0.4*
Clethodim sulfone	*ND*	*0.3*	*0.7*	*ND*	*ND*	*ND*	*ND*
Clethodim sulfoxide	*7.1*	*53.6*	*53.7*	*32.3*	*4.4*	*3.0*	*1.9*
Clethodim imine sulfoxide	*ND*	*2.2*	*3.5*	*5.3*	*4.2*	*4.2*	*3.0*
Clethodim oxazole sulfoxide	*ND*	*0.5*	*0.6*	*1.9*	*2.2*	*2.5*	*2.2*
Unknowns[a]	*ND*	*2.8*	*7.1*	*9.0*	*11.4*	*14.7*	*16.0*
$^{14}CO_2$	-	< 0.1	< 0.1	0.3	1.4	2.0	2.7
Volatiles in ethylene glycol	-	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted	2.9	10.0	26.0	49.5	69.2	73.5	70.5
Total	102.2	103.0	100.6	98.3	94.5	101.2	97.1
Dark control							
Extract	99.3	100.9	97.4	97.4	94.1	94.3	89.6
Clethodim	*92.2*	*86.6*	*58.7*	*40.3*	*14.8*	*4.1*	*3.2*
Clethodim sulfoxide	*7.1*	*14.3*	*35.6*	*53.9*	*74.5*	*88.1*	*81.1*
Clethodim imine sulfoxide	*ND*	*ND*	*ND*	*0.9*	*2.1*	*1.5*	*1.7*
Clethodim oxazole sulfoxide	*ND*	*ND*	*ND*	*0.5*	*2.0*	*2.1*	*3.3*
Clethodim imine	*ND*	*ND*	*1.0*	*0.7*	*0.5*	*ND*	*ND*
Unknowns	*ND*	*ND*	*1.1*	*1.3*	*ND*	*ND*	*ND*
$^{14}CO_2$	-	< 0.1	< 0.1	< 0.1	0.1	0.2	0.2
Volatiles in ethylene glycol	-	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted	2.9	2.3	3.7	5.8	7.7	8.4	10.0
Total	102.2	103.1	101.1	103.2	101.8	102.8	99.7

[a] The components did not individually exceed 3.9% AR.

[Allyl-2-^{14}C]-clethodim disappeared very rapidly from the irradiated soil surface representing just 45.1% AR after 4 hours of irradiation. By day 1, it had decreased to below 2% AR. At least seven photodegradates were formed including the major photodegradate clethodim sulfoxide. Clethodim sulfoxide accounted for a maximum value of 60.4% AR on day 1 and decreased rapidly representing 1.5% AR after 15 days of irradiation. Besides clethodim sulfoxide, two additional significant degradates, M(A)9 and M26/M27, were formed. The metabolite M(A)9 was characterised and identified by LC/MS as trans-3-chloro-acrylic acid. It reached a maximum mean amount of 18.1% AR on day 3 and decreased to 4.1% at the end of irradiation. M26/M27 was identified by LC/MS and LC/NMR as 2-[3-chloroallyloxyimino] butanoic acid isomers and increased to 18.7% AR at the end of the irradiation period. Additionally, a minor radioactive fraction M8, characterised as chloroallyl alcohol was detected representing maximum of 3.0% AR. All other degradates remained ≤ 2.9% AR.

[Allyl-2-^{14}C]-clethodim also steadily disappeared from the dark control samples, representing 48.1% and 2.0% AR on days 3 and 15, respectively. The only degradation product formed was clethodim sulfoxide, steadily increasing to reach a maximum value of 89.2% AR on day 15.

Table 20 Pattern of degradation products in the irradiated/dark control samples treated with [Allyl-2-^{14}C]-clethodim (% of applied radioactivity)

	Irradiation time in days						
	0	0.17	1	3	6	10	15
Irradiated							
Extract	104.9	98.1	72.7	60.2	37.6	34.5	26.1
Clethodim	*103.0*	*45.1*	*1.9*	*ND*	*ND*	*ND*	*ND*
Clethodim sulfoxide	*1.9*	*48.1*	*60.4*	*23.9*	*11.2*	*4.6*	*1.5*
Chloroallyl alcohol	*ND*	*ND*	*ND*	*3.0*	*1.2*	*0.6*	*ND*
Chloroacrylic acid	*ND*	*1.0*	*5.2*	*18.1*	*9.8*	*12.0*	*4.1*

	Irradiation time in days						
	0	0.17	1	3	6	10	15
[Chloroallyloxyimino]butanoic acid	*ND*	*3.9*	*5.2*	*13.5*	*13.6*	*13.9*	*18.7*
Unknowns	*ND*	*ND*	*ND*	*1.7*	*1.7*	*3.4*	*1.8*
$^{14}CO_2$	-	0.2	7.6	12.0	20.9	31.1	40.0
Volatiles in ethylene glycol	-	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted	2.7	4.0	11.0	18.9	27.9	30.1	31.1
Total	107.6	102.6	91.3	91.2	86.4	95.8	97.3
Dark							
Extract	104.9	-	96.1	94.0	94.3	92.9	91.3
Clethodim	*103.0*	-	*63.2*	*48.1*	*27.8*	*8.5*	*2.0*
Clethodim sulfoxide	*1.9*	-	*31.0*	*45.6*	*66.5*	*84.3*	*89.2*
Chloroallyl alcohol	*ND*	-	*1.1*	*0.3*	*ND*	*ND*	*ND*
Chloroacrylic acid	*ND*	-	*0.8*	*ND*	*ND*	*ND*	*ND*
$^{14}CO_2$	-	-	< 0.1	0.6	0.6	0.7	1.0
Volatiles in ethylene glycol	-	-	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Unextracted	2.7	-	2.6	3.6	4.5	5.5	6.8
Total	107.6	-	98.7	98.3	99.4	99.1	99.1

DT_{50} values for clethodim in the samples were calculated applying a series of first-order reaction kinetics. The major photodegradation product of clethodim on soil, clethodim sulfoxide, was also rapidly photodegraded in the irradiated samples. Clethodim sulfoxide was however stable under the same conditions but in the dark. Another major photodegradation product of clethodim on soil, trans-3-chloro-acrylic acid (allyl label), was also photodegraded in the irradiated samples.

The results therefore show that ^{14}C-Clethodim, as well as its major photodegradation products clethodim sulfoxide and trans-3-chloro-acrylic acid, will be prone to photodegradation in soil. The major route of dissipation will be degradation to 2-[3- chloroallyloxyimino] butanoic acid, formation of bound residues and CO_2. The formation of less significant metabolites will be a secondary route of disappearance.

Table 21 Half-lives of clethodim and metabolites in irradiated and dark samples

"Suntest" irradiation	Clethodim						Net irradiation
	Irradiated samples			Dark samples			
	Ring-label	Allyl-label	Mean	Ring-label	Allyl-label	Mean	Mean
DT_{50} (days)	0.13	0.16	0.15	2.41	2.88	2.65	0.15
DT_{50} (hours)	3.1	3.8	3.5	57.8	69.1	63.5	3.6

"Suntest" irradiation	Clethodim sulfoxide			trans-3-chloro-acrylic acid
	Irradiated samples			Irradiated samples
	Ring-label	Allyl-label	Mean	Allyl-label
DT_{50} (days)	1.55	1.48	1.52	6.5

Soil degradation

Study 1

The degradation rate of clethodim and formation/decline of four known metabolites in three soils (German standard soil LUFA 2.2, LUFA 2.4 and LUFA 5M) was studied under aerobic conditions at 20 °C in the dark (Persch, 2012: S12-00097). The study was performed with non-labelled clethodim metabolites over periods of 58 days.

Test soil	LUFA 2.2	LUFA 2.4	LUFA 5M
Batch No.	F 2.2 1212	F 2.4 1312	F 5M 1312
Texture Class (USDA classification)	Sandy loam	Loam	Sandy loam
Sand (%)	72.0	33.0	57.4
Silt (%)	18.0	40.9	30.4
Clay (%)	10.0	26.1	12.2
pH (0.01 M $CaCl_2$)	5.36	7.42	7.38
Organic Matter (%)	2.95	3.22	1.86

Test soil	LUFA 2.2	LUFA 2.4	LUFA 5M
Batch No.	F 2.2 1212	F 2.4 1312	F 5M 1312
Organic Carbon(%)	1.71	1.87	1.08
Cation Exchange Capacity (mval/100 g)	10.4	32.4	17.6
MWHC (g/100 g dry soil)	41.7	45.4	45.5
Bulk Density (disturbed) (g/cm^3)	1.277	1.225	1.150

The application rate of clethodim was 11.2 µg per vessel containing 50 g (dried weight) soil, which was equivalent to 0.224 mg clethodim/kg soil. The average soil moisture content was 45% of the maximum water holding capacity over the entire period of the study.

Two flasks were taken for analysis at 0, 2, 8, 14, 41 and 58 days and were extracted immediately with methanol/ water (4/1, v/v) after sampling and extracts were stored at -18 °C prior to analysis. At every sampling date five untreated samples per soil were taken for concurrent recoveries and blank determination. Two samples were fortified with the same amount of test item as the treated flasks, two with an amount of 5% of the application rate and one sample was used as a blank. The biomass of the soil was measured before incubation, at the start of incubation, and at the end of the study.

Extracts were analysed using HPLC/MS/MS within 3 days of the soil sampling, using a fully validated analytical method. The LOQ for each test item (including clethodim oxazole sulfoxide) was 0.012 mg/kg. The limit of detection (LOD) was defined as 20 % of the limit of quantification and hence reads 0.0024 mg/kg.

Clethodim was degraded from an actual amount of 0.224 mg/kg to values below LOQ or LOD within 2 days in the respective soils. After 2 days clethodim sulfoxide was formed with maximum concentrations of 0.056-0.131 mg/kg in three soils. Clethodim sulfoxide was degraded below LOQ after 8 days in LUFA 2.2 and after 14 days in LUFA 2.4 and LUFA 5M. After 2 days clethodim sulfone was formed with maximum concentrations of 0.039 mg/kg in LUFA 2.2. After 8 days clethodim sulfone was formed with maximum concentrations of 0.075 mg/kg and 0.103 mg/kg in LUFA 2.4 and 5M, respectively. Clethodim sulfone was degraded below LOQ after 14 days in LUFA 2.2 and after 41 days in LUFA 2.4 and 5M, respectively. Clethodim oxazole sulfoxide and clethodim oxazole sulfone were not formed in significant amounts (>LOQ) in the respective soils.

Due to the rapid degradation of the test item within two days no dissipation time (DT_{50} and DT_{90}) could be calculated for clethodim. For clethodim oxazole sulfoxide and clethodim oxazole sulfone kinetic evaluation was not reasonable, as they were formed in amounts below LOQ or LOD.

Table 12 DT_{50} and DT_{90} values (single first-order) for clethodim sulfoxide and clethodim sulfone

Soil	Clethodim sulfoxide		Clethodim sulfone	
	DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)
LUFA 2.2	1.6	5.4	3.8	12.8
LUFA 2.4	2.1	6.9	7.8	25.8
LUFA 5M	2.5	8.4	10.4	34.4

Table 3 Degradation pattern of clethodim in soils

Sampling Interval (days)	% of applied (metabolites as molar fraction)				
	Clethodim	Clethodim sulfoxide	Clethodim sulfone	Clethodim oxazole sulfoxide	Clethodim oxazole sulfone
LUFA 2.2					
0	97.9, 96.1	5.1, 4.8	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ
2	2.5, 1.9	26.5, 21.7	14.4, 17.3	<LOQ, <LOQ	2.0, 1.8
8	<LOQ, <LOQ	2.0, 1.8	6.0, 6.5	<LOQ, <LOQ	4.3, 3.1
14	<LOQ, <LOQ	<LOQ, <LOQ	1.2, <LOQ	<LOQ, <LOQ	2.0, 2.1
41	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, 2.5
58	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	1.4, 2.0

Sampling Interval (days)	% of applied (metabolites as molar fraction)				
	Clethodim	Clethodim sulfoxide	Clethodim sulfone	Clethodim oxazole sulfoxide	Clethodim oxazole sulfone
LUFA 2.4					
0	104.1, 99.8	1.3, 1.8	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ
2	<LOQ, <LOQ	44.4, 44.8	18.1, 16.9	<LOQ, <LOQ	<LOQ, <LOQ
8	<LOQ, <LOQ	5.9, 6.1	28.8, 33.0	<LOQ, <LOQ	<LOQ, <LOQ
14	<LOQ, <LOQ	<LOQ, 1.2	17.2, 21.1	<LOQ, <LOQ	<LOQ, <LOQ
41	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ
58	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ
LUFA 5M					
0	98.8, 99.0	1.5, 1.4	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ
2	<LOQ, <LOQ	54.5, 58.0	17.3, 17.9	<LOQ, <LOQ	<LOQ, <LOQ
8	<LOQ, <LOQ	9.8, 12.1	43.9, 40.4	<LOQ, <LOQ	<LOQ, <LOQ
14	<LOQ, <LOQ	2.6, 1.5	33.6, 32.5	<LOQ, <LOQ	<LOQ, <LOQ
41	<LOQ, <LOQ	<LOQ, <LOQ	1.8, 1.6	<LOQ, <LOQ	<LOQ, <LOQ
58	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ	<LOQ, <LOQ

Study 2

The aerobic soil degradation of the clethodim oxazole sulfone metabolite M4 was studied using three soils, a sandy loam (LUFA Speyer 2.3), a loamy sand (LUFA Speyer 2.2) and a clay soil (LUFA Speyer 6S) (Class, 2009: B 1460 G). Clethodim oxazole sulfone metabolite M4 was applied at about 0.2 mg/kg to bulk soil, which corresponds to about 0.8 mg parent clethodim/kg soil, presuming a M4 formation of 25% from parent. Assuming a soil depth of 5 cm and a soil density of 1 g/cm^3, this dose corresponds to the maximum application rate of clethodim of 384 g ai/ha.

Soil	LUFA Speyer 2.3	LUFA Speyer 2.2	LUFA Speyer 6S
Soil Type	Sandy loam	Loamy sand	Clay
Maximum water holding capacity (g/100 g dry soil)	34.4	48.2	40.7
Organic Carbon	0.98 ± 0.05	2.16 ± 0.40	1.75 ± 0.1
pH	6.4 ± 0.6	5.4 ± 0.1	7.2 ± 0.1
Cation Exchange Capacity (mval/100 g)	8±2	10 ± 1	22 ± 6
Microbial carbon activity, (mg Carbon/100 g dry soil) after acclimatization	18	17	77

50 g of dry soil equivalents were measured from the dosed and homogenized soils into incubation flasks. The 1 L incubation flasks were loosely covered to allow aeration and to reduce loss of water. The flasks were placed in a thermostatic cabinet and incubated at 20 ± 2 °C in the dark. Loss of water was controlled and re-adjusted with distilled water twice per week. The soil moisture contents were adjusted to 40-60 % of the maximum water holding capacity and acclimatized for at least 10 days. The microbial biomass was determined (Anderson & Domsch) after acclimatization and after 80 days of incubation.

Duplicate soil incubations were sampled and analysed for remaining M4 after 0 (7 replicates), 3, 7, 15, 22, 30, 51, 62, 80, and 100 days. For LUFA Speyer 2.3 and LUFA Speyer 2.2, one 10 g aliquot per incubated specimen was extracted. For LUFA Speyer 6S three 10 g aliquots per incubated specimen were extracted to compensate for the higher variability observed for clay soil LUFA Speyer 6S. The soil samples were extracted with 100 mL methanol/water (8/2, v/v) by sonication and shaking. The soil/solvent phases were separated by centrifugation; the supernatant filtered and diluted for subsequent LC/MS/MS determination of M4.

The soil degradation rates of the clethodim oxazole sulfone metabolite M4 in three different soils at 20 °C were evaluated for 100 days of incubation applying single first-order kinetics (SFO) to the data to obtain endpoints for modelling.

Table 24: Degradation rate (days) of clethodim oxazole sulfone (M4)

Climatic estimation	LUFA Speyer 2.3	LUFA Speyer 2.2	LUFA Speyer 6S
DT_{50}	20	24	68
DT_{90}	66	79	227

Metabolite M4 is aerobically degraded in the three soils tested at 20 °C over an incubation period of 100 days. The DT_{50} values were 20 days for LUFA 2.3 (sandy loam), 24 days for LUFA 2.2 (loamy sand) and 68 days for LUFA 6S (clay). The respective DT_{90} values were 66, 79 and 227 days.

Study 3

The biotransformation of 2-[3-chloroallyloxyimino][1-^{14}C]-butanoic acid ([1-^{14}C]-CBA) was studied in (a) sand from the UK; (b) loam soil from Switzerland and (c) sandy loam soil from Switzerland for 120 days under aerobic conditions in the dark at 20 ± 2 °C, and a moisture level of pF 2.5 (Turk, 2012: 13917.6137).

Soil (Soil ID)	A1 UK	Horn	Sevelen
Soil Ref. No	11-1567	12-96	12-95
Texture Class (USDA classification)	Sand	Loam	Sandy loam
% Sand	92.0	47.0	59.0
% Silt	4.0	33.0	37.0
% Clay	4.0	20.0	4.0
pH (0.01 M $CaCl_2$)	4.5	7.4	7.6
Organic Matter (%)	2.4	4.1	2.5
Organic Carbon (%)	1.4	2.4	1.5
Cation Exchange Capacity (meq/100 g)	6.2	17.0	6.8
MWHC (g/100 g dry soil)	6.3	33.7	23.6
Bulk Density (disturbed) (g/cm^3)	1.38	1.14	1.03

Flasks containing 50 g dry weight equivalents were adjusted to 45% of the MWHC and treated with an acetone/water (1:1) solution of [1-^{14}C]CBA, equivalent to an application rate of 0.05 mg/kg. The flasks were incubated at 20 °C under aerobic conditions in the dark and were maintained at 45% of the MWHC. The test systems were aerated continuously with hydrated air and volatile components were trapped in ethylene glycol, to trap volatile organics and 1.0 M KOH to trap $^{14}CO_2$. Two flasks were taken for analysis at 0, 3, 10, 25, 50, 85 and 120 days and were extracted immediately with acetonitrile / water (50:50, v/v) followed by a further extraction with acetonitrile / water (80:20, v:v).

Radioactivity in the hydroxide traps was confirmed as $^{14}CO_2$ for selected traps by barium carbonate precipitation using barium chloride and analysing with LSC prior to and after precipitation. The biomass of the soil was measured before and after incubation by fumigation and extraction method. Portions of the soil extracts containing >2% of applied radioactivity were concentrated and analysed using HPLC with UV and radioactivity detector within one day of the soil sampling.

Microbial biomass measurements confirmed a viable microbial population was present for the duration of the study (>1% organic carbon as viable microbial biomass).

The overall recovery of radioactivity from the soils decrease from 100.2% at time 0 to 85% after 120 days. [1-^{14}C]CBA degraded steadily and completely in all soils to form mainly $^{14}CO_2$ and some unextracted residue. Unextracted residues reach a maximum of 11.2%, 22.4 and 22.4% in the A1 UK, Horn and Sevelen soils, respectively, and declined to 6.4%, 19.2% and 13.6% at the end of the study. Other components present in the extracts reached a maximum of 1.6% of applied radioactivity.

The photolysis product CBA was completely degraded to CO_2 and bound residue in all soils within 50 days. The degradation followed SFO kinetics and a mean DT_{50} of 5.5 days was calculated.

Table 25 Degradation rate (days) of 2-[3-chloroallyloxyimino]-butanoic acid (CBA)

Soil	DT_{50} (days)	DT_{90} (days)
A1 UK (sand)	4.5	15.0
Horn (loam)	7.0	23.3
Sevelen (sandy loam)	4.9	16.2
Mean	5.5	18.2
Geometric Mean	5.4	17.8

Environmental fate in water

The Meeting received information on hydrolytic degradation. Because clethodim is intend for use as herbicide for weed in crops, hydrolytic degradation study relevant to the current evaluations were reported below (FAO Manual Third edition, 2016).

Hydrolysis

The hydrolysis of [Propyl-1-^{14}C]- and [Allyl-2-^{14}C]-clethodim was studied in sterile aqueous buffer solutions at pH 5, 7 and 9 at 25 ± 0.1 °C (Pack, 1988: MEF-0013). The concentration of the test substances was 5-10 mg/L.

Sterile aqueous buffer solutions were prepared at pH 5, 7 and 9 containing [Propyl-1-^{14}C]-clethodim (5 mg/L), or at pH 5 and 7 containing [Allyl-2-^{14}C]-clethodim (10 mg/L). Test solutions contained ≤ 0.1% (v/v) acetonitrile. Aliquots (0.5 mL) were transferred to HPLC auto injector vials, which were capped and incubated for up to 32 days in the dark at 25 °C.

Duplicate samples were taken at 4 hours and 1, 4, 7, 14 and 32 days (propyl-label) or 1, 3, 7, 14, 21 and 30 days (allyl-label). The samples were analysed directly by reversed phase HPLC with confirmation by normal phase TLC. Compound identification was by co-chromatography with unlabelled reference standards. The identity of the hydrolysis products 3-chloroallyl alcohol and clethodim oxazole was confirmed by GC-MS of fractions isolated from test solutions of [allyl]- or [propyl]-clethodim, respectively, of concentration 500 and 50 mg/L incubated for 2 and 6 weeks.

Clethodim represented 97.4-98.2% AR on day 0 (4 hours). In the tests with the propyl-label, clethodim represented 43.0, 90.9 and 91.0% AR at the end of the test (day 32) at pH 5, 7 and 9, respectively. The corresponding DT_{50} values, determined by first order regression analysis, were 28, 297 and 307 days (r^2 values 0.99, 0.96 and 0.96). In the tests with the allyl-label, clethodim represented 64.9 and 94.4% AR at the end of the test (day 30) at pH 5 and 7, respectively. The corresponding DT_{50} values, determined by first order regression analysis, were 54 and 499 days (r^2 values 0.94 and 0.82).

In test solutions from the propyl-label, the major hydrolysis product was clethodim oxazole (maximum levels recorded after 32 days: 50.5, 6.8 and 4.9% at pH 5, 7 and 9, respectively). In test solutions from the allyl-label, the major hydrolysis product was chloroallyl alcohol (maximum levels recorded after 30 days were 30.7 and 4.3% at pH 5 and 7, respectively). Clethodim sulfoxide, which was present as an impurity in the starting material, was found at low levels in nearly all samples (maximum levels per test ranged between 1.2 and 4.7% AR). Low levels (≤ 4.7% AR) of unidentified compounds were detected during the tests.

Rotational crop studies

Confined rotational crop study

Crops were planted in sandy loam soil that had been treated at 1.12 kg ai/ha with [Ring-4,6-^{14}C]-clethodim and then aged for fallow periods of 30, 120 and 365 days in the greenhouse (Gaddamidi, 1988: MEF-0036). Crops were lettuce, carrot and wheat representing a leafy vegetable, a root and tuber vegetable and a small grain.

Carrots, lettuce and wheat were harvested at immaturity (23-41 days after planting) and at maturity (52-119 days after planting). At immaturity, the whole plants were analysed (lettuce: leaf only). At maturity, carrot roots, crowns and leaves, lettuce leaves and wheat grain, hulls and straw were analysed separately. After homogenization, total radioactive residues (TRR) were determined by combustion/LSC. Each matrix was extracted with subsequently dichloromethane/methanol (1:1, v/v) (3 or 4×) and methanol/water (3:1, v/v) (3 or 4×). Following evaporation of the dichloromethane, the dichloromethane/methanol extract was partitioned with hexane, after which the aqueous fraction was combined with the methanol/water extract. The combined extract was adjusted to 30% water in methanol and partitioned with dichloromethane. All soil samples were extracted with methanol (3×), except the t=0 soils which were extracted with dichloromethane and dichloromethane/methanol (2:1; v/v). Unextracted residues were quantified by combustion/LSC. Each fraction was concentrated for HPLC and TLC analysis and compared with reference standards; quantification of metabolites was by LSC of spots scraped off the TLC plates.

The aqueous methanol fractions of carrot leaf (30 and 120 days), lettuce leaf (30 days), wheat straw (30 and 120 days) and wheat hulls (30 days) were refluxed in 2N hydrochloric acid (2 hr) and extracted with ethyl acetate. The aqueous solution was then brought to pH 6.6 and extracted with ethyl acetate. Finally, the aqueous phase was adjusted to pH 11.0 and extracted with ethyl acetate. The ethyl acetate fractions and the aqueous fractions were subjected to HPLC and LC/MS.

Table 26 Total radioactive residue (TRR) in soil following a single treatment of [Ring-4,6-^{14}C]-clethodim at 1.12 kg ai/ha

Plant-back Interval (days)	Crop	Days after application	TRR (mg eq/kg)	Methanol extract (A)		Unextracted		Recovery (%TRR)
				mg eq/kg	%TRR	mg eq/kg	%TRR	
30	Carrot	0	0.960	1.10	114	0.008	0.8	115
		30 (planting)	0.130	0.068	52	0.109	84	136
		136 (harvest)	0.096	0.034	35	0.087	91	126
	Lettuce	0	0.964	1.14	119	0.016	1.7	120
		30 (planting)	0.168	-	-	-	-	-
		94 (harvest)	0.146	0.046	32	0.120	82	114
	Wheat	0	0.992	1.10	111	0.009	0.9	112
		30 (planting)	0.156	-	-	-	-	-
		136 (harvest)	0.106	0.035	33	0.088	83	116
120	Carrot	0	0.955	1.17	123	0.009	0.9	124
		120 (planting)	0.185	0.073	39	0.150	81	121
		239 (harvest)	0.074	0.028	38	0.084	14	151
	Lettuce	0	0.977	1.07	109	0.008	0.8	110
		120 (planting)	0.192	0.069	36	0.160	83	119
		171 (harvest)	0.083	0.030	36	0.064	77	113
	Wheat	0	0.962	1.11	115	0.008	0.8	116
		120 (planting)	0.188	0.068	36	0.144	77	113
		199 (harvest)	0.093	0.026	28	0.094	101	129
365	Carrot	0	0.984	1.07	108	0.006	0.6	109
		366 (planting)	0.084	0.026	31	0.073	87	118
		484 (harvest)	0.061	0.005	8.2	0.082	134	143
	Lettuce	0	0.955	1.08	113	0.008	0.8	114
		366 (planting)	0.080	0.024	30	0.067	84	114
		427 (harvest)	0.068	0.016	24	0.075	110	134
	Wheat	0	0.984	1.11	112	0.006	0.6	113
		366 (planting)	0.107	0.020	19	0.086	80	110
		472 (harvest)	0.060	0.010	17	0.057	95	112

Table 27 Identification of metabolites in methanol extracts of planting soil by TLC following a single treatment of [Ring-4,6-^{14}C]-clethodim at 1.1 kg ai/ha

	Carrot		Lettuce		Wheat	
	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
PBI 30 Days						
TRR	0.130	–		–		–
Imine sulfoxide	0.004	3.1	NA	NA	NA	NA
Oxazole sulfoxide	0.016	12	NA	NA	NA	NA
Oxazole sulfone	0.015	12	NA	NA	NA	NA
Polar fraction (origin)	0.005	3.8	NA	NA	NA	NA
Others	0.012	9.2	NA	NA	NA	NA
PBI 120 Days						
TRR	0.185	–	0.192	–	0.188	–
Imine sulfoxide	< 0.001	< 0.1	0.001	0.5	0.001	0.5
Oxazole sulfoxide	0.003	1.6	0.008	4.2	0.012	6.4
Oxazole sulfone	0.005	2.7	0.013	6.8	0.015	8.0
Polar fraction (origin)	0.001	0.5	0.001	0.5	0.001	0.5
Others	< 0.001	< 0.1	0.002	1.0	0.002	1.1
PBI 365 Days						
TRR	0.084	–	0.080 [a]	–	0.107	–
Imine sulfoxide	< 0.001	< 0.1	< 0.001	< 0.1	< 0.001	< 0.1
Oxazole sulfoxide	0.002	2.4	0.025	31	0.001	0.9
Oxazole sulfone	0.008	9.5	0.083	104	0.003	2.8
Polar fraction (origin)	< 0.001	< 0.1	0.003	3.8	< 0.001	< 0.1
Others	< 0.001	< 0.1	< 0.001	< 0.1	< 0.001	< 0.1

[a] Extract contained only 30% TRR/ 0.024 mg eq/kg. Metabolite concentrations appear to be unrealistic

NA: Not analysed

The radioactivity levels in the soil immediately after treatment with [Ring-4,6-^{14}C]-clethodim to bare soil were within the range 0.955-0.992 mg eq/kg. At planting, no clethodim was detected and identified soil metabolites (at planting) were imine sulfoxide, oxazole sulfoxide and oxazole sulfone. At planting, total radioactive residues in soil had decreased to 0.130-0.168 mg eq/kg (30 days), 0.185-0.192 mg eq/kg (120 days) and 0.080-0.107 mg eq/kg (366 days).

Table 28 Total radioactive residue (TRR) in rotational crops following a single treatment of [Ring-4,6-^{14}C]-clethodim at 1.1 kg ai/ha

Plant Part	TRR	Hexane extract		Dichloromethane extract		Water/methanol extract		Unextracted		Recovery
	mg eq/kg	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	%TRR
PBI 30 Days										
Carrot Leaf	0.342	0.001	0.3	0.094	27	0.061	18	0.063	18	64
Lettuce Leaf	0.084	0.002	2.4	0.045	54	0.021	25	0.014	17	102
Wheat Straw	0.478	0.001	0.2	0.090	19	0.170	36	0.206	43	98
Wheat Hull	0.304	< 0.001	0.0	0.067	22	0.080	26	0.196	64	100
PBI 120 Days										
Carrot Leaf	0.424	0.001	0.2	0.059	14	0.222	52	0.100	24	90
Wheat Straw	0.654	0.002	0.3	0.148	23	0.166	25	0.445	68	116
Wheat Hull	0.568	0.002	0.4	0.115	20	0.111	20	0.340	60	100
PBI 365 Days										
Carrot Leaf	0.053	0.001	1.9	0.018	34	0.035	66	0.013	25	126
Wheat Straw	0.418	0.001	0.2	0.111	27	0.154	37	0.274	66	129
Wheat Hull	0.364	0.001	0.3	0.080	22	0.123	34	0.165	45	101

Table 29 Identification of metabolites in dichloromethane extracts of rotational crops

	Carrot Leaf		Lettuce Leaf		Wheat Straw		Wheat Hulls	
	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
PBI 30 Days								
TRR (extract)	0.094	27	0.045	54	0.090	19	0.067	22
Imine sulfoxide	*0.034*	*9.9*	*0.016*	*19*	*0.018*	*3.8*	*0.023*	*7.6*
Oxazole sulfoxide	*0.011*	*3.2*	*0.003*	*3.6*	*0.017*	*3.6*	*0.012*	*3.9*
Oxazole sulfone	*0.006*	*1.8*	*0.006*	*7.1*	*0.016*	*3.3*	*0.024*	*7.9*
Polar material at origin	*0.004*	*1.2*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
Others	*0.021*	*6.1*	*0.006*	*7.1*	*< 0.001*	*< 0.1*	*0.012*	*3.9*
Recovery (TLC) [a]	0.076	81	0.031	69	0.051	57	0.071	106
PBI 120 Days								
TRR (extract)	0.059	14	–	–	0.148	23	0.115	20
Imine sulfoxide	*0.021*	*5.0*	–	–	*0.016*	*2.4*	*0.040*	*7.0*
Oxazole sulfoxide	*< 0.001*	*< 0.1*	–	–	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
Oxazole sulfone	*0.007*	*1.7*	–	–	*0.030*	*4.6*	*0.025*	*4.4*
Polar material at origin	*< 0.001*	*< 0.1*	–	–	*0.013*	*2.0*	*0.017*	*3.0*
Others	*< 0.001*	*< 0.1*	–	–	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
Recovery (TLC) [a]	0.028	47	–	–	0.059	40	0.082	71
PBI 366 Days								
TRR (extract)	0.018	34	–	–	0.111	27	0.080	22
Imine sulfoxide	*0.006*	*11*	–	–	*0.026*	*6.2*	*0.016*	*4.4*
Oxazole sulfoxide	*< 0.001*	*< 0.1*	–	–	*< 0.001*	*< 0.1*	*0.009*	*2.5*
Oxazole sulfone	*< 0.001*	*< 0.1*	–	–	*0.028*	*6.7*	*0.029*	*8.0*
Polar material at origin	*< 0.001*	*< 0.1*	–	–	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
Others	*< 0.001*	*< 0.1*	–	–	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
Recovery (TLC) [a]	0.006	33	–	–	0.054	49	0.054	68

[a] By TLC; (sum TLC fractions)/(total extract analysed) ×100

Table 30 Distribution of radioactivity in methanol/water fraction of rotational crop extracted after hydrolysis and partitioning

Plant Part	Water/methanol Fraction		Organic Phase (EtOAc)		Aqueous Phase	
	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR
PBI 30 Days						
Carrot leaf	0.061	18	0.048	14	0.038	11
Lettuce leaf	0.021	25	0.017	20	0.022	26
Wheat Straw	0.170	36	0.095	20	0.058	12
Wheat hulls	0.196	64	0.045	15	0.034	11
PBI 120 Days						
Carrot leaf	0.222	52	0.13	31	0.064	15
Wheat Straw	0.166	25	0.11	17	0.068	10

Total residues in mature rotational crops (carrot, lettuce and wheat) planted 30, 120 or 366 days after an application of [Ring-4,6-^{14}C]-clethodim to bare soil were < 0.05 mg eq/kg in carrot root and crown, lettuce leaf (120 and 366 days) and wheat grain. In carrot leaf, lettuce leaf (30 days) and wheat straw and hull the radioactive residue was in the range 0.053- 0.654 mg eq/kg.

Total extracts in mature carrot leaf were 45-102% TRR and unextracted residues were 18-25% of TRR. Total extracts in mature lettuce leaf were 81% TRR and unextracted residues were 17% TRR. Total extracts in wheat straw and hull were 40-64% TRR and unextracted residues were 43-68% TRR. No parent was detected in any of the analysed extracts. Small amounts of imine sulfoxide, oxazole sulfoxide and oxazole sulfone were detected. Other metabolite fractions were all <10% TRR and < 0.05 mg eq/kg.

Summary of metabolism in rotational crops

The metabolites in rotational crops, clethodim oxazole sulfoxide and clethodim oxazole sulfone were soil metabolites of clethodim. Their occurrence in rotational crops is due to the uptake by plant roots.

ANIMAL METABOLISM

The Meeting received studies on the metabolism of clethodim in lactating goat and laying hens. The metabolism of clethodim in laboratory animals (rats) was summarized and evaluated by the WHO Core Assessment Group of the 2019 JMPR.

Lactating goat

The metabolism, excretion and distribution profile of ^{14}C-clethodim were studied in the lactating goat (Rose and Suzuki, 1988: MEF-0038). A lactating goat received orally (by balling gun) daily at 1.16 mg/kg bw/day (equivalent to 24 ppm in alfalfa diet) [Propyl-1-^{14}C]-clethodim divided into three equal doses (14.2 mg/dose) for 3 days and one dose (14.2 mg) on the morning of the fourth day. A control goat received the same number of empty gelatin capsules. Body weights, food consumption and general health and behaviour were monitored and recorded throughout the test period. Weights and volumes of total production of milk (twice per day), urine and faeces (once per day) were recorded and aliquots of each removed for radiochemical analysis. The animals were sacrificed approximately 4 hours after the final dose. Hindquarter and forequarter muscle, peritoneal and subcutaneous fat, liver, kidneys, heart and blood were collected for metabolite characterization.

Urine and blood were not processed before analysis. Tissues and faeces were homogenised in a blender with dry ice. The radioactive residue in tissues, faeces and blood was determined by combustion/LSC. Radioactivity in urine was determined by LSC. The radioactive residue in milk was determined both by combustion/LSC and direct LSC.

Milk (all samples) was lyophilised and extracted with subsequently hexane (3×), acetonitrile (3×) and methanol (3×). The acetonitrile extracts were partitioned with the hexane extracts. The organic extracts were concentrated. The hexane and acetonitrile extracts were analysed by TLC with reference standards (quantification by LSC of spots scraped off the plate). The acetonitrile extract was also analysed by HPLC with references, both separately and after combination with the methanol extract. An attempt was made to extract clethodim from the hexane extract by partitioning with 1N NaOH. Additionally, an attempt was made to cleave clethodim fatty acid or triglyceride conjugates by dissolving the hexane extract in methanol and 1N NaOH (60 °C for 4 h). Unextracted radioactivity was quantified by combustion/LSC and the residue was suspended in water and 1N HCl (at room temperature, and after 2 h refluxing), followed by extraction with ethyl acetate. The amount of radioactivity present as casein in the solid residue was determined by precipitation of casein at pH 4.5 in the day 2 pm milk sample, followed by combustion of the precipitate. The presence of radioactive lactose was confirmed by isotopic dilution in aqueous suspensions of the unextracted residue of the day 2 pm and day 4 am milk samples.

Tissues and blood were extracted with acetone (3×) and methanol: water (1:1, v/v, 3×). The acetone extract was concentrated and partitioned between hexane and acetonitrile. Unextracted radioactivity was quantified by combustion/LSC. The methanol:water extract and the acetonitrile fraction were subjected to TLC. The hexane extracts were not further analysed. Additionally, an attempt was made to solubilize the liver unextracted residue by adding 50 mL 1N HCl (80 °C for 3 h), followed by centrifugation and combustion of the pellet.

Most of the total administered dose was found in the urine (56.4%) and faeces (34.4%). The total recovery of radioactivity was about 92%. The concentration of radioactivity in the milk reached a plateau of about 0.035 mg eq/L by day 2. The radioactivity in the blood (0.166 mg eq/L) was higher than found in muscle (forequarter: 0.033 mg eq/kg, hindquarter: 0.034 mg eq/kg) or fat (subcutaneous: 0.079 mg eq/kg, peritoneal: 0.047 mg eq/kg) and, therefore, there appears to be little potential for accumulation. Somewhat higher radioactivity was found in the liver (0.414 mg eq/kg) and kidney (0.378 mg eq/kg).

Table 31 Recovery of radioactivity in lactating goats following oral administration of [Propyl-1-^{14}C]-clethodim

Sample		% of administered dose (mg eq/kg)				
		Day 1	Day 2	Day 3	Day 4	Total
Urine		16.2 (12.4)	16.0 (9.28)	19.5 (9.86)	4.66 (16.1)	56.4
Faeces		7.98 (4.85)	9.48 (4.87)	11.4 (5.26)	5.52 (5.23)	34.4
Milk	am	< 0.01 (< 0.001)	0.02 (0.026)	0.02 (0.032)	0.03 (0.036)	0.14
	pm	0.01 (0.019)	0.02 (0.033)	0.02 (0.034)	0.01 (0.049)	
Liver		-	-	-	-	0.24 (0.414)
Kidney		-	-	-	-	0.04 (0.378)
Muscle, hindquarter		-	-	-	-	0.03 (0.034)
Muscle, forequarter		-	-	-	-	0.02 (0.033)
Fat, subcutaneous		-	-	-	-	0.02 (0.079)
Fat, peritoneal		-	-	-	-	0.02 (0.047)
Heart		-	-	-	-	0.01 (0.058)
Blood		-	-	-	-	0.22 (0.166)
Total		-	-	-	-	91.5

Table 32 Distribution of radioactivity in milk of lactating goats

Day	Extracted						Unextracted		Total	
	Hexane		Acetonitrile		Methanol					
	mg eq/L	% TRR	mg eq/L	% TRR	mg eq/L	% TRR	mg eq/L	% TRR	mg eq/L	%TRR
1 am[a]	-	-	-	-	-	-	-	-	-	-
1 pm	< 0.001	2.7	0.002	9.7	0.004	19.8	0.012	65.7	0.019	97.8
2 am	0.001	4.0	0.006	23.0	0.003	12.2	0.014	54.1	0.024	93.3
2 pm	0.003	9.1	0.009	26.2	0.007	19.7	0.014	42.0	0.032	97.0
3 am	0.002	6.9	0.008	24.9	0.006	18.1	0.014	44.4	0.030	94.2
3 pm	0.004	12.4	0.009	26.6	0.004	10.4	0.017	49.4	0.034	98.7
4 am	0.002	6.5	0.011	31.6	0.003	8.6	0.016	43.4	0.032	90.0
4 sacrifice	0.005	10.3	0.012	23.7	0.013	27.1	0.015	29.8	0.045	91.0

[a] Before first dosing

Table 33 Identification of radioactivity in milk of lactating goats

Day	Clethodim		Clethodim sulfoxide		S-methyl sulfoxide		Lactose		Total	
	mg eq/L	% TRR	mg eq/L	% TRR	mg eq/L	% TRR	mg eq/L	% TRR	mg eq/L	%TRR
1 am[a]	-	-	-	-	-	-	-	-	-	-
1 pm	< 0.001	< 0.1	0.006	29.4	< 0.001	< 0.1	< 0.001	< 0.1	0.006	29.4
2 am	< 0.001	< 0.1	0.005	19.2	0.002	6.9	0.014	54.1	0.021	80.2
2 pm	< 0.001	< 0.1	0.007	20.2	0.002	5.5	0.014	42.0	0.023	67.7
3 am	< 0.001	< 0.1	0.006	18.0	< 0.001	< 0.1	0.014	44.4	0.020	62.4
3 pm	< 0.001	< 0.1	0.005	14.7	0.001	4.3	0.017	49.4	0.023	68.4
4 am	0.001	3.3	0.006	17.7	0.002	5.7	0.016	43.4	0.025	70.1
4 sacrifice	< 0.001	< 0.1	0.013	27.0	0.005	11.1	0.015	29.8	0.033	67.9

[a] Before first dosing

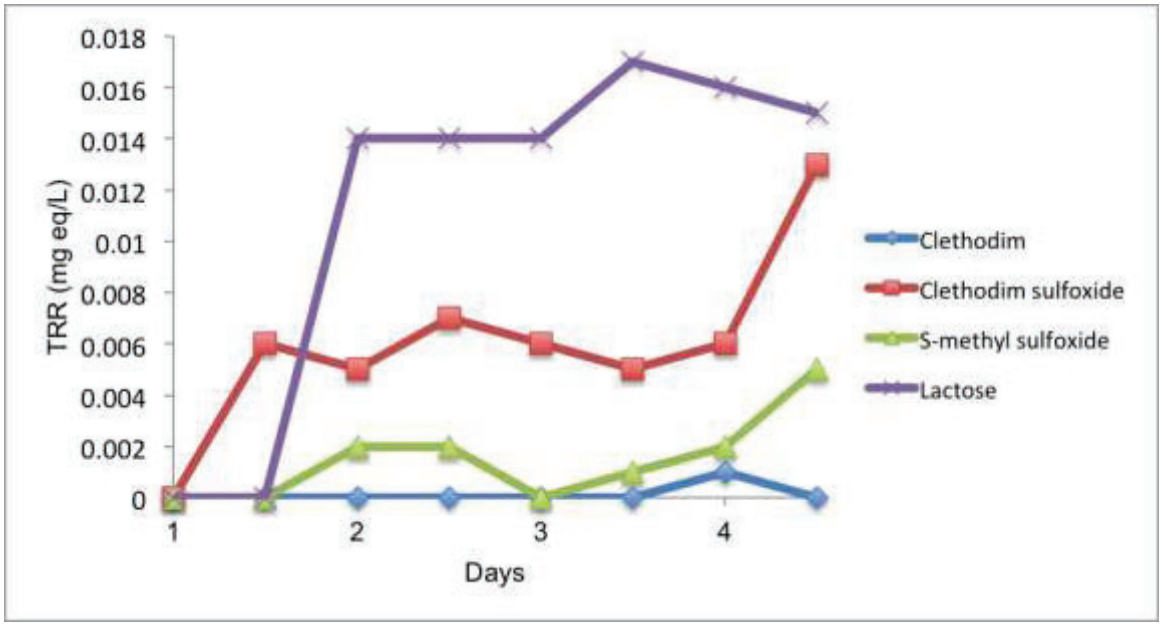


Figure 5 Residues in milk following dosing with [Propyl-1-^{14}C]-clethodim

Milk samples were lyophilised and extracted with organic solvents of increasing polarity. Most of extracted radioactive residue was found in acetonitrile (10-32%) and methanol (9-27%). Metabolites in these extracts were identified as clethodim sulfoxide (0.005-0.013 mg eq/L), S-methyl sulfoxide (0.001-0.005 mg eq/L) and clethodim (≤ 0.001 mg eq/L). Some solvent-front-eluting material was observed in the HPLC analysis. This is most likely ^{14}C-lactose extracted from the PES by methanol. Most of the milk radioactivity was not extracted by organic solvents and remained in the PES. All of the PES radioactivity was soluble in water and was identified as lactose.

Table 34 Summary of radioactive residues in tissues and blood of lactating goats

	Liver		Kidney		Muscle, hindquarter		Muscle, forequarter	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Extract	0.320	77.2	0.344	90.8	0.032	92.5	0.030	90.1
Acetone → Hexane	0.007	1.6	0.004	1.1	< 0.001	0.7	< 0.001	1.4
→ Acetonitrile	0.256	61.8	0.304	80.4	0.028	81.0	0.026	80.1
Methanol/water	0.057	13.8	0.035	9.3	0.004	10.8	0.003	8.6
Unextracted	0.064	15.5	0.025	6.7	0.002	6.8	0.003	8.1
TRR	0.384	92.7	0.369	97.5	0.034	99.3	0.033	98.2
Identified	0.295	71.2	0.276	73.1	0.025	73.1	0.026	80.1
Clethodim	*0.114*	*27.6*	*0.005*	*1.3*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
Clethodim sulfoxide	*0.137*	*33.2*	*0.139*	*36.9*	*0.014*	*40.7*	*0.017*	*51.6*
Clethodim sulfone	*0.013*	*3.2*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
S-methyl sulfoxide	*0.025*	*6.2*	*0.116*	*30.8*	*0.011*	*32.4*	*0.009*	*28.5*
Imine sulfoxide	*0.006*	*1.5*	*0.016*	*4.1*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
5-OH sulfone	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*	*< 0.001*	*< 0.1*
Unidentified	0.016	4.0	0.037	9.8	< 0.001	< 0.1	0.003	7.9
	Heart		Blood		Fat, subcutaneous		Fat, peritoneal	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Extract	0.054	92.0	0.158	93.3	0.075	95.4	< 0.001	2.4
Acetone → Hexane	0.006	10.1	0.002	1.1	0.003	3.6	< 0.001	0.6
→ Acetonitrile	0.044	76.6	0.145	85.7	0.064	81.1	< 0.001	0.2
Methanol/water	0.003	5.3	0.011	6.5	0.008	10.7	< 0.001	1.6
Unextracted	0.003	6.0	0.008	4.6	0.003	3.5	< 0.001	1.5
TRR	0.057	98.0	0.164	97.9	0.078	98.4	0.002	3.9
Identified	0.046	80.4	0.148	89.0	0.066	83.7	-	-
Clethodim	*< 0.001*	*< 0.1*	*0.047*	*28.0*	*0.002*	*2.8*	-	-
Clethodim sulfoxide	*0.025*	*43.2*	*0.067*	*39.9*	*0.037*	*47.2*	-	-
Clethodim sulfone	*< 0.001*	*< 0.1*	*0.006*	*3.8*	*< 0.001*	*< 0.1*	-	-

	Liver		Kidney		Muscle, hindquarter		Muscle, forequarter	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
S-methyl sulfoxide	*0.021*	*37.2*	*0.019*	*11.6*	*0.023*	*29.0*	-	-
Imine sulfoxide	*< 0.001*	*< 0.1*	*0.005*	*3.0*	*0.004*	*4.7*	-	-
5-OH sulfone	*< 0.001*	*< 0.1*	*0.004*	*2.7*	*< 0.001*	*< 0.1*	-	-
Unidentified	< 0.001	< 0.1	0.005	3.2	0.006	8.1	-	-

The highest tissue radioactive residue was found in liver (0.414 mg eq/kg). Most (77.2% TRR) of it was extracted with organic solvents. Liver metabolites were clethodim sulfoxide (0.137 mg eq/kg, 33.2% TRR), clethodim (0.114 mg eq/kg, 27.6% TRR), S-methyl sulfoxide (0.025 mg eq/kg, 6.2% TRR), clethodim sulfone (0.013 mg eq/kg, 3.2% TRR), and imine sulfoxide (0.006 mg eq/kg, 1.5% TRR). The highest concentration of unextracted residue was that of liver (15.5% TRR).

Most (90.8% TRR) of radioactive residue in kidney (0.378 mg eq/kg) was extracted into organic solvents. Kidney metabolites were clethodim sulfoxide (0.139 mg eq/kg, 36.9% TRR), S-methyl sulfoxide (0.116 mg eq/kg, 30.8% TRR), imine sulfoxide (0.016 mg eq/kg, 4.1% TRR), and clethodim (0.005 mg eq/kg, 1.3% TRR). Some (9.8% TRR) of the extracted radioactivity was unidentified. It was polar and remained at the origin (TLC) or in the void volume (HPLC).

Forequarter and hindquarter muscle had approximately equivalent (0.033 mg eq/kg) concentration of radioactivity. Likewise, the extraction and distribution of radioactivity was nearly identical for both tissues. Very little (< 9% TRR) of the total radioactivity was not extracted. Clethodim sulfoxide (0.014-0.017 mg eq/kg, 40.7-51.6% TRR) and S-methyl sulfoxide (0.009-0.011 mg eq/kg, 28.5-32.4% TRR) were metabolites in both muscles.

Combustion analysis of fat samples indicated higher radioactive concentrations in subcutaneous fat (0.079 mg eq/kg) relative to peritoneal fat (0.047 mg eq/kg). When peritoneal fat was extracted with organic solvents, virtually no radioactivity was found in them or in the resulting unextracted residue. By contrast, the ^{14}C accountability for the subcutaneous fat was very high (98.4% TRR). This anomalous disappearance of radioactivity remains unexplained. The metabolites identified were clethodim sulfoxide (0.037 mg eq/kg, 47.2% TRR), S-methyl sulfoxide (0.023 mg eq/kg, 29.0% TRR), imine sulfoxide (0.004 mg eq/kg, 4.7% TRR) and clethodim (0.002 mg eq/kg, 2.8% TRR).

The terminal residues found in plant metabolism studies were free and conjugated sulfoxides and sulfones. No clethodim-related sulphides were observed. Because S-methyl compounds are biosynthesised only from clethodim (or related sulphides) and no sulphides are present in plant terminal residues, it is extremely unlikely that animals would be exposed to them in feedstuff. S-methyl compounds were not observed as plant metabolites. S-methyl metabolites have significance only when parent clethodim is fed to animals.

Laying hens

A poultry metabolism study was conducted with [Ring-4,6-^{14}C]-clethodim (Lee, 1988: MEF-0089). Eight laying hens (white leghorn) received daily oral doses (directly in the proventriculus) of [^{14}C]-clethodim, contained in gelatin capsules for 5 consecutive days at a rate of 27 ppm diet as received (2.1 mg/kg bw per day). Another eight hens were treated identically, but received a higher dose (707 ppm diet as received, 51.3 mg/kg bw per day) to facilitate identification of unknown metabolites. Twelve control hens were included in the study.

Eggs were collected twice daily and separated into white, yolk and shell. Excreta were collected once daily commencing the day before treatment. The hens were sacrificed approximately 4 h after administration of the last dose. Tissues were collected from each hen and frozen at -20 °C. Tissues collected included thigh and breast muscles, abdominal fat, gizzard, liver, kidney, heart, skin, gastrointestinal tract with contents and reproductive organs.

Tissues, eggs and excreta samples were homogenised in a blender with dry ice. The radioactive residue was determined by combustion/LSC.

Liver, kidney, heart, gizzard, thigh and breast muscles and excreta were extracted with methanol (2×) followed by methanol:water (7:3, 2×). Skin, fat and egg yolks were extracted with acetone (2×) and then methanol:water (1:1, 2×). The extracts were combined and evaporated to near dryness, followed by partitioning between hexane and acetonitrile. The acetonitrile fraction was concentrated and analysed by TLC (quantitation by LSC of spots scraped off the plate) and/or HPLC. Egg whites were lyophilised followed by extraction with methanol (2×). The combined extracts were concentrated and subjected to TLC and/or HPLC. Radioactivity in the post-extraction residue was determined by combustion/LSC.

Unextracted residues of kidney and liver (> 0.05 mg eq/kg) were refluxed with 1N HCl (2 h), followed by refluxing with 20% NaOH (16 h). Both acid and base hydrolysates were saturated with ammonium sulfate and extracted with dichloromethane.

After five daily dose administrations of [Ring-4,6-^{14}C]-clethodim at 2.1 mg/kg bw/day, 78% of the total dose had been recovered in excreta. The total recovery (tissues, eggs, excreta) was 80% (tissues 1.9% and eggs 0.1%).

Radioactive residues in tissues were highest in kidney (1.2 mg eq/kg) and liver (0.7 mg eq/kg), and in the GI tract (2.8 mg eq/kg). Residue levels in skin, heart, fat, reproductive organs, gizzard, thigh muscle and breast muscle were all within the range 0.1-0.3 mg eq/kg. Residue levels in eggs were ≤ 0.22 mg eq/kg (maximum at day 4 in egg white). Radioactivity levels in egg yolk and egg white did not reach a plateau within the 4-day study period.

Table 35 Recovery of radioactivity in laying hens following oral administration of [Ring-4,6-^{14}C]-clethodim

Sample	% of administered dose[a] (mg eq/kg) [2.1 mg/kg bw]					
	Day 0[b]	Day 1[b]	Day 2[b]	Day 3[b]	Day 4[b]	Total
Excreta	13 (19.4)	14 (14.3)	17 (12.1)	17 (11.8)	18 (15.6)	78
Egg yolk	< 0.01 (0.01)	< 0.01 (0.02)	< 0.01 (0.04)	< 0.01 (0.05)	< 0.01 (0.07)	0.1
Egg white	< 0.01 (0.03)	0.01 (0.15)	0.02 (0.20)	0.02 (0.19)	0.02 (0.22)	
Egg shell	< 0.01 (0.01)	< 0.01 (0.06)	< 0.01 (0.09)	< 0.01 (0.08)	< 0.01 (0.10)	
Liver	-	-	-	-	-	0.16 (0.7)
Kidney	-	-	-	-	-	0.04 (1.2)
Muscle, thigh	-	-	-	-	-	0.01 (0.2)
Muscle, breast	-	-	-	-	-	0.02 (0.1)
Fat	-	-	-	-	-	0.02 (0.3)
Skin	-	-	-	-	-	0.01 (0.3)
Heart	-	-	-	-	-	0.01 (0.3)
Reproductive organs	-	-	-	-	-	0.08 (0.2)
Gizzard	-	-	-	-	-	0.02 (0.2)
GI tract	-	-	-	-	-	1.5 (2.8)
Total	-	-	-	-	-	80
Sample	% of administered dose[a] (mg eq/kg) [51.3 mg/kg bw]					
	Day 0[b]	Day 1[b]	Day 2[b]	Day 3[b]	Day 4[b]	Total
Excreta	12 (408.7)	14 (274.9)	21 (371.2)	18 (267.5)	20 (342.1)	85
Egg yolk	< 0.01 (0.05)	< 0.01 (0.77)	0.01 (1.38)	0.01 (1.97)	0.01 (2.51)	0.3
Egg white	< 0.01 (1.10)	0.04 (5.88)	0.08 (9.45)	0.07 (7.67)	0.06 (8.82)	
Egg shell	< 0.01 (0.35)	0.01 (2.59)	0.01 (4.28)	0.01 (3.40)	0.01 (3.51)	
Liver	-	-	-	-	-	0.02 (16.2)
Kidney	-	-	-	-	-	0.1 (25.9)
Muscle, thigh	-	-	-	-	-	0.02 (5.1)
Muscle, breast	-	-	-	-	-	0.05 (4.5)
Fat	-	-	-	-	-	0.02 (4.8)
Skin	-	-	-	-	-	0.01 (6.2)
Heart	-	-	-	-	-	0.02 (9.4)
Reproductive organs	-	-	-	-	-	0.2 (8.2)
Gizzard	-	-	-	-	-	0.1 (6.8)
GI tract	-	-	-	-	-	3.6 (98.2)
Total	-	-	-	-	-	89

[a] Calculated from total radioactive residue in mg eq/kg, total % of dose in tissues/eggs/excreta and total tissue/egg/excreta weight

[b] Means values for composite sample per day calculated in a mass weighted average for am and pm samples.

Table 36 Summary of radioactive residues in tissues and egg of laying hens following oral administration of [Ring-4,6-^{14}C]- clethodim at 2.1 mg/kg bw per day

	Liver		Kidney		Muscle, thigh		Muscle, breast		Fat	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Extract	0.57	83.6	1.15	96.2	0.14	88.1	0.08	87.9	0.3	100.9
Acetonitrile	0.57	83.6	1.13	94.5	0.14	87.0	0.03	87.8	0.3	100.2
Clethodim	*0.05*	*7.5*	*0.03*	*2.7*	*ND*	*2.4*	*ND*	*4.1*	*0.20*	*64.9*
Clethodim sulfoxide	*0.22*	*33.2*	*0.51*	*42.5*	*0.10*	*50.5*	*0.04*	*36.8*	*0.04*	*14.5*
Clethodim sulfone	*0.15*	*21.1*	*0.33*	*27.8*	*0.05*	*26.7*	*0.03*	*31.2*	*0.03*	*10.2*
Unidentified	*0.08*	*10.9*	*0.06*	*4.7*	*ND*	*ND*	*0.01*	*11.0*	*0.01*	*4.6*
Origin	*0.02*	*2.3*	*0.06*	*5.4*	*0.02*	*9.1*	*ND*	*1.4*	*0.01*	*2.5*
Hexane	ND	ND	0.02	1.7	ND	1.1	ND	0.1	ND	0.7
Unextracted	0.11	17.0	0.14	11.4	ND	7.4	ND	10.6	ND	1.6
TRR	0.68	100.6	1.29	107.6	0.14	95.4	0.1	98.5	0.3	102.5
	Skin		Heart		Gizzard		Egg yolk[a]		Egg white[a]	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Extract	0.28	85.4	0.24	83.7	0.19	113.0	0.03	97.0	0.16	96.3
Acetonitrile	0.28	83.8	0.23	80.6	0.19	111.5	0.03	97.0	0.16	96.3
Clethodim	*0.01*	*4.6*	*0.01*	*1.6*	*0.03*	*1.3*	-	-	-	-
Clethodim sulfoxide	*0.17*	*56.9*	*0.14*	*48.0*	*0.09*	*44.8*	-	-	-	-
Clethodim sulfone	*0.05*	*16.7*	*0.06*	*21.6*	*0.04*	*21.3*	-	-	-	-
Unidentified	*0.02*	*7.2*	*0.02*	*8.2*	*0.01*	*6.2*	-	-	-	-
Origin	*0.02*	*5.9*	*0.07*	*2.5*	*0.01*	*2.7*	-	-	-	-
Hexane	ND	1.6	0.01	3.1	ND	1.5	ND	ND	ND	ND
Unextracted	0.02	6.2	0.04	13.5	0.02	11.9	0.01	14.1	0.01	4.8
TRR	0.30	91.6	0.28	97.2	0.21	124.9	0.04	111.1	0.17	101.1

[a] Mean values for the total sample collected over 5 days

Table 37 Extraction and identification of radioactivity in eggs following oral administration of [Ring-4,6-^{14}C]- clethodim at 2.1 mg/kg bw per day

	Day 0		Day 1		Day 2		Day 3		Day 4	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
	Egg yolk									
Clethodim	*-[a]*	-	*0.01*	*34.4*	*0.01*	*18.8*	*0.01*	*24.2*	*0.01*	*16.5*
Clethodim sulfoxide	-	-	*0.01*	*36.9*	*0.01*	*31.7*	*0.01*	*25.1*	*0.02*	*36.7*
Clethodim sulfone	-	-	*0.02*	*10.6*	*0.01*	*26.7*	*ND*	*10.8*	*0.01*	*14.6*
Unidentified	-	-	*ND*	*7.2*	*ND*	*4.7*	*0.01*	*18.2*	*ND*	*< 0.1*
Origin	-	-	*ND*	*< 0.1*	*ND*	*1.3*	*ND*	*1.7*	*ND*	*3.2*
	Egg white									
Clethodim	*ND*	*2.3*	*0.01*	*5.7*	*0.01*	*6.3*	*0.01*	*6.4*	*0.01*	*4.7*
Clethodim sulfoxide	*0.02*	*82.2*	*0.09*	*38.7*	*0.09*	*45.8*	*0.05*	*25.9*	*0.06*	*25.8*
Clethodim sulfone	*ND*	*11.2*	*0.06*	*37.1*	*0.07*	*34.2*	*0.07*	*38.2*	*0.03*	*14.8*
Unidentified	*ND*	*ND*	*0.02*	*10.3*	*0.02*	*7.7*	*0.04*	*22.6*	*0.05*	*24.4*
Origin	*ND*	*1.9*	*0.01*	*5.2*	*ND*	*1.6*	*ND*	*1.8*	*0.01*	*3.4*

[a] Insufficient for metabolite identification

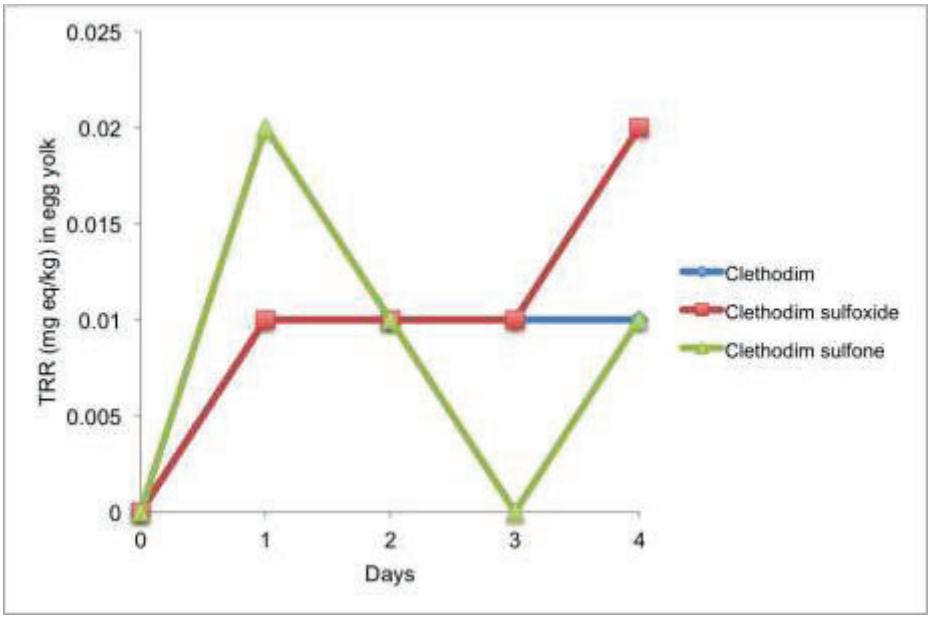


Figure 6a Residues in egg yolk following dosing with [Ring-4,6-^{14}C]-clethodim at 2.1 mg/kg bw per day

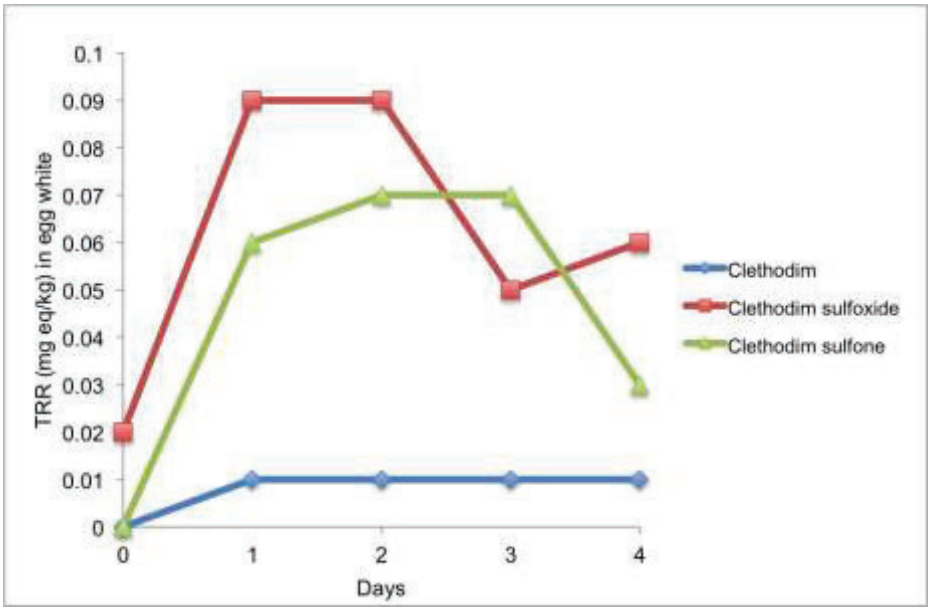


Figure 6b Residues in egg white following dosing with [Ring-4,6-^{14}C]-clethodim at 2.1 mg/kg bw per day

Table 38 Extraction and identification of radioactivity in tissues following oral administration of [Ring-4,6-^{14}C]- clethodim at 51.3 mg/kg bw per day

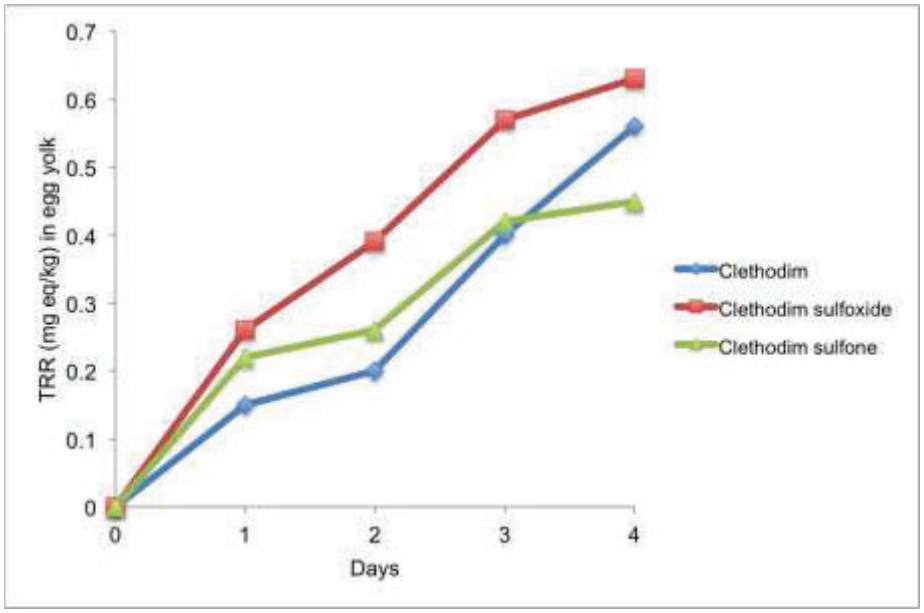
	Liver		Kidney		Muscle, thigh		Muscle, breast	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Clethodim	*0.41*	*2.5*	*1.18*	*4.6*	*0.03*	*0.5*	*0.05*	*1.2*
Clethodim sulfoxide	*5.00*	*30.9*	*10.2*	*39.5*	*2.22*	*43.5*	*2.13*	*47.3*
Clethodim sulfone	*4.34*	*26.8*	*6.49*	*25.1*	*1.69*	*33.2*	*1.51*	*33.6*
Unidentified	*2.17*	*12.1*	*2.91*	*11.3*	*0.77*	*15.2*	*0.17*	*3.8*
Origin	*0.28*	*1.8*	*0.86*	*3.3*	*0.07*	*1.4*	*0.02*	*0.5*
	Fat		Skin		Heart		Gizzard	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR

	Liver		Kidney		Muscle, thigh		Muscle, breast	
Clethodim	*1.61*	*33.5*	*0.20*	*6.3*	*0.05*	*0.5*	*0.40*	*5.8*
Clethodim sulfoxide	*1.98*	*41.3*	*2.95*	*47.5*	*3.50*	*37.3*	*2.60*	*30.3*
Clethodim sulfone	*0.75*	*15.7*	*1.72*	*27.8*	*2.62*	*27.9*	*2.26*	*33.2*
Unidentified	*0.24*	*5.0*	*0.62*	*10.1*	*1.10*	*11.8*	*0.62*	*9.0*
Origin	*0.08*	*1.8*	*0.06*	*1.0*	*0.26*	*2.8*	*0.09*	*1.4*

Table 39 Extraction and identification of radioactivity in eggs following oral administration of [Ring-4,6-^{14}C]- clethodim at 51.3 mg/kg bw per day

	Day 0		Day 1		Day 2		Day 3		Day 4	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
	Egg yolk									
Clethodim	[a]	-	*0.15*	*19.7*	*0.20*	*14.8*	*0.40*	*20.2*	*0.56*	*22.4*
Clethodim sulfoxide	-	-	*0.26*	*33.9*	*0.39*	*28.2*	*0.57*	*29.0*	*0.63*	*25.0*
Clethodim sulfone	-	-	*0.22*	*29.1*	*0.26*	*18.7*	*0.42*	*21.3*	*0.45*	*17.8*
Unidentified	-	-	*0.03*	*3.4*	*0.27*	*19.8*	*0.08*	*4.4*	*0.16*	*6.1*
Origin	-	-	*0.01*	*0.9*	*0.03*	*2.4*	*0.04*	*2.2*	*0.04*	*1.5*
	Egg white									
Clethodim	*0.05*	*5.9*	*0.83*	*10.1*	*0.43*	*4.5*	*0.39*	*5.1*	*0.37*	*4.2*
Clethodim sulfoxide	*0.58*	*65.9*	*3.68*	*44.7*	*4.48*	*47.2*	*3.42*	*44.6*	*3.47*	*39.4*
Clethodim sulfone	*0.09*	*9.9*	*2.18*	*26.6*	*3.44*	*36.3*	*1.42*	*18.5*	*0.94*	*10.7*
Unidentified	*0.11*	*12.4*	*0.80*	*9.7*	*0.30*	*3.1*	*2.86*	*26.6*	*3.35*	*38.0*
Origin	*0.04*	*4.3*	*0.10*	*1.2*	*0.16*	*1.7*	*0.10*	*1.2*	*0.22*	*2.6*

[a] Insufficient for metabolite identification



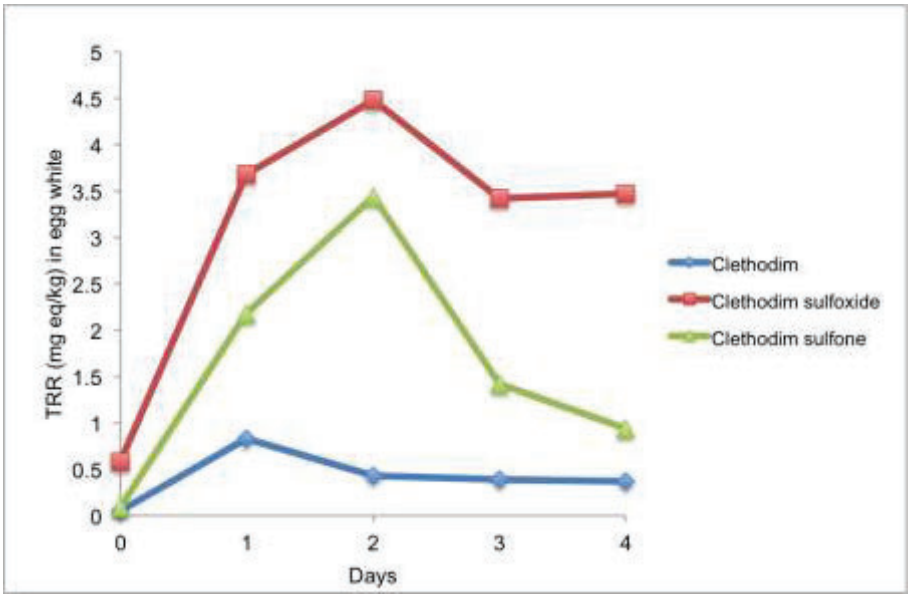


Figure 7 Residues in egg yolk and white following dosing with [Ring-4,6-^{14}C]-clethodim at 51.3 mg/kg bw per day

In kidney, liver, skin, heart, gizzard, breast and thigh muscle, major (> 10% TRR) identified metabolites were clethodim sulfoxide (30.3–56.9% TRR) and clethodim sulfone (15.7–33.6% TRR). Clethodim was also detected (0.5–7.5% TRR). No other metabolites were identified. Unextracted residues represented 6.2–17.0% TRR.

After refluxing the solid residue of kidney and liver after extraction with 1 N HCl and 20% NaOH, < 2 0% was extracted with dichloromethane, indicating that few conjugates had been hydrolysed. It was assumed that the radioactive carbon in the solid residue had been incorporated into natural tissue components.

In fat, major (> 10% TRR) components were clethodim (33.5–64.9% TRR), clethodim sulfoxide (14.5–41.3% TRR) and clethodim sulfone (10.2–15.7% TRR). No other metabolites were identified. Unextracted residue was 1.6% TRR.

The egg white extract contained maximum 10.1% TRR clethodim. Major (> 10% TRR) identified metabolites in egg white were clethodim sulfoxide (25.8–82.2% TRR) and clethodim sulfone (9.9–38.2% TRR). Unextracted residue represented 4.8% TRR on average. In egg yolk, major (> 10% TRR) identified components were clethodim (14.8–34.4% TRR), clethodim sulfoxide (25.0–36.9% TRR) and clethodim sulfone (10.6–29.1% TRR). Unextracted residue represented 14.1% TRR on average.

Summary of animal metabolism

In goat study, clethodim is oxidized to clethodim sulfoxide (major) and further to clethodim sulfone. Clethodim is also converted to the *S*-methyl analogue via a sulfonium cation intermediate and then either converted to imine or hydroxylated at the 5 position. The proposed *S*-methyl-clethodim would follow the dominant metabolic process and form the observed *S*-methyl sulfoxide and smaller amounts of *S*-methyl sulfone. Similarly, the imine would rapidly be oxidized to imine sulfoxide and imine sulfone. Any 5-hydroxy-clethodim formed (not detected) would be rapidly oxidized to the observed 5-hydroxy sulfoxide and sulfone.

In the hen study, the metabolic pathway was simpler than that observed in goat. None of the imine analogues, 5-hydroxy analogues or *S*-methyl analogues identified in goat were found in the hen.

A special case can be seen for the *S*-methyl analogues. S-methyl clethodim is directly formed from parent clethodim and then oxidized to S-methyl sulfoxide. Therefore, parent clethodim needs to

be present in the feed as a precursor to build these compounds. As it is highly unlikely that parent clethodim is present in the feed, the *S*-methyl analogues cannot be formed in the animal and are therefore not expected in edible animal products.

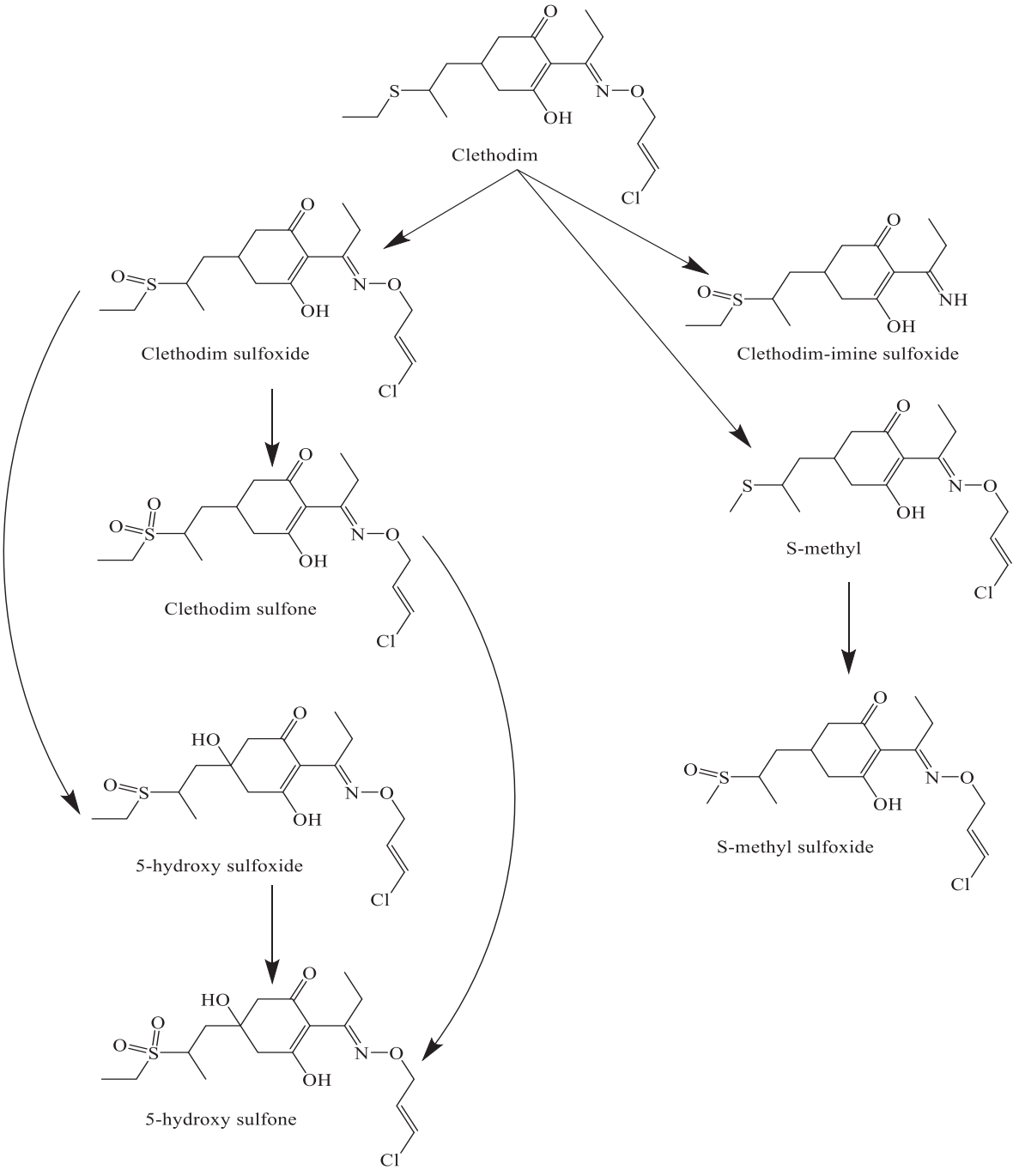


Figure 8 Metabolic pathway of clethodim in animals

METHODS OF RESIDUE ANALYSIS

Analytical methods

Descriptions of analytical methods together with validation data for residues of clethodim and its metabolites in plant and animal matrices were submitted to the Meeting. There are two types of methods of plant matrices, one is a common moiety method and the other is a specific individual method. The common moiety methods of plant matrices rely on an initial extraction, usually with methanol/water. After alkaline precipitation, oxidation and methylation into common moiety DME or

DME-OH, they are prepared for GC analysis. Their residues can be measured by flame photometric detector (FPD) in sulfur mode. The specific individual method relies on an initial extraction with methanol/water and then clethodim and its metabolites are prepared for LC analysis. Their residues can be measured by mass spectrometric detector (MS/MS), to an LOQ of 0.005 mg/kg. Since the methods use standard extraction solvents and standard detection techniques, they have the potential to be incorporated into existing multi-residue methods.

Detailed descriptions of all these analytical methods are presented below.

Plant matrices

Rape seed (EDB.896/Report 170D, 170U, 170V)

Analyte:	Metabolites that were degraded by oxidative decomposition into the common moiety "3-[2-(ethyl-sulfonyl) propyl]- pentanedioic acid, dimethyl ester" (also called DME) and metabolites that were degraded into the common moiety 3-[2-(ethylsulfonyl) propyl]-3-hydroxy-pentanedioic acid, dimethyl ester" (also called DME-OH)	GC-FPD	PAM II. Sec. 180.412
LOQ:	0.05 mg/kg (expressed as clethodim equivalents)		
Description	Samples were extracted with methanol and water and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned with dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in concentrated hydrochloric acid and anhydrous methanol (methylation step) and partitioned into dichloromethane. If necessary, silica gel column clean-up was carried out. Residues of DME and DME-OH were determined by GC using a flame photometric detector (GC-FPD) in sulfur mode.		

Sugar beet (TSR 5068 SGBT)

Analyte:	Metabolites that were degraded into DME and metabolites that were degraded into DME-OH	GC-FPD	RM-26B-1
LOQ:	Metabolites that were converted into the DME moiety: 0.2 mg/kg Metabolites that were converted into the DME-OH moiety: 0.2 mg/kg (expressed as clethodim equivalents)		
Description	Samples were extracted with methanol (and water only for soapstock) and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned into dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in concentrated hydrochloric acid and anhydrous methanol (methylation step) and partitioned into dichloromethane. Silica gel column clean-up and C18-SPE clean-up is optional. Residues of DME and DME-OH were determined by GC-FPD in sulfur mode. Note: This method version is developed to include all metabolites that can be converted into the S-methyl-DME moiety for analysis in animal commodities.		

Cabbage (223/AU/94/100/SV01), Rape seed (EDB.896/Report 170E, 170F, 170G), Cranberry (IR-4 PR No.05358), Strawberry (IR-4 PR No.05230), Broccoli (IR-4 PR No.05215), Cucumber (IR-4 PR No.05219), Carrot (IR-4 PR No.05217)

Analyte:	Metabolites that were degraded into DME and metabolites that were degraded into DME-OH	GC-FPD	RM-26A-1 RM-26B-2
LOQ:	Metabolites that were converted into the DME moiety: 0.05 mg/kg Metabolites that were converted into the DME-OH moiety: 0.05 mg/kg (expressed as clethodim equivalents)		

Description Samples were extracted with methanol and/or water and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned with dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in concentrated hydrochloric acid and anhydrous methanol (methylation step) and partitioned into dichloromethane. If necessary, silica gel column clean-up and C18-SPE clean-up was carried out. Residues of DME and DME-OH were determined by GC-FPD in sulfur mode.
For cabbage, the GC-FPD determination was exchanged for a GC-MS determination.

Tomato, Soya bean, Soya bean oil, Sugar beet roots and Sugar beet top (ML01-0941-TOM), Pear (IR-4 PR No.06874), Cherry (IR-4 PR No.06877), Peach (IR-4 PR No.06875), Plum (IR-4 PR No.06948), Lettuce (IR-4 PR No.07694)

Analyte:	Metabolites that were degraded into DME and metabolites that were degraded into DME-OH	GC-FPD, GC-MS	RM-26B-3
LOQ:	Metabolites that were converted into the DME moiety: 0.095 mg/kg Metabolites that were converted into the DME-OH moiety: 0.088 mg/kg (expressed as clethodim equivalents)		

Description This method modified RM-26B-2 for measurement parameters, calculation procedures and the optional silica gel column cleanup procedure.
Samples were extracted with methanol and/or water (oils were extracted with hexane-saturated acetonitrile) and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned with dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in concentrated hydrochloric acid and anhydrous methanol (methylation step) and partitioned into dichloromethane. If necessary, silica gel column clean-up was carried out. Residues of DME and DME-OH were determined by GC-FPD in sulfur mode.
For cherry and plum, the GC-FPD determination was exchanged for a GC-MS determination.
For lettuce, silica gel column clean-up was exchanged for a C18-SPE clean-up

Hops (IR-4 PR No.A8086)

Analyte:	Metabolites that were degraded by oxidative decomposition into clethodim sulfone (m/z 392→300 for quantification) and metabolites that were degraded into 5-OH clethodim sulfone (m/z 408→204 for quantification)	LC-MS/MS	RM-26B-3 for hops
LOQ:	0.10 mg/kg for both analytes		

Description Samples were extracted with methanol and cleaned up by HAX solid phase extraction. After addition of NaCl saturated water, the extracts were partitioned with dichloromethane. The concentrated residue was oxidized to form clethodim sulfone and 5-OH clethodim sulfone with m-chloroperoxybenzoic acid and the sulfones were partitioned into dichloromethane. After a Cucarb SPE clean-up was carried out, residues of the sulfones were determined by LC-MS/MS. (The methylation was omitted.)

Rape seed (V-23595)

Analyte:	Metabolites that were degraded into DME and metabolites that were degraded into DME-OH	GC-FPD, GC-MS	RM-26B-4
LOQ:	Metabolites that were converted into the DME moiety: 0.10 mg/kg Metabolites that were converted into the DME-OH moiety: 0.10 mg/kg (expressed as clethodim equivalents)		

Description This method modified RM-26B-3 to shorten the initial extraction process and change determination method to improve method recoveries for rape seed matrices.
Samples were extracted with methanol/water (4/1, v/v) (oils were extracted with acetonitrile) and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned with dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in concentrated hydrochloric acid and methanol (methylation step) and partitioned into dichloromethane. After a Silica SPE clean-up was carried out, residues of DME and DME-OH were determined by GC-MS.

Apple (IR-4 PR No.06873), Blueberry (IR-4 PR No.05234), Artichoke (IR-4 PR No.09013)

Analyte:	Metabolites that were degraded into DME and metabolites that were degraded into DME-OH	GC-FPD	CAL Vers. 15
LOQ:	Metabolites that were converted into the DME moiety: 0.095 mg/kg Metabolites that were converted into the DME-OH moiety: 0.088 mg/kg (expressed as clethodim equivalents)		
Description	This method was adapted with minor modification from RM-26B-3. Samples were extracted with methanol and/or water and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned with dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in acidic methanol (methylation step) and partitioned into dichloromethane. Residues of DME and DME-OH were determined by GC-FPD in sulfur mode.		

Sugar beet (roots), Sugar beet (leaves), Soya bean, Proteaginous peas (RCC 855262), Wheat, Grapes (IF-11/02129995)

Analyte:	Clethodim (m/z 360→164 for quantification, m/z 360→166 for confirmation) Clethodim sulfoxide (m/z 376→206 for quantification, m/z 376→164 for confirmation) Clethodim sulfone (m/z 392→300 for quantification, m/z 392→164 for confirmation)	LC-MS/MS	RCC 855262
LOQ:	0.005 mg/kg for all analytes		
Description	Samples (10 g) were extracted with methanol/water (4/1, v/v), homogenized, shaken and filtered. The extracts were analysed with LC-MS/MS.		

Wheat (straw), Onion, Sunflower, Strawberry

Analyte:	M17R (m/z 249→171 or m/z 249→127) M18R (m/z 265→64 or m/z 265→93)	LC-MS/MS	S12-03244
LOQ:	0.01 mg/kg for both analytes		
Description	Samples (10 g) were extracted with methanol/water (4/1, v/v), homogenized, shaken and filtered. The extracts were analysed with LC-MS/MS.		

Validation data for methods on plant matrices are summarized in Table 40.

Table 40 Summary of Recovery Data for clethodim and metabolites fortified into plant matrices

Commodity	Compound (Transition)	Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Method Reference
Rape seed (seed) (CR)	Clethodim	0.06 0.1 0.5	6 13 2	85-120 65-125 90-91	96 87 90	16 24 -	PAM II. Sec. 180.412 KDB.896/ Report 170D, 170U, 170V Bruce, 1996
Cabbage (head) (CR)	Clethodim	0.13 0.25	2 1	57-70 56	64 -	- -	RM-26A-1 223/AU/94/100/SV01 Roberts, 1994
	5-OH-Clethodim Sulfone	0.22 0.43	2 1	86-87 84	87 -	- -	
Rape seed (seed) (CR)	Clethodim Sulfoxide	0.05 0.20	5 7	100-146 68-125	119 94	15 20	RM-26A-1 KDB.896/ Report 170E, 170F, 170G Bruce, 1996
	5-OH-Clethodim Sulfone	0.05 0.20	5 7	97-178 107-134	133 122	22 7.8	
Sugar beet (root) (CR)	Clethodim	0.2 0.5	4 4	61-83 69-81	72 75	13 7.3	RM-26B-1 TSR 5068 SGBT Lai, 1992
	5-OH-Clethodim Sulfone	0.2 0.5	5 4	64-114 89-107	93 100	24 7.9	
Sugar beet (tops) (CR)	Clethodim	0.2 0.5	4 4	65-121 74-86	89 81	27 6.3	
	5-OH-Clethodim Sulfone	0.2 0.5	4 4	106-130 105-116	117 108	8.5 4.8	
Cranberry (berry) (MV)	Clethodim Sulfoxide	0.05 0.50 1.0	3 4 5	96-110 67-83 66-81	101 76 74	7.5 8.7 8.4	RM-26B-2 IR-4 PR No. 05358 Samoil, 1999
	5-OH-Clethodim Sulfone	0.05 0.50 1.0	3 4 5	116-124 84-114 72-106	121 98 92	3.8 13 15	
Strawberry (berry) (MV)	Clethodim Sulfoxide	0.05 2.0 20	3 3 3	82-96 44-86 77-86	89 64 81	7.9 33 5.6	RM-26B-2 IR-4 PR No. 05230 Braverman and Curry, 1999
	5-OH-Clethodim Sulfone	0.05 2.0 20	3 3 3	70-92 43-85 71-78	78 63 73	16 33 5.5	
Broccoli (head) (MV)	Clethodim Sulfoxide	0.05 1.0 2.0	4 4 4	100-100 47-73 53-58	100 57 56	0 20 3.9	RM-26B-2 IR-4 PR No. 05215 Braverman, 2000
	5-OH-Clethodim Sulfone	0.05 1.0 2.0	4 4 4	100-120 66-93 71-86	115 77 79	8.7 16 8.9	
Cucumber (fruit) (MV)	Clethodim Sulfoxide	0.15	4	95-117	105	19	RM-26B-2 IR-4 PR No. 05219 Leavitt and Rathke, 1996
	5-OH-Clethodim Sulfone	0.14	4	87-94	91	3.3	
Carrot (root) (MV)	Clethodim Sulfoxide	0.15	7	111-122	117	3.1	RM-26B-2 IR-4 PR No. 05217 Lai *et al*, 1999
	5-OH-Clethodim Sulfone	0.12	7	113-151	135	9.4	
Tomato (fruit) (MV)	Clethodim (primary method)	0.01 0.10	5 5	87-104 79-91	94 86	6.9 5.1	RM-26B-3

Commodity	Compound (Transition)	Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Method Reference
	Clethodim (confirmatory method)	0.01 0.10	5 5	99-106 79-92	105 86	3.6 5.5	ML01-0941-TOM Brookey, 2003
	Clethodim Sulfoxide (primary method)	0.01 0.10	4 5	102-108 86-100	106 94	2.4 5.9	
	Clethodim Sulfoxide (confirmatory method)	0.01 0.10	4 5	93-110 86-100	102 94	6.8 5.7	
	5-OH-Clethodim Sulfone (primary method)	0.01 0.10	5 5	87-104 71-82	97 77	7.2 5.2	
	5-OH-Clethodim Sulfone (confirmatory method)	0.01 0.10	5 5	97-106 77-86	103 84	4.1 4.7	
Soya bean (seed) (MV)	Clethodim (primary method)	0.05 0.50	5 5	92-98 86-90	95 86	2.5 4.4	
	Clethodim (confirmatory method)	0.05 0.50	5 5	75-78 78-89	77 85	2.0 4.9	
	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	90-110 87-97	101 91	7.6 4.6	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	78-92 86-92	88 89	6.8 3.3	
	5-OH-Clethodim Sulfone (primary method)	0.05 0.50	5 5	84-92 71-84	89 79	3.3 6.5	
	5-OH-Clethodim Sulfone (confirmatory method)	0.05 0.50	5 5	81-87 70-81	84 76	3.9 5.3	
Soya bean (oil) (MV)	Clethodim (primary method)	0.10 1.0	5 5	86-90 82-93	89 85	1.9 5.3	
	Clethodim (confirmatory method)	0.10 1.0	5 5	84-89 78-91	87 83	2.7 5.9	
	Clethodim Sulfoxide (primary method)	0.10 1.0	4 5	76-93 82-90	86 84	8.8 3.9	
	Clethodim Sulfoxide (confirmatory method)	0.10 1.0	4 5	76-93 84-89	86 86	8.8 2.5	
	5-OH-Clethodim Sulfone (primary method)	0.10 1.0	5 5	83-86 77-88	85 80	1.3 5.5	
	5-OH-Clethodim Sulfone (confirmatory method)	0.10 1.0	5 5	82-87 73-85	85 77	2.1 6.3	
Sugar beet (root) (MV)	Clethodim (primary method)	0.05 0.50	4 5	75-82 81-88	78 84	4.0 3.1	
	Clethodim (confirmatory method)	0.05 0.50	4 5	78-84 83-90	82 85	3.5 3.6	
	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	80-93 78-92	88 84	7.5 6.9	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	79-97 76-85	90 81	9.7 4.5	
	5-OH-Clethodim Sulfone (primary method)	0.05 0.50	4 5	67-84 75-82	76 79	9.9 3.3	
	5-OH-Clethodim Sulfone (confirmatory method)	0.05 0.50	4 5	67-87 76-83	78 79	12 3.4	
Sugar beet (top) (MV)	Clethodim (primary method)	0.05 0.50	5 5	97-110 82-86	103 84	4.6 2.1	
	Clethodim (confirmatory method)	0.05 0.50	5 5	95-103 100-108	100 103	3.1 2.9	

Commodity	Compound (Transition)	Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Method Reference
	Clethodim Sulfoxide (primary method)	0.05 0.50	5 4	98-116 73-79	110 76	6.3 4.0	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 4	80-120 91-98	102 94	14 3.4	
	5-OH-Clethodim Sulfone (primary method)	0.05 0.50	5 5	100-114 80-89	107 85	4.7 4.0	
	5-OH-Clethodim Sulfone (confirmatory method)	0.05 0.50	5 5	104-117 94-108	110 100	4.2 5.3	
Pear (fruit) (MV)	Clethodim Sulfoxide	0.1 1.0	4 3	104-114 83-98	109 89	5.0 9.2	RM-26B-3 IR-4 PR No. 06874 Homa, 2011
	5-OH-Clethodim Sulfone	0.1 1.0	4 3	106-111 81-93	108 87	2.2 7.0	
Cherry (fruit) (MV)	Clethodim Sulfoxide	0.1 1.0	4 3	98-114 98-104	104 102	6.9 3.4	RM-26B-3 IR-4 PR No. 06877 Homa, 2013
	5-OH-Clethodim Sulfone	0.1 1.0	4 3	69-71 73-74	70 73	1.6 0.8	
Peach (fruit) (MV)	Clethodim Sulfoxide	0.1 1.0	7 6	103-142 74-91	116 84	11 8.0	RM-26B-3 IR-4 PR No. 06875 Samoil, 2008
	5-OH-Clethodim Sulfone	0.1 1.0	7 6	91-140 71-82	113 78	15 4.8	
Plum (fruit) (MV)	Clethodim Sulfoxide	0.1 1.0	6 3	54-74 78-98	69 86	11 13	RM-26B-3 IR-4 PR No. 06948 Homa, 2011
	5-OH-Clethodim Sulfone	0.1 1.0	6 3	54-79 77-97	72 86	13 12	
Plum (dried) (MV)	Clethodim Sulfoxide	0.1 1.0	6 6	59-83 65-79	71 72	11 7.9	
	5-OH-Clethodim Sulfone	0.1 1.0	6 6	86-106 73-89	93 82	8.5 7.4	
Lettuce (leaves) (MV)	Clethodim Sulfoxide	0.1 1.0 2.4	3 3 3	101-119 79-83 71-82	112 81 77	8.8 2.6 7.2	RM-26B-3 IR-4 PR No. 07694 Braverman, 2004
	5-OH-Clethodim Sulfone	0.1 1.1 2.7	3 3 3	76-84 61-73 63-69	81 67 66	5.2 9.0 4.5	
Hops (dry cone) (MV)	Clethodim Sulfoxide (m/z 392→300)	0.1 1.0	3 3	68-82 102-114	74 108	10 5.6	RM-26B-3 IR-4 PR No. A8086 Jolly, 2014
	5-OH-Clethodim Sulfone (m/z 408→204)	0.1 1.0	3 3	56-85 86-88	68 87	22 1.3	
Rape seed (seed) (CR)	Clethodim Sulfoxide	0.1 0.2 0.5	4 2 5	76-113 88-106 85-106	99 97 99	17 - 8.6	RM-26B-4 V23595 Stearns, 2002
	5-OH-Clethodim Sulfone	0.1 0.2 0.5	4 2 5	88-114 89-93 71-104	102 91 87	11 - 18	
Rape seed (oil) (CR)	Clethodim Sulfoxide	0.1 0.2 0.5	1 1 1	93 85 84	- - -	- - -	
	5-OH-Clethodim Sulfone	0.1 0.2 0.5	1 1 1	79 87 67	- - -	- - -	
Rape seed (meal) (CR)	Clethodim Sulfoxide	0.1 0.2 0.5	1 1 1	119 104 113	- - -	- - -	

Commodity	Compound (Transition)	Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Method Reference
	5-OH-Clethodim Sulfone	0.1 0.2 0.5	1 1 1	114 90 97	- - -	- - -	
Apple (fruit) (MV)	Clethodim Sulfoxide	0.1 1.0	3 3	78-90 78-80	85 79	7.2 1.5	CAL vers. 15 IR-4 PR No. 06873 Homa, 2012
	5-OH-Clethodim Sulfone	0.1 1.0	3 3	80-86 80-82	83 81	3.7 1.4	
Apple (pomace) (MV)	Clethodim Sulfoxide	0.1 1.0	3 3	97-101 83-84	99 83	2.0 0.7	
	5-OH-Clethodim Sulfone	0.1 1.0	3 3	81-85 81-82	83 81	2.5 0.7	
Apple (juice) (MV)	Clethodim Sulfoxide	0.1 1.0	3 3	82-84 81-86	83 83	1.4 3.0	
	5-OH-Clethodim Sulfone	0.1 1.0	3 3	82-84 80-80	83 80	1.2 0	
Blueberry (berry) (MV)	Clethodim Sulfoxide	0.1 1.0	3 3	85-99 79-85	94 82	8.1 3.7	CAL vers. 15 IR-4 PR No. 05234 Samoil, 2008
	5-OH-Clethodim Sulfone	0.1 1.0	3 3	82-89 80-89	85 85	4.5 5.5	
Artichoke (buds) (MV)	Clethodim Sulfoxide	0.1 1.0 10	3 3 3	97-109 85-87 78-86	105 86 82	6.4 1.3 4.9	CAL vers. 15 IR-4 PR No. 09013 Samoil, 2008
	5-OH-Clethodim Sulfone	0.1 1.0 10	3 3 3	108-118 91-97 84-92	114 95 88	4.6 3.4 4.6	
Sugar beet (root) (MV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	93-99 96-103	96 99	2.2 2.7	RCC 855262 Tribolet, 2005
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	96-103 95-107	98 100	3.1 4.7	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	84-90 86-94	88 91	2.9 3.5	
Sugar beet (top) (MV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	87-107 99-114	98 107	9.2 5.3	
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	90-95 93-95	93 94	2.1 0.7	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	78-83 82-85	79 83	2.7 1.3	
Soya bean (seed) (MV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	90-103 77-112	95 96	5.1 16	
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	79-82 69-76	80 73	1.8 3.8	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	76-81 67-76	78 72	3.1 6.4	
Proteginous peas (seed) (MV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	67-78 67-77	73 72	5.7 5.5	
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	85-90 93-100	88 96	2.4 2.9	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	97-102 98-105	99 100	2.2 3.0	
Wheat (grain) (MV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	100-118 88-109	108 97	6.4 8.1	RCC 855262 IF-11/02129995 Holzer, 2012
	Clethodim (m/z 360→166)	0.005 0.05	5 5	98-116 83-108	107 94	6.5 9.4	
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	63-76 84-90	71 90	6.9 3.3	
	Clethodim Sulfoxide (m/z 376→164)	0.005 0.05	5 5	70-72 84-99	71 91	1.3 6.4	

Commodity	Compound (Transition)	Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Method Reference
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	90-98 92-97	94 94	3.6 2.3	
	Clethodim Sulfone (m/z 392→164)	0.005 0.05	5 5	87-97 87-94	93 93	5.2 3.1	
Grapes (bunches) (MV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	82-93 90-101	88 93	5.6 4.9	
	Clethodim (m/z 360→166)	0.005 0.05	5 5	78-93 90-102	87 95	7.5 5.0	
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	92-94 94-98	93 96	1.2 2.1	
	Clethodim Sulfoxide (m/z 376→164)	0.005 0.05	5 5	94-101 93-99	97 95	3.1 2.7	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	96-98 94-98	97 96	0.6 1.4	
	Clethodim Sulfone (m/z 392→164)	0.005 0.05	5 5	99-103 91-97	101 95	1.6 2.2	
Sugar beet (root) (ILV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	90-111 84-97	97 89	8.6 5.7	RCC 855262 20061020/01 -RVP Mende, 2006
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	100-115 98-103	108 100	5.7 2.3	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	80-113 96-109	98 102	15 4.6	
Soya bean (seed) (ILV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	88-109 82-90	100 86	8.3 3.5	
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	95-105 85-95	100 90	4.2 4.4	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	90-114 89-102	99 96	9.0 5.9	
Grapes (bunches) (ILV)	Clethodim (m/z 360→164)	0.005 0.05	5 5	92-92 81-89	86 85	4.7 3.6	RCC 855262 S14-03347 Wiesner and Breyer, 2014
	Clethodim (m/z 360→166)	0.005 0.05	5 5	81-90 79-87	85 83	4.3 4.0	
	Clethodim Sulfoxide (m/z 376→206)	0.005 0.05	5 5	81-93 82-88	87 86	4.9 2.9	
	Clethodim Sulfoxide (m/z 376→164)	0.005 0.05	5 5	81-94 80-88	88 86	6.1 3.7	
	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	86-96 82-89	90 86	5.2 3.2	
	Clethodim Sulfone (m/z 392→164)	0.005 0.05	5 5	85-95 80-87	89 85	5.0 3.3	
Rape seed (seed) (ILV)	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	79-106 76-91	93 83	12 7.9	RCC 855262 S16-03427 Wiesner and Breyer, 2016
	Clethodim Sulfone (m/z 392→164)	0.005 0.05	5 5	79-103 73-87	94 80	11 7.7	
Sugar beet (top) (ILV)	Clethodim Sulfone (m/z 392→300)	0.005 0.05	5 5	83-94 78-97	90 86	4.6 8.3	
	Clethodim Sulfone (m/z 392→208)	0.005 0.05	5 5	95-109 77-96	102 85	5.0 8.6	
Wheat (straw) (MV)	M17R (m/z 249→171)	0.01 0.1	4 5	79-99 67-78	86 71	11 6.1	S12-03244 Lindner and Giesau, 2012
	M17R (m/z 249→127)	0.01 0.1	4 5	81-98 69-75	89 71	7.8 3.5	
	M18R (m/z 265→64)	0.01 0.1	4 5	78-100 66-74	85 70	12 4.3	
	M18R (m/z 265→93)	0.01 0.1	4 5	77-100 68-75	85 71	13 3.7	
Onion (bulb) (MV)	M17R (m/z 249→171)	0.01 0.1	4 5	84-90 66-74	87 70	3.0 4.3	

Commodity	Compound (Transition)	Fortification mg/kg	N	Range Recovery (%)	Mean recovery (%)	% RSD	Method Reference
	M17R (m/z 249→127)	0.01 0.1	4 5	84-90 66-83	86 74	3.3 8.4	
	M18R (m/z 265→64)	0.01 0.1	4 5	72-81 67-76	78 71	5.2 4.7	
	M18R (m/z 265→93)	0.01 0.1	4 5	75-84 66-77	80 72	5.3 5.6	
Sunflower (seeds) (MV)	M17R (m/z 249→171)	0.01 0.1	5 5	80-88 72-76	84 75	4.0 2.2	
	M17R (m/z 249→127)	0.01 0.1	5 5	88-95 72-77	91 75	3.1 3.2	
	M18R (m/z 265→64)	0.01 0.1	5 5	81-84 66-74	83 70	1.8 4.6	
	M18R (m/z 265→93)	0.01 0.1	5 5	80-88 66-74	84 70	3.8 4.6	
Strawberry (fruit) (MV)	M17R (m/z 249→171)	0.01 0.1	5 5	77-92 72-80	86 76	6.5 5.3	
	M17R (m/z 249→127)	0.01 0.1	5 5	81-92 72-82	88 77	4.7 5.2	
	M18R (m/z 265→64)	0.01 0.1	5 5	78-92 72-82	87 78	6.6 5.4	
	M18R (m/z 265→93)	0.01 0.1	5 5	77-96 72-82	86 78	7.9 5.6	

CR: Concurrent Recovery, MV: Method Validation, ILV: Independent Laboratory Validation

Animal matrices

Bovine liver, kidney, muscle, fat and milk (ADC 1124), Poultry liver, muscle, fat, gizzard and egg (88 EM 9)

Analyte: Metabolites that were degraded into DME and metabolites that were degraded into DME-OH — GC-FPD — RM-26A-1

LOQ: Metabolites that were converted into the DME moiety: 0.013 mg/kg for milk and 0.05 mg/kg for egg and tissues
Metabolites that were converted into the DME-OH moiety: 0.013 mg/kg for milk and 0.05 mg/kg for egg and tissues
(expressed as clethodim equivalents)

Description: Samples were extracted with methanol and/or water and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned with dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in concentrated hydrochloric acid and anhydrous methanol (methylation step) and partitioned into dichloromethane. If necessary, silica gel column clean-up was carried out. Residues of DME and DME-OH were determined by GC-FPD in sulfur mode.

Bovine liver, kidney, muscle, fat, milk, poultry muscle and egg (ML01-0941-TOM)

Analyte: Metabolites that were degraded into DME for all matrices and metabolites that were degraded into S-methyl-DME for milk only — GC-FPD — RM-26B-3

LOQ: Metabolites that were converted into the DME moiety: 0.05 mg/kg
Metabolites that were converted into the S-methyl-DME: 0.05 mg/kg for milk

Description Samples were extracted with methanol and cleaned up alkaline precipitation with calcium hydroxide. After addition of hydrochloric acid and sodium chloride, the extracts were partitioned with dichloromethane. The concentrated residue was dissolved in barium hydroxide solution and refluxed with hydrogen peroxide (oxidation step to form the common moieties). After excess hydrogen peroxide removal, the residue was refluxed in concentrated hydrochloric acid and anhydrous methanol (methylation step) and partitioned into dichloromethane. If necessary, silica gel column clean-up was carried out. Residues of DME and DME-OH were determined by GC-FPD in sulfur mode.

Validation data for methods on animal matrices are summarized in Table 41.

Table 41 Summary of recovery data for clethodim and metabolites fortified into animal matrices

Commodity	Mass transition	Fortification mg/kg	N	Range of Recovery (%)	Mean recovery (%)	% RSD	Reference
Bovine Liver (MV)	Clethodim	0.05 0.5 5.0	2 2 1	105, 105 75, 77 98	105 76 -	- - -	RM-26A-1 ADC 1124 Weissenburger and Kruplak, 1988
	5-OH-Clethodim Sulfone	0.05 0.5 5.0	2 2 1	97, 108 69, 73 81	103 71 -	- - -	
Bovine Kidney (MV)	Clethodim	0.05 0.5	2 2	107, 116 93, 96	112 95	- -	
	5-OH-Clethodim Sulfone	0.05 0.5	2 2	103, 119 87, 93	111 90	- -	
Bovine Muscle (MV)	Clethodim	0.05 0.5	2 2	117, 123 86, 95	120 91	- -	
	5-OH-Clethodim Sulfone	0.05 0.5	2 2	119, 119 87, 96	119 92	- -	
Bovine Fat (MV)	Clethodim	0.05 0.5	2 3	91, 97 70-85	94 77	- 9.9	
	5-OH-Clethodim Sulfone	0.05 0.5	2 3	93, 103 65-93	98 76	- 20	
Milk (MV)	Clethodim	0.013 0.05 0.5	2 2 2	95, 101 86, 97 78, 83	98 92 81	- - -	
	5-OH-Clethodim Sulfone	0.013 0.05 0.5	2 2 2	106, 116 74, 87 91, 96	111 81 94	- - -	
Eggs (MV)	Clethodim	0.1 0.5 1	2 2 2	74, 91 56, 76 53, 76	83 66 65	- - -	RM-26A-1 88 EM 9 Fletcher and Pedersen, 1988
	5-OH-Clethodim Sulfone	0.1 0.5 1	2 2 2	104, 106 68, 75 57, 72	105 72 65	- - -	
	S-Meth-Clethodim	0.1 0.5 1	2 2 2	74, 87 54, 69 52, 69	81 62 61	- - -	
Poultry Fat (MV)	Clethodim	0.1 0.5 1	2 2 2	90, 94 73, 83 72, 73	92 78 73	- - -	
	5-OH-Clethodim Sulfone	0.1 0.5 1	2 2 2	89, 92 73, 81 63, 67	91 77 65	- - -	
	S-Meth-Clethodim	0.1 0.5 1	2 2 2	79, 83 67, 76 63, 64	81 72 64	- - -	
Poultry Gizzard (MV)	Clethodim	0.1 0.5 1	2 1 1	87, 90 85 87	89 - -	- - -	

Commodity	Mass transition	Fortification mg/kg	N	Range of Recovery (%)	Mean recovery (%)	% RSD	Reference
	5-OH-Clethodim Sulfone	0.1 0.5 1	2 1 1	62, 83 82 71	73 - -	- - -	
	S-Meth-Clethodim	0.1 0.5 1	2 1 1	77, 82 75 75	80 - -	- - -	
Poultry Liver (MV)	Clethodim	0.1 0.5 1	2 2 2	103, 111 83, 93 79, 87	107 88 83	- - -	
	5-OH-Clethodim Sulfone	0.1 0.5 1	2 2 2	107, 112 82, 85 75, 76	110 84 76	- - -	
	S-Meth-Clethodim	0.1 0.5 1	2 2 2	96, 98 74, 83 72, 81	97 79 77	- - -	
Poultry Muscle (MV)	Clethodim	0.1 0.5 1	1 2 2	90 83, 93 55, 79	- 88 67	- - -	
	5-OH-Clethodim Sulfone	0.1 0.5 1	1 2 2	91 79, 84 68, 74	- 82 71	- - -	
	S-Meth-Clethodim	0.1 0.5 1	1 2 2	89 72, 79 54, 73	- 76 64	- - -	
Bovine Kidney (MV)	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	108-116 76-83	111 78	3.2 3.4	RM-26B-3 ML01-0941-TOM Brookey, 2003
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	109-119 79-85	115 81	3.4 3.1	
Bovine Liver (MV)	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	94-108 67-104	102 93	5.8 16	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	97-120 66-106	112 94	8.5 17	
Bovine Fat (MV)	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	73-97 71-79	87 75	11 3.9	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	74-97 74-81	87 77	9.6 3.4	
Bovine Muscle (MV)	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	83-101 83-91	94 87	8.6 4.3	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	89-103 82-87	97 83	7.5 2.6	
Poultry Muscle (MV)	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	93-119 71-80	102 76	10 4.8	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	94-120 76-83	106 79	9.1 4.2	
Eggs (MV)	Clethodim Sulfoxide (primary method)	0.05 0.50	5 5	80-97 71-81	87 76	9.3 5.1	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	78-112 76-87	94 81	13 5.5	
Milk (MV)	Clethodim Sulfoxide (primary method)	0.05 0.50	5	85-94 78-100	90 86	4.4 10	
	Clethodim Sulfoxide (confirmatory method)	0.05 0.50	5 5	88-95 74-85	90 80	3.7 5.3	
	S-Meth-Clethodim Clethodim Sulfone (primary method)	0.05 0.50	5 5	92-105 82-115	98 94	5.8 14	
	S-Meth-Clethodim Clethodim Sulfone (confirmatory method)	0.05 0.50	5 5	92-105 79-89	98 85	5.0 5.0	

MV: Method Validation

Stability of pesticide residues in stored analytical samples

The Meeting received data on the storage stability of clethodim and its metabolites in samples for plant and animal commodities stored frozen.

The stability of clethodim and 5-OH-clethodim sulfone in sugar beet roots and tops was investigated by fortification of roots and tops with clethodim or 5-OH-clethodim sulfone at 0.5 mg/kg and analysis after storage at about -20 °C for up to 346 days for roots and up to 273 days for tops (Lai, 1992: TSR5068SGBT). Levels of clethodim and 5-OH-clethodim sulfoxide in stored samples were determined using the residue analytical method RM-26B-1, with an LOQ of 0.1 mg clethodim eq/kg.

Table 42 Recovery of clethodim and 5-OH-clethodim sulfone from stored fortified samples of sugar beet

Storage interval (days/ months)	Recovery (%) [0.5 mg/kg fortification]					
	DME			DME-OH		
	Procedural	% remaining	Mean of % remaining	Procedural	% remaining	Mean of % remaining
Sugar beet root						
0	-	103, 100	102	-	114, 106	110
91 / 3	102	98, 96	97	104	112, 104	108
200 / 7	106	74, 82	78	84	70, 92	81
280 / 9	73	92, 82	87	92	106, 90	98
346 / 11	82	76, 80	78	90	100, 100	100
Sugar beet top						
0	-	80, 106	93	-	78, 98	88
109 / 4	106	85, 88	87	86	98, 100	99
189 / 6	82	66, 72	69	100	68, 76	72
273 / 9	96	70, 68	69	100	76. 86	81

A deep-freezer storage stability study was conducted with clethodim, clethodim sulfoxide and clethodim sulfone in alfalfa (Wiesner, 2010: S09-00224). Samples were fortified with 0.10 mg/kg of clethodim, clethodim sulfoxide or clethodim sulfone, respectively. All samples were stored in amber glass jars at ≤-18 °C.

The samples were analysed using a validated residue analytical method employing extraction with a methanol/water mixture using a high speed homogenizer. The extracts were filtered, diluted and analysed for residues of clethodim, clethodim sulfoxide or clethodim sulfone, by the specific LC-MS/MS method RCC 855262. The LOQ was 0.005 mg/kg for all three analytes.

Table 43 Recovery of clethodim, clethodim sulfoxide and clethodim sulfone from stored fortified samples of alfalfa

Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
	Procedural	% remaining	Mean of % remaining
Clethodim			
0	-	79, 82, 82	81
30 / 1	105	1, 1	1
92 / 3	101	0, 0	0
183 / 6	75	0, 0	0
Clethodim sulfoxide			
0	-	95, 94, 100	96
30 / 1	107	107, 105	106
92 / 3	99	90, 87	89
183 / 6	77	74, 85	80
Clethodim sulfone			
0	-	94, 91, 83	89
30 / 1	110	92, 101	97
92 / 3	91	77, 66	72

Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
	Procedural	% remaining	Mean of % remaining
183 / 6	82	57, 64	61

A deep-freezer storage stability study was conducted with clethodim, clethodim sulfoxide and clethodim sulfone in potato tubers (Wiesner, 2010: S09-00225). Samples were fortified with 0.10 mg/kg of clethodim, clethodim sulfoxide or clethodim sulfone, respectively. All samples were stored in amber glass jars at ≤-18 °C.

The samples were analysed using a validated residue analytical method employing extraction with a methanol/water mixture using a high speed homogenizer. The extracts were filtered, diluted and analysed for residues of clethodim, clethodim sulfoxide or clethodim sulfone, by the specific LC-MS/MS method RCC 855262. The LOQ was 0.005 mg/kg for all three analytes.

Table 44 Recovery of clethodim, clethodim sulfoxide and clethodim sulfone from stored fortified samples of potato tubers

Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
	Procedural	% remaining	Mean of % remaining
Clethodim			
0	-	88, 88, 90	89
30 / 1	107	10, 26	18
99 / 3	71	7, 9	8
183 / 6	85	6, 7	7
Clethodim sulfoxide			
0	-	94, 99, 90	94
30 / 1	101	90, 104	102
99 / 3	100	81, 84	83
183 / 6	91	71, 76	74
Clethodim sulfone			
0	-	98, 96, 98	97
30 / 1	110	106, 105	106
99 / 3	105	90, 92	91
183 / 6	81	77, 96	87

A deep-freezer storage stability study was conducted with clethodim in alfalfa and potato tubers (Wiesner, 2010: S09-03263). Samples were fortified with 0.10 mg/kg of clethodim. All samples were stored in amber glass jars at ≤-18 °C.

The samples were analysed using a validated residue analytical method employing extraction with a methanol/water mixture using a high speed homogenizer. The extracts were filtered, diluted and analysed for residues of clethodim, clethodim sulfoxide or clethodim sulfone by the specific LC-MS/MS method RCC 855262. The LOQ was 0.005 mg/kg for all three analytes.

Table 45 Recovery of clethodim, clethodim sulfoxide and clethodim sulfone from stored fortified samples of alfalfa and potato

Analyte	Storage interval (days/months)	Recovery (mg/kg) [clethodim 0.10 mg/kg fortification]		
		Procedural	Storage sample	Mean (mg/kg)
Alfalfa				
Clethodim	0	-	0.097, 0.090, 0.089	0.092
	32 / 1	0.11	0.002, 0.001	0.002
	62 / 2	0.10	0.001, 0	0.001
	92 / 3	0.083	0, 0	0
	103 / 3.3	0.082	0, 0	0
Clethodim sulfoxide	0	-	0.014, 0.011, 0.010	0.012
	32 / 1	0.015	0.089, 0.092	0.091
	62 / 2	0.012	0.082, 0.080	0.081
	92 / 3	0.020	0.047, 0.081	0.064
	103 / 3.3	0.011	0.050, 0.058	0.054

Analyte	Storage interval (days/months)	Recovery (mg/kg) [clethodim 0.10 mg/kg fortification]		
		Procedural	Storage sample	Mean (mg/kg)
Clethodim sulfone	0	-	0, 0, 0	0
	32 / 1	0	0, 0	0
	62 / 2	0	0, 0	0
	92 / 3	0	0, 0	0
	103 / 3.3	0	0, 0	0
Total residue as clethodim equivalents	0	-	0.11, 0.10, 0.099	0.10
	32 / 1	0.12	0.091, 0.093	0.092
	62 / 2	0.11	0.083, 0.080	0.082
	92 / 3	0.10	0.047, 0.081	0.064
	103 / 3.3	0.093	0.050, 0.058	0.054
Potato tubers				
Clethodim	0	-	0.10, 0.10, 0.096	0.10
	31 / 1	0.10	0.029, 0.029	0.029
	61 / 2	0.11	0.016, 0.008*	0.016
	91 / 3	0.074	0.013, 0.017	0.015
	105 / 3.4	0.10	0.006, 0.016	0.011
Clethodim sulfoxide	0	-	0, 0, 0	0
	31 / 1	0.002	0.068, 0.054	0.061
	61 / 2	0.001	0.050, 0.026*	0.050
	91 / 3	0	0.057, 0.067	0.062
	105 / 3.4	0.001	0.090, 0.072	0.081
Clethodim sulfone	0	-	0, 0, 0	0
	31 / 1	0	0, 0	0
	61 / 2	0	0, 0	0
	91 / 3	0	0, 0	0
	105 / 3.4	0	0, 0	0
Total residue as clethodim equivalents	0	-	0.10, 0.10, 0.096	0.10
	31 / 1	0.10	0.097, 0.083	0.090
	61 / 2	0.11	0.066, 0.034*	0.066
	91 / 3	0.074	0.070, 0.084	0.077
	105 / 3.4	0.10	0.096, 0.088	0.092

* The sample was considered to be an outlier.

A deep-freezer storage stability study has been conducted with clethodim, clethodim sulfoxide and clethodim sulfone in oilseed rape seed (Brumhard, 2011: 1094.004.865). Samples were fortified with 0.10 mg/kg of clethodim, clethodim sulfoxide or clethodim sulfone, respectively. All samples were stored in amber glass jars at ≤-18 °C.

The samples were analysed for clethodim, clethodim sulfoxide and clethodim sulfone using the validated residue analytical method RCC 855262, employing extraction with a methanol/water mixture using a high speed homogenizer. The extracts were filtered, diluted and analysed for residues of clethodim and its metabolites by LC-MS/MS. The LOQ was 0.005 mg/kg for all three analytes.

Table 46 Recovery of clethodim, clethodim sulfoxide and clethodim sulfone from stored fortified samples of oilseed rape seeds

Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
	Procedural	% remaining	Mean of % remaining
Clethodim			
0	98.8, 107	92.0, 114, 119, 95.1, 116	107
90 / 3	117, 109	102, 106, 114	107
198 / 6.5	67.0, 69.9	111, 105, 93.4	103
Clethodim sulfoxide			
0	76.9, 74.2	84.2, 66.7, 72.2, 71.6, 76.0	74.2
90 / 3	80.8, 82.3	93.8, 104, 98.0	98.7
198 / 6.5	92.1, 93.0	92.5, 96.1, 98.5	95.7
Clethodim sulfone			
0	84.8, 80.7	87.2, 90.3, 81.2, 87.3, 90.2	87.2

Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
	Procedural	% remaining	Mean of % remaining
90 / 3	83.0, 84.6	86.5, 85.4, 85.9	85.9
198 / 6.5	95.2, 87.6	106, 86.0, 91.1	94.5

A storage stability study was conducted to investing the deep-freezer storage stability of clethodim and its metabolites clethodim sulfoxide, clethodim sulfone, M17R and M18R in four different plant matrices during storage at ≤-18 °C for a period of up to 9 months (Wiesner, 2014: S12-04386). At day 0, samples of potato, oilseed rape seeds, grapes and dry peas were separately fortified at the level of 0.10 mg/kg with clethodim sulfoxide, clethodim sulfone, M17R or M18R, respectively, then stored deep-frozen and analysed after 1, 3, 6 and 9 months or after 9 months only. Additional samples of oilseed rape seeds and dry peas were fortified with clethodim, and then treated likewise. At each analysis time point from month 1 to month 9, samples of the relevant matrices were freshly fortified at the level of 0.10 mg/kg with clethodim or mixtures of clethodim sulfoxide and clethodim sulfone or mixtures of M17R and M18R, respectively, and analysed together with the stored fortified samples.

The samples were analysed for clethodim, clethodim sulfoxide and clethodim sulfone using the validated residue analytical method RCC 855262, employing extraction with a methanol/water mixture using a high speed homogenizer. The extracts were filtered, diluted and analysed for residues of clethodim and its metabolites by LC-MS/MS. The LOQ for clethodim, clethodim sulfoxide and clethodim sulfone was 0.005 mg/kg each. For M17R and M18R, the LOQ was 0.01 mg/kg each.

At day 0, one control sample and three fortified samples were analysed. At each time point after day 0, one control sample and three stored fortified samples were analysed together with two freshly fortified samples.

Table 47 Recovery of clethodim, clethodim sulfoxide, clethodim sulfone, M17R and M18R from stored fortified samples of potato, oilseed rape seeds, grapes and dry peas

Commodity	Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
		Procedural (mean)	% remaining	Mean of % remaining
Potato	Clethodim sulfoxide			
	0	-	78, 82, 78	79
	284 / 9	90	77, 78, 75	77
	Clethodim sulfone			
	0	-	71, 78, 77	75
	284 / 9	90	77, 74, 74	75
	M17R			
	0	-	98, 92, 100	97
	36 / 1	88	80, 83, 84	82
	92 / 3	99	79, 94, 81	85
	182 / 6	99	96, 99, 98	98
	274 / 9	95	91, 92, 98	94
	M18R			
	0	-	95, 98, 120	104
	36 / 1	91	86, 88, 86	87
	92 / 3	100	86, 93, 86	88
	182 / 6	96	98, 97, 101	99
	274 / 9	90	94, 80, 91	88
Oilseed rape seeds	Clethodim			
	0	-	75, 75, 94	81
	275 / 9	83	60, 63, 63	62
	Clethodim sulfoxide			
	0	-	73, 79, 77	76
	275 / 9	81	92, 91, 83	89
	Clethodim sulfone			
	0	-	78, 75, 79	77
	275 / 9	83	68, 69, 59	65

Commodity	Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
		Procedural (mean)	% remaining	Mean of % remaining
	M17R			
	0	-	87, 101, 92	93
	37 / 1	76	77, 72, 78	76
	91 / 3	82	78, 82, 78	79
	181 / 6	78	87, 85, 82	85
	275 / 9	88	104, 105, 99	103
	M18R			
	0	-	93, 89, 85	89
	37 / 1	77	80, 79, 84	81
	91 / 3	93	85, 84, 89	86
	181 / 6	83	89, 90, 90	90
	275 / 9	90	93, 96, 98	96
Dry peas	Clethodim			
	0	-	95, 77, 91	88
	35 / 1	98	89, 94, 63	82
	91 / 3	91	74, 75, 70	73
	185 / 6	79	70, 69, 69	69
	279 / 9	93	79, 77, 83	80
	Clethodim sulfoxide			
	0	-	92, 95, 85	91
	35 / 1	106	104, 99, 112	105
	91 / 3	81	77, 80, 76	78
	0	-	73, 76, 70	73
	184 / 6	80	80, 69, 67	72
	276 / 9	92	74, 71, 71	72
	Clethodim sulfone			
	0	-	87, 84, 90	87
	35 / 1	80	61, 88, 95	81
	91 / 3	79	70, 78, 80	76
	0	-	74, 72, 74	73
	184 / 6	83	78, 90, 91	86
	276 / 9	95	78, 73, 75	75
	M17R			
	0	-	104, 102, 101	102
	31 / 1	84	87, 91, 88	89
	91 / 3	107	94, 96, 98	96
	184 / 6	85	80, 86, 83	83
	276 / 9	101	99, 98, 101	99
	M18R			
	0	-	104, 92, 92	96
	31 / 1	85	92, 90, 90	91
	91 / 3	104	91, 89, 76	85
	184 / 6	86	87, 94, 96	92
	276 / 9	95	92, 95, 92	93
Grapes	Clethodim sulfoxide			
	0	-	84, 87, 85	85
	36 / 1	89	78, 97, 82	86
	92 / 3	80	83, 89, 73	82
	0	-	80, 76, 76	77
	185 / 6	94	76, 86, 68	77
	280 / 9	93	73, 79, 78	77
	Clethodim sulfone			
	0	-	64, 85, 81	77
	36 / 1	81	75, 76, 90	80
	92 / 3	76	81, 70, 79	77
	0	-	80, 79, 74	78
	185 / 6	92	71, 79, 75	75
	280 / 9	93	79, 72, 71	74
	M17R			

Commodity	Storage interval (days/months)	Recovery (%) [0.10 mg/kg fortification]		
		Procedural (mean)	% remaining	Mean of % remaining
	0	-	102, 102, 100	101
	36 / 1	89	96, 95, 97	96
	92 / 3	105	108, 106, 104	106
	189 / 6	96	95, 96, 92	94
	284 / 9	90	100, 94, 99	98
	M18R			
	0	-	105, 100, 100	102
	36 / 1	88	98, 99, 98	98
	92 / 3	102	101, 103, 108	104
	189 / 6	93	88, 87, 91	89
	284 / 9	92	93, 98, 90	94

The stability of clethodim and 5-OH-clethodim sulfone in processed fractions of cotton seed was investigated from incurred residues obtained from a processing study on cotton seed (MRID 410302-19). Two applications of 240 g/L EC formulation were applied to cotton at 2.2 kg ai/ha in 187 L/ha. The treated cotton was harvested and processed into hulls, meal, crude oil, refined oil, soapstock and delinted cottonseed. After an initial analysis of the common moieties DME and DME-OH following the residue analytical method RM-26A-1 representing day zero of the stability determination, the analysis was repeated at two to four intervals up to 14 months after frozen storage at -20 °C (Ho, 1990: T-6912SS).

Table 48 Recovery of clethodim and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of cotton processed commodities

Analyte	Storage interval (days/months)	Procedural (%)	Residues (mg/kg)	% remaining
Hulls				
DME	0	85.4	0.78	-
	62 / 2.1	81.7	0.91	117
	158 / 5.3	82.0	0.67	85.9
DME-OH	0	78.1	ND	-
	62 / 2.1	120	ND	-
	158 / 5.3	89.8	ND	-
Meal				
DME	0	86.1	0.94	-
	62 / 2.1	80.5	0.96	102
	158 / 5.3	69.3	0.97	103
DME-OH	0	85.8	0.41	-
	62 / 2.1	109	0.72	-
	158 / 5.3	92.4	0.42	-
Total residues	0	-	1.35	-
	62 / 2.1	-	1.68	124
	158 / 5.3	-	1.39	103
Crude oil				
DME	0	77.1	0.14	-
	126 / 4.2	76.4	0.14	100
	224 / 7.5	44.9	0.12	85.7
	307 / 10.2	46.1	0.11	78.6
	434 / 14.5	92.2	0.16	114
DME-OH	0	57.0	ND	-
	126 / 4.2	89.5	ND	-
	224 / 7.5	39.3	ND	-
	307 / 10.2	97.7	ND	-
	434 / 14.5	86.9	ND	-
Soapstock				
DME	0	81.5	0.65	-
	292 / 9.7	46.1	0.56	86.2
	440 / 14.7	95.4	0.71	109

Analyte	Storage interval (days/months)	Procedural (%)	Residues (mg/kg)	% remaining
DME-OH	0	56.0	ND	-
	292 / 9.7	105	ND	-
	440 / 14.7	99.9	ND	-

The stability of clethodim and 5-OH-clethodim sulfone in processed fractions of soya been seed was investigated from incurred residues obtained from a processing study on cotton seed (MRID 410302-20). Two applications of 240 g/L EC formulation were applied to cotton at 2.2 kg ai/ha in 374 L/ha. The treated cotton was harvested and processed into hulls, meal, crude oil, refined oil, soapstock, degummed oil and crude lecithin. After an initial analysis of the common moieties DME and DME-OH following the residue analytical method RM-26A-1 representing day zero of the stability determination, the analysis was repeated at two to four intervals up to 13 months after frozen storage at -20 °C (Ho, 1990: T-6921SS).

Table 49 Recovery of clethodim and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of soya been processed commodities

Analyte	Storage interval (days/months)	Procedural (%)	Residues (mg/kg)	% remaining
Hulls				
DME	0	89.1	17.3	-
	75 / 2.5	66.5	15.8	91.2
	179 / 6	65.9	13.8	79.7
	395 / 13.2	104	17.7	102
DME-OH	0	113	9.13	-
	75 / 2.5	57.3	6.50	-
	179 / 6	69.2	5.68	-
	395 / 13.2	101	8.19	-
Total residues	0	-	26.4	-
	75 / 2.5	-	22.3	84.3
	179 / 6	-	19.5	73.7
	395 / 13.2	-	25.9	97.8
Meal				
DME	0	75.6	22.0	-
	129 / 4.3	122	22.9	104
	156 / 5.2	67.1	21.3	96.8
	260 / 8.7	63.7	18.1	82.2
DME-OH	0	64.4	5.20	-
	129 / 4.3	116	12.8	-
	156 / 5.2	59.9	9.57	-
	260 / 8.7	67.4	8.11	-
Total residues	0	-	27.2	-
	129 / 4.3	-	35.7	131
	156 / 5.2	-	30.9	113
	260 / 8.7	-	26.2	96.3
Crude oil				
DME	0	73.4	2.60	-
	126 / 4.2	68.3	2.56	98.5
	224 / 7.5	64.4	2.09	80.4
DME-OH	0	72.5	0.17	-
	126 / 4.2	84.5	0.28	-
	224 / 7.5	85.5	0.25	-
Total residues	0	-	2.77	-
	126 / 4.2	-	2.84	103
	224 / 7.5	-	2.34	84.5
Soapstock				
DME	0	84.9	31.8	-
	252 / 8.4	46.1	21.4	67.2
	379 / 12.6	114	21.7	68.1

Analyte	Storage interval (days/months)	Procedural (%)	Residues (mg/kg)	% remaining
DME-OH	0	120	1.56	-
	252 / 8.4	106	0.99	-
	379 / 12.6	116	1.52	-
Total residues	0	-	33.4	-
	252 / 8.4	-	22.4	67.0
	379 / 12.6	-	23.2	69.5
Crude lecithin				
DME	0	82.0	36.1	-
	263 / 8.8	42.9	28.2	78.1
	390 / 13	104	39.9	111
DME-OH	0	99.5	6.11	-
	263 / 8.8	103	4.75	-
	390 / 13	101	5.94	-
Total residues	0	-	42.2	-
	263 / 8.8	-	33.0	97.2
	390 / 13	-	45.8	109

Aliquots (10 g) of apple fruit, pomace or juice were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfoxide, both at a level of 1.0 mg/kg, corresponding to 0.95 mg/kg and 0.88 mg/kg clethodim equivalents, respectively (Homa, 2012: IR-4 PR No. 06873). Storage temperatures remained at -21 ± 7 °C. The maximum sample storage duration was 567 days for apple fruit, 609 days for pomace and 615 days for juice (calculated from sampling to extraction); Day 0 samples were not analysed.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfoxide in stored samples were determined using the residue analytical method RM-26B-3, with an LOQ of 0.095 mg/kg for clethodim and all metabolites that can be converted to DME and an LOQ of 0.088 mg/kg for all 5-OH-metabolites that can be converted to DME-OH, respectively, all expressed as clethodim equivalents.

Table 50 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfoxide analysed as DME and DME-OH from stored fortified samples of apple commodities

Analyte	Storage interval (days/months)	Recovery (%)		
		Procedural	% remaining	Mean of % remaining
Fruit				
DME	567 / 19	95, 88	86, 85, 78	83
DME-OH	567 / 19	84, 84	73, 72, 70	72
Pomace				
DME	609 / 20	90, 93	84, 85, 86	85
DME-OH	609 / 20	80, 80	73, 70, 73	72
Juice				
DME	615 / 20.5	86, 90	93, 89, 93	92
DME-OH	615 / 20.5	80, 80	77, 73, 76	75

Aliquots (20 g) of homogenized peach fruits were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 1.0 mg/kg, corresponding to 0.95 mg/kg and 0.88 mg/kg clethodim equivalents, respectively (Samoil, 2008: IR-4 PR No. 06875). Storage temperatures remained at -12 to -22 °C.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-3, with an LOQ of 0.1 mg/kg for clethodim sulfoxide and 5-OH-clethodim sulfone. Following the total residue method, clethodim sulfoxide and 5-OH-clethodim sulfone are representing all metabolites that can be converted to DME and all 5-OH-metabolites that can be converted to DME-OH, respectively. Day 0 samples were not analysed.

Table 51 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of peach

Analyte	Storage interval (days/months)	Recovery (%) [1.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	700 / 23	95	87, 80, 83	83
DME-OH	700 / 23	86	86, 83, 87	85

Aliquots (10 g) of homogenized plum fruits were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 1.0 mg/kg, corresponding to 0.95 mg/kg and 0.88 mg/kg clethodim equivalents, respectively (Homa, 2011, IR-4 PR No. 06948). Storage temperatures remained at -4 to -22 °C.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-3, with an LOQ of 0.1 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 52 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of plum

Analyte	Storage interval (days/months)	Recovery (%) [1.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
Plum (fresh)				
DME	875 / 29	91, 89	70, 70, 75	72
DME-OH	875 / 29	87, 89	72, 72, 77	74
Plum (dried)				
DME	820 / 27	89, 91	70, 51, 69	63
	828 / 27	96, 98	75, 74	74
DME-OH	820 / 27	84, 83	71, 52, 73	65
	828 / 27	91, 93	79, 77	78

Aliquots (10 g) of homogenized blueberries were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 1.0 mg/kg (Samoil, 2008: IR-4 PR No. 05234). Storage temperatures remained at -21 ± 7 °C.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-3, with an LOQ of 0.1 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 53 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of blueberry

Analyte	Storage interval (days/months)	Recovery (%) [1.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	144 / 4.7	79	85, 85	85
	161 / 5.3	85, 90	92	-
DME-OH	144 / 4.7	86	91, 87	89
	161 / 5.3	89, 99	97	-

Homogenized samples (20 g) of cranberries were fortified individually with clethodim and 5-OH clethodim sulfone at a concentration of 0.2 mg/kg (Samoil, 1999: IR-4 PR No. 05358). Triplicate samples of each matrix were analysed for the analytes after frozen storage at -12 to -22 °C for 673 days.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-2, with an LOQ of 0.05 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 54 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of cranberry

Analyte	Storage interval (days/months)	Recovery (%) [2.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	673 / 22	118, 89	76, 64, 64	68
DME-OH	673 / 22	156, 108	88, 75, 78	80

Aliquots (20 g) of homogenized strawberries were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 2.0 mg/kg (Braverman, 1999: IR-4 PR No. 05230). Storage temperatures remained at -21 ± 7 °C

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-2, with an LOQ of 0.05 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 55 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of strawberry

Analyte	Storage interval (days/months)	Recovery (%) [2.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	805 / 26	70	71, 60	65
	810 / 27	77	81	-
DME-OH	805 / 26	81	71, 64	67
	810 / 27	92	91	-

Aliquots (20 g) of homogenized broccoli were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 1.0 mg/kg (Braverman, 2000: IR-4 PR No. 05215). Storage temperatures remained at -12 to -22 °C.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-2, with an LOQ of 0.05 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 56 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of broccoli

Analyte	Storage interval (days/months)	Recovery (%) [1.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	943 / 31	91	68, 69, 69	69
DME-OH	943 / 31	100	78, 79, 75	77

Aliquots (10 g) of homogenized head lettuce were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 1.0 mg/kg (Braverman, 2004: IR-4 PR No. 07694). Storage temperatures remained at -10 to -29 °C.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-3, with an LOQ of 0.1 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 57 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of head lettuce

Analyte	Storage interval (days/months)	Recovery (%) [1.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	346 / 11	95	95, 89, 95	93
DME-OH	328 / 11	118	83, 81, 83	82

Aliquots (10 g) of homogenized carrot roots were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone at a level of 2.3 mg/kg and 2.1 mg/kg, respectively (Lai *et al*., 1999: IR-4 PR No. 05217).

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-2, with an LOQ of 0.11 mg/kg and 0.10 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 58 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of carrot root

Analyte	Storage interval (days/months)	Recovery (%) [2.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	713 / 23	77	76, 73	75
	720 / 24	74	69, 77	73
DME-OH	713 / 23	75	66, 64	65
	720 / 24	72	69, 73	71

Aliquots (20 g) of homogenized dry pea seeds were fortified with a mixture of clethodim, 5-OH-clethodim and clethodim imine sulfone at levels of 0.05 mg/kg, 0.5 mg/kg and 1.0 mg/kg (Grigg, 1995: IR-4 PR No. 05204).

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-2, with an LOQ of 0.05 mg/kg for DME and DME-OH, respectively. Both clethodim imine sulfone and clethodim are converted to DME during the analytical procedure which accounts for the abnormally high recovery values for this compound. Equal weights of clethodim and clethodim imine sulfone produce nearly equal molar amounts of DME because they have similar molecular weights, and as a result, the values reported for DME were twice as high as they should have been. To correct for the error, the DME values were multiplied by 0.5 and the corrected values were reported.

Table 59 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of dry pea

Analyte	Fortification level (mg/kg)	Storage interval (days/months)	Recovery (%)	
			Procedural	% remaining
DME	0.05	532 / 17	86	82
		537 / 18	-	85
		593 / 19	102	99
	0.5	532 / 17	-	73
		537 / 18	73	80
	1.0	532 / 17	-	69
		537 / 18	-	70
DME-OH	0.05	532 / 17	90	114
		537 / 18	-	124
		593 / 19	46	82
	0.5	532 / 17	-	112
		537 / 18	80	87
	1.0	532 / 17	-	108
		537 / 18	-	74

Aliquots (10 g) of homogenized hops cones were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 1.0 mg/kg (Jolly, 2014: IR-4 PR No. A8086). Storage temperatures remained at -20 °C.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-3, with an LOQ of 0.1 mg/kg for DME and DME-OH, respectively. Day 0 samples were not analysed.

Table 60 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of hop cones

Analyte	Storage interval (days/months)	Recovery (%) [1.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	309 / 10	90, 88	73, 76, 71	73
DME-OH	309 / 10	108, 105	85, 88, 80	84

Aliquots (10 g) of homogenized artichoke flower buds were fortified with a mixture of clethodim sulfoxide and 5-OH-clethodim sulfone, both at a level of 1.0 mg/kg (Samoil, 2008: IR-4 PR No. 09013). Storage temperatures remained at -21 ± 7 °C.

Levels of clethodim sulfoxide and 5-OH-clethodim sulfone in stored samples were determined using the residue analytical method RM-26B-3, with an LOQ of 0.1 mg/kg for clethodim sulfoxide and 5-OH-clethodim sulfone, respectively. Day 0 samples were not analysed.

Table 61 Recovery of clethodim sulfoxide and 5-OH-clethodim sulfone analysed as DME and DME-OH from stored fortified samples of artichoke

Analyte	Storage interval (days/months)	Recovery (%) [1.0 mg/kg fortification]		
		Procedural	% remaining	Mean of % remaining
DME	109 / 3.5	87	87, 85	86
	115 / 4	97, 87	82	-
DME-OH	109 / 3.5	86	87, 86	87
	115 / 4	89, 83	80	-

Samples (50 mL) of unpasteurized whole milk and bovine tissue (fat, kidney, liver, muscle, each 25 g) were fortified with clethodim, 5-OH clethodim sulfone and S-methyl clethodim sulfoxide all at levels of 0.25 mg/kg (tissue) and 0.05 mg/kg (milk) (Weissenburger, 1989: ADC1124). Two fortified samples were stored with three control samples at or below -20 °C. Two of the control samples were freshly fortified with clethodim, with 5-OH clethodim sulfone and with S-methyl clethodim sulfoxide at 0.25 mg/kg (tissue) and 0.05 mg/kg (milk) at the time of analysis. The method is a common moiety method. Clethodim and clethodim-like metabolites containing the 5-(2- ethyl-thiopropyl) cyclohexene-3-one moiety are converted to DME, 5-OH clethodim and 5-OH clethodim like metabolites containing the 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moiety are converted to DME-OH and S-methyl-clethodim and S-methyl like metabolites are converted to S-methyl-DME. The residues are expressed as clethodim equivalents.

Table 62 Recovery of clethodim and its metabolites analysed as DME, S-methyl DME and DME-OH from stored fortified samples of ruminant tissues and milk

Analyte	Fortification level (mg/kg)	Storage interval (days/months)	Recovery (%)		
			Procedural	% remaining	Mean of % remaining
Milk					
DME	0.05	0	-	94, 91	93
		31 / 1	84, 78	80	-
		63 / 2	202*, 80*	27*, 14*	19*
		91 / 3	39, 41	73, 75	74
		105 / 3.5	86, 89	83, 79	81
		121 / 4	76, 72	74, 80	77
		151 / 5	78, 64	70, 94	82
S-methyl DME	0.05	0	-	98, 92	95
		31 / 1	91, 83	88	-
		63 / 2	68*, 81*	56*, 56*	56*
		91 / 3	46, 46	79, 82	80

Analyte	Fortification level (mg/kg)	Storage interval (days/months)	Recovery (%)		
			Procedural	% remaining	Mean of % remaining
		105 / 3.5	82, 90	89, 84	87
		121 / 4	76, 80	78, 92	85
		151 / 5	87, 65	72, 114	93
DME-OH	0.05	0	-	117, 109	113
		31 / 1	107, 99	102	-
		63 / 2	76*, 92*	65*, 62*	63*
		91 / 3	44, 44	86, 97	91
		105 / 3.5	101, 103	95, 90	93
		121 / 4	94, 89	91, 107	99
		151 / 5	92, 75	80, 116	98
Fat					
DME	0.25	0	-	79, 79	79
		31 / 1	101, 89	83, 82	83
		63 / 2	95, 87	82, 71	77
		91 / 3	89, 80	77, 75	76
		121 / 4	62, 79	83, 80	82
		151 / 5	78	78, 90	84
S-methyl DME	0.25	0	-	83, 85	84
		31 / 1	91, 91	96, 93	95
		63 / 2	92, 82	82, 78	80
		91 / 3	91, 83	82, 75	78
		121 / 4	77, 86	92, 89	91
		151 / 5	84	85, 97	91
DME-OH	0.25	0	-	107, 99	103
		31 / 1	118, 101	106, 101	103
		63 / 2	94, 88	82, 82	82
		91 / 3	90, 83	88, 83	85
		121 / 4	87, 96	100, 98	99
		151 / 5	83	89, 104	97
Kidney					
DME	0.25	0	-	88, 77	83
		31 / 1	85, 79	84, 80	82
		63 / 2	87, 80	69, 71	70
		91 / 3	78, 74	81, 78	80
		121 / 4	79, 75	84, 79	81
		151 / 5	88, 77	82, 80	81
S-methyl DME	0.25	0	-	90, 77	83
		31 / 1	80, 79	82, 85	83
		63 / 2	87, 80	74, 67	70
		91 / 3	84, 74	87, 83	85
		121 / 4	81, 76	84, 79	81
		151 / 5	94, 81	86, 93	89
DME-OH	0.25	0	-	113, 94	104
		31 / 1	109, 101	98, 98	98
		63 / 2	98, 87	81, 81	82
		91 / 3	74, 71	88, 85	86
		121 / 4	95, 82	95, 95	95
		151 / 5	86, 77	86, 91	89
Liver					
DME	0.25	0	-	70, 70	70
		31 / 1	78, 79	71, 69	70
		63 / 2	78, 78	65, 71	68
		91 / 3	79, 82	76, 68	72
		121 / 4	73, 80	75, 90	82
		151 / 5	81, 98	82, 72	77
S-methyl DME	0.25	0	-	78, 78	78
		31 / 1	74, 79	70, 70	70
		63 / 2	80, 81	75, 81	79
		91 / 3	86, 89	87, 77	82
		121 / 4	75, 82	75, 95	85

Analyte	Fortification level (mg/kg)	Storage interval (days/months)	Recovery (%)		
			Procedural	% remaining	Mean of % remaining
		151 / 5	79, 98	87, 74	81
DME-OH	0.25	0	-	79, 72	76
		31 / 1	102, 102	80, 97	88
		63 / 2	84, 79	79, 84	81
		91 / 3	83, 83	103, 91	97
		121 / 4	84, 97	93, 113	103
		151 / 5	81, 101	89, 85	87
Muscle					
DME	0.25	0	-	80, 80	80
		31 / 1	83, 88	73, 76	74
		63 / 2	71, 92	76, 80	78
		91 / 3	77, 72	94, 74	84
		121 / 4	83, 81	78, 79	79
		151 / 5	76, 82	76, 214*	76
S-methyl DME	0.25	0	-	88, 88	88
		31 / 1	90, 93	89, 90	90
		63 / 2	80, 94	86, 92	89
		91 / 3	84, 74	106, 86	96
		121 / 4	89, 86	90, 92	91
		151 / 5	86, 95	99, 95	97
DME-OH	0.25	0	-	98, 91	94
		31 / 1	88, 94	94, 100	97
		63 / 2	87, 97	92, 97	95
		91 / 3	78, 74	111, 103	107
		121 / 4	103, 99	103, 110	106
		151 / 5	91, 94	98, 98	98

* Samples and controls were found to be contaminated; control levels were subtracted from sample results; results reported as questionable

Samples of chicken eggs and tissue (fat, gizzard, liver and muscle) were fortified with clethodim, 5-OH clethodim sulfone and S-methyl clethodim sulfoxide at 1 and 2 mg/kg (eggs) or 1 mg/kg (fat, kidney, liver, muscle and gizzard) and stored at approximately -18 °C (range -13 °C to -29 °C) (Lear, 1989: 129-003). Controls and freshly fortified samples were included. Analysis was according to Chevron method RM-26A with modifications. The method is a common moiety method. Clethodim and clethodim-like metabolites containing the 5-(2-ethylthiopropyl) cyclohexene-3-one moiety are converted to DME, 5-OH clethodim and 5-OH clethodim like metabolites containing the 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moiety are converted to DME-OH and S-methyl-clethodim and S-methyl like metabolites are converted to S-methyl-DME. The residues are expressed as clethodim equivalents.

Table 63 Recovery of clethodim and its metabolites analysed as DME, S-methyl DME and DME-OH from stored fortified samples of poultry tissues and eggs

Analyte	Fortification level (mg/kg)	Storage interval (days/months)	Recovery (%)		
			Residue (mg/kg)	% remaining	Mean of % remaining
Eggs					
DME	1.03	0	0.853, 0.710	83, 69	76
	1.07	34 / 1	0.919, 0.984, 0.841	86, 92, 79	85
	2.14	60 / 2	1.82, 1.81, 1.78	85, 84, 83	84
S-methyl DME	1.05	0	0.807, 0.679	77, 65	71
	1.05	34 / 1	0.822, 0.892, 0.747	78, 85, 71	78
	2.10	60 / 2	1.67, 1.66, 1.65	80, 79, 78	79
DME-OH	1.02	0	0.925, 0.769	90, 75	83
	1.00	34 / 1	0.777, 0.839, 0.747	78, 84, 75	79
	1.99	60 / 2	1.77, 1.65, 1.73	89, 83, 87	86
Gizzard					
DME	1.03	0	0.786, 0.827, 0.864	76, 80, 84	80
	1.03	21 / 0.7	0.724, 0.785, 0.802	70, 76, 78	75

Analyte	Fortification level (mg/kg)	Storage interval (days/months)	Recovery (%)		
			Residue (mg/kg)	% remaining	Mean of % remaining
	1.07	42 / 1.4	0.874, 0.907, 0.820	82, 85, 76	81
S-methyl DME	1.05	0	0.734, 0.796, 0.807	70, 76, 77	74
	1.05	21 / 0.7	0.709, 0.759, 0.787	67, 72, 75	71
	1.05	42 / 1.4	0.779, 0.812, 0.732	74, 77, 70	74
DME-OH	1.02	0	0.831, 0.860, 0.874	81, 84, 85	83
	1.02	21 / 0.7	0.791, 0.803, 0.840	77, 78, 82	79
	1.00	42 / 1.4	0.714, 0.739, 0.695	72, 74, 70	72
Liver					
DME	1.03	0	0.870, 0.867, 0.847	84, 84, 82	83
	1.03	21 / 0.7	0.830, 0.856, 0.851	81, 83, 83	82
	1.07	42 / 1.4	0.914, 0.856, 0.759	85, 80, 71	79
S-methyl DME	1.05	0	0.799, 0.814, 0.817	76, 77, 78	77
	1.05	21 / 0.7	0.806, 0.837, 0.803	77, 80, 76	78
	1.05	42 / 1.4	0.810, 0.769, 0.703	77, 73, 67	72
DME-OH	1.02	0	0.858, 0.851, 0.858	84, 83, 84	84
	1.02	21 / 0.7	0.857, 0.870, 0.825	84, 85, 81	83
	1.00	42 / 1.4	0.755, 0.704, 0.687	76, 71, 69	72
Muscle					
DME	1.03	0	0.780, 0.751, 0.821	76, 73, 80	76
	1.03	21 / 0.7	0.727, 0.768, 0.719	70, 74, 70	72
	1.07	42 / 1.4	0.793, 0.806, 0.884	74, 75, 82	77
S-methyl DME	1.05	0	0.756, 0.706, 0.781	72, 67, 74	71
	1.05	21 / 0.7	0.694, 0.740, 0.702	66, 70, 67	68
	1.05	42 / 1.4	0.710, 0.696, 0.788	68, 66, 75	70
DME-OH	1.02	0	0.805, 0.781, 0.852	79, 76, 83	79
	1.02	21 / 0.7	0.741, 0.782, 0.747	72, 76, 73	74
	1.00	42 / 1.4	0.636, 0.535, 0.729	64, 54, 73	64
Fat					
DME	1.03	0	0.697, 0.852, 0.780	68, 83, 76	75
	1.03	21 / 0.7	0.776, 0.815, 0.744	75, 79, 72	75
	1.07	42 / 1.4	0.794, 0.827, 0.833	74, 77, 78	76
S-methyl DME	1.05	0	0.728, 0.805, 0.750	69, 77, 71	72
	1.05	21 / 0.7	0.749, 0.795, 0.724	71, 76, 69	72
	1.05	42 / 1.4	0.691, 0.717, 0.743	66, 68, 71	68
DME-OH	1.02	0	0.702, 0.902, 0.816	69, 88, 80	79
	1.02	21 / 0.7	0.846, 0.909, 0.818	83, 89, 80	84
	1.00	42 / 1.4	0.703, 0.752, 0.741	71, 76, 74	74

USE PATTERN

Clethodim is a systematic and selective herbicide of the chemical group of cyclohexanedione. It delivers efficacy against annual and perennial weeds. The Meeting received labels for uses in Australia, Croatia, Estonia, Finland, France, Italy, Lithuania, Netherlands, Poland, Romania, Slovakia, Spain, Sweden, Switzerland and the USA. The information available to the Meeting on registered uses of clethodim is summarized in the table below.

Labels indicate to avoid contact of clethodim with grass crops such as corn, rice, sorghum, small grains, etc. as grass crops are highly sensitive to clethodim.

Table 64 Registered uses of clethodim for crops

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
Pome Fruit	Switzerland	EC	120 g/L	spray	0.24		1	-	Before flowering
Pome Fruit	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a]	4	14	PHI 14

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
Stone Fruit	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a]	4	14	PHI 14
Peach	USA	EC	120 g/L	spray[c]	0.079-0.14 max 0.56 /season	47-374a 28-94[b]	4	14	PHI 14 Application towards the basis of the plant
		EC	360 g/L	spray[c]	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14 Application towards the basis of the plant
Bushberry (for High bush)	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 14
Berry and Small Fruit Crops; Bushberry (for High bush)	USA	EC	120 g/L	spray[c]	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14 Application towards the basis of the plant
		EC	360 g/L	spray[c]	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14 Application towards the basis of the plant
Berry Low Growing (except Cranberry and Strawberry)	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 45
Cranberry	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374 [a] 28-94[b]	4	14	PHI 30 Do not apply between the “hook” stage and full fruit set.
		EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30 Do not apply between the “hook” stage and full fruit set.
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30 Do not apply between the “hook” stage and full fruit set.
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30 Do not apply between the “hook” stage and full fruit set.
Strawberry	Estonia	EC	120 g/L	spray	0.24	200-400	1	-	PHI 30 (BBCH 12-59, 91-97)
Strawberry	Finland	EC	120 g/L	spray	0.12-0.24	200-400			PHI 30 (BBCH 12-59, or after harvest)
Strawberries	Lithuania	EC	120 g/L	spray	0.12-0.24	200-400	1	-	PHI 30 (BBCH 12-59)
Strawberry	Netherlands	EC	120 g/L	spray	0.12-0.24	150-800	1	-	PHI 30 (BBCH 11-59, 91-93)
Strawberry	Poland	EC	120 g/L	spray	0.24	200-300	1	-	PHI 30 (BBCH 12-59, 91-93)
Strawberry	Romania	EC	120 g/L	spray	0.18-0.24				Postemergence
Strawberry	Slovakia	EC	120 g/L	spray	0.24	200-300	1	-	PHI 30 (BBCH 12-59, 91-93)
Strawberry	Sweden	EC	120 g/L	spray	0.24		1	-	PHI 30 (BBCH 12-59, 91-97)

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
Strawberry	Switzerland	EC	120 g/L	spray	0.24		1	-	Before flowering or after harvest
Strawberry	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 4
		EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 4
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 4
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 4
Onions	Australia	EC	120 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	PHI 14
		EC	240 g/L	spray	0.042-0.12	50-150[a] 20-30[b]	1	-	PHI 14
		EC	360 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	PHI 14
Onion	Croatia	EC	123 g/L	spray	0.20-0.25	200-400	1	-	PHI 49
Onion	Estonia	EC	120 g/L	spray	0.24	200-400	1	-	PHI 56 (BBCH 12-45)
Onion	Finland	EC	120 g/L	spray	0.12-0.24	200-400			PHI 56 (BBCH 12-41)
Onion	France	EC	120 g/L	spray	0.12				
		EC	240 g/L	spray	0.18		1	-	PHI 60
Onion	Italy	EC	120 g/L	spray	0.12-0.24	200-400	1	-	PHI 56
Onions	Lithuania	EC	120 g/L	spray	0.12-0.24	200-400	1	-	PHI 56 (BBCH 12-45)
Onions	Netherlands	EC	120 g/L	spray	0.24	200-400	1	-	PHI 56 (BBCH 12-45)
Onion from sowing	Poland	EC	120 g/L	spray	0.24	200-300	1	-	PHI 56 (BBCH 11-18)
Onion	Slovakia	EC	120 g/L	spray	0.24	200-300	1	-	PHI 56 (sowing) (BBCH 11-12)
Onion	Spain	EC	120 g/L	spray	0.12-0.18	200-400	1	-	PHI 56 (BBCH 12-45)
Onions	Sweden	EC	120 g/L	spray	0.24		1	-	BBCH 12-45
Onions	Switzerland	EC	120 g/L	spray	0.24		1	-	Waiting period: 8 weeks (Post-emergence)
Onions	USA	EC	116 g/L	spray	0.076-0.27 max 0.54 /season	187-374[a] 94[b]	2-4	14	PHI 45
		EC	120 g/L	spray	0.079-0.28[d] max 0.56 /season	187-374[a] 94[b]	2	14	PHI 45
		EC	240 g/L	spray	0.11-0.28[d] max 0.56 /season	187-374[a] 94[b]			PHI 45
		EC	360 g/L	spray	0.11-0.28[d] max 0.56 /season	187-374[a] 94[b]	2	14	PHI 45
Cauliflowers (Cauliflower, Broccoli)	Netherlands	EC	120 g/L	spray	0.24	150-600	1	-	PHI 28 (BBCH 12-41)
Cabbage	Australia	EC	120 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	PHI 7
		EC	240 g/L	spray	0.042-0.12	50-150[a] 20-30[b]	1	-	PHI 7

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
		EC	360 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	PHI 7
Cabbage	Estonia	EC	120 g/L	spray	0.24	200-400	1	-	PHI 28 (BBCH 12-41)
Cabbage	Finland	EC	120 g/L	spray	0.12-0.24	200-400			PHI 28 (BBCH 12-41)
Cabbage (headed, Savoy, randonguziai, Brussels)	Lithuania	EC	120 g/L	spray	0.12-0.24	200-400	1	-	PHI 28 (BBCH 12-41)
Cabbage	Netherlands	EC	120 g/L	spray	0.24	200-400	1	-	PHI 28 (BBCH 12-41)
Head cabbage (cultivation from seeding)	Poland	EC	120 g/L	spray	0.24	200-300	1	-	PHI 28 (BBCH 14-19)
Cabbage	Slovakia	EC	120 g/L	spray	0.24	200-300	1	-	PHI 28
Cabbage	Sweden	EC	120 g/L	spray	0.24		1	-	PHI 28 (BBCH 12-41)
Head cabbage	Switzerland	EC	120 g/L	spray	0.24		1	-	Waiting period: 4 weeks (Post-emergence)
Brassica Head and Stem Vegetables	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 30
Head & Stem Brassica Vegetables	USA	EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30
Squash/Cucumber	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 14
Cucurbits	USA	EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14
Lettuce	Australia	EC	120 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	PHI 28
		EC	240 g/L	spray	0.042-0.12	50-150[a] 20-30[b]	1	-	PHI 28
		EC	360 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	PHI 28
Leafy Greens	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 14
		EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 14

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
Pulse crops	Australia	EC	240 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	Adzuki beans: Do not apply after first flower buds are visible. Chickpeas, Faba beans, Broad beans, Field peas: Do not apply beyond full flowering. Lentils: Apply up to the 7 node/early branching stage of crop growth. Lupins: Do not apply after 80% of flowers have opened. Do not graze or cut for stock feed for 21 days after application.
		EC	360 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	Adzuki beans: Do not apply after first flower buds are visible. Chickpeas, Faba beans, Broad beans, Field peas: Do not apply beyond full flowering. Lentils: Apply up to the 7 node/early branching stage of crop growth. Lupins: Do not apply after 80% of flowers have opened. Do not graze or cut for stock feed for 21 days after application.
Chick peas, Faba beans, Field peas, Lupin	Australia	EC	120 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	
Beans	Croatia	EC	123 g/L	spray	0.20-0.25	200-400	1	-	PHI 42
Beans	Finland	EC	120 g/L	spray	0.12	200-400			PHI 30 (BBCH 12-19)
Beans (green, grains)	Lithuania	EC	120 g/L	spray	0.12	200-400	1	-	PHI 30 (BBCH 12-19)
Beans of the field	Romania	EC	120 g/L	spray	0.18-0.24				Post-emergence
Bean and pea (dry)	Spain	EC	120 g/L	spray	0.12	200-400	1	-	PHI 56
Beans/dried and fresh with skins	Sweden	EC	120 g/L	spray	0.12		1	-	BBCH 12-19
Beans	Switzerland	EC	120 g/L	spray	0.24		2		Post-emergence
Beans, Dry Shelled	USA	EC	120 g/L	spray	0.079-0.28 max 0.56 /season	47-374[a] 28-94[b]	2	14	PHI 30
		EC	240 g/L	spray	0.11-0.28 max 0.56 /season	47-374[a] 28-94[b]	2	14	PHI 30
		EC	360 g/L	spray	0.11-0.28 max 0.56 /season	47-374[a] 28-94[b]	2	14	PHI 30

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
Bean, Dry	USA	EC	240 g/L	spray	0.11-0.28 max 0.56 /season	47-374[a] 28-94[b]	2		PHI 30
Dried Shelled Pea and Bean (except Soya bean) Bean, Dry (except Soya bean)	USA	EC	116 g/L	spray	0.076-0.27 max 0.54 /season	47-374[a] 28-94[b]	2-4	14	PHI 30
Pea (dry)	Estonia	EC	120 g/L	spray	0.12	200-400	1	-	PHI 56 (BBCH 12-39)
Pea	Finland	EC	120 g/L	spray	0.12	200-400			PHI 56 (BBCH 12-39)
Fresh Beans and Dried Peas	France	EC	120 g/L	spray	0.12		1	-	PHI 30
		EC	240 g/L	spray	0.12		1	-	PHI 30
Fodder Legumes	France	EC	120 g/L	Spray	0.12				PHI 240
			240 g/L	spray	0.18				PHI 240
Peas for grain	Lithuania	EC	120 g/L	spray	0.12	200-400	1	-	PHI 56 (BBCH 12-39)
Chickpeas	Romania	EC	120 g/L	spray	0.18-0.24				Post-emergence
Peas	Slovakia	EC	120 g/L	spray	0.084-0.096 0.24-0.26	250-400	1	-	BBCH 12-30
Peas / dried	Sweden	EC	120 g/L	spray	0.12		1	-	BBCH 12-39
Peas without pods	Switzerland	EC	120 g/L	spray	0.12		1	-	Post-emergence
Protein pea	Switzerland	EC	120 g/L	spray	0.12		1	-	Before flowering
Pea, Dry Shelled	USA	EC	116 g/L	spray	0.076-0.14 max 0.14 /season	47-374[a] 28-94[b]	1	-	PHI 30 Apply before bloom
		EC	120 g/L	spray	0.079-0.14	47-374[a] 28-94[b]	1	-	PHI 30 For peas apply, before bloom
		EC	240 g/L	spray	0.11-0.14 max 0.54 /season	47-374[a] 28-94[b]	1	-	PHI 30 For peas apply, before bloom
		EC	360 g/L	spray	0.11-0.14	47-374[a] 28-94[b]	1	-	PHI 30 For peas apply, before bloom
Carrot	Estonia	EC	120 g/L	spray	0.24	200-400	1	-	PHI 40 (BBCH 12-45)
Carrot	Finland	EC	120 g/L	spray	0.12-0.24	200-400			PHI 40 (BBCH 12-45)
Carrot	France	EC	120 g/L	spray	0.24[5)]		1	-	PHI 40
		EC	240 g/L	sprat	0.24[5)]		1	-	PHI 40
Carrot	Italy	EC	120 g/L	spray	0.12-0.24	200-400	1	-	PHI 40
Carrots	Lithuania	EC	120 g/L	spray	0.12-0.24	200-400	1	-	PHI 40 (BBCH 12-45)
Carrots	Netherlands	EC	120 g/L	spray	0.24	200-400	1	-	PHI 48 (BBCH 12-45)
Carrot	Poland	EC	120 g/L	spray	0.24	200-300	1	-	PHI 40 (BBCH 12-19)
Carrot	Slovakia	EC	120 g/L	spray	0.24	200-300	1	-	PHI 40 (BBCH 12-19)
Carrot	Spain	EC	120 g/L	spray	0.12-0.18	200-400	1	-	PHI 40 (BBCH 12-45)
Carrot	Sweden	EC	120 g/L	spray	0.24		1	-	PHI 40 (BBCH 12-45)
Carrots	Switzerland	EC	120 g/L	spray	0.24		1	-	Waiting period: 8 weeks (Post-emergence)
Carrot	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 30

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
		EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 30
Artichoke	Spain	EC	120 g/L	spray	0.12-0.18	200-400	1	-	PHI 40 (BBCH 12-51)
Artichoke (Globe)	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 5
		EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 5
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 5
Canola	Australia	EC	120 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	PHI 56
		EC	240 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	Do not apply after flower buds become visible.
		EC	360 g/L	spray	0.036-0.12	50-150[a] 20-30[b]	1	-	Do not apply after flower buds become visible.
Rapeseed	Croatia	EC	123 g/L		0.20-0.25	200-400	1	-	Before the flowering begins
Canola / Winter rape	Estonia	EC	120 g/L	spray	0.12	200-400	1	-	PHI 90 (BBCH 12-50)
Spring and autumn leaves and rapeseed	Finland	EC	120 g/L	spray	0.12	200-400			PHI 90 (BBCH 12-50)
Winter and spring rape	Lithuania	EC	120 g/L	spray	0.12	200-400	1	-	PHI 90 (BBCH 12-30)
Winter rape	Netherlands	EC	120 g/L	spray	0.12	200-400	1	-	PHI 120 (BBCH 12-30)
Winter rape	Poland	EC	120 g/L	spray	0.096	200-300	1	-	PHI 120 (BBCH 12-30)
Rape	Romania	EC	120 g/L		0.096				Post-emergence
Winter rape	Slovakia	EC	120 g/L	spray	0.096	200-300	1	-	PHI 120 (BBCH 12-30)
		EC	120 g/L	spray	0.084-0.096* 0.24-0.26**	250-400	1	-	*autumn application **spring application BBCH 12-30
Rape	Spain	EC	120 g/L	spray	0.12	200-400	1	-	PHI 120 (BBCH 12-32)
Rapes	Sweden	EC	120 g/L	spray	0.12		1	-	BBCH 12-50
Rape	Switzerland	EC	120 g/L	spray	0.12		1	-	Before flowering
Canola	USA	EC	116 g/L	spray	0.076-0.10 max 0.10 /season	47-374[a] 28-94[b]	1	-	PHI 70 Do not apply after crop has begun bolting.
		EC	120 g/L	spray	0.079-0.11 max 0.11 /season	47-374[a] 28-94[b]	-	-	PHI 70 Do not apply after crop has begun bolting.
		EC	240 g/L	spray	0.070-0.11 max 0.28 /season	47-374[a] 28-94[b]			PHI 70 Do not apply after crop has begun bolting.

Crop	Country	Formulation		Application					PHI, days and/or Application timing
		Type	Conc.	Method	Rate kg ai/ha	Water L/ha	No. max	Interval, days	
		EC	240 g/L	spray	0.070-0.11 max 0.11 /season	47-374[a] 28-94[b]			PHI 70 Do not apply after crop has begun bolting.
		EC	360 g/L	spray	0.070-0.14	47-374[a] 28-94[b]			PHI 70 Do not apply after crop has begun bolting.
Safflower	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 70
		EC	120 g/L	spray	0.079-0.14 max 0.28 /season	47-374[a] 28-94[b]	2	14	PHI 70
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]		14	PHI 70
		EC	360 g/L	spray	0.11-0.14 max 0.28 /season	47-374[a] 28-94[b]	2	14	PHI 70
Hops	USA	EC	116 g/L	spray	0.076-0.14 max 0.54 /season	47-374[a] 28-94[b]	4	14	PHI 21
		EC	120 g/L	spray	0.079-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 21
		EC	240 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 21
		EC	360 g/L	spray	0.11-0.14 max 0.56 /season	47-374[a] 28-94[b]	4	14	PHI 21

[a] Ground Application

[b] Aerial Application

[c] Direct the application towards the base of the plant to avoid contact with leaf tissue.

[d] For aerial application do not exceed 0.14 kg ai/ha in a single application to onion.

RESULTS OF SUPERVISED RESIDUE TRIALS ON CROPS

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

Group	Commodity	Table
Pome fruits	Apple	Table 61
	Pear	Table 62
Stone fruits	Cherry	Table 63
	Plum	Table 64
	Peach	Table 65
Berries and other small fruits	Blueberry	Table 66
	Cranberry	Table 67
	Strawberry	Table 68, 69
Bulb vegetables	Onion	Table 70
Brassica vegetables (except Brassica leafy vegetables)	Broccoli	Table 71
	Cabbage	Table 72, 73
Fruiting vegetables, Cucurbits	Cucumber	Table 74

Group	Commodity	Table
Leafy vegetables (including Brassica leafy vegetables)	Lettuce, Head	Table 75
Pulses	Beans (dry)	Table 76
	Peas (dry)	Table 77-79
Root and tuber vegetables	Carrot	Table 80-82
Stalk and stem vegetables	Artichoke	Table 83-84
Oilseed	Rape seed	Table 85-87
Dried herbs	Hops, dry	Table 88
Legume Animal feeds	Bean fodder	Table 89
	Bean forage	Table 90
	Pea fodder	Table 91, 92
	Pea vines	Table 93

Clethodim formulation was applied for broadcast treatment. Each of the field trial sites generally consisted of an untreated control plot and a treated plot. Application rates and residue concentrations have generally been rounded to two significant figures.

Residue values from the trials, which have been used for the estimation of maximum residue levels, STMRs and HRs, are underlined.

Laboratory reports included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Date of analyses and duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables except when residues were found in samples from control plots. Residue data are not corrected for percent recovery.

Conditions of the supervised residue trials were generally well reported in detailed field reports. Most field reports provided data on the applicators used, plot size, field sample size and sampling date.

The residue concentrations are reported for DME moiety and DME-OH moiety in common moiety methods or for clethodim, clethodim sulfoxide and clethodim sulfone in a specific individual method, additionally M17R and M18R in some reports. All residues were expressed as clethodim equivalent using the conversion factors of 1.2 (360/294 = 1.22) for DME, 1.2 (360/310 = 1.16) for DME-OH, 0.96 (360/376 = 0.96) for clethodim sulfoxide, 0.92 (360/392 = 0.92) for clethodim sulfone, 1.44 (360/250 = 1.44) for M17R and 1.35 (360/266 = 1.35) for M18R.

Total residues for estimation of maximum residues levels are calculated by summing up the concentrations of clethodim, clethodim sulfoxide and clethodim sulfone in a specific individual method.

The method for calculation of the total residues for plant commodities using specific individual methods is illustrated below. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone are all 0.005 mg/kg (expressed as clethodim equivalents).

Clethodim	Clethodim sulfoxide	Clethodim sulfone	Total
< 0.005	0.17	0.012	0.19
< 0.005	0.074	< 0.005	0.084
< 0.005	< 0.005	< 0.005	< 0.015

The method for calculation of the total residues for plant commodities using common moiety methods is illustrated below.

DME	DME-OH	Total
< 0.095	< 0.088	< 0.18
0.18	< 0.088	0.27

Pome fruits

Apple

The Meeting received 13 trials (at harvest trials) on apple which were conducted in the USA (Homa, 2012: IR-4 PR No. 06873). In each of these trials, two broadcast or banded applications of an EC formulation (116 g ai/L) directed to the ground were made at a nominal rate of 0.28 kg ai/ha. The first application was made 6-16 days prior to the second application. All applications were made in tank-mix with an adjuvant, non-ionic surfactant (NIS). At each trial, fruits were taken 14 ± 2 days after last application (DALA).

Samples were analysed for total residues of clethodim by the GC-FPD methods CAL version 15. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LODs for DME and DME-OH were both 0.03 mg/kg (expressed as clethodim equivalents). Apple fruit samples were stored at -21 ± 7 °C for a maximum of 19 months between sampling and analysis.

Table 65 Residues of clethodim and metabolites on apple from supervised trials in the USA

Apple country, year (variety)	Application					DALA Days	Residues, mg/kg [b]			Ref
	Form	kg ai /ha	L/ha	Growth Stage [a]	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.54 /year*	-		*4*	*14*				
USA, 2008 Lansing, NY[d] (McIntosh) Outdoor	EC	0.28 0.28	322 320	Fruiting Fruiting (6 days)	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	IR-4 PR No. 06873
USA, 2008 Grand Junction, CO (Gala) Outdoor	EC	0.28 0.29	292 294	Fruiting Fruiting (14 days)	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	Mean recovery for clethodim sulfoxide analysed by DME: 96% (n=14) at 0.1 mg/kg 92% (n=2) at 1.0 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 99% (n=14) at 0.1 mg/kg 84% (n=2) at 1.0 mg/kg Sampling to analysis: 211-567 days
USA, 2008 Sunny Slope, ID (Rome (Law Strain)) Outdoor	EC	0.28 0.28	140 139	Fruiting Fruiting (16 days)	2	12	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2008 Lansing, NY[d] (Empire) Outdoor	EC	0.28 0.28	320 322	Fruiting Fruiting (6 days)	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2008 Prosser, WA[e] (Fuji) Outdoor	EC	0.28 0.27	241 246	Fruiting Fruiting (14 days)	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2008 Prosser, WA[f] (Yellow Delicious) Outdoor	EC	0.28 0.28	247 258	Fruiting Fruiting (14 days)	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2008 Parlier, CA (Fuji) Outdoor	EC	0.29 0.29	295 289	Fruiting Fruiting (14 days)	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2008 North Rosa, NY (Empire) Outdoor	EC	0.29 0.28	190 188	Early Ripening Advanced Ripening (14 days)	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2008 Holt, MI	EC	0.28 0.29	282 192	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18	

Apple country, year (variety)	Application					DALA Days	Residues, mg/kg [b]			Ref
	Form	kg ai /ha	L/ha	Growth Stage [a]	no.		DME	DME -OH	Total	
(Empire) Outdoor				(15 days)					(< 0.18)	
USA, 2008 Lyons, NY (Granny Smith) Outdoor	EC	0.29[c] 0.28[c]	285281	Fruit at 60 % final size Fruit about 90 % final size (14 days)	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Lansing, NY (McIntosh) Outdoor	EC	0.28 0.28	331 316	Fruiting Fruiting (14 days)	2	12	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Holt, MI (Gala) Outdoor	EC	0.28 0.28	187 188	Fruiting Fruiting (13 days)	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Yakima, WA (Granny Smith) Outdoor	EC	0.28 0.29	239 241	Fruiting Fruiting (14 days)	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	

Portion analysed: fruit

[a] Re-treatment interval is given in parenthesis.

[b] Mean of replicate field samples is given in parenthesis.

[c] Banded applications

[d] Address: IR-4 Apple Orchard, located at Lansing Orchards, Cornell University, Sweazey Road, Lansing, NY Tompkins County, Application dates (1st): 22 Aug 2008

[e] Address: IAREC, Roza Farm, Plot D-45, Prosser, WA 99350 Benton County, Application dates (1st): 25 Aug 2008

[f] Address: WSU-IAREC, 24106 N. Bunn Rd., Prosser, WA 99350 Benton County, Application dates (1st): 25 Aug 2008

Pear

The Meeting received six trials (at harvest trials) on pear which were conducted in the USA (Homa, 2011: IR-4 PR No. 06874). In each of these trials, two broadcast spray applications directed to the ground of an EC formulation (116 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 2 days prior to the second application. All applications were made in tank-mix with an adjuvant, NIS or crop oil concentrate (COC). At each trial, fruits were taken 14 ± 2 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-3. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LODs for DME and DME-OH were both 0.02 mg/kg (expressed as clethodim equivalents). Pear fruit samples were stored at -4 to -23 °C for a maximum of 23 months between sampling and analysis.

Table 66 Residues of clethodim and metabolites on pear from supervised trials in the USA

Pear country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.54 /year*	-		*4*	*14*				
USA, 2008 Kingsbury, CA	EC	0.30 0.29	297 341	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18	IR-4 PR No. 06874

Pear country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
(Yoinashi) Outdoor									(≤ 0.18)	Mean recovery for clethodim sulfoxide analysed by DME: 102% (n=9) at 0.1 mg/kg 90% (n=3) at 1.0 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 102% (n=9) at 0.1 mg/kg 88% (n=3) at 1.0 mg/kg Sampling to analysis: 678-713 days
USA, 2008 Courtland, CA (Bartlett) Outdoor	EC	0.27 0.27	209 210	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	
USA, 2008 Sunny Slope, ID (Bartlett) Outdoor	EC	0.28 0.28	234 235	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	
USA, 2008 Lansing, NY (Bosc) Outdoor	EC	0.28 0.28	322 321	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	
USA, 2008 Hood River, OR (Anjou) Outdoor	EC	0.28 0.31	286 308	Green Fruit Fruiting	2	16	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	
USA, 2009 Prosser, WA (Bosc) Outdoor	EC	0.28 0.28	246 252	Fruiting Fruiting	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	

Portion analysed: fruit

[a] Mean of replicate field samples is given in parenthesis.

Stone fruits

Subgroup of Cherries

Cherry

The Meeting received 1five trials (14 trials; at harvest trials, one trial; decline trial) on cherry which were conducted in Canada and the USA (Homa, 2013: IR-4 PR No. 06877). In each of these trials, two or three broadcast or banded applications directed to the ground of an EC formulation (116 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 2 days prior to the second application. All applications were made in tank-mix with an adjuvant, NIS. At each trial, fruits were taken 14 ± 2 DALA. In the decline trial additional samples were collected at 1, 4, 7 and 18 DALA.

Samples were analysed for total residues of clethodim by methods RM-26B-3 using GC-MS instead of GC-FPD. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LOD for DME was 0.03 mg/kg and DME-OH was 0.01 mg/kg (expressed as clethodim equivalents). Cherry fruit samples were stored at -4 to -23 °C for a maximum of 27 months between sampling and analysis.

Table 67 Residues of clethodim and metabolites on cherry from supervised trials in Canada and the USA

Cherry country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*14*				
Cherry, Sweet										IR-4 PR No. 06877
USA, 2009 Tulare, CA[c] (Tulare) Outdoor	EC	0.28 [b] 0.28 [b] 0.28 [b]	249 256 256	Fruiting Fruiting Fruiting	3	1 4 7 14 18	< 0.095 < 0.095 < 0.095 < 0.095 < 0.095 < 0.095 < 0.095 < 0.095 < 0.095 < 0.095	< 0.088 < 0.088 < 0.088 < 0.088 < 0.088 < 0.088 < 0.088 < 0.088 < 0.088 < 0.088	< 0.18 < 0.18 (< 0.18) < 0.18 < 0.18 (< 0.18) < 0.18 < 0.18 (< 0.18) < 0.18 < 0.18 (< 0.18) < 0.18 < 0.18 (< 0.18)	Mean recovery for clethodim sulfoxide analysed by DME: 89% (n=36) at 0.1 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 75% (n=36) at 0.1 mg/kg Sampling to analysis: 722-811 days
USA, 2009 Tulare, CA[c] (Brooks) Outdoor	EC	0.27 [b] 0.28 [b]	285 294	Fruit set Fruiting	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Holt, MI (Ulster) Outdoor	EC	0.28 0.28	190 186	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Clarksville, MI (Ulster) Outdoor	EC	0.30 0.30	198 198	Fruiting Fruiting	2	16	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Filer, ID (Bing) Outdoor	EC	0.28 0.28	187 188	Fruit fill Fruit fill	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Prosser, WA (Sweetheart) Outdoor	EC	0.28 0.27	252 216	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Moxee, WA (Bing) Outdoor	EC	0.28 0.28	307 308	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
Canada, 2009 Jordan Station, ON (Vogue) Outdoor	EC	0.29 0.29	257 262	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
Cherry, Tart										
USA, 2009 Holt, MI[d] (Montmorency) Outdoor	EC	0.28 0.29	190 194	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Clarksville, MI (Montmorency) Outdoor	EC	0.29 0.28	191 189	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Fennville, MI (Montmorency)	EC	0.29 0.29	194 193	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	

Cherry country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
Outdoor										
USA, 2009 Holt, MI[e] (Montmorency) Outdoor	EC	0.28 0.29	190 192	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Hotchkiss, CO (Montmorency) Outdoor	EC	0.28 0.28	262 255	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2009 Lansing, NY (Galaxy) Outdoor	EC	0.28 0.28	312 332	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
Canada, 2009 Niagra-on-the-Lake, ON (Montmorency) Outdoor	EC	0.29 0.29	259 257	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	

Portion analysed: fruit

[a] Mean of replicate field samples is given in parenthesis.

[b] Banded applications

[c] Address: Lagomarsino Farming LLC, 12704 Avenue 232, Tulare, CA Tulare County, Application dates (1st): 2 Apr 2009

[d] Address: Horticulture Teaching and Research Center: HTRC, 3291 College Rd. Holt, MI 48842 Ingham County
Application dates (1st): 29 Jun 2009

[e] Address: Botany / Plant Pathology Farm, 3291 College Road, Holt, MI Ingham County
Application dates (1st): 15 Jun 2009

Subgroup of Plums

Plum

The Meeting received six trials (at harvest trials) on plum which were conducted in the USA (Homa, 2011: IR-4 PR No. 06948). In each of these trials, two broadcast or banded applications directed to the ground of an EC formulation (116 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 2 days prior to the second application. All applications were made in tank-mix with an adjuvant, NIS or COC. At each trial, fruits were taken 14 ± 2 DALA.

Samples were analysed for total residues of clethodim by methods RM-26B-3 using GC-MS instead of GC-FPD. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LOD for DME was 0.03 mg/kg and DME-OH was 0.02 mg/kg (expressed as clethodim equivalents). Plum fruit samples were stored at -4 to -22 °C for a maximum of 28 months between sampling and analysis.

Table 68 Residues of clethodim and metabolites on plum from supervised trials in the USA

Plum country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*14*				
USA, 2008 Parlier, CA[c] (Black Amber) Outdoor	EC	0.29 [b] 0.28 [b]	295 306	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	IR-4 PR No. 06948
USA, 2008 Parlier, CA[d] (French) Outdoor	EC	0.28 [b] 0.29 [b]	322 327	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	Mean recovery for clethodim sulfoxide analysed by DME: 89% (n=14) at 0.1 mg/kg
USA, 2008 Winters, CA[e] (French Prune) Outdoor	EC	0.29 0.28	220 216	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	
USA, 2008 Winters, CA[f] (French Prune) Outdoor	EC	0.27 0.28	207 215	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	Mean recovery for 5-OH clethodim sulfone analtsed by DME-OH: 75% (n=14) at 0.1 mg/kg
USA, 2008 Holt, MI (Stanley) Outdoor	EC	0.28 0.27	282 272	Fruiting Fruiting	2	12	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	
USA, 2008 Salem, OR (Brooks) Outdoor	EC	0.29 [b] 0.28 [b]	288 287	Green plums Fruiting, not ripe yet	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (≤ 0.18)	Sampling to analysis: 763-840 days

Portion analysed: fruit

[a] Mean of replicate field samples is given in parenthesis.

[b] Banded applications

[c] Address: UC Kearney Research and Extension Center, 9240 S. Riverbend Ave., Parlier, CA 93648 Fresno County

Application dates: 28 May (1st) and 9 June (2nd) 2008

[d] Address: UC Kearney Research and Extension Center, 9240 S. Riverbend Ave., Parlier, CA 93648 Fresno County

Application dates: 31 Jul (1st) and 14 Aug (2nd) 2008

[e] Address: U.C. Davis Plant Science Dept., Wolfskill Experimental Farm, 4334 Putah Creek Rd., Winters, CA Solano County

Application dates (1st): 30 Jul 2008

[f] Address: U.C. Davis Plant Science Dept., Wolfskill Field Research Station, 4334 Putah Creek Rd., Winters, CA Solano County

Application dates (1st): 6 Aug 2008

Subgroup of Peaches

Peach

The Meeting received 9 trials (at harvest trials) on peach which were conducted in the USA (Samoil, 2008: IR-4 PR No. 06875). In each of these trials, two broadcast spray applications directed to the ground of an EC formulation (113 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 2 days prior to the second application. All applications were made in tank-mix with an adjuvant, COC. At each trial, fruits were taken 14 ± 2 DALA except in one trial which fruits were sampled 8 DALA because of an unexpected early ripening.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-3. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LOD for DME was 0.03 mg/kg and DME-OH was 0.04 mg/kg (expressed as clethodim equivalents). Peach fruit samples were stored at -12 to -22 °C for a maximum of 22 months between sampling and analysis.

Table 69 Residues of clethodim and metabolites on peach from supervised trials in the USA

Peach country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*14*				
USA, 2004 Davis, CA (Fay Elberta) Outdoor	EC	0.28 0.28	278 276	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	IR-4 PR No. 06875
USA, 2004 Parlier, CA (Flavorcrest) Outdoor	EC	0.28 0.28	231 234	Immature fruit Immature fruit (2-3 inch diameter)	2	12	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	Mean recovery for clethodim sulfoxide analysed by DME: 107% (n=10) at 0.1 mg/kg 109% (n=2) at 1.0 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 94% (n=10) at 0.1 mg/kg 95% (n=2) at 1.0 mg/kg Sampling to analysis: 606-677 days
USA, 2004 Madera, CA (Last Chance) Outdoor	EC	0.28 0.28	230 232	Coloring fruit Coloring fruit	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2004 Holt, MI (Red Haven) Outdoor	EC	0.28 0.28	185 188	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2004 Bridgeton, NJ (Dixie Red) Outdoor	EC	0.27 0.27	201 200	Fruiting Fruiting	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2004 Lansing, NY (Harrow Diamond/ Lovell) Outdoor	EC	0.30 0.31	296 310	Fruiting (2-3 inch diameter) Fruiting (3-4 inch diameter)	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2004 Jackson Springs, NC[b] (Contender) Outdoor	EC	0.28 0.28	332 327	Fruiting Fruiting	2	12	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2004 Jackson Springs, NC[c] (Emery) Outdoor	EC	0.27 0.29	276 289	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2004 Fredricksburg, TX (Gold Prince) Outdoor	EC	0.28 0.28	238 237	Green fruit the size of a golf ball Fruit is red in color, commercially harvestable	2	8	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	

Portion analysed: fruit

[a] Mean of replicate field samples is given in parenthesis.

[b] Address: Field C5C, Sandhills Research Station, 2148 Windblow Road,Jackson Springs, NC 27281-9124
Application dates (1st): 13 Jun 2004

[c] Address: Field F3C, Sandhills Research Station, 2148 Windblow Road,Jackson Springs, NC 27281-9124
Application dates (1st): 9 Jul 2004

Berries and other small fruits

Subgroup of Bush berries

Blueberry

The Meeting received 9 trials (at harvest trials) on blueberry which were conducted in Canada and the USA (Samoil, 2008: IR-4 PR No. 05234). In each of these trials, two banded applications directed to the ground (highbush variety, 8 trials) or broadcast applications over the top (lowbush variety, one trial) of an EC formulation (113 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 1 days prior to the second application. All applications were made in tank-mix with an adjuvant, COC. At each trial, berries were taken 13-20 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods CAL version 15. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LODs for DME and DME-OH were both 0.02 mg/kg (expressed as clethodim equivalents). Blueberry samples were stored at -21 ± 7 °C for a maximum of 4 months between sampling and analysis.

Table 70 Residues of clethodim and metabolites on blueberry from supervised trials in Canada and the USA

Blueberry country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*14*				
USA, 2005 Creston, CA (Misty) Outdoor	EC	0.29 0.29	293 287	Fruiting Fruiting	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (<u>≤ 0.18</u>)	IR-4 PR No. 05234
USA, 2004 Jonesboro, ME (Wild)[b] Outdoor	EC	0.28 0.29	190 195	Fruiting Fruiting	2	14	1.6 2.0	0.46 0.53	2.1 2.5 (2.3)	Mean recovery for clethodim sulfoxide analysed by DME: 102% (n=9) at 0.1 mg/kg 82% (n=3) at 3.0 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 99% (n=9) at 0.1 mg/kg 74% (n=3) at 3.0 mg/kg Sampling to analysis: 87-132 days
USA, 2004 Holt, MI (Jersey) Outdoor	EC	0.28 0.29	190 197	Bloom Fruiting	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (<u>≤ 0.18</u>)	
USA, 2004 Chatsworth, NJ (Bluecrop) Outdoor	EC	0.27 0.27	166 166	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (<u>≤ 0.18</u>)	
USA, 2004 Castle Hayne, NC [c] (Croatan) Outdoor	EC	0.28 0.28	304 304	Fruiting Fruiting	2	15	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (<u>≤ 0.18</u>)	
USA, 2004 Castle Hayne, NC [d] (NC2678) Outdoor	EC	0.28 0.28	302 298	Fruiting Fruiting	2	20	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	
USA, 2004 Aurora, OR (Bluecrop) Outdoor	EC	0.30 0.30	299 295	Green fruit Green fruit	2	14	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (<u>≤ 0.18</u>)	
Canada, 2004 Matsqui, BC	EC	0.29 0.29	165 169	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18	

Blueberry country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
(Bluecrop) Outdoor									(< 0.18)	
Canada, 2004 St-Paul d'Abbotsford, QC (Northland) Outdoor	EC	0.27 0.29	225 244	Fruiting Fruiting	2	13	< 0.095 < 0.095	< 0.088 < 0.088	< 0.18 < 0.18 (< 0.18)	

Portion analysed: berry

[a] Mean of replicate field samples is given in parenthesis.

[b] Low bush variety. Broadcast applications over the top.

[c] Address: Field F1, Ideal Blueberry Tract, Horticultural Crops Research Station, 3800 Castle Hayne Road, Castle Hayne, NC 28429-6519

Application dates (1st): 4 May 2004

[d] Address: Field F1, Ideal Blueberry Tract, Horticultural Crops Research Station, 3800 Castle Hayne Road, Castle Hayne, NC 28429-6519

Application dates (1st): 11 May 2004

Subgroup of Low growing berries

Cranberry

The Meeting received three trials (at harvest trials) on cranberry which were conducted in the USA (Samoil, 1999: IR-4 PR No. 05358). In each of these trials, two foliar broadcast applications of an EC formulation (113 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 or 21 days prior to the second application. All applications were made in tank-mix with an adjuvant, COC. At each trial, berries were taken 29-30 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.05 mg/kg (expressed as clethodim equivalents). Cranberry samples were stored at -12 to -22 °C for a maximum of 24 months between sampling and analysis.

Table 71 Residues of clethodim and metabolites on cranberry from supervised trials in the USA

Cranberry country, year (variety)	Application					DALA Days	Residues, mg/kg [b]			Ref
	Form	kg ai /ha	L/ha	Growth Stage [a]	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*30*				
USA, 1994 Warrens, WI (Searles) Outdoor	EC	0.31 0.27	187 189	Green berries Green berries (14 days)	2	29	0.18 0.15	0.14 0.13	0.32 0.28 (0.30)	IR-4 PR No. 05358 Mean recovery for clethodim sulfoxide analysed by DME: 115% (n=2) at 0.05 mg/kg 70% (n=1) at 0.5 mg/kg

Cranberry country, year (variety)	Application					DALA Days	Residues, mg/kg [b]			Ref
	Form	kg ai /ha	L/ha	Growth Stage [a]	no.		DME	DME -OH	Total	
USA, 1994 Long Beach, WA (McFarland) Outdoor	EC	0.28 0.27	255 241	Green berries Ripening fruit (14 days)	2	29	0.08 0.07	0.08 0.06	0.16 0.13 (0.15)	74% (n=4) at 1.0 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 151% (n=2) at 0.05 mg/kg 97% (n=1) at 0.5 mg/kg 89% (n=4) at 1.0 mg/kg Sampling to analysis: 692-731 days
USA, 1994 Wareham, MA (Early Black) Outdoor	EC	0.28 0.28	468 468	Early fruit Fruit (21 days)	2	30	0.14 0.13	0.14 0.14	0.29 0.27 (0.28)	

Portion analysed: berry

[a] Re-treatment interval is given in parenthesis.

[b] Mean of replicate field samples is given in parenthesis.

Strawberry

The Meeting received 8 trials (decline trials) on strawberry which were conducted in Europe (Balluff, 2000: 99182/E1-FPST and Brielbeck, 2000: AB 94510-RU-010C). In each of these trials, one foliar broadcast application of an EC formulation (240 g ai/L) was made at a nominal rate of 0.24 kg ai/ha. All applications were made in tank-mix with an adjuvant, COC. At each trial, berries were taken at four sampling events in the range of 13-47 DALA (Balluff, 2000) or at two sampling events at 28 and 35 DALA (Brielbeck, 2000).

Samples (Balluff, 2000) were analysed for total residues of clethodim by methods RM-26B-2 using GC-MS instead of GC-FPD. The LOQ for total clethodim was 0.05 mg/kg. The LOD for DME was 0.01 mg/kg and DME-OH was 0.015 mg/kg (expressed as clethodim equivalents). Strawberry samples were stored at ≤-18 °C for a maximum of 7 months between sampling and analysis.

Samples (Brielbeck, 2000) were analysed for total residues of clethodim by methods RM-26B-2 using GC-NPD instead of GC-FPD. The LOQ for total clethodim was 0.11 mg/kg. Strawberry samples were stored at -20 °C between sampling and analysis.

Table 72 Residues of clethodim and metabolites on strawberry from supervised trials in Europe

Strawberry country, year (variety)	Application					DALA Days	Residues, mg/kg			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
GAP, Netherlamds etc	*EC*	*0.24*	*200-400*		*1*	*30*				
Germany, 1999 Esterbrügge Lower Saxonia[a]	EC	0.27	307	63	1	18 25 29	0.33 0.11 0.07	0.42 0.22 0.15	0.75 0.33 0.22	99182/E1-FPST Mean recovery for

Strawberry country, year (variety)	Application					DALA Days	Residues, mg/kg			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
(Symphony) Outdoor						34	0.05	0.12	0.17	clethodim analysed by DME: 95% (n=2) at 0.05 mg/kg 79% (n=1) at 0.5 mg/kg Sampling to analysis: 135-212 days
Germany, 1999 Esterbrügge Lower Saxonia[b] (Honeone) Outdoor	EC	0.27	304	59	1	23 29 33 38	0.07 0.03 0.02 0.01	0.13 0.06 0.04 0.03	0.20 <u>0.09</u> 0.06 < 0.05	
UK, 1999 Upton Bishop (Everest) Outdoor	EC	0.28	205	61	1	13 19 25 32	0.16 0.09 0.06 0.03	0.21 0.14 0.10 0.06	0.37 0.23 0.16 <u>0.09</u>	
UK, 1999 Ightham (Bolero) Outdoor	EC	0.27	199	61	1	27 34 41 47	0.03 0.02 0.01 < 0.01	0.04 0.03 < 0.015 < 0.015	<u>0.07</u> 0.05 < 0.05 < 0.05	
Germany, 2000 Münster (-) Outdoor	EC	0.24	-	-	1	28 36	Not reported		<u>0.22</u> 0.17	AB 94510-RU-010C Mean recovery for clethodim: 89% (n=3) at 0.11 mg/kg 96% (n=3) at 0.28 mg/kg 97% (n=3) at 0.56 mg/kg 101% (n=3) at 1.1 mg/kg Sampling to analysis: not reported
Germany, 2000 Vechta (-) Outdoor	EC	0.24	-	-	1	28 35	Not reported		<u>0.19</u> 0.12	
Germany, 2000 Karlsruhe (-) Outdoor	EC	0.24	-	-	1	28 35	Not reported		0.14 <u>0.16</u>	
Germany, 2000 Jork (-) Outdoor	EC	0.24	-	-	1	28 35	Not reported		<u>0.13</u> 0.12	

Portion analysed: berry

[a] Address:-, Application dates: 20 May 1999

[b] Address:-, Application dates: 31 May 1999

The Meeting received 7 trials (decline trials) on strawberry which were conducted in the USA (Braverman and Curry, 1999: IR-4 PR No. 05230). In each of these trials, two foliar broadcast applications of an EC formulation (113 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 1 days prior to the second application. All applications were made in tank-mix with an adjuvant, COC. At each trial, fruits were taken 4 ± 1 and 7 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.05 mg/kg (expressed as clethodim equivalents). Strawberry fruit samples were stored at -12 to -22 °C or below for a maximum of 28 months between sampling and analysis.

Table 73 Residues of clethodim and metabolites on strawberry from supervised trials in the USA

Strawberry country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*4*				
USA, 1994 Gainesville, FL (Sweet Charlie)	EC	0.27 0.29	273 302	not reported	2	4	0.33 0.36	0.20 0.17	0.52 0.53 (0.53)	IR-4 PR No. 05230

Strawberry country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
Outdoor						7	0.15 0.20	0.12 0.14	0.27 0.34 (0.31)	Mean recovery for clethodim sulfoxide analysed by DME: 96% (n=15) at 0.05 mg/kg 74% (n=2) at 0.5 mg/kg 61% (n=1) at 1.0 mg/kg 65% (n=13) at 2.0 mg/kg 57% (n=3) at 20 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 102% (n=15) at 0.05 mg/kg 83% (n=2) at 0.5 mg/kg 84% (n=1) at 1.0 mg/kg 71% (n=13) at 2.0 mg/kg 49% (n=3) at 20 mg/kg Sampling to analysis: 357-842 days
USA, 1994 Prosser, WA (Sumas) Outdoor	EC	0.28 0.28	210 205		2	4 7	0.43 0.52 0.37 0.35	0.46 0.57 0.46 0.43	0.89 1.1 (0.99) 0.83 0.77 (0.80)	
USA, 1994 Salinas, CA (Selva) Outdoor	EC	0.27 0.27	563 569		2	3 7	0.60 0.63 0.54 0.50	0.18 0.16 0.27 0.27	0.78 0.78 (0.78) 0.81 0.77 (0.79)	
USA, 1995 Salinas, CA (Commander) Outdoor	EC	0.27 0.26	415 403		2	4 7	< 0.05 1.7 0.57 0.40	< 0.05 0.22 0.10 0.08	< 0.10 2.0 (1.0) 0.67 0.47 (0.57)	
USA, 1995 Bridgeton, NJ (Early Glow) Outdoor	EC	0.28 0.28	390 390		2	4 7	1.1 1.0 0.87 1.0	0.66 0.62 0.80 0.89	1.7 1.7 (1.7) 1.7 1.9 (1.8)	
USA, 1995 Lansing, MI (Honeoye) Outdoor	EC	0.28 0.29	184 192		2	4 7	0.96 0.93 0.62 0.77	0.76 0.80 0.74 0.84	1.7 1.7 (1.7) 1.3 1.6 (1.5)	
USA, 1995 Raleigh, NC (Appollo) Outdoor	EC	0.28 0.30	179 193		2	4 7	0.47 0.44 0.29 0.32	0.33 0.28 0.30 0.34	0.80 0.72 (0.76) 0.59 0.65 (0.62)	

Portion analysed: berry

[a] Mean of replicate field samples is given in parenthesis.

Bulb vegetables

Subgroup of Bulb Onions

Onion

The Meeting received 2 trials (at harvest trials) on onion conducted in Norway (Klump, 2000: 20001029/01-RP). In each of these trials, an EC formulation (240 g ai/L) was applied to three different plots. In a first and second plot one application was made at either 0.090 kg ai/ha or 0.18 kg ai/ha, respectively, and in a third plot two applications were made at 0.090 kg ai/ha. At each trial, bulbs were taken 36 or 59 DALA.

Samples were analysed for total residues of clethodim by methods RM-26B-2 using GC-MS instead of GC-FPD. The LOQ for clethodim was 0.05 mg/kg. The LODs for DME and DME-OH were both 0.01 mg/kg (expressed as clethodim equivalents). Onion bulb samples were stored at <-20 °C for a maximum of 6.6 months between sampling and analysis.

Table 74 Residues of clethodim and metabolites on onion from supervised trials in Norway

Onion country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
GAP, Netherlands etc	*EC*	*0.24*	*200-400*		*1*	*56*				
Norway, 1999 Rygge (Jumbo) Outdoor	EC	0.090	250	20	1	36	0.02	< 0.01	< 0.05	20001029/01-RP
		0.18	250	20	1	36	0.01	< 0.01	< 0.05	Mean recovery for clethodim analysed by DME: 80% (n=2) at 0.05 mg/kg
		0.090 0.090	250 250	14 20	2	36	0.03	< 0.01	< 0.05	
Norway, 1999 Stavern (-) Outdoor	EC	0.090	250	17	1	59	< 0.01	< 0.01	< 0.05	
		0.18	250	-	1	59	< 0.01	< 0.01	< 0.05	
		0.090 0.090	250 250	16 17	2	59	< 0.01	< 0.01	< 0.05	Sampling to analysis: 181-200 days

[a] Portion analysed: bulbs

Brassica vegetables (except Brassica leafy vegetables)

Subgroup of Flowerhead Brassicas

Broccoli

The Meeting received six trials (at harvest trials) on broccoli which were conducted in the USA (Braverman, 2000: IR-4 PR No. 05215). In each of these trials, two foliar broadcast applications of an EC formulation (113 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 1 days prior to the second application. All applications were made in tank-mix with an adjuvant, COC. At each trial, heads were taken 30 ± 1 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.05 mg/kg (expressed as clethodim equivalents). Broccoli head samples were stored at -12 to -22 °C for a maximum of 32 months between sampling and analysis.

Table 75 Residues of clethodim and metabolites on broccoli from supervised trials in the USA

Broccoli country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*30*				
USA, 1996 St. Salinas, CA[b] (Everest) Outdoor	EC	0.27 0.27	291 240	Post-thinning Vegetative 6-9 leaves	2	30	< 0.05 < 0.05	< 0.05 < 0.05	< 0.10 < 0.10 (< 0.10)	IR-4 PR No. 05215
USA, 1996 St. Salinas, CA[c] (Patriot) Outdoor	EC	0.28 0.28	357 253	6-8 leaf Vegetative growth Vegetative per heading	2	29	0.43 0.47	0.43 0.44	0.86 0.91 (0.89)	Mean recovery for clethodim sulfoxide analysed by DME: 95% (n=8) at 0.05 mg/kg 60% (n=8) at 2.0 mg/kg
USA, 1996 St. Salinas, CA[d] (Patriot) Outdoor	EC	0.28 0.28	239 292	6-8 leaf Vegetative growth Vegetative per heading, 8-10 leaf	2	30	0.25 0.24	0.26 0.27	0.51 0.51 (0.51)	Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 98% (n=8) at 0.05 mg/kg

Broccoli country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
USA, 1996 St. Salinas, CA[d] (Everest) Outdoor	EC	0.28 0.28	239 292	6-8 leaf Vegetative growth Vegetative per heading, 8-10 leaf	2	31	0.42 0.35	0.53 0.41	0.95 0.76 (0.86)	79% (n=8) at 2.0 mg/kg Sampling to analysis: 728-962 days
USA, 1996 Weslaco, TX (Baccus) Outdoor	EC	0.38 0.38	370 370	6-8 leaf Vegetative per heading, 10-14 leaf	2	31	0.53 0.43	0.55 0.49	1.1 0.92 (1.0)	
USA, 1995 Aurora, OR (Gem) Outdoor	EC	0.28 0.28	215 161	6 leaf 7-8 leaf	2	29	0.36 0.35	0.71 0.74	1.1 1.1 (1.1)	

Portion analysed: head

[a] Mean of replicate field samples is given in parenthesis.

[b] Address: Spence Field, USDA ARS 1636 East Alisal St. Salinas, CA. 93905, Application dates (1st): 30 May 1996

[c] Address: Spence Field, USDA ARS 1636 East Alisal St. Salinas, CA. 93905, Application dates (1st): 23 Oct 1996

[d] Address: Field B, USDA ARS 1636 East Alisal St. Salinas, CA. 93905, Application dates (1st): 10 Oct 1996

Subgroup of Head Brassicas

Cabbages, Head

The Meeting received one trial (decline trial) on cabbage conducted in Australia (Roberts, 1994: 223/AU/94/100/SV01). One foliar spray application of an EC formulation (240 g ai/L) was made at a nominal rate of 0.12 kg ai/ha in the first plot and at a nominal rate of 0.24 kg ai/ha in the second plot. All applications were made in tank-mix with an adjuvant, D-C-Trate. Heads were taken at 1 and 7 DALA.

Samples were analysed for total residues of clethodim by the methods RM-26A-1 using GC-MS instead of GC-FPD. The LOD was 0.02 mg/kg. Cabbage head samples were stored at -20 °C for a maximum of 3 months between sampling and analysis.

Table 76 Residues of clethodim and metabolites on cabbage from supervised trials in Australia

Cabbage country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, Australia	*EC*	*0.12*			*1*	*7*				
Australia, 1994 Cranbourne, Victoria (Green Coronet) Outdoor	EC	0.12	125	Mature	1	1 7	Not reported		0.11 0.07	223/AU/94/100/SV01 Mean recovery for clethodim: 61% (n=3) at 0.13-0.25 mg/kg Mean recovery for 5-OH-clethodim sulfone: 86% (n=3) at 0.10-0.20 mg/kg Sampling to analysis: 96 days
	EC	0.24	125	Mature	1	1 7	Not reported		0.52 0.20	

Portion analysed: head

[a] Results have been corrected for the mean recovery of clethodim (61%) and for the mean recovery of 5-OH-clethodim sulfone (86%) and reported as clethodim equivalents

The Meeting received 20 trials on head cabbage which were conducted in Europe (Grote, 2009: S08-02085, Grote, 2010: S09-01365, Grote, 2015: S14-03658 and Grote, 2016: S15-03506). In each of these trials, one foliar spray application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.24 kg ai/ha. At each trial, heads were taken 26-31 DALA. In some trials (Grote, 2015 and Grote, 2016) an additional sampling event was included immediately after the application, when the spray deposit had dried.

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). In some trials (Grote, 2015 and Grote, 2016) two additional metabolites, M17R and M18R were analysed by methods No. S12-03244. The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Cabbage head samples were stored at ≤-18 °C for a maximum of 3 months between sampling and analysis.

Table 77 Residues of clethodim and metabolites on head cabbage from supervised trials in Europe

Cabbage, country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Netherlands etc	*EC*	*0.24*	*200-400*		*1*	*28*						
UK, 2008 Langrick, Lincolnshire (Attraction) Outdoor	EC	0.24	294	45	1	27	< 0.005	0.17	0.012	-	-	S08-02085 Mean recovery for clethodim: 86% (n=2) at 0.005/ 0.05 mg/kg
							Total: 0.19					
UK, 2008 Gosberton Clough, Lincolnshire (Clarissa F1) Outdoor	EC	0.24	295	42	1	29	< 0.005	0.32	0.027	-	-	Mean recovery for clethodim sulfoxide: 97% (n=4) at 0.005/ 0.05/0.50 mg/kg
							Total: 0.35					
France, 2008 Limersheim, Alsace (Atria) Outdoor	EC	0.27	330	48	1	27	< 0.005	0.074	< 0.005	-	-	
							Total: 0.084					
France, 2008 Meistratzheim Alsace (Brigadier) Outdoor	EC	0.25	307	48	1	27	< 0.005	0.096	< 0.005	-	-	Mean recovery for clethodim sulfone: 97% (n=2) at 0.005/ 0.05 mg/kg
							Total: 0.11					
Germany, 2008 Rutesheim- Perouse, Baden-Württemberg[b] (Ramco) Outdoor	EC	0.26	327	48	1	28	< 0.005	0.15	0.006	-	-	Sampling to analysis: 57-84 days
							Total: 0.16					

Cabbage, country, year (variety)	Application					DALA	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.	Days	clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
Germany, 2008 Rutesheim- Perouse, Baden-Württemberg[c] (Kraut-Kaiser) Outdoor	EC	0.24	297	48	1	27	< 0.01	0.037	< 0.005	-	-	
							Total: 0.052					
France, 2009 Hindisheim, Bas-Rhin (Atria) Outdoor	EC	0.24	302	44	1	28	< 0.005	0.046	0.006	-	-	S09-01365 Mean recovery for clethodim: 109% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 90% (n=3) at 0.005/ 0.05/0.10 mg/kg
							Total: 0.057					
Germany, 2009 Maxdorf, Rheinland-Pfalz (Destiny) Outdoor	EC	0.26	323	43	1	31	< 0.005	0.069	0.011	-	-	Mean recovery for clethodim sulfone: 90% (n=3) at 0.005/ 0.05/0.10 mg/kg Sampling to analysis: 14-92 days
							Total: 0.085					
Germany, 2014 Kirchheim, Baden-Württemberg (Mandy) Outdoor	EC	0.26	323	44	1	0	0.023	0.019	< 0.005	< 0.01	< 0.01	S14-03658 Mean recovery for clethodim: 96% (n=15) at 0.005/ 0.05/1.0 mg/kg Mean recovery for clethodim sulfoxide: 103% (n=14) at 0.005/0.05/ 1.0/2.0 mg/kg Mean recovery for clethodim sulfone: 102% (n=12) at 0.005/0.05 mg/kg
							Total: 0.047					
						28	< 0.005	0.054	< 0.005	< 0.01	< 0.01	
							Total: 0.064					
France, 2014 Villejust, Essonne (Guard) Outdoor	EC	0.25	315	41	1	0	0.071	0.037	< 0.005	< 0.01	< 0.01	
							Total: 0.11					
						28	< 0.005	0.15	0.014	< 0.01	< 0.01	
							Total: 0.16					
Italy, 2014 Granarolo, Emilia Romagna (Bronco) Outdoor	EC	0.25	317	41-43	1	0	< 0.005	< 0.005	< 0.005	< 0.01	< 0.01	Mean recovery for M17R: 96% (n=14) at 0.01/0.10 mg/kg Mean recovery for M18R: 96% (n=14) at 0.01/0.10 mg/kg
							Total: < 0.015					
						28	< 0.005	0.14	0.009	< 0.01	< 0.01	
							Total: 0.15					

Cabbage, country, year (variety)	Application					DALA	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.	Days	clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
Spain, 2014 L´Acudia, Valencia (Ducatti) Outdoor	EC	0.25	312	41	1	0	0.71	1.7	0.011	0.04	< 0.01	Sampling to analysis: 2-10 days
							Total: 2.4					
						28	< 0.005	0.072	0.006	< 0.01	< 0.01	
							Total: 0.083					
Germany, 2015 Altenbruch, Niedersachsen (Lennox) Outdoor	EC	0.25	309	46	1	0	< 0.005	0.049	< 0.005	< 0.01	< 0.01	S15-03506 Mean recovery for clethodim: 100% (n=25) at 0.005/0.05/ 4.0 mg/kg Mean recovery for clethodim sulfoxide: 102% (n=25) at 0.005/0.05/ 8.0 mg/kg Mean recovery for clethodim sulfone: 103% (n=24) at 0.005/0.05 mg/kg Mean recovery for M17R: 100% (n=24) at 0.01/0.10 mg/kg Mean recovery for M18R: 104% (n=23) at 0.01/0.10 mg/kg
							Total: 0.059					
						28	< 0.005	0.16	0.006	< 0.01	< 0.01	
							Total: 0.17					
France, 2015 Limersheim, Bas-Rhin (Cilion) Outdoor	EC	0.25	317	46	1	0	< 0.005	< 0.005	< 0.005	0.01	0.01	
							Total: < 0.015					
						27	< 0.005	0.048	< 0.005	< 0.01	< 0.01	
							Total: 0.058					
UK, 2015 Banks, Lancashire (Clarissa) Outdoor	EC	0.24	293	41 - 43	1	0	0.71	1.4	< 0.005	< 0.01	< 0.01	
							Total: 2.2					
						28	< 0.005	0.55	0.048	< 0.01	< 0.01	
							Total: 0.60					
Poland, 2015 Uscikowo, Wielkopolska (Ramkila) Outdoor	EC	0.25	309	42	1	0	< 0.005	0.033	< 0.005	< 0.01	< 0.01	
							Total: 0.043					
						26	< 0.005	0.19	0.017	< 0.01	< 0.01	
							Total: 0.21					
Italy, 2015 Lovoleto, Bologna (Miramonte) Outdoor	EC	0.25	313	41	1	0	0.025	0.14	< 0.005	< 0.01	< 0.01	Sampling to analysis: 2-10 days
							Total: 0.17					
						28	< 0.005	0.062	0.010	< 0.01	< 0.01	
							Total: 0.077					
Spain, 2015 Alcudia Carlet, Valencia (Ducati) Outdoor	EC	0.26	324	35	1	0	2.2	4.9	0.026	< 0.01	< 0.01	
							Total: 7.1					
						27	< 0.005	0.041	0.009	< 0.01	< 0.01	
							Total: 0.055					
Bulgaria, 2015 Lenitsa, Letnitsa (Kiose) Outdoor	EC	0.25	317	41	1	0	2.0	6.2	0.017	0.09	< 0.01	
							Total: 8.2					
						28	< 0.005	0.095	0.013	< 0.01	< 0.01	

Cabbage, country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
							Total: 0.11					
Bulgaria, 2015 Ognyanovo, Pazardjik (Pruktur) Outdoor	EC	0.25	313	41	1	0	< 0.005	0.011	< 0.005	< 0.01	< 0.01	
							Total: 0.021					
						30	< 0.005	0.089	0.006	< 0.01	< 0.01	
							Total: 0.10					

Portion analysed: head

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

[b] Address: 71277 Rutesheim-Perouse, Baden-Württemberg, Germany, Application dates: 18 Aug 2008

[c] Address: 71277 Rutesheim-Perouse, Baden-Württemberg, Germany, Application dates: 19 Aug 2008

Fruiting vegetables, Cucurbits

Subgroup of Fruiting vegetables, Cucurbits – Cucumber and Summer squashes

Cucumber

The Meeting received six trials (at harvest trials) on cucumber which were conducted in the USA (Leavitt and Rathke, 1996: IR-4 PR No. 05219). The field phase report of this study was not available but at each trial, fruit samples were taken 14 ± 1 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQ for clethodim and all metabolites that can be converted to DME was 0.14 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.13 mg/kg (expressed as clethodim equivalents). Cucumber fruit samples were stored at -20 ± 5 °C for a maximum of 15 months between sampling and analysis.

Table 78 Residues of clethodim and metabolites on cucumber from supervised trials in the USA

Cucumber country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*14*				
USA, 1994 Gainesville, FL (-)	Not reported	0.28 0.28	Not reported		2	14	< 0.14 < 0.14	< 0.13 < 0.13	< 0.27 < 0.27 (≤ 0.27)	IR-4 PR No. 05219 Mean recovery for clethodim sulfoxide analysed by DME: 102% (n=12) at 0.12 mg/kg 97% (n=2) at 1.2 mg/kg Mean recovery for 5-OH clethodim sulfone analysed
USA, 1994 Freeville, NY (-)	Not reported	0.28 0.28	Not reported		2	14	< 0.14 < 0.14	< 0.13 < 0.13	< 0.27 < 0.27 (≤ 0.27)	
USA, 1994 East Lansing, MI (-)	Not reported	0.28 0.28	Not reported		2	13	< 0.14 < 0.14	< 0.13 < 0.13	< 0.27 < 0.27 (≤ 0.27)	
USA, 1994 Arlington, WI (-)	Not reported	0.28 0.28	Not reported		2	14	< 0.14 < 0.14	< 0.13 < 0.13	< 0.27 < 0.27 (≤ 0.27)	

Cucumber country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
USA, 1995 Charleston, SC (-)	Not reported	0.28 0.28	Not reported		2	13	< 0.14 < 0.14	< 0.13 < 0.13	< 0.27 < 0.27 (< 0.27)	by DME-OH: 105% (n=12) at 0.093-0.11 mg/kg 107% (n=2) at 0.92 mg/kg Sampling to analysis: 27-458 days
USA, 1995 Weslaco, TX (-)	Not reported	0.28 0.28	Not reported		2	14	< 0.14 < 0.14	< 0.13 < 0.13	< 0.27 < 0.27 (< 0.27)	

Portion analysed: fruit

[a] Mean of replicate field samples is given in parenthesis.

Leafy vegetables (including Brassica leafy vegetables)

Subgroup of Leafy greens

Lettuce, Head

The Meeting received six trials (at harvest trials) on head lettuce which were conducted in the USA (Braverman, 2004: IR-4 PR No. 07694). In each of these trials, two foliar broadcast applications of an EC formulation (113 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 1 days prior to the second application. All applications were made in tank-mix with an adjuvant, COC. In each trial, head lettuce with wrapper leaves and head lettuce without wrapper leaves samples were taken 14 ± 1 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-3. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.10 mg/kg (expressed as clethodim equivalents). The LODs for DME and DME-OH were both 0.03 mg/kg (expressed as clethodim equivalents). Lettuce head samples were stored at -10 to -29 °C or below for a maximum of 5.7 months between sampling and analysis.

Table 79 Residues of clethodim and metabolites on head lettuce from supervised trials in the USA

Head lettuce country, year (variety)	Application					DALA Days	Residues, mg/kg With wrapper leaves Without wrapper leaves			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.54 /year*	-		*4*	*14*				
USA, 2000 St. Salinas, CA[b] (Titan head) Outdoor	EC	0.28 0.28	336 356	Vegetative, small heads, diameter 3-4 in. Vegetative, almost mature heads	2	13	0.18 0.22	< 0.10 < 0.10	0.28 0.32	IR-4 PR No. 07694 Mean recovery for clethodim sulfoxide: 112% (n=9) at 0.10-0.11 mg/kg
USA, 2000 St. Salinas, CA[c] (Titan head) Outdoor	EC	0.29 0.27	360 303	Vegetative, too many leaves to count, centre Vegetative, small to medium sized heads	2	15	0.29 0.14	< 0.10 < 0.10	0.39 0.24	
USA, 2000 St. Salinas,	EC	0.29	327	Vegetative, 10-12 true leaves	2	13	0.18[a]	< 0.10	0.28	Mean recovery for

Head lettuce country, year (variety)	Application					DALA Days	Residues, mg/kg			Ref
							With wrapper leaves			
							Without wrapper leaves			
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
CA[d] (Titan head) Outdoor		0.28	307	Vegetative, small to medium sized heads forming			0.24	< 0.10	0.34	5-OH clethodim sulfone: 100% (n=9) at 0.10-0.11 mg/kg Sampling to analysis: 12-174 days
USA, 2000 Coalinga, CA (Spector) Outdoor	EC	0.28 0.29	216 218	Vegetative Vegetative	2	14	0.20	< 0.10	0.30	
							0.18	< 0.10	0.28	
USA, 2000 Five Points, CA (Annie) Outdoor	EC	0.29 0.29	206 211	Vegetative, 10 leaves Vegetative	2	14	0.34	< 0.10	0.44	
							0.17	< 0.10	0.27	
USA, 2000 Wilsonville, OR (Summertime) Outdoor	EC	0.28 0.29	285 288	9 leaf Early maturity, small heads	2	14	0.12	< 0.10	0.22	
							< 0.10	< 0.10	< 0.20	

Portion analysed: With wrapper leaves (up), Without wrapper leaves (down)

[a] It is likely that the treated sample with wrapper leaves was switched with the control sample without wrapper leaves during preparation. For reporting purposes, the sample containing residues is listed here. As analysed, the control sample contained 0.18 ppm and the treated sample (analysed twice) contained < 0.10 ppm.

[b] Address: Block 4 South, USDA-ARS Spence Field, 1572 Old Stage Rd., Salinas, Monterey County, CA
Application dates: 27 Jul 2000

[c] Address: Field A, USDA-ARS Research Station, East Alisal St., Salinas, Monterey County, CA
Application dates: 09 Aug 2000

[d] Address: Field B, USDA-ARS Research Station, East Alisal St., Salinas, Monterey County, CA
Application dates: 04 Oct 2000

Pulses

Subgroup of Dry beans

Beans (dry)

The Meeting received four trials on beans (dry) conducted in Europe (Grote, 2016: S14-03657). In each of these trials, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.29 or 0.12 kg ai/ha. In each trial, seeds were taken at commercial harvest, 51-57 DALA.

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262, additionally M17R and M18R by methods No. S12-03244. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Dry bean seeds were stored at ≤-18 °C for a maximum of 16 days between sampling and analysis.

Table 80 Residues of clethodim and metabolites on dry bean from supervised trials in Europe

Beans (dry) country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Croatia	*EC*	*0.20-0.25*	*200-400*		*1*	*42*						
UK, 2014 King's Newton, Leicestershire (Fuego) Outdoor	EC	0.35	338	79 - 83	1	51	0.006	0.35	0.092	< 0.01	< 0.01	S14-03657 Mean recovery for clethodim: 91% (n=6) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 100% (n=6) at 0.005/ 0.05/0.50 mg/kg Mean recovery for clethodim sulfone: 105% (n=7) at 0.005/ 0.05/0.50 mg/kg Mean recovery for M17R: 93% (n=6) at 0.01/0.10 mg/kg Mean recovery for M18R: 89% (n=6) at 0.01/0.10 mg/kg Sampling to analysis: 3-16 days
							Total: 0.45					
France, 2014 Mespuits, Essonne (Diva) Outdoor	EC	0.31	322	69	1	56	< 0.005	0.11	0.087	< 0.01	< 0.01	
							Total: 0.20					
Spain, 2014 Torrellano, Alicante (Reina Mosa) Outdoor	EC	0.14	345	71	1	56	< 0.005	0.15	0.078	0.01	< 0.01	
							Total: 0.23					
Spain, 2014 Novelda, Alicante (Flor de Otoño) Outdoor	EC	0.13	335	71	1	57	< 0.005	0.16	0.083	0.01	< 0.01	
							Total: 0.25					

Portion analysed: seed

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

Subgroup of Dry peas

Peas (dry)

The Meeting received 2 trials (at harvest trials) on peas (dry) which were conducted in the USA (Grigg, 1995: IR-4 05204). In each of these trials, two applications of an EC formulation were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 ± 1 days prior to the second application. In each trial, seeds were taken 20 or 21 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.05 mg/kg (expressed as clethodim

equivalents). Dry pea seeds were stored at -12 to -25 °C for a maximum of 18 months between sampling and analysis.

Table 81 Residues of clethodim and metabolites on dry pea from supervised trials in the USA

Peas (dry) country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.27 0.54/ year*			*2-4*	*30*				
USA, 1993 Prosser, WA (-) Outdoor	EC	0.28 0.28	not reported		2	21	2.9 2.6 3.2 3.7	1.1 1.0 1.3 1.3	4.0 3.5 4.5 5.0 (4.3)	IR-4 05204 Mean recovery for clethodim analysed by DME: 90% (n=12) at 0.05-10 mg/kg
USA, 1994 Prosser, WA (-) Outdoor	EC	0.28 0.28			2	20	5.1 4.8	1.9 1.5	7.0 6.3 (6.7)	Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 93% (n=12) at 0.15-10 mg/kg Sampling to analysis: 539-560 days

Portion analysed: seed

[a] Mean of replicate field samples is given in parenthesis.

The Meeting received 2 trials (at harvest trials) on peas (dry) which were conducted in France (Balluff, 1998: 97065/F1-FPPS). In each of these trials, one foliar application of an EC formulation (240 g ai/L or 120 g ai/L) was made at a nominal rate of 0.19 or 0.13 kg ai/ha. In each trial, seeds were taken 58 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQ for clethodim was 0.07 mg/kg. Dry pea seed samples were stored for a maximum of 4 months between sampling and analysis.

Table 82 Residues of clethodim and metabolites on dry pea from supervised trials in France

Peas (dry) country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
GAP, Slovakia	*EC*	*0.24-0.26*	*250-400*	*12-30*	*1*					
France, 1997 Taize, Deux-Sevres (Baccara) Outdoor	240 g/L EC	0.19	296	51	1	58	0.05	0.7	0.12	97065/F1-FPPS Mean recovery for clethodim analysed by DME: 95% (n=2) at 0.07 mg/kg 82% (n=1) at 0.7 mg/kg Sampling to analysis: 130-131 days
	120 g/L EC	0.20	311	51	1	58	0.20	0.21	0.41	
		0.13	305	51	1	58	0.12	0.14	0.26	
France, 1997 Curçay sur Dive, Vienne (Alladin) Outdoor	240 g/L EC	0.19	307	49	1	58	0.02	0.05	0.07	
	120 g/L EC	0.19	297	49	1	58	0.07	0.16	0.23	
		0.13	299	49	1	58	0.03	0.07	0.10	

Portion analysed: seed

The Meeting received 24 trials on peas (dry) which were conducted in Europe (Grote, 2009: S08-01827, Grote, 2009: S08-02048, Grote, 2009: S08-02069, Grote, 2010: S09-01362, Grote, 2010: S09-01363, Grote, 2010: S10-00568, Grote, 2010: S10-00569 and Grote, 2016: S15-03508). In the 2008-2010 trials, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.30 kg ai/ha. In each trial, seeds were taken at commercial harvest, 51-69 DALA. In the 201five trials, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.29 or 0.12 kg ai/ha. In each trial, seeds were taken at commercial harvest, 55-67 DALA.

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). In the 201five trials additionally two metabolites, M17R and M18R were analysed by methods No. S12-03244. The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Dry pea seeds were stored at ≤-18 °C for a maximum of 3.1 months between sampling and analysis.

Table 83 Residues of clethodim and metabolites on dry pea from supervised trials in Europe

Peas (dry) country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Slovakia	*EC*	*0.26*	*250-400*	*12-30*	*1*							
Hungary, 2008 Adony, Fejér (Grana) Outdoor	EC	0.31	307	59	1	55	< 0.005	0.068	0.039	-	-	S08-01827 Mean recovery for clethodim: 85% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 91% (n=3) at 0.005/ 0.05/0.10 mg/kg Mean recovery for clethodim sulfone: 98% (n=3) at 0.005/ 0.05/0.10 mg/kg Sampling to analysis: 54-94 days
							Total: 0.11					
Hungary, 2008 Székesfehérvá, Fejér (Mastin) Outdoor	EC	0.32	317	55	1	56	< 0.005	0.14	0.12	-	-	
							Total: 0.27					
UK, 2008 Alderminster[b] (Nitouche) Outdoor	EC	0.31	307	35 - 51	1	69	< 0.005	0.031	0.015	-	-	
							Total: 0.047					
UK, 2008 Alderminster[c] (Einstein) Outdoor	EC	0.30	304	51 - 55	1	56	< 0.005	0.15	0.039	-	-	S08-02048 Mean recovery for clethodim: 96% (n=2) at 0.005/

Peas (dry) country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
							Total: 0.19					0.05 mg/kg Mean recovery for clethodim sulfoxide: 105% (n=3) at 0.005/ 0.05/0.50 mg/kg Mean recovery for clethodim sulfone: 104% (n=3) at 0.005/ 0.05/0.50 mg/kg Sampling to analysis: 52-92 days
Hungary, 2008 Aba, Fejér (ZKI 01-30) Outdoor	EC	0.31	313	55	1	51	< 0.005	0.38	0.17	-	-	
							Total: 0.56					
Spain, 2008 Almansa, Albacete (Baccara) Outdoor	EC	0.31	407	69	1	55	< 0.005	0.22	0.047	-	-	S08-02069 Mean recovery for clethodim: 98% (n=4) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 96% (n=4) at 0.005/ 0.05/0.50 mg/kg Mean recovery for clethodim sulfone: 95% (n=4) at 0.005/ 0.05/0.50 mg/kg Sampling to analysis: 83-92 days
							Total: 0.27					
Spain, 2008 Barrax, Albacete (Messire) Outdoor	EC	0.33	435	35	1	56	< 0.005	0.078	0.057	-	-	
							Total: 0.14					
Greece, 2008 Nea Apollonia, Thessaloniki[d] (Argos) Outdoor	EC	0.29	385	73 - 74	1	56	< 0.005	0.74	0.16	-	-	
							Total: 0.91					
Greece, 2008 Nea Apollonia, Thessaloniki[e] (Urano) Outdoor	EC	0.31	418	73 - 75	1	57	0.005	0.64	0.16	-	-	
							Total: 0.81					
Greece, 2008 Nea Apollonia, Thessaloniki[f] (Ojo) Outdoor	EC	0.31	412	73	1	54	0.006	0.67	0.17	-	-	
							Total: 0.85					
Hungary, 2009 Ráclamás, Fejér (Oasis) Outdoor	EC	0.29	294	65	1	56	0.009	0.95	0.30	-	-	S09-01362 Mean recovery for clethodim: 76% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 82% (n=3) at 0.005/
							Total: 1.3					

Peas (dry) country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
												0.05/1.0 mg/kg Mean recovery for clethodim sulfone: 91% (n=3) at 0.005/ 0.05/1.0 mg/kg Sampling to analysis: 85 days
Spain, 2009 Lliria, Valencia (Tristan G) Outdoor	EC	0.33	325	32	1	56	< 0.005	0.29	0.069	-	-	S09-01363 Mean recovery for clethodim: 85% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 93% (n=3) at 0.005/ 0.05/0.25 mg/kg
							Total: 0.36					
Greece, 2009 Apollonia, Thessaloniki (Early Onward) Outdoor	EC	0.29	288	51	1	56	< 0.005	0.080	0.045	-	-	Mean recovery for clethodim sulfone: 89% (n=3) at 0.005/ 0.05/0.25 mg/kg Sampling to analysis: 71-92 days
							Total: 0.13					
UK, 2010 Kiddington, Oxfordshire (Profit) Outdoor	EC	0.31	310	65	1	54	< 0.005	0.65	0.27	-	-	S10-00568 Mean recovery for clethodim: 95% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 100% (n=3) at 0.005/ 0.05/1.0 mg/kg
							Total: 0.93					
UK, 2010 Hanby, Lincs	EC	0.27	273	61	1	51	< 0.005	0.28	0.15	-	-	Mean recovery for clethodim

Peas (dry) country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
(Genki) Outdoor							Total: 0.44					sulfone: 99% (n=3) at 0.005/ 0.05/1.0 mg/kg Sampling to analysis: 47-56 days
Spain, 2010 Barax, Albacete (Cartouche) Outdoor	EC	0.29	287	33	1	54	< 0.005	0.11	0.033	-	-	S10-00569 Mean recovery for clethodim: 90% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 85% (n=3) at 0.005/ 0.05/0.15 mg/kg Mean recovery for clethodim sulfone: 87% (n=2) at 0.005/ 0.05 mg/kg Sampling to analysis: 57 days
							Total: 0.15					
Germany, 2015 Buxtehude, Niedersachsen (Alvetsa) Outdoor	EC	0.31	317	39	1	63	< 0.005	0.34	0.10	< 0.01	< 0.01	S15-03508 Mean recovery for clethodim: 94% (n=12) at 0.005/ 0.05 mg/kg
							Total: 0.45					
Poland, 2015 Kluczewo Huby, Wielkopolska (Wenus) Outdoor	EC	0.31	324	39	1	67	< 0.005	0.030	0.011	< 0.01	< 0.01	Mean recovery for clethodim sulfoxide: 96% (n=13) at 0.005/ 0.05/0.50 mg/kg
							Total: 0.046					
UK, 2015 Heather, Leicestershire (Kabuki) Outdoor	EC	0.28	293	33	1	62	< 0.005	0.10	0.041	< 0.01	< 0.01	Mean recovery for clethodim sulfone: 94% (n=13) at 0.005/ 0.05/0.50 mg/kg Mean recovery for M17R: 104% (n=13) at 0.01/0.10 mg/kg
							Total: 0.15					
Germany, 2015 Ahrensfelde, Brandenburg (Navarro) Outdoor	EC	0.27	277	39	1	59	< 0.005	0.14	0.081	< 0.01	< 0.01	
							Total: 0.23					
						64	< 0.005	0.16	0.086	< 0.01	< 0.01	

Peas (dry) country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
							Total: 0.25					Mean recovery for M18R: 104% (n=13) at 0.01/0.10 mg/kg Sampling to analysis: 3-18 days
Italy, 2015 Idice, Bologna (Ideal) Outdoor	EC	0.12	303	71	1	57	< 0.005	0.024	0.006	< 0.01	< 0.01	
							Total: 0.035					
Spain, 2015 Cutanda, Aragon (Capuchino) Outdoor	EC	0.13	312	39 - 51	1	57	< 0.005	< 0.005	< 0.005	< 0.01	< 0.01	
							Total: < 0.015					
Greece, 2015 Stephanina, Thessaloniki (Jof) Outdoor	EC	0.12	310	61	1	55	< 0.005	0.11	0.039	< 0.01	< 0.01	
							Total: 0.15					
Bulgaria, 2015 Chernogorovo, Pazardjik (Denitsa) Outdoor	EC	0.12	310	39	1	61	< 0.005	< 0.005	< 0.005	< 0.01	< 0.01	
							Total: < 0.015					

Portion analysed: seed

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

[b] Address: CU37 8PC, Alderminster, UK, Application dates: 03 Jun 2008

[c] Address: CU37 8PC, Alderminster, UK, Application dates: 19 Jun 2008

[d] Address: 57015, Nea Apollonia, Thessaloniki, Greece, Application dates: 20 May 2008

[e] Address: 57015, Nea Apollonia, Thessaloniki, Greece, Application dates: 15 May 2008

[f] Address: 57014, Nea Apollonia, Thessaloniki, Greece, Application dates: 15 May 2008

Root and tuber vegetables

Subgroup of Root vegetables

Carrot

The Meeting received two trials (at harvest trials) on carrot which were conducted in Norway (Klump, 2000: 20001029/01-RP). In each of these trials, an EC formulation (240 g ai/L) was applied to three different plots. In a first and second plot one application was made at either 0.090 kg ai/ha or 0.18 kg ai/ha, respectively and in a third plot two applications were made at 0.090 kg ai/ha. In each trial, roots were taken 51-70 DALA.

Samples were analysed for total residues of clethodim by methods RM-26B-2 using GC-MS instead of GC-FPD. The LOQ for clethodim was 0.05 mg/kg. The LODs for DME and DME-OH were both 0.015 mg/kg (expressed as clethodim equivalents). Root samples were stored at <-20 °C for a maximum of 5.8 months between sampling and analysis.

Table 84 Residues of clethodim and metabolites on carrot from supervised trials in Norway

Carrot country, year (variety)	Application					DALA Days	Residues, mg/kg[1)]			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
GAP, Slovakia	*EC*	*0.24*	*200-400*	*12-45*	*1*	*40*				
Norway, 1999 Overhalla (Panto)	EC	0.090	250	20	1	64	< 0.05	< 0.05	< 0.10	20001029/01-RP

Carrot country, year (variety)	Application					DALA Days	Residues, mg/kg[1)]			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
Outdoor		0.18	250	21	1	51	0.05	< 0.05	0.10	Mean recovery for clethodim analysed by DME: 92% (n=2) at 0.05 mg/kg
		0.090 0.090	250 250	14 20	2	64	< 0.05	< 0.05	< 0.10	
Norway, 1999 Ridabu, Hedmark (Panther) Outdoor	EC	0.090	250	18	1	70	< 0.05	< 0.05	< 0.10	Sampling to analysis: 170-175 days
		0.18	250	18	1	70	< 0.05	< 0.05	< 0.10	
		0.090 0.090	250 250	13 18	2	70	< 0.05	< 0.05	< 0.10	

Portion analysed: root

The Meeting received 20 trials on carrot which were conducted in Europe (Roussel, 2009: ChR-08-4437, Grote, 2010: S09-02141, Grote, 2010: S09-02224, Hauck, 2011: IF-10/01643313, and Grote, 2013: S12-01198). In each of these trials, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.24 kg ai/ha. In each trial, roots were taken at 37-52 DALA. In the 2012 trials, additionally whole plants were taken at, 0, 10 ± 1 and 20 ± 1 DALA.

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). In the 2012 trials additionally two metabolites, M17R and M18R were analysed by methods No. S12-03244. The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Carrot root samples were stored at ≤-18 °C for a maximum of 4.6 months between sampling and analysis.

Table 85 Residues of clethodim and metabolites on carrot from supervised trials in Europe

Carrot country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Slovakia etc	*EC*	*0.24*	*200 - 400*	*12-45*	*1*	*40*						
France, 2008 Warmeriville, Champagne Ardennes (Kabro) Outdoor	EC	0.25	310	43	1	48	< 0.005	0.078	0.007	-	-	ChR-08-4437 Mean recovery for clethodim: 90% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 95% (n=2) at 0.005/
							Total: 0.090					

Carrot country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai/ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
France, 2008 Berthenay, Centre (Katop) Outdoor	EC	0.24	300	42	1	50	< 0.005	0.008	< 0.005	-	-	0.05 mg/kg Mean recovery for clethodim sulfone: 93% (n=2) at 0.005/ 0.05 mg/kg Sampling to analysis: 44-51 days
							Total: 0.018					
Hungary, 2009 Saponya, Fejèr (Bangor-F1) Outdoor	EC	0.25	317	45	1	50	< 0.005	0.030	< 0.005	-	-	S09-02141 Mean recovery for clethodim: 97% (n=4) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 99% (n=5) at 0.005/ 0.05/0.10 mg/kg Mean recovery for clethodim sulfone: 103% (n=4) at 0.005/ 0.05 mg/kg Sampling to analysis: 32-87 days
							Total: 0.040					
Hungary, 2009 Bordáany, Csongràd (Napa F1) Outdoor	EC	0.26	327	45	1	52	< 0.005	< 0.005	< 0.005	-	-	
							Total: < 0.015					
France, 2009 Saulx-les-Chartreux, Essonne (Symphonie) Outdoor	EC	0.26	319	43	1	51	< 0.005	0.054	0.006	-	-	
							Total: 0.065					
UK, 2009 Scarisbrick, Lancashire (Maestro) Outdoor	EC	0.25	307	43	1	51	< 0.005	0.085	0.008	-	-	
							Total: 0.098					
UK, 2009 Shenstone, Staffordshire (Nairobi) Outdoor	EC	0.26	320	46	1	49	< 0.005	0.039	< 0.005	-	-	
							Total: 0.049					
Germany, 2009 Dreetz, Brandenburg (Bangor) Outdoor	EC	0.26	328	46-47	1	48	< 0.005	0.045	0.006	-	-	
							Total: 0.056					
Spain, 2009 Conil de la Frontera (Maestro)	EC	0.25	313	41	1	42	< 0.005	0.037	0.006	-	-	S09-02224 Mean recovery for clethodim:

Carrot country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai/ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
Outdoor							Total: 0.048					105% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 110% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfone: 105% (n=2) at 0.005/ 0.05 mg/kg Sampling to analysis: 21-91 days
Bulgaria, 2009 Mokrishte Pazardjik (Pordone) Outdoor	EC	0.26	327	45	1	41	< 0.005	< 0.005	< 0.005	-	-	
							Total: < 0.015					
France, 2010 St Laurent d'Algouze (Carlo) Outdoor	EC	0.26	424	44	1	40	< 0.005	0.016	< 0.005	-	-	IF-10/01643313 Mean recovery for clethodim: 88% (n=10) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 92% (n=10) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfone: 93% (n=10) at 0.005/ 0.05 mg/kg Sampling to analysis: not reported
							Total: 0.026					
France, 2010 Bleujac (Bolero) Outdoor	EC	0.23	290	42	1	41	< 0.005	0.014	< 0.005	-	-	
							Total: 0.024					
Greece, 2010 Nea Chalkidona (Tempo F1) Outdoor	EC	0.25	408	44	1	41	< 0.005	0.009	< 0.005	-	-	
							Total: 0.019					
Spain, 2010 Malaga (Nantesa) Outdoor	EC	0.24	303	42	1	40	< 0.005	0.016	< 0.005	-	-	
							Total: 0.026					
Spain, 2010 Lebrija (Navelino) Outdoor	EC	0.25	307	44	1	41	< 0.005	0.010	< 0.005	-	-	
							Total: 0.020					
Spain, 2010 Sanlucar de Barrameda (Navelino) Outdoor	EC	0.25	310	42	1	41	< 0.005	0.016	< 0.005	-	-	
							Total: 0.026					
Germany, 2012 Kutenholz, Lower Saxony (Nantaise DP	EC	0.25	315	46	1	40	< 0.005	0.015	< 0.005	< 0.01	< 0.01	S12-01198 Mean recovery for clethodim: 104% (n=2) at
							Total: 0.025					
					1	0	0.26	1.1	0.009	0.07	< 0.01	
							Total: 1.4					

Carrot country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
44) Outdoor						10	< 0.005	0.047	0.006	0.03	< 0.01	0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 89% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfone: 88% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for M17R: 92% (n=4) at 0.01/0.10 mg/kg Mean recovery for M18R: 92% (n=4) at 0.01/0.10 mg/kg Sampling to analysis: 41-139 days
							Total: 0.058					
						21	< 0.005	0.021	< 0.005	0.03	< 0.01	
							Total: 0.031					
UK, 2012 Bilsthorpe, Nottinghamshire (Nairobi) Outdoor	EC	0.25	313	42-44	1	40	< 0.005	0.027	< 0.005	< 0.01	< 0.01	
							Total: 0.037					
					1	0	0.33	0.78	0.006	0.06	< 0.01	
							Total: 1.1					
						10	< 0.005	0.088	0.006	0.04	< 0.01	
							Total: 0.099					
						20	< 0.005	0.074	0.006	0.04	< 0.01	
							Total: 0.085					
Italy, 2012 Bosco Mesoia, Ferrara (Dordonia) Outdoor	EC	0.26	320	41-43	1	37	< 0.005	0.009	< 0.005	< 0.01	< 0.01	
							Total: 0.019					
					1	0	5.0	16	0.072	0.32	< 0.01	
							Total: 21					
						9	0.028	0.58	0.033	0.24	0.03	
							Total: 0.64					
						22	0.006	0.065	0.010	0.04	< 0.01	
							Total: 0.081					
France, 2012 Angees-Sur-Mer, Pyrenees-Orientales (Chambord) Outdoor	EC	0.23	285	41	1	40	< 0.005	0.008	< 0.005	< 0.01	< 0.01	
							Total: 0.018					
					1	0	1.1	3.8	0.017	0.14	< 0.01	
							Total: 4.9					
						10	0.011	0.14	0.011	0.23	0.04	
							Total: 0.16					
						20	< 0.005	0.034	< 0.005	0.04	< 0.01	
							Total: 0.044					

Portion analysed: root (up), whole plant (down) in the 2012 trials, root only in the other trials.

a Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

The Meeting received 8 trials (at harvest trials) on carrot which were conducted in the USA (Lai, Kunkel and Corley, 1999: IR-4 PR No. 05217). In each of these trials, two foliar broadcast applications of an EC formulation (113 g ai/L) were made at a nominal rate of 0.28 kg ai/ha. The first application was made 14 or 15 days prior to the second application. All applications were made in tank-mix with an adjuvant, COC. In each trial, roots were taken 30 ± 1 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQ for clethodim and all metabolites that can be converted to DME was 0.14 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.11 mg/kg (expressed as clethodim equivalents). Carrot root samples were stored at -20 ± 5 °C for a maximum of 22 months between sampling and analysis.

Table 86 Residues of clethodim and metabolites on carrot from supervised trials in the USA

Carrot country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME-OH	Total	

Carrot country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*30*				
USA, 1994 Salinas, CA (Six Pak)	EC	0.28 0.27	436 575	Vegetative 4-6 leaf stage Vegetative 7-10 leaves	2	29	< 0.14 < 0.14	< 0.11 < 0.11	< 0.25 < 0.25 (< 0.25)	IR-4 PR No. 05217 Mean recovery for clethodim sulfoxide analysed by DME: 118% (n=16) at 0.15 mg/kg 76% (n=2) at 3.0 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 130% (n=16) at 0.12 mg/kg 74% (n=2) at 2.4mg/kg Sampling to analysis: 222-659 days
USA, 1994 Gainesville, FL (Altona F1)	EC	0.28 0.28	305 301	Vegetative Vegetative	2	30	< 0.14 < 0.14	< 0.11 < 0.11	< 0.25 < 0.25 (< 0.25)	
USA, 1995 Salinas, CA [b] (Six Pak)	EC	0.27 0.27	778 805	Vegetative Vegetative	2	31	< 0.14 < 0.14	< 0.11 < 0.11	< 0.25 < 0.25 (< 0.25)	
USA, 1995 Prossner, WA (Scarlet Nantes)	EC	0.28 0.27	295 298	Vegetative 4-5 leaf stage Vegetative	2	31	< 0.14 < 0.14	< 0.11 < 0.11	< 0.25 < 0.25 (< 0.25)	
USA, 1995 East Lansing, MI (Caro Pride)	EC	0.28 0.27	183 176	Vegetative 5-7 leaf stage Vegetative/ Roots 1/2" dia	2	31	< 0.14 < 0.14	< 0.11 < 0.11	< 0.25 < 0.25 (< 0.25)	
USA, 1995 Salinas, CA [c] (Caramba)	EC	0.29 0.29	405 402	Vegetative Vegetative	2	31	< 0.14 < 0.14	< 0.11 < 0.11	< 0.25 < 0.25 (< 0.25)	
USA, 1995 Salinas, CA[d] (Caramba)	EC	0.27 0.27	459 498	Vegetative Vegetative	2	29	0.25 0.22	< 0.11 < 0.11	0.36 0.33 (0.35)	
USA, 1995 Weslaco, TX (Royal Chantenay)	EC	0.29 0.29	283 283	Vegetative Vegetative	2	29	0.18 0.28	< 0.11 < 0.11	0.29 0.39 (0.34)	

Portion analysed: root

[a] Mean of replicate field samples is given in parenthesis.

[b] Address: USDA-ARS Spence Field, Blk 3 Salinas, CA, Application dates (1st): 10 Feb 1995

[c] Address: USDA-ARS Spence Field, Blk 3 Salinas, CA, Application dates (1st): 31 Jul 1995

[d] Address: USDA-ARS Field B Salinas, CA, Application dates (1st): 30 Aug 1995

Stalk and stem vegetables

Subgroup of Stalk and stem vegetables-Others

Artichoke, Globe

The Meeting received four trials (at harvest trials) on artichoke which were conducted in Europe (Grote, 2010: S09-02223 and Hauck, 2011: IF-10/01643302). In the 2009 trials (Grote, 2010), one soil application between the rows with an EC formulation (120 g ai/L) was made at a rate of 0.36 or 0.39 kg ai/ha. In the 2010 trials (Hauck, 2011), one foliar application of an EC formulation (120 g ai/L) was made at a rate of 0.36 or 0.34 kg ai/ha. In each trial, flower heads were taken 40 ± 1 DALA.

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed

as clethodim equivalents). Artichoke head samples were stored at ≤ -18 °C for a maximum of 3 months between sampling and analysis.

Table 87 Residues of clethodim and metabolites on artichoke from supervised trials in Europe

Artichoke country, year (variety)	Application					DALA Days	Residues, mg/kg[a]				Ref
	Form	kg ai /ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	Total	
GAP, Spain	*EC*	*0.18*	*200-400*	*12-51*	*1*	*40*					
Greece, 2009 Gomoston, Achaia (Italia) Outdoor	EC	0.36[b]	301	39	1	40	< 0.005	< 0.005	< 0.005	< 0.015	S09-02223 Mean recovery for clethodim: 80% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 96% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfone: 85% (n=2) at 0.005/ 0.05 mg/kg Sampling to analysis: 27-85 days
Spain, 2009 Benisano, Valencia (Blanca de Rudela) Outdoor	EC	0.39[b]	324	19	1	41	< 0.005	< 0.005	< 0.005	< 0.015	
Greece, 2010 Iria, Argelida (Irion) Outdoor	EC	0.36[c]	401	33	1	40	< 0.005	0.014	0.0074	0.026	IF-10/01643302 Recovery for clethodim: 103% (n=1) at 0.10 mg/kg Recovery for clethodim sulfoxide: 90% (n=1) at 0.10 mg/kg Recovery for clethodim sulfone: 89% (n=1) at 0.10 mg/kg Sampling to analysis: not reported
Spain, 2010 Zafarraya, Granada (Alhambra) Outdoor	EC	0.34[c]	287	43	1	41	< 0.005	0.061	0.016	0.082	

Portion analysed: flower head

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

[b] Soil application

[c] foliar application

The Meeting received three trials (two trials; at harvest trials, one trial; decline trial) on artichoke which were conducted in the USA (Samoil, 2008: IR-4 PR No. 09013). In each of these trials, two broadcast applications of an EC formulation (113 g ai/L) were made at a rate in the range of 0.41-0.46 kg ai/ha. The first application was made 14 ± 1 days prior to the second application. All

applications were made in tank-mix with an adjuvant, COC. In each trial, buds were taken 5 DALA. In the decline trial additional samples were collected at 3, 7 and 12 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods CAL vers. 13. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). Artichoke bud samples were stored at -21 ± 7 °C for a maximum of 3 months between sampling and analysis.

Table 88 Residues of clethodim and metabolites on artichoke from supervised trials in the USA

Artichoke country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.14 0.54 /year*	-		*4*	*5*				
USA, 2004 Moss Landing, CA (Green Globe) Outdoor	EC	0.46 0.45	150 150	Producing Producing	2	5	0.69 0.78	< 0.088 < 0.088	0.78 0.87 (0.82)	IR-4 PR No. 09013 Mean recovery for clethodim sulfoxide analysed by DME: 98% (n=4) at 0.1 mg/kg 102% (n=2) at 1.0 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 92% (n=4) at 0.1 mg/kg 111% (n=2) at 1.0 mg/kg Sampling to analysis: 83-105 days
USA, 2004 Salinas, CA (Green Globe) Outdoor	EC	0.45 0.46	748 767	Producing Producing	2	5	0.74 1.0	< 0.088 0.10	0.83 1.1 (0.96)	
USA, 2004 Castroville, CA (Green Globe) Outdoor	EC	0.45 0.41	1132 1029	Producing Producing	2	3 5 7 12	0.56 0.58 0.64 0.66 0.38 0.39 0.45 0.46	< 0.088 < 0.088 0.10 0.10 < 0.088 < 0.088 0.10 0.12	0.65 0.67 (0.66) 0.74 0.76 (0.75) 0.47 0.48 (0.47) 0.55 0.58 (0.57)	

Portion analysed: buds

[a] Mean of replicate field samples is given in parenthesis.

Oilseed

Subgroup of Small seed oilseeds

Rape seed

The Meeting received 13 trials on rape seed conducted in Europe (Bruce, 1996: EDB.896).

In French trials (EDB.896/Report 171U and 171V), one application of an EC formulation (240 g ai/L) was made at a nominal rate of 0.18, 0.36, 0.48 or 0.96 kg ai/ha. In each trial, seeds were taken 98-305 DALA. Samples were analysed for total residues of clethodim by the GC-FPD methods PAM II. Sec. 180.412. The LOQ for clethodim was 0.1 mg/kg. Rape seed samples were stored at -20 °C for a maximum of 19 months between sampling and analysis.

In trials conducted in the UK (EDB.896/Report 195X), one application of an EC formulation (240 g ai/L) was made at a nominal rate of 0.36 or 0.72 kg ai/ha. In each trial, seeds were taken 258 or 294 DALA. Samples were analysed for total residues of clethodim by the GC-FPD methods PAM II. Sec. 180.412. The LOQ for clethodim was 0.1 mg/kg. Rape seed samples were stored at -20 °C for a maximum of 4 months between sampling and analysis.

Table 89 Residues of clethodim and metabolites on rape seed from supervised trials in Europe

Rape seed country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, Slovakia	*EC*	*0.24-0.26*	*200-400*	*12-30*	*1*					
France, 1986 Azay-sur-Cher (Jet Neuf)	EC	0.36	400	not reported	1	98	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	EDB.896/ Report 171U and 171V Mean recovery for clethodim analysed by DME: 96% (n=6) at 0.06 mg/kg 94% (n=9) at 0.1 mg/kg 90% (n=2) at 0.5 mg/kg Sampling to analysis: 65-566 days
France, 1985 Fontaine-Denis (Bienvenu)	EC	0.18	400		1	253	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	253	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
France, 1985-1986 Licy-Clignon (Bienvenu)	EC	0.18	400		1	126 305	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
France, 1985 Reugny (Bienvenu)	EC	0.18	400		1	248	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	248	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
France, 1985-1986 Réveillon (Bienvenu)	EC	0.18	400		1	117 299	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
France, 1985 Ville gongis (Bienvenu)	EC	0.18	400		1	253	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	253	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
France, 1986-1987 Vué (Bienvenu)	EC	0.18	400		1	108 283	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	283	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.48	400		1	108 283	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
France, 1986-1987 Levroux (Bienvenu)	EC	0.18	400		1	106 267	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	106 267	< 0.1 < 0.1 < 0.1 < 0.1	0.11 < 0.1 < 0.1 < 0.1	0.21 < 0.2 (0.21) < 0.2 < 0.2	

Rape seed country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
									(< 0.20)	
	EC	0.48	400		1	106 267	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
	EC	0.96	400		1	106	< 0.1 < 0.1	0.12 0.11	0.22 0.21 (0.22)	
France, 1986-1987 Azay-sur-Cher (Bienvenu)	EC	0.18	400		1	107 268	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	107 268	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
	EC	0.48	400		1	107 268	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 (< 0.2) < 0.2 < 0.2 (< 0.2)	
	EC	0.96	400		1	107	< 0.1 < 0.1	< 0.0 < 0.1	< 0.2 < 0.2 (< 0.2)	
France, 1986 Fontaine-Denis (Bienvenu)	EC	0.18	400		1	288	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	288	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.48	400		1	288	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.20)	
France, 1986 Bléré (Bienvenu)	EC	0.18	400		1	268	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.36	400		1	268	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
	EC	0.48	400		1	268	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
UK, 1987 Gt. Green, Thurston, Suffolk (Bienvenu)	EC	0.36	300	GS 1,6	1	258	< 0.1	< 0.1	< 0.2	EDB.896/ Report 195X Recovery for clethodim analysed by DME: 112% Sampling to analysis: 4 months
UK, 1987 Humby Hall, Ingoldsby, Lincolnshire (Bienvenu)	EC	0.36	300	GS 1,5	1	294	< 0.1	< 0.1	< 0.2	
	EC	0.72	300	GS 1,5	1	294	< 0.1	< 0.1	< 0.2	

Portion analysed: seed

[a] Mean of replicate field samples is given in parenthesis.

The Meeting received 9 trials on rape seed conducted in Canada (Bruce, 1996: EDB.896).

In the trials conducted in 1989 (EDB.896/Report 170G), an EC formulation (240 g ai/L) was applied to four different plots. In a first and second plot one or two applications were made at a nominal rate of 0.060 kg ai/ha in tank-mix with an adjuvant, CC16255. In a third and fourth plot one or two applications were made at a nominal rate of 0.11 kg ai/ha in tank-mix with an adjuvant, COC. In each trial, seeds were taken 70-103 DALA. In a trial conducted in 1986 (EDB.896/Reports 170E and 170F), one application of an EC formulation (240 g ai/L) was made at a nominal rate of 0.21 kg ai/ha in tank-mix with an adjuvant, COC and seeds were taken 70 DALA. Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26A-1. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.05 mg/kg (expressed as clethodim equivalents). Rape seed samples were stored at -20 °C between sampling and analysis.

In another trial conducted in 1986 (EDB.896/Report 170D), one application of an EC formulation (240 g ai/L) was made at a nominal rate of 0.12 kg ai/ha or 0.24 kg ai/ha and seeds were taken 74-86 DALA. Samples were analysed for total residues of clethodim by the GC-FPD methods PAM II. Sec. 180.412. The LOQ for clethodim was 0.05 mg/kg.

Table 90 Residues of clethodim and metabolites on rape seed from supervised trials in Canada

Rape seed country, year (variety)	Application				DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.11 0.28/year*		*2-3*	*70*				
Canada, 1989 Speers, Saskatchewan (Westar)	EC	0.060[b]	not reported	1	70	< 0.05 < 0.05	0.11 0.098	0.16 0.15 (0.15)	EDB.896/ Report 170G Mean recovery for clethodim sulfoxide analysed by DME: 103% (n=9) at 0.05/0.20 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 132% (n=9) at 0.05/0.20 mg/kg Sampling to analysis: not reported
	EC	0.060 0.060[b]		2	70	0.072 < 0.05	0.25 0.10	0.32 0.15 (0.24)	
	EC	0.11[c]		1	70	0.050 0.069	0.16 0.22	0.21 0.29 (0.25)	
	EC	0.11 0.11[c]		2	70	< 0.05 < 0.05	0.10 0.15 (0.13)	0.15 0.20 (0.18)	
Canada, 1989 Speers, Saskatchewan (Tobin)	EC	0.060[b]		1	70	0.056 0.12	0.14 0.18 c 0.053	0.20 0.31 (0.25) c 0.053	
	EC	0.060 0.060[b]		2	70	0.10 0.086	0.25 0.21 c 0.053	0.35 0.30 (0.33) c 0.053	
	EC	0.11[c]		1	70	0.051 0.065	0.10 0.14 c 0.053	0.16 0.20 (0.18) c 0.053	
	EC	0.11 0.11[c]		2	70	0.19 0.15	0.35 0.32 c 0.053	0.54 0.47 (0.50) c 0.053	
Canada, 1989 Indus, Alberta (Westar)	EC	0.060[b]		1	103	< 0.05 < 0.05	< 0.05 < 0.05	< 0.10 < 0.10 (< 0.10)	
	EC	0.060 0.060[b]		2	103	< 0.05 < 0.05	< 0.05 < 0.05	< 0.10 < 0.10 (< 0.10)	

Rape seed country, year (variety)	Application				DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	Growth Stage	no.		DME	DME -OH	Total	
	EC	0.11[c]		1	103	< 0.05 < 0.05	< 0.05 < 0.05	< 0.10 < 0.10 (< 0.10)	
	EC	0.11 0.11[c]		2	103	< 0.05 < 0.05	< 0.05 < 0.05	< 0.10 < 0.10 (< 0.10)	
Canada, 1989 Olds, Alberta (Tobin)	EC	0.060[b]		1	86	< 0.05 0.060	< 0.05 < 0.05	< 0.10 0.11 (0.11)	
	EC	0.060 0.060[b]		2	86	0.064 0.055	< 0.05 < 0.05	0.11 0.11 (0.11)	
	EC	0.11[c]		1	86	0.065 0.054	< 0.05 < 0.05	0.11 0.11 (0.11)	
	EC	0.11 0.11[c]		2	86	< 0.05 < 0.05	< 0.05 < 0.05	< 0.10 < 0.10 (< 0.10)	
Canada, 1986 Poplar Point, Manitoba (Westar)	EC	0.21	HB 2.2-2.6 canola leaf stage	1	75	0.078 0.065 c 0.080	0.12 0.12	0.20 0.19 (0.19) c 0.080	EDB.896/ Report 170E and 170F Mean recovery for clethodim sulfoxide analysed by DME: 107% (n=3) at 0.05/0.20 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 111% (n=3) at 0.05/0.20 mg/kg Sampling to analysis: not reported
Canada, 1986 Miami, Manitoba (Westar)	EC	0.12	not reported	1	74	0.06	< 0.05	0.11	EDB.896/ Report 170D Mean recovery for clethodim analysed by DME: 71% (n=4) at 0.1mg/kg Sampling to analysis: not reported
	EC	0.24		1	74	0.05	< 0.05	0.10	
Canada, 1986 Miami, Manitoba (Westar)	EC	0.12		1	86	< 0.05	< 0.05	< 0.10	
	EC	0.24		1	86	< 0.05	< 0.05	< 0.10	
Canada, 1986 Miami, Manitoba (Westar)	EC	0.12		1	75	< 0.05	< 0.05	< 0.10	
	EC	0.24		1	75	< 0.05	< 0.05	< 0.10	

Portion analysed: seed

[a] Mean of replicate field samples is given in parenthesis.

[b] in tank-mix with an adjuvant, CC16255

[c] in tank-mix with an adjuvant, COC

The Meeting received 7 trials on rape seed conducted in the USA (Stearns, 2002: V-23595). In each of these trials, two foliar broadcast applications of an EC formulation (240 g ai/L) were made at a nominal rate of 0.11 kg ai/ha. The first application was made 14 ± 1 days prior to the second

application. All applications were made in tank-mix with an adjuvant, COC. In each trial, seeds were taken 57-61 DALA.

Samples were analysed for total residues of clethodim by the GC-MS methods RM-26B-4. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.1 mg/kg (expressed as clethodim equivalents). Rape seed samples were stored at -20 °C for a maximum of 13 months between sampling and analysis.

Table 91 Residues of clethodim and metabolites on rape seed from supervised trials in the USA

Rape seed country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		DME	DME -OH	Total	
GAP, USA	*EC*	*0.11 0.28 /year*			*2-3*	*70*				
USA, 2002 Jamesville, NC (Flint)	EC	0.11 0.11	179 168	Not reported	2	58	0.10 < 0.1	0.30 0.14	0.40 0.24 (0.32)	V-23595 Mean recovery for clethodim sulfoxide analysed by DME: 98% (n=11) at 0.10-0.50 mg/kg Mean recovery for 5-OH clethodim sulfone analysed by DME-OH: 93% (n=11) at 0.10-0.50 mg/kg Sampling to analysis: 41-382 days
USA, 2001 Arkansaw, WI (Hyola 420)	EC	0.11 0.11	186 185		2	61	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
USA, 2001 Barnard, SD (Minot Roundup Ready)	EC	0.11 0.11	150 150		2	60	< 0.1 < 0.1	0.10 0.12	0.20 0.22 (0.21)	
USA, 2001 New Rockford, ND (Quantum)	EC	0.11 0.11	168 170		2	60	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
USA, 2001 Seymour, IL (Pioneer 46A65)	EC	0.11 0.11	190 187		2	60	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2 (< 0.2)	
USA, 2002 Walla Walla, WA (Ceres)	EC	0.11 0.11	187 187		2	57+15[b]	< 0.1 < 0.1	0.11 0.19	0.21 0.29 (0.25)	
USA, 2002 Umapine, OR (Ceres)	EC	0.11 0.11	191 191		2	57+15[b]	< 0.1 < 0.1	0.13 0.17	0.23 0.27 (0.25)	

Portion analysed: seed

[a] Mean of replicate field samples is given in parenthesis.

[b] The canola was cut 57 DALA, and allowed to dry in the field for 15 days before sampling the seed.

Dry herbs

Hops, dry

The Meeting received four trials (two trials; at harvest trials, two trials; decline trial) on hops conducted in the USA (Jolly, 2014: IR-4 PR No. A8086). In each of these trials, four banded to the ground applications of an EC formulation (116 g ai/L) were made at a nominal rate of 0.14 kg ai/ha. Applications occurred at 14 ± 1 day intervals. All applications were made in tank-mix with an adjuvant, NIS or COC. In each trial, dry cones were taken 21 ± 1 DALA. In the decline trials additional samples were collected at 7, 15 and 28 ± 1 DALA.

Samples were analysed for total residues of clethodim by methods RM-26B-3 with final determination of clethodim sulfone and 5-OH clethodim sulfone (omitting the methylation step) by LC-MS/MS. The LOQs for clethodim sulfone and 5-OH clethodim sulfone was 0.1 mg/kg and 0.09 mg/kg, respectively (expressed as clethodim equivalents). The LOD for clethodim sulfone was

0.03 mg/kg and 5-OH clethodim sulfone was 0.04 mg/kg (expressed as clethodim equivalents). Hops, dry cone samples were stored at < -20 °C for a maximum of 11 months between sampling and analysis.

Table 92 Residues of clethodim and metabolites on hops (dried) from supervised trials in the USA

Hops, dry country, year (variety)	Application					DALA Days	Residues, mg/kg [a]			Ref
	Form	kg ai /ha	L/ha	Growth Stage	no.		Clethodim sulfone	5-OH Clethodim sulfone	Total	
GAP, USA	*EC*	*0.14 0.56 /year*	-		*4*	*21*				
USA, 2012 Parma, ID (Newport) Outdoor	EC	0.14 0.14 0.14 0.15	187 187 187 206	Vegetative Vegetative Vegetative Maturing	4	21	< 0.1 < 0.1	< 0.09 < 0.09	< 0.19 < 0.19 (< 0.19)	IR-4 PR No. A8086
USA, 2012 Hubbard, OR (Nugget) Outdoor	EC	0.14 0.14 0.14 0.14	384 374 384 384	Flowering Flowering Immature cones Corn forming	4	7 15 22 29	< 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1	< 0.09 < 0.09 < 0.09 < 0.09 < 0.09 < 0.09	< 0.19 < 0.19 (< 0.19) < 0.19 < 0.19 (< 0.19) < 0.19 < 0.19 (< 0.19)	Mean recovery for clethodim sulfoxide: 91% (n=7) at 0.1mg/kg 89% (n=2) at 1.0 mg/kg Mean recovery for 5-OH clethodim sulfone: 95% (n=7) at 0.1mg/kg 107% (n=2) at 1.0 mg/kg Sampling to analysis: 322-344 days
USA, 2012 Prosser, WA [b] (Warrior) Outdoor	EC	0.14 0.14 0.15 0.14	486 477 496 496	Vegetative Vegetative Vegetative Vegetative	4	7 15 21 28	< 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1	< 0.09 < 0.09 < 0.09 < 0.09 < 0.09 < 0.09	< 0.19 < 0.19 (< 0.19) < 0.19 < 0.19 (< 0.19) < 0.19 < 0.19 (< 0.19)	
USA, 2012 Prosser, WA [c] (Nugget) Outdoor	EC	0.14 0.14 0.14 0.14	159 150 150 159	Budding Bud & bloom Fruiting Fruiting	4	20	< 0.1 < 0.1	< 0.09 < 0.09	< 0.19 < 0.19 (< 0.19)	

Portion analysed: dry cone

[a] Mean of replicate field samples is given in parenthesis.

[b] Address: Washington State University, IAREC 24106 N. Bunn Rd., Prosser, WA Singleton HQ H-19 Hop yard II, Application dates (1st): 9 Jul 2012

[c] Address: WSU, IAREC 24106 N. Bunn Rd. Prosser, WA, Roza Farm B-49, Application dates (1st): 10 Jul 2012

Animal feeds

Legume animal feeds

Bean fodder

The Meeting received four trials on bean forage conducted in Europe (Grote, 2016: S14-03657). In each of these trials, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.29 or 0.12 kg ai/ha. In each trial, straw samples were taken at commercial harvest, 51-57 DALA (BBCH 89-97).

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262, additionally M17R and M18R by methods No. S12-03244. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Bean straw samples were stored at ≤-18 °C for a maximum of 17 days between sampling and analysis.

Table 93 Residues of clethodim and metabolites on bean straw from supervised trials in Europe

Bean straw country, year (variety)	Application					DALA Days	Residues, mg/kg [a]					Ref
	Form	kg ai/ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Croatia	*EC*	*0.20 - 0.25*	*200 - 400*		*1*	*42*						
UK, 2014 King's Newton, Leicestershire (Fuego) Outdoor	EC	0.35	338	79 - 83	1	51	< 0.005	0.13	0.034	0.17	0.09	S14-03657 Mean recovery for clethodim: 82% (n=6) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 103% (n=6) at 0.005/ 0.05/0.50 mg/kg Mean recovery for clethodim sulfone: 97% (n=7) at 0.005/ 0.05/0.50 mg/kg Mean recovery for M17R: 96% (n=8) at 0.01-1.0 mg/kg Mean recovery for M18R: 93% (n=7) at 0.01/0.10/ 0.20 mg/kg Sampling to analysis: 6-17 days
							Total: 0.17					
France, 2014 Mespuits, Essonne (Diva) Outdoor	EC	0.31	322	69	1	56	< 0.005	0.040	0.020	0.13	0.03	
							Total: 0.065					
Spain, 2014 Torrellano, Alicante (Reina Mosa) Outdoor	EC	0.14	345	71	1	56	< 0.005	0.050	0.021	0.88	0.16	
							Total: 0.076					
Spain, 2014 Novelda, Alicante (Flor de Otoño) Outdoor	EC	0.13	335	71	1	57	< 0.005	0.070	0.028	0.60	0.11	
							Total: 0.10					

Portion analysed: straw

[a] Total residue is the sum of residues of clethodim, clethodim sulfoxide and clethodim sulfone.

Bean forage

The Meeting received four trials on bean forage conducted in Europe (Grote, 2016: S14-03657). In each of these trials, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.29 or 0.12 kg ai/ha. In each trial, whole plant samples were taken at 0 DALA (BBCH 69-73).

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262, additionally M17R and M18R by methods No. S12-03244. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Bean whole plant samples were stored at ≤-18 °C for a maximum of 17 days between sampling and analysis.

Table 94 Residues of clethodim and metabolites on bean forage from supervised trials in Europe

Bean forage country, year (variety)	Application					DALA Days	Residues, mg/kg[a]					Ref
	Form	kg ai/ha	L/ha	BBCH	no.		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Croatia	*EC*	*0.20 - 0.25*	*200 - 400*		*1*							
UK, 2014 King's Newton, Leicestershire (Fuego) Outdoor	EC	0.35	338	79 - 83	1	0	0.85	1.8	0.011	0.01	< 0.01	S14-03657 Mean recovery for clethodim: 86% (n=7) at 0.005/ 0.05/5.0 mg/kg Mean recovery for clethodim sulfoxide: 105% (n=8) at 0.005- 12 mg/kg Mean recovery for clethodim sulfone: 105% (n=6) at 0.005/ 0.05 mg/kg Mean recovery for M17R: 96% (n=6) at 0.01/0.10 mg/kg Mean recovery for M18R: 93% (n=5) at 0.01/0.10 mg/kg Sampling to analysis: 11-17 days
							Total: 2.7					
France, 2014 Mespuits, Essonne (Diva) Outdoor	EC	0.31	322	69	1	0	4.4	2.7	0.016	0.04	< 0.01	
							Total: 7.1					
Spain, 2014 Torrellano, Alicante (Reina Mosa) Outdoor	EC	0.14	345	71	1	0	0.77	2.8	0.034	0.04	< 0.01	
							Total: 3.6					
Spain, 2014 Novelda, Alicante (Flor de Otoño) Outdoor	EC	0.13	335	71	1	0	0.79	2.0	0.016	0.01	< 0.01	
							Total: 2.8					

Portion analysed: whole plant

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

Pea fodder

The Meeting received 2 trials (at harvest trials) on pea straw which were conducted in France (Balluff, 1998: 97065/F1-FPPS). In each of these trials, one foliar application of an EC formulation (240 g ai/L or 120 g ai/L) was made at a nominal rate of 0.19 or 0.13 kg ai/ha. At each trial, straw samples were taken 58 DALA (BBCH 89).

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26B-2. The LOQ for clethodim was 0.07 mg/kg. The LODs for DME and DME-OH were 0.03 mg/kg and 0.04 mg/kg, respectively (expressed as clethodim equivalents). Pea straw samples were stored for a maximum of 4 months between sampling and analysis.

Table 95 Residues of clethodim and metabolites on pea straw from supervised trials in France

Pea straw country, year (variety)	Application					DALA Days	Residues, mg/kg[a]			Ref
	Form	kg ai /ha	L/ha	BBCH	no.		DME	DME -OH	Total	
GAP, Slovakia	*EC*	*0.24-0.26*	*250-400*	*12-30*	*1*					
France, 1997 Taize, Deux-Sevres (Baccara) Outdoor	240 g/L EC	0.19	296	51	1	58	0.12	< 0.04	0.16	97065/F1-FPPS Mean recovery for clethodim: 92% (n=2) at 0.07 mg/kg 97% (n=1) at 0.7 mg/kg Sampling to analysis: 132 days
	120 g/L EC	0.20	311	51	1	58	0.20	0.05	0.25	
		0.13	305	51	1	58	0.23	0.04	0.27	
France, 1997 Curçay sur Dive, Vienne (Alladin) Outdoor	240 g/L EC	0.19	307	49	1	58	0.06	< 0.04	0.10	
	120 g/L EC	0.19	297	49	1	58	0.09	< 0.04	0.13	
		0.13	299	49	1	58	0.05	< 0.04	0.09	

Portion analysed: straw

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

The Meeting received 24 trials on pea straw conducted in Europe (Grote, 2009: S08-01827, Grote, 2009: S08-02048, Grote, 2009: S08-02069, Grote, 2010: S09-01362, Grote, 2010: S09-01363, Grote, 2010: S10-00568, Grote, 2010: S10-00569 and Grote, 2016: S15-03508). In the trials conducted between 2008-2010, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.30 kg ai/ha. In each trial, straw samples were taken at commercial harvest, 51-69 DALA. In the trials conducted in 2015, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.29 or 0.12 kg ai/ha. In each trial, straw samples were taken at commercial harvest, 55-67 DALA (BBCH 87-89).

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). In the trials conducted in 2015 two additional metabolites, M17R and M18R were analysed by methods No. S12-03244. The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Pea straw samples were stored at ≤-18 °C for a maximum of 3.1 months between sampling and analysis.

Table 96 Residues of clethodim and metabolites on pea straw from supervised trials in Europe

Pea straw country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg [a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Slovakia	*EC*	*0.24-0.26*	*250-400*	*12-30*	*1*							
Hungary, 2008 Adony, Fejér (Grana) Outdoor	EC	0.31	307	59	1	55	< 0.005	0.046	0.064	-	-	S08-01827 Mean recovery for clethodim: 74% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 85% (n=3) at 0.005/ 0.05/0.10 mg/kg Mean recovery for clethodim sulfone: 85% (n=3) at 0.005/ 0.05/0.10 mg/kg Sampling to analysis: 54-94 days
							Total: 0.12					
Hungary, 2008 Székesfehérvá, Fejér (Mastin) Outdoor	EC	0.32	317	55	1	56	< 0.005	0.060	0.073	-	-	
							Total: 0.14					
UK, 2008 Alderminster[b] (Nitouche) Outdoor	EC	0.31	307	35 - 51	1	69	< 0.005	0.011	0.005	-	-	
							Total: 0.021					
UK, 2008 Alderminster[c] (Einstein) Outdoor	EC	0.30	304	51 - 55	1	56	< 0.005	0.019	0.007	-	-	S08-02048 Mean recovery for clethodim: 90% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 83% (n=3) at 0.005/ 0.05/0.50 mg/kg Mean recovery for clethodim sulfone: 87% (n=3) at 0.005/ 0.05/0.50 mg/kg Sampling to analysis: 52-92 days
							Total: 0.031					
Hungary, 2008 Aba, Fejér (ZKI 01-30) Outdoor	EC	0.31	313	55	1	51	< 0.005	0.17	0.15	-	-	
							Total: 0.33					

Pea straw country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg [a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
Spain, 2008 Almansa, Albacete (Baccara) Outdoor	EC	0.31	407	69	1	55	< 0.005	0.38	0.22	-	-	S08-02069 Mean recovery for clethodim: 82% (n=4) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 98% (n=4) at 0.005/ 0.05/0.50 mg/kg Mean recovery for clethodim sulfone: 93% (n=4) at 0.005/ 0.05/0.50 mg/kg Sampling to analysis: 79-92 days
							Total: 0.61					
Spain, 2008 Barrax, Albacete (Messire) Outdoor	EC	0.33	435	35	1	56	< 0.005	0.011	0.007	-	-	
							Total: 0.023					
Greece, 2008 Nea Apollonia, Thessaloniki [d] (Argos) Outdoor	EC	0.29	385	73 - 74	1	56	< 0.005	0.075	0.026	-	-	
							Total: 0.11					
Greece, 2008 Nea Apollonia, Thessaloniki [e] (Urano) Outdoor	EC	0.31	418	73 - 75	1	57	< 0.005	0.086	0.028	-	-	
							Total: 0.12					
Greece, 2008 Nea Apollonia, Thessaloniki [f] (Ojo) Outdoor	EC	0.31	412	73	1	54	< 0.005	0.11	0.033	-	-	
							Total: 0.15					
Hungary, 2009 Ráclamás, Fejér (Oasis) Outdoor	EC	0.29	294	65	1	56	< 0.005	0.082	0.042	-	-	S09-01362 Mean recovery for clethodim: 86% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 89% (n=3) at 0.005/ 0.05/1.0 mg/kg Mean recovery for clethodim sulfone: 77% (n=2) at 0.005/ 0.05 mg/kg Sampling to analysis: 85 days
							Total: 0.13					

Pea straw country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg [a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
Spain, 2009 Lliria, Valencia (Tristan G) Outdoor	EC	0.33	325	32	1	56	< 0.005	0.008	0.008	-	-	S09-01363 Mean recovery for clethodim: 73% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 96% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfone: 79% (n=2) at 0.005/ 0.05 mg/kg Sampling to analysis: 71-92 days
							Total: 0.021					
Greece, 2009 Apollonia, Thessaloniki (Early Onward) Outdoor	EC	0.29	288	51	1	56	< 0.005	0.020	0.022	-	-	
							Total: 0.047					
UK, 2010 Kiddington, Oxfordshire (Profit) Outdoor	EC	0.31	310	65	1	54	< 0.005	0.037	0.017	-	-	S10-00568 Mean recovery for clethodim: 87% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 91% (n=3) at 0.005/ 0.05/0.10 mg/kg Mean recovery for clethodim sulfone: 90% (n=3) at 0.005/ 0.05/0.10 mg/kg Sampling to analysis: 47-56 days
							Total: 0.059					
UK, 2010 Hanby, Lincs (Genki) Outdoor	EC	0.27	273	61	1	51	< 0.005	0.073	0.047	-	-	
							Total: 0.13					
Spain, 2010 Barax, Albacete (Cartouche)	EC	0.29	287	33	1	54	< 0.005	0.11	0.056	-	-	S10-00569 Mean recovery for clethodim:

Pea straw country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg [a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
Outdoor							Total: 0.17					86% (n=2) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 82% (n=3) at 0.005/ 0.05/0.15 mg/kg Mean recovery for clethodim sulfone: 77% (n=3) at 0.005/ 0.05/0.15 mg/kg Sampling to analysis: 57 days
Germany, 2015 Buxtehude, Niedersachsen (Alvetsa) Outdoor	EC	0.31	317	39	1	63	< 0.005	0.060	0.035	0.06	0.03	S15-03508 Mean recovery for clethodim: 90% (n=9) at 0.005/ 0.05 mg/kg Mean recovery for clethodim sulfoxide: 96% (n=9) at 0.005-1.0 mg/kg Mean recovery for clethodim sulfone: 98% (n=9) at 0.005-1.0 mg/kg Mean recovery for M17R: 91% (n=8) at 0.01-0.20 mg/kg Mean recovery for M18R: 93% (n=8) at 0.01-0.20 mg/kg Sampling to analysis: 5-18 days
							Total: 0.10					
Poland, 2015 Kluczewo Huby, Wielkopolska (Wenus) Outdoor	EC	0.31	324	39	1	67	< 0.001	0.013	0.012	0.04	0.01	
							Total: 0.030					
UK, 2015 Heather, Leicestershire (Kabuki) Outdoor	EC	0.28	293	33	1	62	< 0.005	0.11	0.081	0.14	0.09	
							Total: 0.20					
Germany, 2015 Ahrensfelde, Brandenburg (Navarro) Outdoor	EC	0.27	277	39	1	59	< 0.005	0.037	0.033	0.06	0.03	
							Total: 0.075					
						64	< 0.005	0.035	0.029	0.06	0.03	
							Total: 0.069					
Italy, 2015 Idice, Bologna (Ideal) Outdoor	EC	0.12	303	71	1	57	< 0.005	0.014	0.040	0.07	0.04	
							Total: 0.059					
Spain, 2015 Cutanda, Aragon (Capuchino) Outdoor	EC	0.13	312	39 - 51	1	57	< 0.005	< 0.005	< 0.005	< 0.01	< 0.01	
							Total: < 0.015					
Greece, 2015 Stephanina, Thessaloniki (Jof) Outdoor	EC	0.12	310	61	1	55	< 0.005	0.009	0.006	0.03	0.01	
							Total: 0.020					
Bulgaria, 2015 Chernogorovo, Pazardjik	EC	0.12	310	39	1	61	< 0.005	< 0.005	< 0.005	< 0.01	< 0.01	

Pea straw country, year (variety)	Application					DALA Days	Residues expressed as clethodim, mg/kg [a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
(Denitsa) Outdoor							Total: < 0.015					

Portion analysed: straw

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

[b] Address: CU37 8PC, Alderminster, UK, Application dates: 03 Jun 2008

[c] Address: CU37 8PC, Alderminster, UK, Application dates: 19 Jun 2008

[d] Address: 57015, Nea Apollonia, Thessaloniki, Greece, Application dates: 20 May 2008

[e] Address: 57015, Nea Apollonia, Thessaloniki, Greece, Application dates: 15 May 2008

[f] Address: 57014, Nea Apollonia, Thessaloniki, Greece, Application dates: 15 May 2008

Pea vines

The Meeting received eight trials on pea vines conducted in Europe (Grote, 2016: S15-03508). In each of these trials, one foliar application of an EC formulation (120 g ai/L) was made at a nominal rate of 0.29 or 0.12 kg ai/ha. In each trial, whole plant samples were taken at 0 DALA (BBCH 33-71).

Samples were analysed for residues of clethodim, clethodim sulfoxide and clethodim sulfone by methods RCC 855262, and additionally M17R and M18R by methods No. S12-03244. The LOQs for clethodim, clethodim sulfoxide and clethodim sulfone were all 0.005 mg/kg (expressed as clethodim equivalents). The LODs for clethodim, clethodim sulfoxide and clethodim sulfone were 0.0015 mg/kg, 0.0014 mg/kg and 0.0014 mg/kg, respectively (expressed as clethodim equivalents). The LOQs for M17R and M18R were both 0.01 mg/kg (expressed as clethodim equivalents). The LODs for M17R and M18R were both 0.004 mg/kg (expressed as clethodim equivalents). Pea whole plant samples were stored at ≤-18 °C for a maximum of 18 days between sampling and analysis.

Table 97 Residues of clethodim and metabolites on pea vines from supervised trials in Europe

Pea vines country, year (variety)	Application					DALA Days	Residues, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
GAP, Slovakia	*EC*	*0.24-0.26*	*250-400*	*12-30*	*1*	-						
Germany, 2015 Buxtehude, Niedersachsen (Alvetsa) Outdoor	EC	0.31	317	39	1	0	1.9	4.6	0.015	0.03	< 0.01	S15-03508 Mean recovery for clethodim: 81% (n=13) at 0.005-5.0 mg/kg Mean recovery for clethodim sulfoxide: 91% (n=13) at 0.005/ 0.05/8.0 mg/kg Mean recovery for clethodim sulfone: 94% (n=12) at 0.005/ 0.05 mg/kg Mean recovery for M17R: 85% (n=12) at
							Total: 6.5					
Poland, 2015 Kluczewo Huby, Wielkopolska (Wenus) Outdoor	EC	0.31	324	39	1	0	4.6	7.4	0.016	0.06	< 0.01	
							Total: 12					
UK, 2015 Heather, Leicestershire (Kabuki) Outdoor	EC	0.28	293	33	1	0	4.1	6.1	0.032	0.06	< 0.01	
							Total: 10					
Germany, 2015 Ahrensfelde, Brandenburg (Navarro) Outdoor	EC	0.27	277	39	1	0	1.9	5.3	0.017	0.03	< 0.01	
							Total: 7.2					

Pea vines country, year (variety)	Application					DALA Days	Residues, mg/kg[a]					Ref
	Form	kg ai /ha	L/ha	BBCH	no		clethodim	clethodim sulfoxide	clethodim sulfone	M17R	M18R	
Italy, 2015 Idice, Bologna (Ideal) Outdoor	EC	0.12	303	71	1	0	0.17	2.2	0.028	< 0.01	< 0.01	0.01/0.10 mg/kg Mean recovery for M18R: 87% (n=12) at 0.01/0.10 mg/kg Sampling to analysis: 1-18 days
							Total: 2.4					
Spain, 2015 Cutanda, Aragon (Capuchino) Outdoor	EC	0.13	312	39 - 51	1	0	0.48	4.0	0.028	0.07	< 0.01	
							Total: 4.5					
Greece, 2015 Stephanina, Thessaloniki (Jof) Outdoor	EC	0.12	310	61	1	0	0.45	2.9	0.024	0.06	< 0.01	
							Total: 3.4					
Bulgaria, 2015 Chernogorovo, Pazardjik (Denitsa) Outdoor	EC	0.12	310	39	1	0	0.30	4.1	0.039	0.03	< 0.01	
							Total: 4.4					

Portion analysed: whole plant

[a] Total residue is sum of residues for clethodim, clethodim sulfoxide and clethodim sulfone.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In Processing

The Meeting received information on high temperature hydrolysis of clethodim and clethodim sulfoxide, and the fate of clethodim residues during the processing of apple, plum and oilseed rape.

Crops that the Meeting received supervised field trial information for may be processed prior to consumption. Processing factors have been calculated for clethodim residues in oilseed rape.

High temperature hydrolysis

Study 1 (Clethodim)

The hydrolysis of [Ring-4,6-^{14}C]-clethodim was studied in sterile buffered solutions of pH 4, 5 and 6 (Persch, 2013: S12-00895). The buffered solutions used in these studies were 0.05 M citrate (pH 4 and pH 6), and 0.05 M acetate (pH 5). The test systems were treated under conditions that simulate the effects of pasteurization (pH 4, 90 °C for 20 min), baking/boiling (pH 5, 100 °C for 60 min), and sterilization (pH 6, 120 °C for 20 min). The initial concentration of the test item in 50 mL buffer solution was 2.58 mg/L. The test was performed in the dark with two independent (duplicate) samples. The test vessels were weighed before and after processing, and the weight of the sample in each vessel was calculated. An aliquot was taken from the test vessel. Analysis was performed using LSC, HPLC and LC-MS.

There was no significant change in total radioactivity following processing. In addition, no significant change in sample weight was obtained following processing. Results of quantification of radioactivity by LSC for each set of vessels subjected to simulated conditions showed recovery after processing of 104% at pH4 (pasteurization), 101% at pH5 (baking/boiling) and 105% at pH 6 (sterilization).

Under representative condition of pasteurization the degradation product clethodim oxazole was formed with an amount of 13.5%. Under representative condition of baking/brewing/boiling and sterilization clethodim oxazole was formed with amounts of 80.4% and 96.3%, respectively, and an additional degradation product, clethodim trione with amounts of 5.4% and 3.8%, respectively.

Table 98 Identification of radioactivity under the conditions for processing simulation

Conditions	Recovery of Applied Radioactivity (%)			
	Clethodim	Clethodim oxazole	Clethodim trione	Total (mean)
pH 4, 90 °C, 20min	85.1, 88.0	14.9, 12.1	-	104
pH 5, 100 °C, 60 min	13.6, 14.8	81.1, 79.7	5.3, 5.5	101
pH 6, 120 °C, 20 min	NA, NA	95.5, 97.2	4.6, 3.0	105

NA: not applicable

Study 2 (Clethodim sulfoxide)

The hydrolysis of [Ring-4,6-^{14}C]-clethodim sulfoxide was studied in sterile buffered solutions of pH 4, 5 and 6 (Bloβ, 2018: S18-02073). The buffered solutions used in these studies were 0.05 M citrate (pH 4, 5 and 6). The test systems were treated under conditions that test the effects of pasteurization (pH 4, 90 °C for 20 min), baking/boiling (pH 5, 100 °C for 60 min), and sterilization (pH 6, 120 °C for 20 min). The initial concentration of test item in 15 mL buffer solution was 3.97-4.16 mg/L. The test was performed in the dark with two independent (duplicate) samples. An aliquot of 2 mL was taken from the test vessel and stabilised with 10% acetonitrile. An aliquot of 0.1 mL was analysed by LSC. The LSC and radio-HPLC samples were taken before and after the respective processing.

There was no significant change in total radioactivity following processing. Results of quantification of radioactivity by LSC for each set of vessels subjected to simulated conditions showed recovery after processing of 102.1% at pH4 (pasteurization), 101.4% at pH5 (baking/boiling) and 101.3% at pH 6 (sterilization).

^{14}C-clethodim sulfoxide degraded during all processing conditions and one major degradation product, clethodim oxazole sulfoxide, was formed under conditions representative of simulating pasteurisation, baking/brewing/boiling and sterilisation. After processing at pH 4 at 90 °C for 20 minutes, which simulates the pasteurization process, ^{14}C-clethodim sulfoxide degraded from 95.5% before processing to 4.9% after processing, while clethodim oxazole sulfoxide increased from 4.7% before processing to 89.4% after processing. After processing at pH 5 at 100 °C for 60 minutes which simulates the baking/brewing/boiling process, ^{14}C- clethodim sulfoxide degraded from 100.0 % before processing to 2.3% after processing, while clethodim oxazole sulfoxide increased from 0.0% before processing to 93.7% after processing. After processing at pH 6 at 120 °C for 20 minutes which simulates the sterilisation process, ^{14}C-clethodim sulfoxide degraded from 100.0% before processing to 0.0% after processing, while clethodim oxazole sulfoxide increased from 0.0% before processing to 98.0% after processing.

Table 99 Identification of radioactivity under the conditions for processing simulation

Conditions	Recovery of Applied Radioactivity (%)					
	Clethodim sulfoxide	Clethodim oxazole sulfoxide	Clethodim trione sulfoxide	M4	M5	Total
pH 4, 90 °C, 20min	6.2, 3.5	88.9, 89.8	7.1, 6.7	0.0, 1.9	0.0, 0.0	102.3, 101.9
pH 5, 100 °C, 60 min	2.0, 2.6	94.0, 93.4	5.7, 5.2	0.0, 0.0	0.0, 0.0	101.7, 101.2
pH 6, 120 °C, 20 min	0.0, 0.0	97.6, 98.4	2.9, 2.5	0.0, 0.0	1.1, 0.0	101.6, 100.9

Apple

The study was conducted to determine the magnitude of residues of clethodim in/on raw apple fruits and processed fractions of apple fruits. One test was carried out in the USA following exaggerated treatment with clethodim 116 g ai/L EC formulation during the 2008 growing season (Homa, 2012: IR-4 PR No. 06873). In the test, two broadcast applications directed to the ground were made to the crop each at a rate of 1.4 kg ai/ha, 5 × the critical US GAP, with a 14-day interval. Samples of apple were taken 14 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods CAL vers. 15. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LODs for DME and DME-OH were 0.03 mg/kg on fresh fruit and 0.01 mg/kg on pomace and juice (expressed as clethodim equivalents). The overall mean recoveries from concurrent fortifications for clethodim sulfoxide and 5-OH clethodim sulfone in each matrix were within 70-120%. Processed apple samples were stored at -21 ± 7 °C for a maximum of 20 months between sampling and analysis.

Table 100 Residues of clethodim in processed commodities of apple

Apple country, year (variety)	Application kg ai/ha	Application no.	DALA Days	Commodity	Residues, mg/kg DME	Residues, mg/kg DME-OH	Residues, mg/kg Total	Processing Factor
USA, 2008 North Rosa, NY (Empire) Outdoor	1.4	2	14	Fruit	< 0.095	< 0.088	< 0.18	
	1.4			Pomace	< 0.095	< 0.088	< 0.18	-
				Juice	< 0.095	< 0.088	< 0.18	-

Plum

The study was conducted to determine the magnitude of residues of clethodim in/on raw plum fruits and processed fractions of plum fruits. One test was carried out in the USA following exaggerated treatment with clethodim 116 g ai/L EC formulation during the 2008 growing season (Homa, 2011: IR-4 PR No. 06948). In the test, two banded applications directed to the ground were made to the crop each at a rate of 1.4 kg ai/ha, 5 × the critical US GAP, with a 14-day interval. Samples of apple were taken 13 DALA.

Samples were analysed for total residues of clethodim by methods RM-26B-3 using GC-MS instead of GC-FPD. The LOQ for clethodim and all metabolites that can be converted to DME was 0.095 mg/kg (expressed as clethodim equivalents) and the LOQ for all 5-OH-metabolites that can be converted to DME-OH was 0.088 mg/kg (expressed as clethodim equivalents). The LOD was 0.03 mg/kg for DME and 0.02 mg/kg for DME-OH on fresh fruit; and 0.05 mg/kg and 0.02 mg/kg, respectively, on dried fruit (expressed as clethodim equivalents). The overall mean recoveries from concurrent fortifications for clethodim sulfoxide and 5-OH clethodim sulfone in each matrix were within 70-120%. Processed plum samples were stored at -4 to -22 °C for a maximum of 28 months between sampling and analysis.

Table 101 Residues of clethodim in processed commodities of plum

Plum country, year (variety)	Application kg ai/ha	Application no.	DALA Days	Commodity	Residues, mg/kg DME	Residues, mg/kg DME-OH	Residues, mg/kg Total	Processing Factor
USA, 2008 Parlier, CA (French) Outdoor	1.4	2	14	Fruit	< 0.095	< 0.088	< 0.18	
	1.4			Dried	< 0.095	< 0.088	< 0.18	-

Oilseed rape

The study was conducted to determine the magnitude of residues of clethodim in/on raw rape seeds and processed fractions of rape seeds. Seven tests were carried out in France (Bruce, 1996: EDB.896/Report 171U and 171V), Canada (Bruce, 1996: EDB.896/Reports 170E and 170F) and the USA (Stearns, 2002: V-23595).

Five tests were carried out in France following treatment with clethodim 240 g ai/L EC formulation. One application was made to the crop at a rate of 0.18 kg ai/ha or 0.48 kg ai/ha. Samples of rape seed were taken 106-305 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods PAM II. Sec. 180.412. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.1 mg/kg (expressed as clethodim equivalents). The recoveries from concurrent fortifications (0.06 and 0.10 mg/kg) for clethodim in oil were 102 and 138%, respectively. Processed rape seed samples were stored at -20 °C for a maximum of 15 months between sampling and analysis.

One test was carried out in Canada following exaggerated treatment with clethodim 240 g ai/L EC formulation. One application was made to the crop at a rate of 0.24 kg ai/ha, 2.3 × the critical US GAP. Samples of rape seed were taken 67 DALA.

Samples were analysed for total residues of clethodim by the GC-FPD methods RM-26A-1. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.05 mg/kg (expressed as clethodim equivalents). The overall mean recoveries from concurrent fortifications for clethodim sulfoxide and 5-OH clethodim sulfone in crude oil were within 70-120% but in canola meal were over 120%.

One test was carried out in the USA following exaggerated treatment with a clethodim 240 g ai/L EC formulation. Two broadcast applications were made to the crop each at a rate of 0.32 kg ai/ha, 3 × the critical US GAP. Samples of rape seed were taken 60 DALA.

Samples were analysed for total residues of clethodim by the GC-MS methods RM-26B-4. The LOQs for clethodim and all metabolites that can be converted to DME and for all 5-OH-metabolites that can be converted to DME-OH were both 0.1 mg/kg (expressed as clethodim equivalents). The overall mean recoveries from concurrent fortifications for clethodim sulfoxide and 5-OH clethodim sulfone in each matrix were within 70-120%. Processed rape seed samples were stored at -20 °C for a maximum of 12 months between sampling and analysis.

Table 102 Residues of clethodim in processed commodities of rape seed

Rape seed country, year (variety)	Application		DALA Days	Commodity	Residues, mg/kg			Processing Factor
	kg ai/ha	no.			DME	DME -OH	Total	
France, 1985-1986 Licy-Clignon (Bienvenu)	0.18	1	126	Seed	< 0.1	< 0.1	< 0.2	
				Oil	< 0.1	< 0.1	< 0.2	<1
			305	Seed	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean < 0.2	
				Oil	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean < 0.2	<1
France, 1985-1986 Réveillon (Bienvenu)	0.18	1	117	Seed	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean < 0.2	
				Oil	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean < 0.2	<1
			299	Seed	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean< 0.2	
				Oil	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean < 0.2	<1
France, 1986-1987 Voué (Bienvenu)	0.48	1	108	Seed	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean < 0.2	
				Oil	< 0.1	< 0.1	< 0.2	
					< 0.1	< 0.1	< 0.2	
							mean < 0.2	<1

Rape seed country, year (variety)	Application kg ai/ha	Application no.	DALA Days	Commodity	Residues, mg/kg DME	Residues, mg/kg DME -OH	Residues, mg/kg Total	Processing Factor
France, 1986-1987 Levroux (Bienvenu)	0.48	1	106	Seed Oil	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 mean < 0.2 < 0.2 < 0.2 mean < 0.2	 <1
France, 1986-1987 Azay-sur-Cher (Bienvenu)	0.18	1	107	Seed Oil	< 0.1 < 0.1	< 0.1 < 0.1	< 0.2 < 0.2	<1
	0.48	1	107	Seed Oil	< 0.1 < 0.1 < 0.1 < 0.1	< 0.1 < 0.1 < 0.1 < 0.1	< 0.2 < 0.2 mean < 0.2 < 0.2 < 0.2 mean < 0.2	 <1
Canada, 1986 Speers, Saskatchewan (Tobin)	0.24	1	67	Seed Meal Crude oil	0.077, 0.099, 0.067 0.16, 0.52, < 0.05 < 0.05, < 0.05, < 0.05	0.21, 0.23, 0.22 < 0.05, 0.055, < 0.05 < 0.05, < 0.05, < 0.05	0.29, 0.33, 0.29 mean 0.30 0.17, 0.58, < 0.10 mean 0.28 < 0.10, < 0.10, < 0.10 mean < 0.10	 0.93 < 0.33
USA, 2001 Seymour, IL (Pioneer 46A65)	0.32 0.32	2	60	Seed Seed (processed) Meal Oil	< 0.1, < 0.1 < 0.1, < 0.1 < 0.1, < 0.1 < 0.1, < 0.1	0.19, 0.12 0.21, 0.20 0.13, 0.10 < 0.1, < 0.1	0.29, 0.22 mean 0.26 0.31, 0.30 mean 0.31 0.23, 0.20 mean 0.22 < 0.2, < 0.2 mean < 0.2	 1.2 0.85 < 0.77

Processing Factor = Clethodim residues in processed commodity/ Clethodim residues in rape seeds (prior to processing)

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

The Meeting received lactating dairy cow and laying hens feeding studies.

Lactating dairy cow

Three groups of four lactating dairy cows (Holstein) were administered gelatin capsules containing 5% clethodim and 95% clethodim sulfoxide once a day for 28 consecutive days (Weissenburger *et al.*, 1989: ADC1124). The dose levels were equivalent to 0.53, 1.7 and 5.7 ppm in the feed as received for clethodim and 10, 32 and 107 ppm in the feed as received for clethodim sulfoxide (expressed as clethodim). A control group (2 animals) was included, to which empty capsules were administered. One cow per treatment group was left untreated for a further 3 days after the 28-day dosing period. The times of preparation and administration of the clethodim/clethodim sulfoxide dosing capsules were 8-10:30 a.m. and 11:00 a.m., respectively. Cows were milked twice daily. After each evening milking event, duplicate evening milk samples (250 mL each) were mixed with duplicate morning milk (250 mL each) and stored (3-4 months) immediately at or below -20 °C for later analysis. On day 1 and 31, milk samples contained evening milk (500 mL) and morning milk (500 mL) only, respectively. On the 25th, 26th and 27th days of dosing, additional milk subsamples were taken for pasteurization and fractionation into skim milk and cream (control and highest dose group only).

At the end of the 28-day dosing period (between 22-24 hours after the last dose), three animals of each group and one control animal were slaughtered. Liver, kidney, composite muscle and composite (subcutaneous and peritoneal) fat samples (approximately 1 kg each) were removed and immediately stored (3-4 months) at ≤-20 °C for later analysis.

Samples were analysed in duplicate according to Chevron method RM-26A, which was slightly modified for analysis of cream samples. RM-26A is a common moiety method. Clethodim and clethodim-like metabolites containing the 5-(2-ethylthiopropyl) cyclohexene-3-one moiety are converted to DME, 5-OH clethodim and 5-OH clethodim like metabolites containing the 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moiety are converted to DME-OH and S-methyl-clethodim and S-methyl like metabolites are converted to S-methyl-DME. The residues are expressed as clethodim equivalents. The LOQs were 0.0125 mg/kg for milk and milk products and 0.05 mg/kg for tissues. Freshly fortified samples (all matrices) at the LOQ and up to 100 × LOQ were included within most analytical series yielding recoveries (generally) within 70-110%.

The cows remained in good health during the study. No treatment-related effects on bodyweight, milk production, milk composition (% fat) or feed intake during the dosing period were observed, apart from one cow in the highest treatment group, which showed a 15% decline in feed consumption. At post-mortem, no treatment-related abnormalities were observed in the respiratory, alimentary, urinary and reproductive systems of the cows.

Table 103 Residues in cow milk (mg clethodim eq/kg)

Study Day	DME							
	Control		0.53/10 ppm (1×)		1.7/32 ppm (3×)		5.7/107 ppm (10×)	
	Individual	Mean	Individual	Mean	Individual	Mean	Individual	Mean
-1	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
1	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, 0.0228, 0.0207, 0.0269	0.021	0.0703, 0.0769, 0.0694, 0.0812	0.074
2	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0158, 0.0133, 0.0133, 0.0172	0.015	0.0551, 0.0541, 0.0681, 0.0602	0.059
4	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0148, 0.0170, 0.0184, 0.0207	0.018	0.0524, 0.0346, 0.0516, 0.0518	0.048
7	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0137, <LOQ, 0.0151, 0.0148	0.014	0.0472, 0.0496, 0.0454, 0.0485	0.048
12	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0181, 0.0172, <LOQ, <LOQ	0.015	0.0558, 0.0558, 0.0665, 0.0693	0.062
16	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0158, 0.0145, 0.0190, 0.0199	0.017	0.0626, 0.0703, 0.0632, 0.0788	0.069
20	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0221, <LOQ, 0.0178, 0.0174	0.017	0.0789, 0.0655, 0.0679, 0.0684	0.070
24	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0217, 0.0169, 0.0205, 0.0270	0.022	0.0545, 0.0704, 0.0441, 0.0667	0.059
28	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0234, <LOQ, 0.0200, 0.0334	0.022	0.0713, 0.0591, 0.0669, 0.0724	0.067
1 (D) 2 (D) 3 (D)	<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ		0.0130 <LOQ <LOQ	
Study Day	S-methyl DME							
	Control		0.53/10 ppm (1×)		1.7/32 ppm (3×)		5.7/107 ppm (10×)	
	Individual	Mean	Individual	Mean	Individual	Mean	Individual	Mean
-1	<LOQ		<LOQ		<LOQ, <LOQ,	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
1	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, 0.0144, <LOQ	0.013
2	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0152, 0.0316, 0.0172, <LOQ	0.019
4	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0146, <LOQ, <LOQ, <LOQ	0.013

Study Day	DME							
	Control		0.53/10 ppm (1×)		1.7/32 ppm (3×)		5.7/107 ppm (10×)	
	Individual	Mean	Individual	Mean	Individual	Mean	Individual	Mean
7	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, 0.0139, <LOQ	0.013
12	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0138, 0.0133, 0.0164, <LOQ	0.014
16	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0164, 0.0151, 0.0151, <LOQ	0.015
20	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, 0.0137, 0.0156, 0.0137	0.014
24	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0141, 0.0136, <LOQ, <LOQ	0.013
28	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	0.0138, <LOQ, 0.0150, <LOQ	0.013
1 (D) 2 (D) 3 (D)	<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ	
Study Day	DME-OH							
	Control		0.53/10 ppm (1×)		1.7/32 ppm (3×)		5.7/107 ppm (10×)	
	Individual	Mean	Individual	Mean	Individual	Mean	Individual	Mean
-1	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
1	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
2	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
4	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
7	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
12	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
16	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
20	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
24	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
28	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ, <LOQ	<LOQ
1 (D) 2 (D) 3 (D)	<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ		<LOQ <LOQ <LOQ	

(D) Depuration phase

LOQ = 0.0125 mg/kg

Table 104 Residues in skim milk and cream (mg clethodim eq/kg)

	Study Day	Control			5.7/107 ppm (10×)		
		DME	S-methyl DME	DME-OH	DME	S-methyl DME	DME-OH
Skim milk (Non-fat solids)	27-28	<LOQ	<LOQ	<LOQ	0.0269	<LOQ	<LOQ
Cream (Fat solids)		<LOQ	<LOQ	<LOQ	0.1096	<LOQ	<LOQ
Pasteurized whole milk		<LOQ	<LOQ	<LOQ	0.0606	0.0139	<LOQ
Acid whey (Lactose)		<LOQ	<LOQ	<LOQ	0.0265	<LOQ	<LOQ

LOQ = 0.0125 mg/kg

No DME-OH residues above the LOQ (0.0125 mg/kg for milk and milk products were found in whole milk, skim milk, pasteurized milk and acid whey (all dose groups).

No residues of S-methyl-DME above the LOQ (0.0125 mg/kg for milk and milk products) were found in milk, skim milk, cream, pasteurized whole milk and acid whey from the control group, the low and middle dose group. The milk samples from the high dose group contained a maximum of 0.032 mg/kg (mean 0.014 mg/kg). S-methyl-DME residues reached a plateau after 1 day of dosing. S-methyl-DME residues were all <LOQ in the milk products, apart from pasteurized whole milk (0.014 mg/kg).

No residues of DME above the LOQ (0.0125 mg/kg for milk and milk products) were found in milk, skim milk, cream, pasteurized whole milk and acid whey from the control group and the low-dose group. DME residues reached a plateau after 1 day of dosing in whole milk samples (middle- and high–dose groups). The maximum values were 0.033 mg/kg (mean 0.018 mg/kg) for the middle-dose group and 0.081 mg/kg (mean 0.062 mg/kg) for the high-dose group. For the high-dose group, DME residues in skim milk, cream, pasteurized whole milk and acid whey were 0.026, 0.11, 0.061 and 0.027 mg/kg, respectively.

Depuration cows did not show any measurable residue in their milk from day 1 after cessation of treatment apart from one cow from the highest dose group showing 0.013 mg/kg DME at day 1 of retrieval.

Table 105 Residues in cow tissues (mg clethodim eq/kg)

	Study Day	Control	0.53/10 ppm (1×)		1.7/32 ppm (3×)		5.7/107 ppm (10×)	
		Individual	Individual	Mean	Individual	Mean	Individual	Mean
Liver								
DME	28	<LOQ	0.054, 0.052, 0.059	0.055	0.070, 0.119, 0.090	0.093	0.222, 0.445, 0.286	0.32
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
S-methyl DME	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	0.058, 0.087, <LOQ	0.065
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
DME-OH	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
Kidney								
DME	28	<LOQ	0.051, <LOQ, <LOQ	0.050	0.134. 0.148, 0.170	0.15	0.408, 0.538, 0.244	0.40
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
S-methyl DME	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	0.056, 0.078, <LOQ	0.061
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
DME-OH	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
Muscle								
DME	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, 0.070, <LOQ	0.057
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
S-methyl DME	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
DME-OH	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
Fat								
DME	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, 0.052	0.051	0.102, 0.153, 0.089	0.11
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	

	Study Day	Control	0.53/10 ppm (1×)		1.7/32 ppm (3×)		5.7/107 ppm (10×)	
		Individual	Individual	Mean	Individual	Mean	Individual	Mean
S-methyl DME	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	
DME-OH	28	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ	<LOQ		<LOQ		<LOQ	

(D) Depuration phase

LOQ = 0.050 mg/kg

No DME-OH residues above the LOQ (0.05 mg/kg for tissues) were found in any of the following samples from all dose groups: liver, kidney, muscle and fat.

The cows receiving the lowest dose showed up to 0.051 mg/kg (individual cow) of DME in kidney (mean 0.05 mg/kg), 0.059 mg/kg in liver (mean 0.055 mg/kg) and < 0.05 mg/kg in muscle and fat (subcutaneous and peritoneal). DME residues found in the middle dose group were maximum 0.17 mg/kg in kidney (mean 0.15 mg/kg), 0.12 mg/kg in liver (mean 0.093 mg/kg), 0.052 mg/kg in fat (mean 0.051 mg/kg) and ≤0.05 mg/kg in muscle samples. DME residues found in the high dose group were a maximum of 0.54 mg/kg in kidney (mean 0.40 mg/kg), 0.45 mg/kg in liver (mean 0.32 mg/kg), 0.070 mg/kg in muscle (mean 0.057 mg/kg) and 0.15 mg/kg in fat (mean 0.10 mg/kg). Hence, DME residues measured in kidney and liver samples were roughly proportional with the dose rate.

No S-methyl-DME residues were found in any of the tissue samples from the low-dose group, middle-dose group and all the depuration cows. S-methyl-DME residues of the high-dose group were maximum 0.078 mg/kg in kidney (mean 0.061 mg/kg), 0.087 mg/kg in liver (mean 0.065 mg/kg) and < 0.05 mg/kg in muscle and fat samples.

Laying hen

Three groups of twenty-six-month old White Leghorn chickens (Gallus gallus) were administered gelatin capsules containing 5% clethodim and 95% clethodim sulfoxide in corn oil once a day for 28 consecutive days (Fletcher and Pedersen, 1988: 88 EM 9).

The dose levels were equivalent to 0.74, 1.9 and 5.5 ppm in the feed as received for clethodim and 11, 34 and 108 ppm in the feed as received for clethodim sulfoxide (expressed as clethodim). A control group (20 animals), administered capsules containing corn oil, was included. Ten laying hens per treatment group were left untreated for a further 2 days after the 28-day dosing period. Clethodim/clethodim sulfoxide dosing capsules were prepared daily from weekly prepared stocks (clethodim in acetone and clethodim sulfoxide in corn oil), which were analysed on day 1 and day 7 after preparation (average concentrations in stock of clethodim/clethodim sulfoxide 91/104% of nominal, range 66-109% / 81-129%). Eggs were collected daily. Egg contents, pooled from 10 birds within each treatment group, were homogenized and frozen immediately until analysis within 68 days.

On day 29, ten randomly chosen animals out of each group and ten control animals were slaughtered. On day 31 the remaining animals in each group were slaughtered. Two composite samples of liver and gizzard (entire organs) per dosage group and three composite samples of muscle (at least 100 g of thigh and breast muscle) and fat (at least 30 g of subcutaneous and abdominal fat) per dosage group were removed and immediately frozen (≤ 56 days) for later analysis.

Samples were analysed in duplicate according to the common moiety method Chevron method RM-26A with minor modifications. Clethodim and clethodim-like metabolites containing the 5-(2-ethylthiopropyl) cyclohexene-3-one moiety are converted to DME, 5-OH clethodim and 5-OH clethodim like metabolites containing the 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moiety are converted to DME-OH and S-methyl-clethodim and S-methyl like metabolites are converted to S-methyl-DME. The residues are expressed as clethodim equivalents. The LOD was 0.05 mg/kg for eggs and for animal tissues. Freshly fortified egg (2 × LOD and 10 × LOD) and tissue samples (2 ×

LOD) were included within the analytical series and gave recoveries between 70 and 110% for muscle, incidentally below 70% or above 110% for gizzard and liver samples and below 70% in approximately 50% of the recoveries obtained for egg and fat samples. The validated LOQ was 0.1 mg/kg for eggs and tissues.

The laying hens remained in good health during the study. No treatment-related effects on bodyweight, behavioural reactions or systemic signs of toxicity, egg production and quality, or feed intake during and after the dosing period were observed. At post-mortem, no treatment-related abnormalities were observed in the respiratory, alimentary and reproductive systems of the laying hens.

Table 106 Residues in hen eggs (mg clethodim eq/kg)

Study Day	Control			0.74/11 ppm (1×)			1.9/34 ppm (3×)			5.5/108 ppm (10×)		
	DME	S-methyl DME	DME -OH	DME	S-methyl DME	DME -OH	DME	S-methyl DME	DME -OH	DME	S-methyl DME	DME -OH
-1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.21	<LOQ	<LOQ
2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.21	<LOQ	<LOQ
4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.19	<LOQ	<LOQ
7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.15	<LOQ	<LOQ
14	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.17	<LOQ	<LOQ
21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.14	<LOQ	<LOQ
28	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.24	<LOQ	<LOQ
1 (D) 2 (D)	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ	<LOQ <LOQ

LOQ = 0.1 mg/kg

Table 107 Residues in hen tissues (mg clethodim eq/kg)

	Study Day	Control		0.74/11 ppm (1×)		1.9/34 ppm (3×)		5.5/108 ppm (10×)	
		Individual	Mean	Individual	Mean	Individual	Mean	Individual	Mean
Liver									
DME	29	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
S-methyl DME	29	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
DME-OH	29	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
Gizzard									
DME	29	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
S-methyl DME	29	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
DME-OH	29	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ	<LOQ, <LOQ	<LOQ
Muscle									

	Study Day	Control		0.74/11 ppm (1×)		1.9/34 ppm (3×)		5.5/108 ppm (10×)	
		Individual	Mean	Individual	Mean	Individual	Mean	Individual	Mean
DME	29	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
S-methyl DME	29	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
DME-OH	29	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
Fat									
DME	29	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
S-methyl DME	29	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
DME-OH	29	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ
	2(D)	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ	<LOQ, <LOQ, <LOQ	<LOQ

(D) Depuration phase

LOQ = 0.1 mg/kg

No residues measured as DME-OH and S-methyl-DME above the LOQ (0.1 mg eq/kg) were found in any of the egg and tissue samples (liver, gizzard, muscle and fat) from all dose groups. No residues measured as DME above the LOQ (0.1 mg eq/kg) were found in any of the egg and tissue samples of the control and the low- and middle-dose groups. Samples (egg) from the high-dose group contained a maximum of 0.24 mg eq/kg DME (mean 0.19 mg eq/kg). Residues measured as DME in eggs reached a plateau after one day of dosing. DME was not found above the LOQ (0.1 mg/kg) in tissue samples.

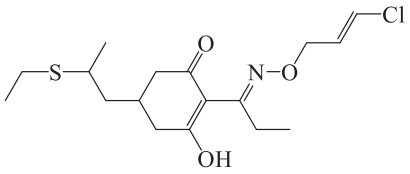
APPRAISAL

Clethodim is a fatty acid synthesis inhibitor herbicide, which interacts with acetyl CoA carboxylase. It stops new cell growth leading to the gradual death of the plant.

Clethodim

Clethodim was first evaluated for toxicology and residues by the JMPR in 1994. Clethodim was scheduled at the Fiftieth Session of the CCPR for periodic evaluation by the 2019 JMPR. The Meeting received information on identity, physical and chemical properties, animal and plant metabolism, rotational crop study, environmental fate, analytical methods, GAP information, storage stability, processing, supervised residue trials and farm animal feeding study.

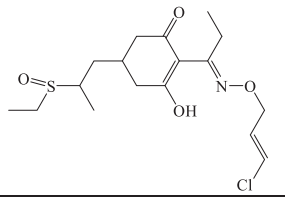
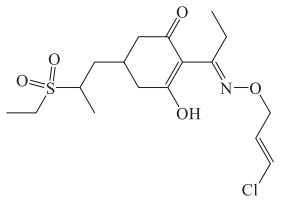
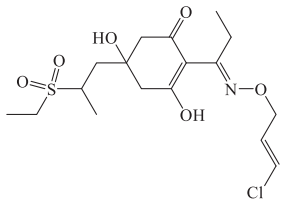
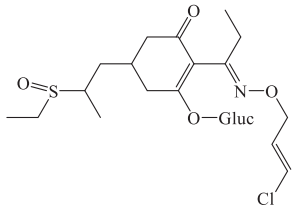
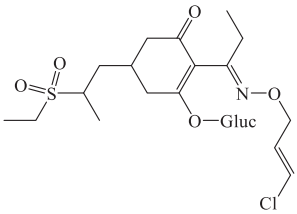
The IUPAC name for clethodim is (5RS)-2-{(1EZ)-1-[(2E)-3-chloroallyloxyimino]propyl}-5-[(2RS)-2-(ethylthio)propyl]-3-hydroxycyclohex-2-en-1-one.

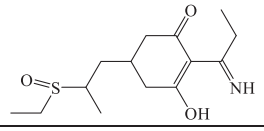
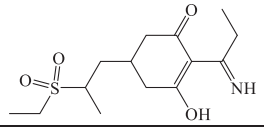
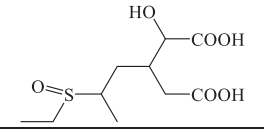
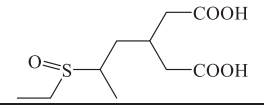
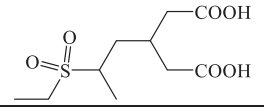
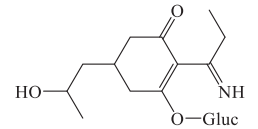
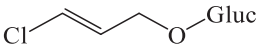
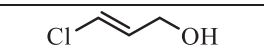
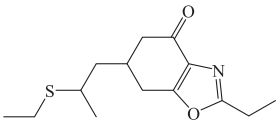
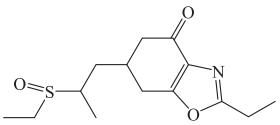
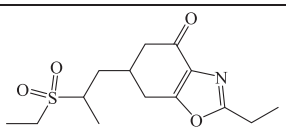
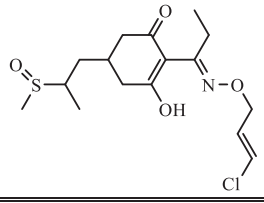


The following abbreviations are used for the major metabolites discussed below:

Metabolites converted to DME (3-[2-(ethylsulfonyl)propyl]-pentanedioic acid, dimethyl ester) or DME-OH (3-[2-(ethylsulfonyl)propyl]-3-hydroxy-pentanedioic acid, dimethyl ester) moieties by common moiety analytical methods are indicated in brackets.

Table 108 Metabolites referred to in this appraisal

Code	Name and Matrix	Structure
Clethodim sulfoxide (DME moiety)	2-((E)-1-((((E)-3-chloroallyl)oxy) imino)propyl)-5-(2-(ethylsulfinyl) propyl)-3-hydroxycyclohex-2-en-1-one Spinach, Soya bean (seeds), Carrot (roots & leaves), Cotton (seeds), Soil, Goat, Hen	
Clethodim sulfone (DME moiety)	2-((E)-1-((((E)-3-chloroallyl)oxy) imino)propyl)-5-(2-(ethylsulfonyl) propyl)-3-hydroxycyclohex-2-en-1-one Spinach, Carrot (outdoor: roots & leaves), Soil, Goat, Hen	
5-hydroxy sulfone (DME-OH moiety)	2-((E)-1-((((E)-3-chloroallyl)oxy) imino)propyl)-5-(2-(ethylsulfonyl) propyl)-3,5-dihydroxycyclohex-2- en-1-one Soya bean (seeds), Carrot (roots)	
Clethodim sulfoxide glucoside (DME moiety)	Conjugates of clethodim sulfoxide Soya bean (seeds & leaves), Carrot (outdoor: leaves) Cotton (leaves)	
Clethodim sulfone glucoside (DME moiety)	Conjugates of clethodim sulfone Soya bean (leaves)	

Code	Name and Matrix	Structure
Clethodim imine sulfoxide (DME moiety)	5-(2-(ethylsulfinyl)propyl)-3- hydroxy-2-(1-iminopropyl) cyclohex-2-en-1-one Soya bean (leaves), Carrot (leaves), Cotton (leaves), Goat	
Clethodim imine sulfone (DME moiety)	5-(2-(ethylsulfonyl)propyl)-3-hydroxy-2-(1-iminopropyl) cyclohex-2-en-1-one Spinach	
M15R	Hydroxy 3-[(2-Ethylsulfinyl) propyl]-pentanedioic acid Spinach, Carrot (outdoor: roots)	
M17R (DME moiety)	3-[(2-Ethylsulfinyl) propyl]- pentanedioic acid Spinach, Carrot (outdoor: leaves & roots)	
M18R (DME moiety)	3-[(2-Ethylsulfonyl) propyl]- pentanedioic acid Spinach, Carrot (outdoor: leaves & roots)	
M19R	3-hydroxy-5-(2-hydroxypropyl)-2- (1-iminopropyl)cyclohex-2-en-1- one glucose conjugate Carrot (outdoor: leaves)	
M15A	3-Chloroallyl alcohol glucoside Spinach	
Chloroallyl alcohol	3-Chloroallyl alcohol Water (hydrolysis)	
Clethodim oxazole (DME moiety)	2-ethyl-6-(2-(ethylthio)propyl)-6,7-dihydrobenzo[*d*]oxazol-4(*5H*)-one High temperature hydrolysis	
Clethodim oxazole sulfoxide (DME moiety)	2-ethyl-6-(2-(ethylsulfinyl)propyl)-6,7-dihydrobenzo[*d*]oxazol-4(*5H*)- one Soil	
Clethodim oxazole sulfone (DME moiety)	2-ethyl-6-(2-(ethylsulfonyl)propyl)-6,7-dihydrobenzo[*d*]oxazol-4(*5H*)- one Soil	
S-methyl sulfoxide	2-((*E*)-1-((((*E*)-3-chloroallyl)oxy) imino)propyl)-3-hydroxy-5-(2- (methylsulfinyl)propyl)cyclohex-2-en-1-one Goat	

PHYSICAL AND CHEMICAL PROPERTIES

Clethodim has a higher solubility in organic solvents in comparison to water and is not volatile. Clethodim was shown to be hydrolytically stable at neutral and basic conditions but photolytically unstable (DT_{50} of < 10 days).

Plant metabolism

The Meeting received plant metabolism studies for clethodim after foliar application to spinach, soya bean, carrot and cotton with clethodim labelled at [Ring-4,6-^{14}C] and [Allyl-2-^{14}C].

Spinach

Outdoor grown spinach received a single foliar application of [^{14}C]-clethodim at a rate of 0.50 kg ai/ha. Treated spinach foliage was harvested 14 days after treatment (DAT) (immature) and 28 DAT (mature). The TRRs in the treated foliage measured by the extraction procedure were 3.4–6.9 mg eq/kg. The residues in immature leaves were greater than residues in the mature leaves. Total extractability was ≥ 81% TRR in immature and mature leaves extracted with acetonitrile/water, acetonitrile and acetonitrile/0.2 N HCl.

Parent clethodim was not detected in either immature or mature foliage. Ring opened metabolites made up the majority of the residues in both immature and mature leaves: M17R (33–35% TRR, 1.2–2.3 mg eq/kg), M15A (21–23% TRR, 0.79–1.1 mg eq/kg), M15R (13–14% TRR, 0.48–0.88 mg eq/kg) and M18R (9.7–13% TRR, 0.42–0.66 mg eq/kg). Clethodim imine sulfoxide was the major ring-intact metabolite in immature spinach leaves (14% TRR, 0.98 mg eq/kg); it was not detected in mature leaves. Clethodim imine sulfone was the major ring-intact metabolite in mature leaves (7.5% TRR, 0.25 mg eq/kg). Clethodim sulfoxide (free: 2.8–6.8% TRR, 0.12–0.35 mg eq/kg) and clethodim sulfone (free: 0.3–0.6% TRR, 0.01–0.03 mg eq/kg) were present in both immature and mature foliage. A multi-component fraction, M3/4A, was also present at 18–21% TRR (0.73–0.90 mg eq/kg) with no individual component greater than 3.6% TRR (0.018 mg eq/kg).

Soya bean

Greenhouse grown soya bean received two foliar applications of [^{14}C]-clethodim of 0.28 kg ai/ha with a 14-day retreatment interval (RTI). The first treatment was applied when the soya bean plants were at the 6–8 leaf stage. The soya bean plants were grown to maturity and harvested at 30 days after the last application (DALA). The TRRs in soya bean were 18–28 mg eq/kg for leaves, 1.6–1.8 mg eq/kg for pods and 3.9–4.3 mg eq/kg for seeds. Total extractability was ≥ 70% TRR in all commodities extracted with hexane, acetone, methanol, methanol/water and methanol/0.2 N HCl.

Parent clethodim was not detected in any of the plant parts. Major metabolites in seeds were clethodim sulfoxide (free: 32% TRR, 1.2–1.3 mg eq/kg; conjugated: 8.5–12% TRR, 0.33–0.49 mg eq/kg) and 5-OH sulfone (10–11% TRR, 0.41–0.43 mg eq/kg), and in leaves were clethodim imine sulfoxide (14% TRR, 3.9 mg eq/kg), conjugates of clethodim sulfoxide (25–27% TRR, 4.7–6.9 mg eq/kg) and conjugates of clethodim sulfone (2.0–12% TRR, 0.56–2.2 mg eq/kg).

Carrot

Greenhouse grown carrots received two foliar applications of [^{14}C]-clethodim at 0.28 kg ai/ha with a 14 day. The treated carrots were harvested at 20 DALA. The TRRs in carrot were 9.2–22 mg eq/kg for leaves and 0.40–0.62 mg eq/kg for carrot roots. Total extractability was ≥ 88% TRR in leaves and roots extracted with acetone, methanol, methanol/water and methanol/0.2 N HCl.

Parent clethodim was only detected in the roots (0.8–1.1% TRR, 0.003–0.007 mg eq/kg). Major metabolites were clethodim sulfoxide (29–34% TRR, 0.11–0.21 mg eq/kg) and 5-OH sulfone (10% TRR, 0.063 mg eq/kg) in roots, and clethodim sulfoxide (11–16% TRR, 0.97–3.5 mg eq/kg) and clethodim imine sulfoxide (22% TRR, 4.9 mg eq/kg) in leaves.

Field grown carrots received a dingle foliar application of [^{14}C]-clethodim at a rate of 0.60 kg ai/ha. Carrot roots and foliage were harvested 21 DAT (immature) and 56 DAT (mature). The TRRs in immature carrots were 3.9–5.7 mg eq/kg for leaves and 0.74–0.82 mg eq/kg for roots. The TRRs in mature carrots were 0.75–0.84 mg eq/kg for leaves and 0.13–0.16 mg eq/kg for roots. Total extractability was ≥ 80% TRR in leaves and roots extracted with acetonitrile/water, acetonitrile and acetonitrile/0.2 N HCl.

Parent clethodim was detected at very low concentrations in immature leaves (0.004–0.005 mg eq/kg) but was not detected in mature leaves. Clethodim sulfoxide (free: 11–22% TRR, 0.095–0.16 mg eq/kg; glucoside: 9.3–15% TRR, 0.078–0.11 mg eq/kg) was the major residue in mature leaves. Metabolites M17R (8.9% TRR, 0.075 mg eq/kg), M18R (8.1% TRR, 0.068 mg eq/kg) and M19R (14% TRR, 0.12 mg eq/kg) were significant in mature leaves. A multi-component fraction, M3A (11–15% TRR, 0.020–0.081 mg eq/kg), was also detected as the major residue in immature and mature leaves with no individual component being greater than 2.4% TRR (0.018 mg eq/kg).

Parent clethodim was not detected in mature roots. Clethodim sulfoxide (18–24% TRR, 0.029–0.032 mg eq/kg), M17R (14% TRR, 0.022 mg eq/kg), M18R (13% TRR, 0.020 mg eq/kg) and M15R (12% TRR, 0.019 mg eq/kg) were present at >10% TRR in mature roots.

The cyclohexene ring opened metabolites, M15R, M17R and M18R observed in the outdoor study were not observed in the study performed in a greenhouse.

Cotton

Greenhouse grown cotton plants received two foliar applications of [^{14}C]-clethodim at 0.28 kg ai/ha with a 14 day RTI. The first treatment was applied when the cotton plants were at the 8–12 leaf stage. Cotton plants were grown to maturity and harvested at 70 DALA. The TRRs in cotton were 6.7–14 mg eq/kg for leaves, 0.47–1.4 mg eq/kg for shell and 0.068–0.22 mg eq/kg for seeds. Total extractability was ≥87% TRR in leaves with acetone, methanol and methanol/water. Total extractability was 39–54% TRR in seeds extracted with hexane, acetone, methanol and methanol/water.

Parent clethodim was not detected in any of the plant parts. The metabolites ≥ 10% TRR in cotton leaves were conjugates of clethodim sulfoxide (10% TRR, 0.67 mg eq/kg) and clethodim imine sulfoxide (18% TRR, 2.4 mg eq/kg). Identified residues in cotton seed were ≤ 0.007 mg eq/kg, with the most abundant residue being clethodim sulfoxide (3.1% TRR).

Conclusions

Parent clethodim is rapidly metabolised in plant commodities. The one major metabolic pathway in plants is sulfoxidation to clethodim sulfoxide followed by further oxidation to clethodim sulfone. Clethodim sulfoxide and clethodim sulfone conjugates were also identified as major or minor metabolites in all crops. Another pathway is elimination of the chloroallyl moiety, leading to the formation of clethodim imine and 3-chlorolally metabolites, including 3-chloroalcohol glucoside (M15A).

The studies in carrots and spinach were performed in outdoor conditions and suggest that the clethodim ring can be opened by a photolytic reaction (also from imine metabolites) to form pentanedioic acids. Metabolites M15R, M17R and M18R belong to the pentanedioic acids.

Environmental fate

The Meeting received aqueous hydrolysis, soil photolysis, aerobic soil metabolism and soil degradation studies for clethodim.

In the aqueous hydrolysis study, clethodim was hydrolytically stable at pH 7 and 9 but degraded at pH 5 with a DT_{50} of 28–54 days at 25 °C. The major hydrolysis products were clethodim oxazole (51% applied residue (AR) after 32 days) and chloroallyl alcohol (31% AR after 30 days). Hydrolysis is unlikely to be a major route of environmental degradation.

In the soil photolysis studies, clethodim was rapidly degraded in irradiated soils (DT_{50} of 0.15–1.8 days) and in non-irradiated soils (DT_{50} of 1.9–3.6 days). Clethodim sulfoxide was the major degradation product on soil and was rapidly photodegraded in the irradiated soils. The major dissipation route of clethodim sulfoxide was degradation to trans-3-chloro-acrylic acid, 2-[3-chloroallyloxyimino] butanoic acid (CBA), formation of bound residues and CO_2. Clethodim is susceptible to photolytic degradation.

In the aerobic soil metabolism studies, clethodim was rapidly degraded in a variety of soils with a DT_{50} of < 2.5 days at 25 °C. Clethodim sulfoxide was the most significant metabolite and other significant soil metabolites were clethodim sulfone, clethodim oxazole sulfoxide and clethodim oxazole sulfone.

The DT_{50}s of clethodim sulfoxide and clethodim sulfone were 1.6–2.5 days and 3.8–10 days, respectively.

The DT_{50} of clethodim oxazole sulfone was 20–68 days. The photolysis product CBA was degraded with a DT_{50} of 5.5 days.

Clethodim was rapidly degraded in the environmental fate studies, and the breakdown products also rapidly degraded to form bound residues and CO_2. Clethodim is not persistent in soil.

Rotational crop metabolism

The Meeting received a confined rotational crop study with ^{14}C-labeled clethodim.

Rotational crops (lettuce, carrots and wheat) were planted in sandy loam soil that had been treated at 1.1 kg ai/ha with [^{14}C]-clethodim and then aged for 30, 120 and 365 days in a greenhouse.

In carrot leaf, lettuce leaf (30 days), and wheat straw and hulls, the radioactive residues were found at > 0.05 mg eq/kg (0.053–0.65 mg eq/kg).

Parent clethodim was not detected in any of the analysed extracts. Small amounts of clethodim imine sulfoxide (2.4–19% TRR, 0.006–0.040 mg eq/kg), clethodim oxazole sulfoxide (< 0.1–3.9 TRR, < 0.001–0.017 mg eq/kg) and clethodim oxazole sulfone (< 0.1–8.0% TRR, < 0.001–0.029 mg eq/kg) were detected.

The results show that the metabolism of clethodim in rotated crops was similar for all crop types. The metabolites in rotational crops, clethodim oxazole sulfoxide and clethodim oxazole sulfone were soil metabolites of clethodim. Their occurrence in rotational crops is due to the uptake by plant roots.

Residues related to clethodim are not expected to be significant in rotational crops as the treated rate in the study was 2 × GAP rate.

Animal metabolism

The Meeting received animal metabolism studies on rats, lactating goats and laying hens where animals were dosed with [^{14}C]-clethodim. The metabolism and distribution of clethodim in farm animals were investigated using the [Propyl-1-^{14}C]-clethodim for lactating goats and the [Ring-4,6-^{14}C]-clethodim for laying hens.

Rats

The metabolism of clethodim in rats was reviewed within the framework of the toxicological evaluation by the WHO Core Assessment Group of the 2019 JMPR.

Lactating goats

Lactating goats received daily oral dosing of [^{14}C]-clethodim at 1.2 mg/kg bw/day (equivalent to 24 ppm in the diet) for 4 consecutive days. The goats were sacrificed 4 hours after the last dose. Most of the total administered dose was found in the urine (56%) and faeces (34%).

Total radioactive residues (TRR) were highest in the liver (0.41 mg eq/kg) and kidney (0.38 mg eq/kg), followed by muscle (forequarter: 0.033 mg eq/kg, hindquarter: 0.034 mg eq/kg) and fat (subcutaneous: 0.079 mg eq/kg, peritoneal: 0.047 mg eq/kg). The concentration of radioactivity in the milk reached a plateau of about 0.035 mg eq/L by day 2.

The majority of the radioactive residues in liver (77% TRR), kidney (91% TRR), muscle (90–93% TRR) and subcutaneous fat (95% TRR) were extracted into organic solvents (acetone and

methanol/water). Most of the milk radioactivity was not extracted by organic solvents and remained in the post-extraction solids (PES)(30–66% TRR).

Clethodim was found in liver (28% TRR, 0.11 mg/kg), kidney (1.3% TRR, 0.005 mg/kg), fat (2.8% TRR, 0.002 mg/kg) and milk on Day 4 (3.3% TRR, 0.001 mg/kg). No clethodim was found in muscle.

Clethodim sulfoxide was major metabolite in milk (15–29% TRR, 0.005–0.013 mg eq/kg) and tissues (33–52% TRR, 0.014–0.14 mg eq/kg).

S-methyl clethodim sulfoxide was also a major metabolite in kidney, muscle and fat (29–32% TRR, 0.009–0.12 mg eq/kg).

Significant residues of the radioactivity in milk were incorporated into natural products; [^{14}C]-lactose was identified in milk (30–54% TRR, 0.014–0.017 mg eq/kg).

Other identified metabolites in milk and tissues, clethodim sulfone, clethodim imine sulfoxide and 5-OH clethodim sulfone were observed at levels below 5% TRR (< 0.016 mg eq/kg).

Laying hens

Laying hens received daily oral doses of [^{14}C]-clethodim for 5 consecutive days at a rate equivalent to 27 ppm in the diet as received (2.1 mg/kg bw per day). Another group of hens were treated identically, but received a higher dose (equivalent to 707 ppm in the diet as received, 51.3 mg/kg bw per day) to facilitate identification of unknown metabolites. The hens were sacrificed 4 hours after the last dose. After administration, 78–85% of the total dose was recovered in excreta.

In the 27 ppm dose group, radioactive residues in tissues were highest in kidney (1.2 mg eq/kg) and liver (0.7 mg eq/kg). Residue levels in skin, fat, thigh muscle and breast muscle were all within the range of 0.1–0.3 mg eq/kg. Residue levels in eggs were ≤ 0.22 mg eq/kg (maximum at day 4 in egg white). Radioactivity levels in egg yolk and egg white did not reach a plateau within the 4-day study period.

Liver, kidney, thigh and breast muscles were extracted with methanol and methanol/water. Skin, fat and egg yolks were extracted with acetone and methanol/water. Good extractability was achieved for all samples (≥ 84% TRR).

In kidney, liver, skin, breast and thigh muscle, major identified metabolites were clethodim sulfoxide (30–57% TRR) and clethodim sulfone (16–34% TRR). Clethodim was also detected (0.5–7.5% TRR). In fat, major components were clethodim (65% TRR), clethodim sulfoxide (15–41% TRR) and clethodim sulfone (10–16% TRR). No other metabolites were identified.

Conclusions

The metabolic pathway of clethodim in rat is consistent with that in ruminants (goat) where clethodim, clethodim sulfoxide, clethodim sulfone and at lower levels 5-hydroxy sulfoxide, 5-hydroxy sulfone, imine sulfoxide, S-methyl clethodim and S-methyl sulfoxide were identified. In hen, the metabolic pathway was simpler than that observed in rat and goat. None of the imine analogues, 5-hydroxy analogues or S-methyl analogues identified in rat and goat were found in hens.

Methods of analysis

The Meeting received information on analytical methods for clethodim and its metabolites in plant and animal matrices. There are two types of methods of plant matrices, one is a common moiety method and the other is a specific individual method.

In the common moiety methods of plant and animal matrices, samples were extracted with methanol/water. All compounds containing the 5-(2-ethylthiopropyl) cyclohexene-3-one moiety were converted into DME and all compounds containing the 5-(2-ethylthiopropyl)-5-hydroxy cyclo-hexene-3-one moiety were converted into DME-OH by alkaline precipitation, oxidation and methylation. The residues can be measured by GC-FPD. Representative compounds that are

converted into DME (clethodim or clethodim sulfoxide) and DME-OH (5-OH clethodim sulfoxide) are used as reference materials for fortification and method validation. The methods of analysis were validated with an LOQ of 0.095 mg/kg expressed as clethodim equivalents for DME and 0.088 mg/kg expressed as clethodim equivalents for DME-OH.

In the specific individual methods of plant matrices, samples were extracted with methanol/water, and then clethodim, clethodim sulfoxide, clethodim sulfone, M17R and M18R (free form of all analytes) can be measured by LC-MS/MS with an LOQ of 0.005 mg/kg for each analyte.

The Meeting concluded that the presented methods were sufficiently validated and are suitable to measure clethodim and its metabolites in plant (common-moiety and individual analyte methods) and animal (common-moiety method only) commodities.

Stability of pesticide residues in stored analytical samples

The Meeting received information on storage stability of clethodim and its metabolites in raw/processed plant and animal commodities.

Storage stability studies using the specific individual analytical method showed that clethodim was stable for at least 6 months at -18 °C in crop commodities representative of the high protein (dry pea) and high oil (oilseed rape) commodity groups, but it was degraded within 30 days in the high water (alfalfa) and high starch (potato) commodity groups.

Storage stability studies using the specific individual analytical method showed that clethodim sulfoxide was stable for at least 6 months at ≤-18 °C in crop commodities representative of the high water (alfalfa), high acid (grape), high starch (potato), high protein (dry pea) and high oil (oilseed rape) commodity groups.

Storage stability studies using the specific individual analytical method showed that clethodim sulfone was stable at <-18 °C for at least 6 months in crop commodities representative of the high acid (grape), high starch (potato), high protein (dry pea) and high oil (oilseed rape) commodity groups, and stable at least 3 months in the high water (alfalfa) commodity group.

Storage stability studies using the specific individual analytical method showed that M17R and M18R were stable for at least 9 months at ≤-18 °C in crop commodities representative of the high acid (grape), high starch (potato), high protein (dry pea) and high oil (oilseed rape) commodity groups.

Storage stability studies fortified with 5-OH clethodim sulfone showed that residues analysed as DME-OH were stable for at least 5 months at -12 to -22 °C in crop commodities representative of the high water (peach, plum, lettuce, sugar beet leaves), high acid (blueberry, cranberry), high starch (carrot roots, sugar beet roots) and high protein (dry pea) commodity groups and hops.

Storage stability studies in animal commodities fortified with clethodim, 5-OH clethodim sulfone and S-methyl clethodim sulfoxide showed that residues analysed as DME, DME-OH and S-methyl DME were stable for at least 5 months at -20 °C in milk and bovine tissues (liver, kidney, muscle and fat), and for at least 1 month at -18 °C in chicken eggs and tissues (liver, muscle and fat).

The Meeting noted that clethodim was unstable in high water and high starch commodity groups during freezer storage. However, the residues analysed as DME by the common moiety analytical methods were stable for at least 5 months in raw/processed plant and animal commodities including the high water and high starch commodities. The Meeting agreed that the demonstrated storage stability on various representative plant and animal commodities using the common moiety analytical methods covered the residue sample storage intervals used in the field trials considered by the current Meeting.

Definition of the residue

Plant commodities

In plant metabolism studies on clethodim in root crops (carrot), leafy crops (spinach) and pulses/oilseeds (soya bean/ cotton), clethodim was extensively metabolized and not detected or occurred in low amounts in mature crops at levels up to 1.1% TRR.

Clethodim sulfoxide (2.8–34% TRR) and clethodim sulfone (0.3–9.9% TRR) were found in all primary crop commodities. Conjugates of clethodim sulfoxide (2.7–27% TRR) and conjugates of clethodim sulfone (0.5–12% TRR) were also identified as metabolites in soya bean (leaves and seeds), carrot (leaves and roots) and cotton (leaves).

5-OH clethodim sulfone was identified in soya bean seeds (10–11% TRR) and carrot roots (7.6–10% TRR). Clethodim imine sulfoxide was found in leaves of immature spinach (14% TRR), soya bean (14% TRR), carrot (13–22% TRR) and cotton (18% TRR). Clethodim imine sulfoxide (2.4–19% TRR) was also determined in rotational crops (carrot, lettuce and wheat). Clethodim imine sulfoxide levels increased with exposure to sunlight.

The ring opened metabolites M15R (7.7–14% TRR), M17R (8.9–35% TRR) and M18R (7.3–13% TRR) belong to the pentanedioic acids and were identified as major metabolites in spinach and carrot grown outdoors. 3-Chloroallyl alcohol glucoside (M15A) was also a major metabolite found in spinach (21–23% TRR).

In rotational crops, the metabolites in soil, clethodim oxazole sulfoxide (< 0.1–3.9% TRR) and clethodim oxazole sulfone (< 0.1–8.0% TRR), were also detected.

In the high temperature hydrolysis study for processed commodities, the major metabolite of plant commodities, clethodim sulfoxide, degraded to clethodim oxazole sulfoxide (pH4: 89% AR, pH5: 94% AR, pH6: 98% AR). This metabolite was not observed in plant metabolism studies.

In a storage stability study conducted in alfalfa and potato tubers, clethodim was decomposed to compounds other than clethodim sulfoxide and clethodim sulfone during freezer storage. Therefore, the sum of clethodim, clethodim sulfoxide and clethodim sulfone would not be appropriate as a marker for monitoring.

Common moiety analytical methods that determined the common moiety DME and DME-OH are available. Parent clethodim, clethodim sulfoxide, clethodim sulfone, clethodim imine sulfoxide, clethodim oxazole sulfoxide, clethodim oxazole sulfone, M17R and M18R (including the free and conjugated forms) are converted into the DME. 5-OH clethodim sulfone and M15R (including the free and conjugated forms) are converted into the DME-OH.

The Meeting noted that the common moiety methods are not specific to monitor clethodim and residues may arise from sethoxydim, no other suitable marker compound and analytical method were available.

The Meeting decided to define the residue for compliance with the MRL for plant commodities as sum of clethodim and its metabolites convertible to dimethyl 3-[2-(ethylsulfonyl)propyl]-pentanedioate (DME) and dimethyl 3-[2-(ethylsulfonyl)propyl]-3-hydroxy-pentanedioate (DME-OH), expressed as clethodim.

In deciding which compounds should be included in the residue definition for dietary risk assessment, the Meeting considered the likely occurrence of the compounds and the toxicological properties of the candidates clethodim sulfone, clethodim oxazole sulfoxide, M19R, M15A and 3-chloroallyl alcohol.

The Meeting concluded that the TTC approach for genotoxicity could be applied for clethodim sulfone, M19R and M15A and the TTC approach using Cramer Class III could be applied for clethodim oxazole sulfoxide.

Clethodim sulfone is measured as DME by the common moiety analytical method but the individual residue cannot be determined. Therefore, the field trial data analysed with a specific analytical method were used for the estimation of exposure. The chronic dietary exposure was estimated based on uses on head cabbage, dry peas, carrot and artichoke because the residue data for clethodim sulfone itself were available.

The Meeting noted that the estimated chronic dietary exposure to clethodim sulfone (0.028 µg/kg bw per day) exceeds the threshold of toxicological concern for genotoxicity (0.0025 µg/kg bw per day).

3-Chloroallyl alcohol was the major hydrolysis product (31% AR after 30 days) and is the free form of M15A (glucose conjugate). M15A was the major residue in spinach (21–23% TRR, 0.79–1.1 mg eq/kg) and M19R was the major residue in carrot mature leaves (14% TRR, 0.12 mg eq/kg) at a 2 × GAP rate of 0.50 kg ai/ha. Those three metabolites cannot be measured by the common moiety analytical method. The Meeting noted that M15A and M19R were not observed in the rat metabolism study and no information is available on their toxicity.

M19R and M15A are expected to occur in leaves with exposure to sunlight. Therefore, the chronic dietary exposure was estimated based on uses on leafy greens and head cabbage. The maximum residues of M19R and M15A in the plant metabolism studies, with adjustment to the GAP rate (50% the rate used in the metabolism studies), were used to estimate the chronic dietary exposure. It was noted that 3-chloroallyl alcohol (free form of M15A) was only detected in the hydrolysis study. Estimated exposures were:

M19R: 0.091 µg/kg bw per day

M15A: 0.84 µg/kg bw per day

The Meeting noted that the estimated exposures to M19R and M15A exceeded the threshold of toxicological concern for genotoxicity (0.0025 µg/kg bw per day).

Clethodim oxazole sulfoxide is generated from clethodim sulfoxide during high temperature processing of plant commodities. This compound can be measured by a common moiety analytical method but individual residues of the compound cannot be determined. The Meeting could not estimate the chronic dietary exposure for clethodim oxazole sulfoxide.

Because the Meeting was unable to conclude on the toxicological relevance of the metabolites clethodim sulfone, M19R, M15A and clethodim oxazole sulfoxide the Meeting could not reach a conclusion on the residue definition for dietary risk assessment.

Animal commodities

In animal metabolism studies, clethodim was rapidly metabolized and not detected or in low amounts in tissues (up to 7.5% TRR) except goat liver, hen fat and egg yolk. Clethodim was the major component of the residue in goat liver (28% TRR), hen fat (34–65% TRR) and egg yolk (15–34%TRR).

Clethodim sulfoxide and clethodim sulfone were identified in goat and hen. Clethodim sulfoxide was a major metabolite in all animal commodities (milk: 15–29% TRR, egg: 25–82% TRR, tissues: 15–57% TRR). Clethodim sulfone was a major metabolite identified in hen commodities (egg yolk: 11–29% TRR, egg white: 9.9–38% TRR, tissues: 10–34% TRR).

S-methyl clethodim sulfoxide, clethodim imine sulfoxide and 5-OH clethodim sulfone were found only in goat. S-methyl clethodim sulfoxide was identified as a major metabolite in kidney (31% TRR), muscle (29–32% TRR) and fat (29% TRR). Clethodim imine sulfoxide and 5-OH clethodim sulfone were present at < 5% TRR in milk and tissues.

In plant metabolism studies, clethodim sulfoxides and clethodim sulfones (free and conjugated) were found but no clethodim was observed. S-methyl clethodim is directly formed from parent clethodim and then oxidized to S-methyl sulfoxide. Therefore, S-methyl clethodim sulfoxide cannot be formed in the animal due to the absence of parent clethodim in feed.

In farm animal feeding studies the administered dose comprised 5% clethodim and 95% clethodim sulfoxide. No residue of 5-OH clethodim sulfone was found in any animal commodities. Therefore, residues that can be converted to the DME-OH moiety are unlikely to be found in animal commodities.

The Meeting decided to define the residue for compliance with the MRL for animal commodities as sum of clethodim and its metabolites convertible to dimethyl 3-[2-(ethylsulfonyl)propyl]-pentanedioate (DME),expressed as clethodim.

In deciding which compounds should be included in the residue definition for dietary risk assessment, the Meeting considered the likely occurrence of the compound and the toxicological properties of the candidate clethodim sulfone.

Clethodim sulfone resides cannot be identified in animal commodities since no specific analytical method is available. However, the estimated chronic dietary exposure to clethodim sulfone from plant commodities exceeds the threshold of toxicological concern for genotoxicity.

Farm animal feeding studies show that DME residues in fat are two times higher than in muscle, and, in cream, more than four times higher than in skimmed milk. The Meeting considered the residue fat-soluble.

Because the Meeting was unable to conclude on the toxicological relevance of the metabolite clethodim sulfone the Meeting could not reach a conclusion on the residue definition for dietary risk assessment.

The Meeting recommended the following residue definitions for clethodim:

Definition of the residue for compliance with the MRL for plant commodities: *Sum of clethodim and its metabolites convertible to dimethyl 3-[2-(ethylsulfonyl)propyl]-pentanedioate (DME) and dimethyl 3-[2-(ethylsulfonyl)propyl]-3-hydroxy-pentanedioate (DME-OH), expressed as clethodim*

Definition of the residue for compliance with the MRL for animal commodities: *Sum of clethodim and its metabolites convertible to dimethyl 3-[2-(ethylsulfonyl)propyl]-pentanedioate (DME), expressed as clethodim*

The Meeting considers the residue to be fat-soluble.

Definition of the residue for dietary risk assessment for plant and animal commodities: *A conclusion could not be reached*

Results of supervised residue trials on crops

Supervised trials were available for the use of clethodim on apple, pear, cherry, plum, peach, blueberry, cranberry, strawberry, onion, broccoli, cabbage, cucumber head lettuce, beans, peas, carrot, artichoke, oilseed rape and hops.

Product labels were available from Australia, European countries and the USA.

Since no residue data were provided for alfalfa fodder, beans (succulent), cotton seed, cotton seed oil, fodder beat, peanut, potato, soya bean, soya bean oil, sugar beet, sunflower seed, sunflower seed oil and tomato, the Meeting withdrew the previous recommendations for maximum residue levels for these commodities.

Total residues for estimation of maximum residue levels in plant commodities are calculated by summing up the concentrations of DME and DME-OH (expressed as clethodim equivalents) in common moiety methods. The method of calculation is illustrated below.

Example of the method for calculation of total residues

DME	DME-OH	Total
< 0.095	< 0.088	< 0.18
0.18	< 0.088	0.27

Pome fruits

The critical GAP for pome fruit (not including persimmon, Japanese) in the USA allows four directed ground sprays of 0.14 kg ai/ha with a maximum seasonal rate of 0.54 kg ai/ha and a PHI of 14 days.

Data were available from supervised trials on apples and pears in the USA.

Total residues of DME and DME-OH in apples from independent trials in the USA with two applications of 0.27–0.29 kg ai/ha at a total application rate of 0.55–0.58 kg ai/ha with a PHI of 12–15 days were (n = 13): < 0.18 (13) mg/kg.

Total residues of DME and DME-OH in pears from independent trials in the USA with two applications of 0.27–0.30 kg ai/ha at a total application rate of 0.54–0.59 kg ai/ha with a PHI of 13–16 days were (n = 6): < 0.18 (6) mg/kg.

Since total residues of DME and DME-OH in apples and pears from the 2 × treated plots were all < 0.18 mg/kg, the Meeting agreed to estimate a maximum residue level of 0.2 (*) mg/kg for the group of pome fruits except persimmon, Japanese.

Stone fruits

The critical GAP for stone fruit or peach in the USA allows four directed ground sprays of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 14 days.

Data were available from supervised trials on cherries (sweet and sour), plums and peaches in Canada and the USA.

Total residues of DME and DME-OH in cherries from independent trials in Canada and the USA with two applications of 0.27–0.30 kg ai/ha at a total application rate of 0.55–0.60 kg ai/ha with a PHI of 13–16 days were (n = 14): < 0.18 (14) mg/kg.

Total residues of DME and DME-OH in plums from independent trials in the USA with two applications of 0.27–0.29 kg ai/ha at a total application rate of 0.55–0.57 kg ai/ha with a PHI of 12–14 days were (n = 5): < 0.18 (5) mg/kg.

Total residues of DME and DME-OH in peaches from independent trials in the USA with two applications of 0.27–0.31 kg ai/ha at a total application rate of 0.54–0.61 kg ai/ha with a PHI of 12–15 days were (n = 7): < 0.18 (7) mg/kg.

Since total residues of DME and DME-OH in cherries, plums and peaches from the 2 × treated plots were all < 0.18 mg/kg, the Meeting agreed to estimate a maximum residue level of 0.2 (*) mg/kg for the group of stone fruits.

Bush berries, Subgroup of

The critical GAP for bush berries (high bush) in the USA allows four directed ground sprays of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 14 days.

Data were available from supervised trials on blueberries in Canada and the USA.

Total residues of DME and DME-OH in blueberries (high bush varieties) from independent trials in Canada and the USA with two applications of 0.27–0.30 kg ai/ha at a total application rate of 0.54–0.60 kg ai/ha with a PHI of 13–15 days were (n = 7): < 0.18 (7) mg/kg.

Since total residues of DME and DME-OH in blueberries (high bush varieties) from the 2 × treated plots were all < 0.18 mg/kg, the Meeting agreed to estimate a maximum residue level of 0.2 (*) mg/kg for the subgroup of bush berries.

The Meeting noted that the US GAP also covered high bush cranberries and elderberry, listed in the Codex Classification as Guelder rose (*Viburnum opulus* L.) and elderberries (*Sambucus* spp.) in the subgroup of large shrub/tree berries, and agreed to extrapolate a maximum residue level of 0.2 (*) mg/kg for Guelder rose and elderberries.

Low growing berries, Subgroup of

Cranberry

Data were available from supervised trials on cranberries in the USA.

The critical GAP for cranberry in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 30 days.

The trials on cranberries in the USA did not match the GAP.

The Meeting could not estimate a maximum residue level for clethodim in cranberry.

Strawberry

Data were available from supervised trials on strawberries in Germany, the UK and the USA.

The critical GAP for strawberry in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 4 days.

The trials on strawberries in the USA did not match the GAP.

The critical GAP for strawberry in the Netherlands allows one spray application of 0.24 kg ai/ha with a PHI of 30 days.

Total residues of DME and DME-OH in strawberries from independent trials in Germany and the UK matching GAP in the Netherlands were (n = 8): 0.07, 0.09 (2), 0.13, 0.16, 0.19 and 0.22 (2) mg/kg.

Based on the residues in strawberries from trials in Germany and the UK, the Meeting estimated a maximum residue level of 0.5 mg/kg for strawberry.

Bulb onions, Subgroup of

Data were available from supervised trials on onion in Norway.

The critical GAP for onions in the Netherlands allows one application of 0.24 kg ai/ha with a PHI of 56 days.

The trials on onions in Norway did not match the GAP.

The Meeting could not estimate a maximum residue level for clethodim in bulb onions.

The Meeting withdrew the previous recommendation for onion and garlic of 0.5 mg/kg.

Flowerhead Brassicas, Subgroup of

Broccoli

Data were available from supervised trials on broccoli in the USA.

The critical GAP for brassica head and stem vegetables in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 30 days.

The trials on broccoli in the USA did not match the GAP.

The Meeting could not estimate a maximum residue level for clethodim in broccoli.

Head Brassicas, Subgroup of

Cabbage, Head

Data were available from supervised trials on head cabbage in Australia and European countries.

The GAP for cabbages in Australia allows one spray application of 0.12 kg ai/ha with a PHI of 7 days.

Total residues of DME and DME-OH in head cabbage from independent trials in Australia matching the Australian GAP were (n = 1): 0.07 mg/kg and the total residues at two times the GAP rate were (n = 1): 0.20 mg/kg.

The critical GAP for head cabbage in the Netherlands allows one spray application of 0.24 kg ai/ha with a PHI of 28 days.

Since the methods of analysis in the European trials did not measure all analytes in the clethodim residue definition, the Meeting could not estimate a maximum residue level for clethodim in the Subgroup of head brassicas.

Fruiting vegetables, Cucurbits – Cucumber and Summer squashes, Subgroup of

Cucumber

Data were available from supervised trials on cucumber in the USA.

The critical GAP for cucurbits in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 14 days.

Total residues of DME and DME-OH in cucumber from independent trials in the USA with two applications of 0.28 kg ai/ha at a total application rate of 0.56 kg ai/ha with a PHI of 13–14 days were (n = 6): < 0.27 (6) mg/kg.

Since total residues of DME and DME-OH in cucumber from the 2 × treated plots were all < 0.27 mg/kg, the Meeting agreed to estimate a maximum residue level of 0.3 (*) mg/kg for cucumber.

Lettuce, Head

Data were available from supervised trials on head lettuce in the USA.

The critical GAP for leafy greens in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 14 days.

The trials on head lettuce in the USA did not match the GAP.

The Meeting could not estimate a maximum residue level for clethodim in leafy greens.

Dry beans, Subgroup of

Data were available from supervised trials on dry beans in European countries.

The critical GAP for dry beans in Croatia allows one spray application of 0.25 kg ai/ha with a PHI of 42 days.

The trials on dry beans in France, Spain and the UK did not match the GAP and the methods of analysis in the European trials did not measure all analytes in the clethodim residue definition.

The Meeting could not estimate a maximum residue level for clethodim in the Subgroup of dry beans.

The Meeting withdrew the previous recommendation for beans (dry) of 2 mg/kg.

Dry peas, Subgroup of

Data were available from supervised trials on dry peas in European countries and the USA.

The GAP for dry peas in the USA allows 2–4 spray applications of up to 0.27 kg ai/ha at a maximum seasonal rate of 0.54 kg ai/ha with a PHI of 30 days, which leads to a critical GAP of 2 applications at 0.27 kg ai/ha.

The trials on dry peas in the USA did not match the GAP.

The critical GAP for dry peas in Slovakia allows one spray application of 0.26 kg ai/ha at application timing of BBCH 12–30.

The trials on dry peas in France did not match the GAP. The methods of analysis in the other European trials did not measure all analytes in the clethodim residue definition.

The Meeting could not estimate a maximum residue level for clethodim in the Subgroup of dry peas.

The Meeting withdrew the previous recommendation for field peas (dry) of 2 mg/kg.

Root vegetables, Subgroup of

Carrot

Data were available from supervised trials on carrot in European countries and the USA.

The critical GAP for carrot in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 30 days.

The trials on carrot in the USA did not match the GAP.

The critical GAP for carrot in Slovakia allows one spray application of 0.24 kg ai/ha with a PHI of 40 days.

The trials on carrot in European countries did not match the GAP and the methods of analysis in the European trials did not measure all analytes in the clethodim residue definition.

The Meeting could not estimate a maximum residue level for clethodim in carrot.

Other stalk and stem vegetables, Subgroup of

Artichoke, globe

Data were available from supervised trials on artichoke in Greece, Spain and the USA.

The critical GAP for artichoke in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 5 days.

The trials on artichoke in the USA did not match the GAP.

The critical GAP for artichoke in Spain allows one spray application of 0.18 kg ai/ha with a PHI of 40 days.

Since the methods of analysis in the trials conducted in Greece and Spain did not measure all analytes in the clethodim residue definition, the Meeting could not estimate a maximum residue level for clethodim in artichoke, globe.

Small seed oilseeds, Subgroup of

Rape seed

Data were available from supervised trials on rape seed in Canada, France, the UK, and the USA.

The critical GAP for rape seed (winter rape) in Slovakia allows one spray application of 0.26 kg ai/ha (for spring application) at an application timing of BBCH 12–30.

The trials on rape seeds in France and the UK did not match the GAP.

The critical GAP for rape seed in the USA allows an application rate of 0.11 kg ai/ha with a maximum seasonal rate of 0.28 kg ai/ha and a PHI of 70 days.

Total residues of DME and DME-OH in rape seeds from independent trials in Canada and the USA matching the US GAP were (n = 4): 0.25 (3) and 0.50 mg/kg. However, the trials for rape seeds in Canada and the USA were insufficient to estimate a maximum residue level for the commodity.

The Meeting could not estimate a maximum residue level for clethodim in rape seed.

The Meeting withdrew the previous recommendation for rape seed of 0.5 mg/kg, rape seed crude oil of 0.5 (*) mg/kg and rape seed edible oil of 0.5 (*) mg/kg.

Hops, dry

Data were available from supervised trials on dried hops in the USA.

The critical GAP for hops in the USA allows four spray applications of 0.14 kg ai/ha with a maximum seasonal rate of 0.56 kg ai/ha and a PHI of 21 days.

Since the methods of analysis in the US trials did not measure all analytes in the clethodim residue definition, the Meeting could not estimate a maximum residue level for clethodim in hops, dry.

Residues in animal feeds

Legume animal feeds

Bean fodder

Data were available from supervised trials on bean fodder in France, Spain and the UK.

The critical GAP for beans in Croatia allows one spray application of 0.25 kg ai/ha with a PHI of 42 days.

The trials on bean fodder in France, Spain and the UK did not match the GAP.

The Meeting could not estimate a maximum residue level for clethodim in the Subgroup of bean fodder.

The Meeting withdrew the previous recommendation for bean fodder of 10 mg/kg.

Bean forage

Data were available from supervised trials on bean forage in France, Spain and UK.

The critical GAP for beans in Croatia allows one spray application of 0.25 kg ai/ha and no instruction for feeding.

Since the methods of analysis in the trials conducted in France, Spain and the UK did not measure all analytes in the clethodim residue definition, the Meeting could not estimate a maximum residue level for clethodim in bean forage.

Pea fodder

Data were available from supervised trials on pea fodder in European countries and the USA.

The critical GAP for peas in Slovakia allows one spray application of 0.26 kg ai/ha at application timing of BBCH 12–30.

The trials on pea fodder in France did not match the GAP.

The methods of analysis in the other European trials did not measure all analytes in the clethodim residue definition.

The Meeting could not estimate a maximum residue level for clethodim in pea fodder.

Pea vines

Data were available from supervised trials on pea vines in European countries.

The critical GAP for peas in Slovakia allows one spray application of 0.26 kg ai/ha at application timing of BBCH 12–30.

Since the methods of analysis in the European trials did not measure all analytes in the clethodim residue definition, the Meeting could not estimate a maximum residue level for clethodim in pea vines.

Fate of residues during processing

High temperature hydrolysis

The hydrolytic stability of [^{14}C]-clethodim and [^{14}C]-clethodim sulfoxide was studied under conditions of high temperature in sterile aqueous buffers at pH 4, 5 and 6 for periods of up to 60 minutes to simulate common processing practices (pasteurization, baking/boiling, and sterilization).

At pH 4 with heating at 90 °C for 20 min, clethodim degraded to clethodim oxazole (14% AR). At pH 5 with heating at 100 °C for 60 min and at pH 6 at 120 °C for 20 min, clethodim oxazole was formed with amounts of 80% and 96% AR, respectively, and an additional degradation product, clethodim trione with amounts of 5.4% and 3.8% AR, respectively.

At pH 4, 5 and 6 with heating, clethodim sulfoxide degraded to clethodim oxazole sulfoxide (89, 94 and 98% AR), and an additional degradation product, clethodim trione sulfoxide with amounts of 6.9%, 5.5% and 2.7% AR, respectively.

Residues in processed commodities

The Meeting received information on the fate of clethodim residues during processing of apples, plums and oilseed rape.

Although the studies on apples and plums were conducted at an exaggerated application rate compared to GAP, residues of clethodim determined as DME and DME-OH in the RAC and the processed fractions (apple: juice and pomace, plum: dried) were all below the respective LOQs of 0.095 mg/kg for DME and 0.088 mg/kg for DME-OH. Processing factors for apple juice, apple pomace and dried plum could not be established.

Processing studies on rape seed did not indicate concentration of residues in the oil.

Residues in animal commodities

Farm animal feeding studies

The Meeting received a lactating dairy cow and a laying hen feeding studies, which provided information on likely residues resulting in animal commodities, milk and eggs from clethodim and clethodim sulfoxide residues in the animal diet.

Lactating dairy cows

Holstein/Friesian dairy cows were dosed with 5% clethodim and 95% clethodim sulfoxide for 28 days at the equivalent of 0.53, 1.7 and 5.7 ppm for clethodim and 10, 32 and 107 ppm for clethodim sulfoxide in the diet. Residues of DME-OH were below the LOQ in milk (< 0.013 mg eq/kg) and tissues (liver, kidney, muscle and fat: < 0.05 mg eq/kg) at all feeding levels. Residues of S-methyl DME were below the LOQ in milk (< 0.013 mg eq/kg) at the 0.53/10 ppm and 1.7/32 ppm feeding levels, below the LOQ in muscle and fat (< 0.05 mg eq/kg) at all feeding levels and were detected in milk (< 0.013–0.032 mg eq/kg), liver (< 0.05–0.087 mg eq/kg) and kidney (< 0.05–0.078 mg eq/kg) at the highest feeding level (5.7/107 ppm).

Residues of DME (expressed as clethodim) were below the LOQ (< 0.05 mg eq/kg) in muscle and fat at the 0.53/10 ppm and 1.7/32 ppm feeding levels. Whole milk contained no residue (< 0.013 mg eq/kg) of DME at the 0.53/10 ppm feeding level. Residues of DME in whole milk achieved a plateau concentration of < 0.013–0.033 mg eq/kg at the 1.7/32 ppm feeding level and 0.035–0.081 mg eq/kg at the 5.7/107 ppm feeding level.

Residues of DME in liver and kidney were < 0.05–0.059 mg eq/kg at the 0.53/10 ppm feeding level, 0.070–0.17 mg/kg at the 1.7/32 ppm feeding level and 0.22–0.54 mg/kg at the 5.7/107 ppm feeding level.

Laying hens

Laying hens were dosed with 5% clethodim and 95% clethodim sulfoxide for 28 days at the equivalent of 0.74, 1.9 and 5.5 ppm for clethodim and 11, 34 and 108 ppm for clethodim sulfoxide in the diet. Residues of DME-OH and S-methyl DME were below the LOQ (0.1 mg/kg) in eggs, liver, muscle and fat at all feeding levels.

Residues of DME (expressed as clethodim) were below the LOQ (0.1 mg/kg) in liver, muscle and fat at all feeding levels. Eggs contained no residue (< 0.1 mg/kg) of DME at the 0.74/11 ppm and the 1.9/34 ppm feeding level. Residues of DME in eggs achieved a plateau concentration of 0.14–0.24 mg/kg at the 5.5/108 ppm feeding level.

Farm animal dietary burden

Dietary burdens were calculated for beef cattle, dairy cattle, broilers and laying poultry based on feed items evaluated by the JMPR.

The only potential feed item was apple wet pomace. Total residues of DME and DME-OH in apple wet pomace are expected to be below the LOQ as residues in apple fruits are below the LOQ.

Animal commodity maximum residue levels

The dietary burden for beef and dairy cattle is 0 ppm. No residues of DME are expected in any tissues or milk. No feed items for poultry were applicable.

The Meeting estimated maximum residue levels at the LOQ of 0.02 (*) mg/kg for milk and 0.05 (*) mg/kg for mammalian meat and mammalian edible offal to replace the previous recommendations for milk of 0.05 (*) mg/kg, mammalian meat of 0.2 (*) mg/kg and mammalian edible offal of 0.2 (*) mg/kg. The Meeting estimated a maximum residue level of 0.05 (*) mg/kg for mammalian fat.

The Meeting estimated maximum residue levels of 0.1 (*) mg/kg for eggs, poultry meat and poultry, edible offal to replace the previous recommendations for eggs of 0.05 (*) mg/kg, poultry meat of 0.2 (*) mg/kg and edible offal of poultry of 0.2 (*) mg/kg. The Meeting estimated a maximum residue level of 0.1 (*) mg/kg for poultry fat.

RECOMMENDATIONS

Definition of the residue for compliance with the MRL for plant commodities: Sum of clethodim and its metabolites convertible to dimethyl 3-[2-(ethylsulfonyl)propyl]-pentanedioate (DME) and dimethyl 3-[2-(ethylsulfonyl)propyl]-3-hydroxy-pentanedioate (DME-OH), expressed as clethodim.

Definition of the residue for compliance with the MRL for animal commodities: Sum of clethodim and its metabolites convertible to dimethyl 3-[2-(ethylsulfonyl)propyl]-pentanedioate (DME), expressed as clethodim.

The residue is fat-soluble.

Definition of the residue for dietary risk assessment for plant and animal commodities: *A conclusion could not be reached*

Table 109 Recommendations of the 2019 JMPR for residues of clethodim

CCN	Commodity	Recommended maximum residue level (mg/kg)		STMR or STMR-P mg/kg	HR or HR-P mg/kg
		New	Previous		
AL 1020	Alfalfa fodder	W	10		
AL 0061	Beans fodder	W	10		
VD 0071	Beans (dry)	W	2		
VP 0061	Beans, except broad bean and soya bean	W	0.5*		
SO 0691	Cotton seed	W	0.5		
OC 0691	Cotton seed oil, crude	W	0.5*		
OR 0691	Cotton seed oil, edible	W	0.5*		
MO 0105	Edible offal (Mammalian)	W	0.2*		
PE 0112	Eggs	W	0.05*		
VD 0561	Field pea (dry)	W	2		
AM 1051	Fodder beet	W	0.1*		
VA 0381	Garlic	W	0.5		
MM 0095	Meat (from mammals other than marine mammals)	W	0.2*		
ML 0106	Milks	W	0.05*		
VA 0385	Onion, Bulb	W	0.5		
SO 0697	Peanut	W	5		
VR 0589	Potato	W	0.5		
PM 0110	Poultry meat	W	0.2*		
PO 0111	Poultry, Edible offal of	W	0.2*		
SO 0495	Rape seed	W	0.5		
OC 0495	Rape seed oil, Crude	W	0.5*		
OR 0495	Rape seed oil, Edible	W	0.5*		
VD 0541	Soya bean (dry)	W	10		
OC 0541	Soya bean oil, crude	W	1		
OR 0541	Soya bean oil, refined	W	0.5*		
VR 0596	Sugar beet	W	0.1		
SO 0702	Sunflower seed	W	0.5		
OC 0702	Sunflower seed oil, crude	W	0.1*		
VO 0448	Tomato	W	1		

DIETARY RISK ASSESSMENT

Because the Meeting was unable to conclude on the toxicological relevance of the metabolites clethodim sulfone, clethodim oxazole sulfoxide, M19R and M15A, the Meeting could not reach a conclusion on the residue definitions for dietary risk assessment for plant and animal commodities.

As a result, long-term and acute dietary risk assessments could not be conducted.

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