

CLETHODIM (187)

EXPLANATION

Clethodim was evaluated by the JMPR in 1994 and 1997. Numerous MRLs were recommended in the first evaluation, but questions were raised at the 1996 CCPR on quantitative aspects of the metabolism study on plants and both the quantities and nature of the goat metabolites. The basis for the limit of determination in animal tissues and the resulting recommendations for MRLs for several animal commodities were also questioned. Specific doubts were expressed in relation to the limit of determination achieved by a compound-specific method and the practical limit of determination claimed for routine monitoring and enforcement.

The manufacturer submitted data on new residue trials on alfalfa, artichokes, cabbages, field peas, lupins, carrots, cauliflower, clover, celery, flax, garlic, cucumbers, leeks, lentils, lettuce, onions, peaches, peppers, spinach, summer squash and tomatoes for the 1997 evaluation. Some of the trials were not reviewed as they were not indicated as required or desirable in the 1994 evaluation, and some did not address the questions raised at the 1996 CCPR. The 1997 JMPR recommended withdrawal of the draft MRLs for beans, sunflower seed and sunflower seed oil (crude and edible).

At the 1999 CCPR, comments were made in relation to the MRLs recommended for cattle meat and cattle offal based on the limits of determination in animal tissues. In addition, it was noted that there was no justification given for the recommended animal commodity MRLs with respect to levels found in animal feed commodities. It was suggested that the JMPR should provide an estimation of the exposure of livestock to residues in treated feed items, to confirm the appropriateness of the animal commodity MRLs.

For the current evaluation, the manufacturer reported new supervised trials on cucumbers, peppers, potatoes, sunflowers and dry beans, and processing studies on cotton, canola (rape seed), peanuts, sugar beets, soya beans, sunflowers and tomatoes. New information on physical and chemical properties and on formulations was provided, and revision of the previously reported specific analytical method was submitted with new validation data. Previously reviewed studies on metabolism in crops, rats, goats and hens and degradation in soil were re-submitted.

IDENTITY

Physical and chemical properties

Pure active ingredient

Solubility in buffer solutions	pH	g/l
	3.7	0.0181 (Willemsz-Geeroms, 1985)
	4.9	0.0718
	5.8	0.479
	6.6	1.74
	7.8	5.4
	8.8	12.4 (cloudy solution, colloidal suspension)
	8.9	10.4 14.8 (cloudy solution, colloidal suspension)

Technical material (Ashworth, 1988)

Colour:	amber
Physical state:	viscous liquid

Odour:	no characteristic odour
Melting point:	liquid at ambient temperatures
Boiling point:	decomposes below boiling point
Density:	1.1395 g/ml at 20°C (Willemsz-Geeroms, 1986)
Solubility:	soluble in most organic solvents, acetone, hexane, ethyl acetate. DMF: >90 g/100 ml at 25°C (Hance, 1988)
pH:	4.15 (1% w/v solution) (Knight, 1986).
Flammability:	flash point 78°C (closed cup, ASTM D-56) (Updyke, 1990)
Stability in sunlight:	half-life 16.3 hours at 23.8°C (Lam, 1987)
Storage stability:	half-life 8.4, 1.2 and 0.7 months at 20°C, 38°C and 50°C respectively. (Jackson, 1988)
Minimum purity:	88% clethodim
Main impurities:	trione 0.7% maximum; alkoxyamine 0.1% maximum

Formulations

EC 12.5% ai; EC 25% ai, manufacturing use product 37 and 70% ai

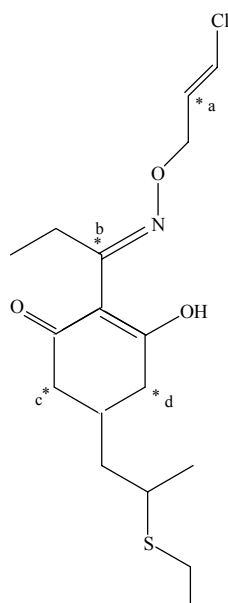
METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Metabolism studies on rats, a lactating goat and laying hens were re-submitted. The goat study (Rose and Suzuki, 1988) was reviewed in 1994 and 1997, and studies on the rat (Rose and Griffis, 1988) and hens (Lee, 1988) in 1994.

The metabolism studies were with [¹⁴C]clethodim labelled in the 1-propyl position for goats, the 4- and 6-hydroxycyclohexenone ring for hens and the 4- and 6-ring and 2-allyl carbons for carrots, soya beans and cotton. The positions of the labels are shown in Figure 1.

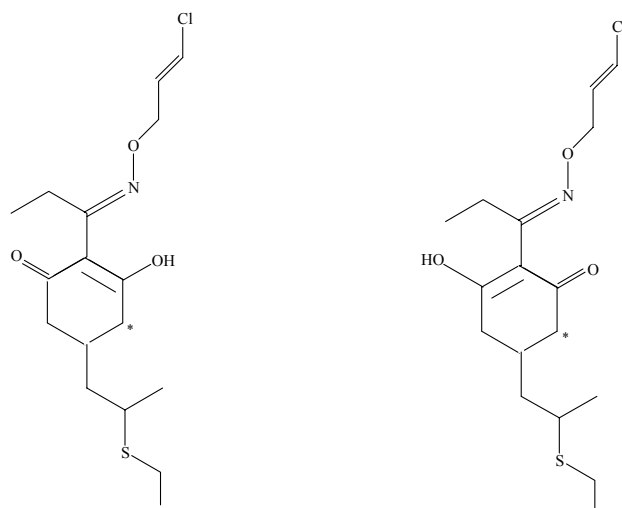
Figure 1.



a: 2-allyl; b: 1-propyl; c, d: 6- and 4- positions of hydroxycyclohex-2-enone ring

The labels in the ring positions are present as a 50/50 mixture owing to keto-enol tautomerism, Figure 2.

Figure 2.



The data from the studies on the goat and hens are repeated below to allow comparison of the distribution of radioactivity in the two species.

Table 1. Distribution of ^{14}C in a lactating goat (Rose & Suzuki, 1988) and laying hens (Lee, 1988).

Species	Dose regime	Sample	^{14}C , % of dose	Reference
Goat	1.16 mg/kg bw/day	Urine	56.43	Rose & Suzuki 1988
	for 3 days	Faeces	34.40	
		Milk	0.11	
		Blood	0.22	
		Tissues	0.37	
Total			91.53	
Hen	2.1 mg/kg bw/day	Excreta	77.9	Lee 1988
	for 5 days	Eggs	0.1	
		Tissues	1.9	
Total			79.9	
Hen	51.3 mg/kg bw/day	Excreta	84.7	Lee 1988
	for 5 days	Eggs	0.3	
		Tissues	4.2	
Total			89.2	

Most of the administered radioactivity was excreted: 90.94% of the dose by the goat and 77.9% and 84.7% of the low and high doses respectively by the hens. Most of the ^{14}C in the goat tissues was extractable with acetonitrile, with some in the methanol/water and hexane extracts and unextracted solids (Table 2). Peritoneal fat was the only substrate which was not easily extractable.

Table 2. Extraction of ^{14}C from goat tissues by various solvent systems.

Sample	% of ^{14}C in sample and (mg/kg clethodim equivalents)				
	Hexane	CH_3CN	$\text{MeOH-H}_2\text{O}$	Solids	Total
Liver	1.6 (0.007)	61.8 (0.256)	13.8 (0.057)	15.5 (0.064)	92.7 (0.384)
Kidney	1.1 (0.004)	80.4 (0.304)	9.3 (0.035)	6.7 (0.025)	97.5 (0.369)
Fat, subcutaneous	3.6 (0.003)	81.1 (0.064)	10.7 (0.008)	3.5 (0.003)	98.4 (0.078)
Fat, peritoneal	0.6 (0.000)	0.2 (0.000)	1.6 (0.000)	1.5 (0.000)	3.9 (0.002)
Muscle, hindquarter	0.7 (0.000)	81.8 (0.028)	10.8 (0.004)	6.8 (0.002)	99.3 (0.034)
Muscle, forequarter	1.4 (0.000)	80.1 (0.026)	8.6 (0.003)	8.1 (0.003)	98.2 (0.033)
Heart	10.1 (0.006)	76.6 (0.044)	5.3 (0.003)	6.0 (0.003)	98.0 (0.057)
Blood	1.1 (0.002)	85.7 (0.145)	6.5 (0.011)	4.6 (0.008)	97.9 (0.164)

The levels of clethodim and metabolites in tissues, organs and blood of the goat were tabulated in the 1997 monograph and the Table is repeated here for convenience. In milk, the radioactivity was associated with the *S*-methyl sulfoxide (5.5%), clethodim sulfoxide (~20%) and lactose derivatives (30-50%).

Table 3. Distribution of clethodim and metabolites in goat tissues, organs and blood after dosing at 1.16 mg/kg body weight/day with [¹⁴C]clethodim.

Compound	% of ¹⁴ C in sample and (mg/kg as clethodim)						
	Liver	Kidney	Fat, subcutaneous	Muscle, forequarter	Muscle, hindquarter	Heart	Blood
Clethodim	27.6 (0.114)	1.3 (0.005)	2.8 (0.002)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	28.0 (0.047)
Clethodim sulfoxide	33.2 (0.137)	36.9 (0.139)	47.2 (0.037)	51.6 (0.017)	40.7 (0.014)	43.2 (0.025)	39.9 (0.067)
Clethodim sulfone	3.2 (0.013)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	3.8 (0.006)
<i>S</i> -methyl sulfoxide	6.2 (0.025)	30.8 (0.116)	29.0 (0.023)	28.5 (0.009)	32.4 (0.011)	37.2 (0.021)	11.6 (0.019)
Imine sulfoxide	1.5 (0.006)	4.1 (0.016)	4.7 (0.004)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	3.0 (0.005)
5-OH sulfone	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	2.7 (0.004)
Unidentified	4.0 (0.016)	9.8 (0.037)		0.0 (0.000)	7.9 (0.003)	0.0 (0.000)	3.2 (0.005)
Total	75.7	82.9	91.8	80.1	81.0	80.4	92.2

The major compound in all the samples was clethodim sulfoxide, accompanied mainly by clethodim in the liver and blood and by the *S*-methyl sulfoxide in the other samples. The imine sulfoxide was present at levels in the range of about 1.5-5% in the liver, kidneys, fat and blood.

The distribution of the radioactivity in extracts of hen tissues and eggs is shown in Table 4 and its distribution among the labelled compounds in each sample in Table 5, after treatment at the high dose of 51.3 mg/kg body weight/day for 5 days.

Table 4. Distribution of extracted radioactivity in hen tissues and eggs.

Sample	% of ¹⁴ C in sample and (mg/kg clethodim equivalents)			
	CH ₃ CN	Hexane	Solids	Total recovered
Liver	83.6 (0.57)	ND	17.0 (0.11)	100.6
Kidney	94.5 (1.13)	1.7 (0.02)	11.4 (0.14)	107.6
Skin	83.3 (0.28)	1.6 (ND)	6.2 (0.02)	91.6
Fat	100.2 (0.06)	0.7 (ND)	1.6 (ND)	102.5
Thigh	87.0 (0.14)	1.1 (ND)	7.4 (ND)	95.4
Breast	87.8 (0.03)	0.1 (ND)	10.6 (ND)	98.5
Heart	80.6 (0.23)	3.1 (0.01)	13.5 (0.04)	97.2
Gizzard	111.5 (0.19)	1.5 (ND)	11.9 (0.02)	124.9
Egg yolk*	97.0 (0.03)	ND	14.1 (0.01)	111.1
Egg white*	96.3 (0.16)	ND	4.8 (0.01)	101.1

*Total from samples collected for 5 days
ND = not detectable.

Table 5. Distribution of clethodim and metabolites in hen tissues, organs and eggs after dosing at 51.3 mg/kg bw/day for 5 days.

Sample	% of ¹⁴ C in sample and (mg/kg clethodim equivalents)				
	Clethodim	Clethodim sulfoxide	Clethodim sulfone	Unidentified*	At origin
Liver	2.5 (0.41)	30.9 (5.00)	26.8 (4.34)	12.1 (2.17)	1.8 (0.28)
Kidney	4.6 (1.18)	39.5 (10.23)	25.1 (6.49)	11.3 (2.91)	3.3 (0.86)
Skin	6.3 (0.20)	47.5 (2.95)	27.8 (1.72)	10.1 (0.62)	1.0 (0.06)
Fat	33.5 (1.61)	41.3 (1.98)	15.7 (0.75)	5.0 (0.24)	1.8 (0.08)
Thigh	0.5 (0.03)	43.5 (2.22)	33.2 (1.69)	15.2 (0.77)	1.4 (0.07)
Breast	1.2 (0.05)	47.3 (2.13)	33.6 (1.51)	3.8 (0.17)	0.5 (0.02)
Heart	0.5 (0.05)	37.3 (3.50)	27.9 (2.62)	11.8 (1.10)	2.8 (0.26)
Gizzard	5.8 (0.40)	30.3 (2.60)	33.2 (2.26)	9.0 (0.62)	1.4 (0.09)
Egg white					
Day 0	5.9 (0.05)	65.9 (0.58)	9.9 (0.09)	12.4 (0.11)	4.3 (0.04)
Day 1	10.1 (0.83)	44.7 (3.68)	26.6 (2.18)	9.7 (0.80)	1.2 (0.10)
Day 2	4.5 (0.43)	47.2 (4.48)	36.3 (3.44)	3.1 (0.30)	1.7 (0.16)
Day 3	5.1 (0.39)	44.6 (3.42)	18.5 (1.42)	26.6 (2.86)	1.2 (0.10)
Day 4	4.2 (0.37)	39.4 (3.47)	10.7 (0.94)	38.0 (3.35)	2.6 (0.22)
Egg yolk **					
Day 1	19.7 (0.15)	33.9 (0.26)	29.1 (0.22)	3.4 (0.09)	0.9 (0.01)
Day 2	14.8 (0.20)	28.2 (0.39)	18.7 (0.26)	19.8 (0.27)	2.4 (0.03)
Day 3	20.2 (0.40)	29.0 (0.57)	21.3 (0.42)	4.4 (0.08)	2.2 (0.04)
Day 4	22.2 (0.56)	25.0 (0.63)	17.8 (0.45)	6.1 (0.16)	1.5 (0.04)

*Composite of multiple TLC bands

** Insufficient yolk sample on day 0 for analysis

Clethodim sulfoxide was the main radioactive residue in all samples except gizzard. Clethodim sulfone was generally the next most prominent, but was exceeded by clethodim in the fat and in one sample of yolk.

Goat liver and kidneys were analysed for clethodim and metabolites by the residue enforcement method described in the 1994 evaluation (King, 1984). The samples were extracted with MeOH. The MeOH was removed *in vacuo* and the residue partitioned with hexane and CH₃CN. In the liver samples 79.9% of the ¹⁴C was found in the CH₃CN and 0.9% in the hexane, and in the kidneys 91.6% in the CH₃CN and 0.2% in the hexane. Aliquots of the CH₃CN phases were concentrated to dryness, transferred to MeOH/H₂O (1:2) and oxidized for analysis. Radioactivity was measured in the remaining CH₃CN fractions after separation by TLC and HPLC. The results of the GLC and total ¹⁴C determination were as shown below.

Residue expressed as	Liver, mg/kg		Kidney, mg/kg	
	Enforcement	¹⁴ C	Enforcement	¹⁴ C
Clethodim	0.196	0.270	0.173	0.160
S-methyl sulfoxide	0.120	0.025	0.094	0.116
5-OH sulfone	0	0	0	0

Clethodim and its sulfoxide and sulfone residues in hen breast muscle from another study in which birds were dosed at 2.1 mg/kg bw were also determined by the enforcement method. The results from the GLC analysis gave 0.12 mg/kg as compared with the total ¹⁴C analysis of 0.07 mg/kg.

Plant metabolism

Metabolism studies on carrots, soya beans and cotton plants were reviewed in 1994 and 1997 (Chen, 1988a,b). The distribution and characterization of the radioactivity after treatment with ring- and allyl-labelled [¹⁴C]clethodim were detailed in the 1997 monograph. The predominant components of the radioactive residue were clethodim sulfoxide and/or the imine sulfoxide. Data from the two studies are shown in Tables 6 and 7.

Table 6. Distribution of ^{14}C in plants treated with [^{14}C]clethodim (Chen, 1988a,b).

Crop	Treatment	PHI, days	Sample	% of total ^{14}C in plant	
				ring label	allyl label
Carrots	2 × 0.28 kg ai/ha at 10.2-15.2 cm long leaves at 14 day interval	20	Leaves	97.3	89.3
			Roots	2.7	10.7
Cotton	2 × 0.28 kg ai/ha at 8-12 leaf stage at 14 day interval	70	Leaves	93.2	85.0
			Stems	2.6	6.0
			Shell	3.6	4.7
			Fibre (cotton)	0.1	1.3
			Seeds	0.2	1.3
			Roots	0.3	1.7
Soya beans	2 × 0.28 kg ai/ha at 6-8 leaf stage at 14 day interval	30	Leaves	83.8	78.4
			Stems	0.8	1.2
			Roots	0.2	0.6
			Pods	5.1	5.6
			Beans	10.1	14.2

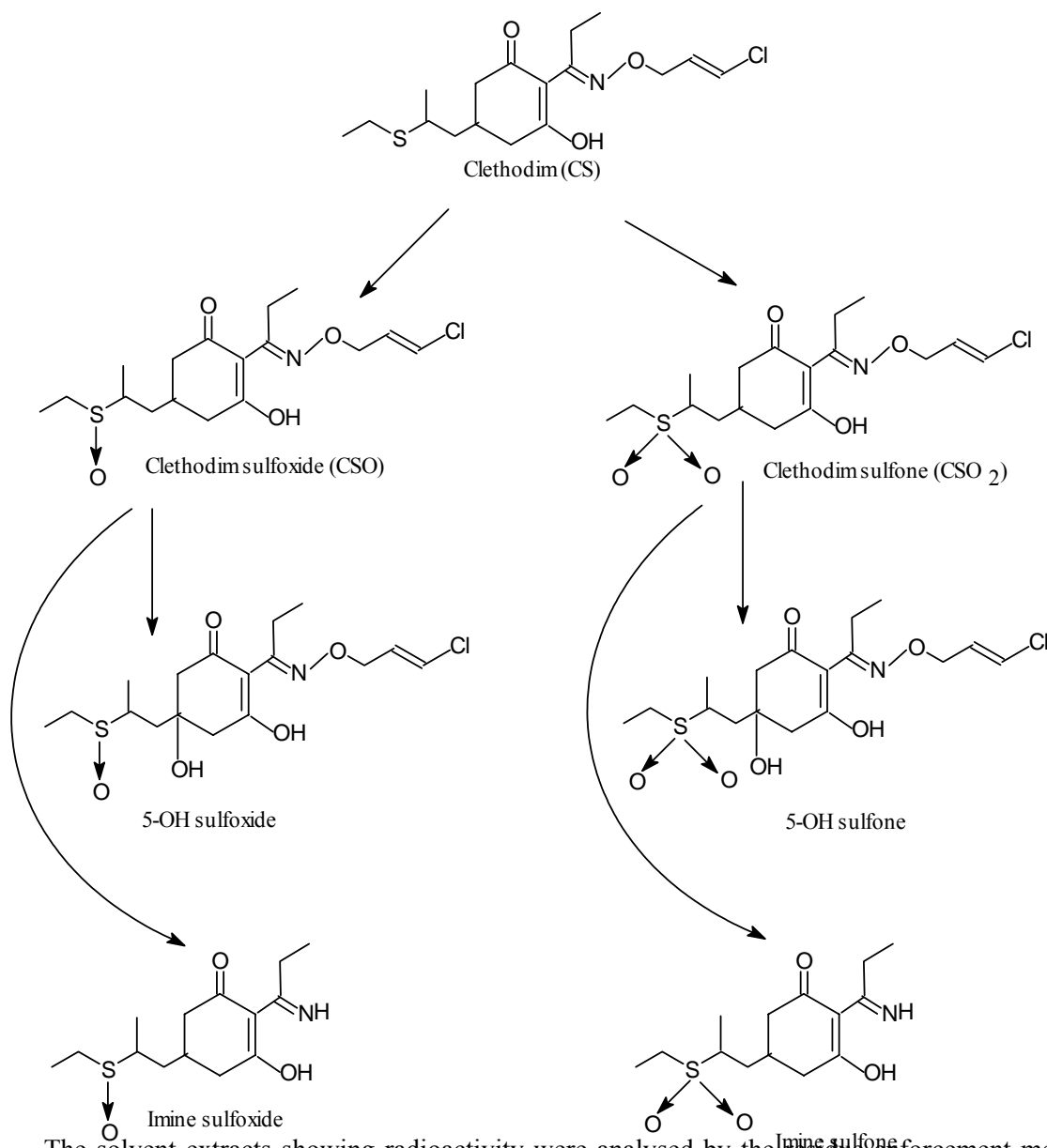
The roman numerals in Table 7 refer to the 4,6-hydroxycyclohexenone label and the italic numerals to the 2-allyl label.

Table 7. Distribution of ^{14}C residues in leaves and roots or seeds of treated crops.

Compound	^{14}C in samples and (mg/kg as clethodim)					
	Carrot leaves	Carrots	Soya bean leaves	Soya beans	Cotton leaves	Cotton seed
Clethodim		0.8 (0.003) <i>1.1 (0.007)</i>				
Clethodim sulfoxide	15.7 (3.50) <i>10.5 (0.97)</i>	28.6 (0.110) <i>33.9 (0.210)</i>	5.9 (1.65) <i>4.5 (0.79)</i>	32.0 (1.240) <i>31.5 (1.340)</i>	4.1 (0.55) <i>5.3 (0.35)</i>	4.3 (0.003) <i>3.1 (0.007)</i>
Clethodim sulfone	0.6 (0.13) <i>1.8 (0.17)</i>	3.4 (0.014) <i>4.6 (0.029)</i>	0.9 (0.25) <i>0.9 (0.16)</i>	4.6 (0.178) <i>5.1 (0.217)</i>	0.4 (0.05) <i>1.8 (0.12)</i>	2.8 (0.002) <i>0.4 (0.001)</i>
Imine sulfoxide	22.1 (4.93) -----	9.9 (0.040) -----	13.9 (3.88) -----	7.8 (0.302) -----	17.8 (2.40) -----	6.0 (0.004) -----
Imine sulfone	5.9 (1.32) -----	8.6 (0.034) -----	8.7 (2.43) -----	8.1 (0.314) -----	4.1 (0.55) -----	2.3 (0.001) -----
5-OH sulfoxide	1.6 (0.36) <i>1.0 (0.09)</i>	6.4 (0.026) <i>7.3 (0.045)</i>	trace <i>1.4 (0.25)</i>	7.1 (0.275) <i>4.0 (0.170)</i>	1.4 (0.19) <i>1.1 (0.07)</i>	0.6 (0.002) <i>0.4 (0.001)</i>
5-OH sulfone	1.9 (0.42) <i>1.7 (0.16)</i>	7.6 (0.030) <i>10.1 (0.063)</i>	3.1 (0.86) <i>2.2 (0.39)</i>	10.7 (0.414) <i>10.1 (0.429)</i>	0.4 (0.05) <i>0.6 (0.04)</i>	1.6 (0.001) <i>0.6 (0.001)</i>
Aromatic sulfone	0.3 (0.07) <i>0.6 (0.06)</i>	1.4 (0.006) <i>0.8 (0.005)</i>	0.5 (0.14) <i>0.4 (0.07)</i>	1.5 (0.058) <i>1.9 (0.081)</i>	0.5 (0.07) <i>0.4 (0.03)</i>	
Clethodim sulfoxide conj.	8.5 (1.90) <i>2.9 (0.27)</i>	5.9 (0.024) <i>8.3 (0.052)</i>	24.8 (6.92) <i>26.7 (4.70)</i>	8.5 (0.329) <i>11.5 (0.489)</i>	2.7 (0.37) <i>10.1 (0.67)</i>	
Clethodim sulfone conj.	0.5 (0.11) <i>4.3 (0.40)</i>	0.5 (0.002) <i>4.3 (0.027)</i>	2.0 (0.56) <i>12.3 (2.17)</i>	1.3 (0.050) <i>2.5 (0.106)</i>	1.3 (0.18) <i>5.0 (0.33)</i>	
Polar conj.	26.8 (5.98) <i>31.6 (2.91)</i>	10.2 (0.041) <i>13.4 (0.083)</i>	18.3 (5.11) <i>31.4 (5.53)</i>	9.9 (0.383) <i>4.3 (0.183)</i>	31.5 (4.25) <i>56.2 (3.75)</i>	29.5 (0.020) <i>28.9 (0.064)</i>
Unextracted	5.3 (1.18) <i>9.3 (0.86)</i>	3.7 (0.015) <i>11.9 (0.074)</i>	8.9 (2.48) <i>12.2 (2.15)</i>	1.5 (0.058) <i>8.9 (0.378)</i>	4.6 (0.62) <i>12.2 (0.81)</i>	46.3 (0.032) <i>61.0 (0.134)</i>

Similar trends were observed for both labels. The main identified components of the radioactive residue were generally clethodim sulfoxide and/or its conjugates. The imine sulfoxide was prominent in the leaves. Much of the residue was characterized only as polar conjugates or, particularly in cotton seed, as unextracted.

Figure 3. Proposed metabolic pathways of clethodim in plants.



The solvent extracts showing radioactivity were analysed by the residue enforcement method (King, 1984). The total extractable residue in the plant samples was oxidized and methylated, and the residues were determined as dimethyl 3-[2-(ethylsulfonyl)propyl]pentanedioate (DME) and the corresponding 5-hydroxy compound (DME-OH). The reaction sequence for DME is shown in Figure 4. TLC and autoradiography methods were used in place of GLC to quantify DME and DME-OH. A comparison with the total extractable ¹⁴C residues, quantified as DME and DME-OH, is shown below. The comparison is also shown for soya beans determined in a separate experiment.

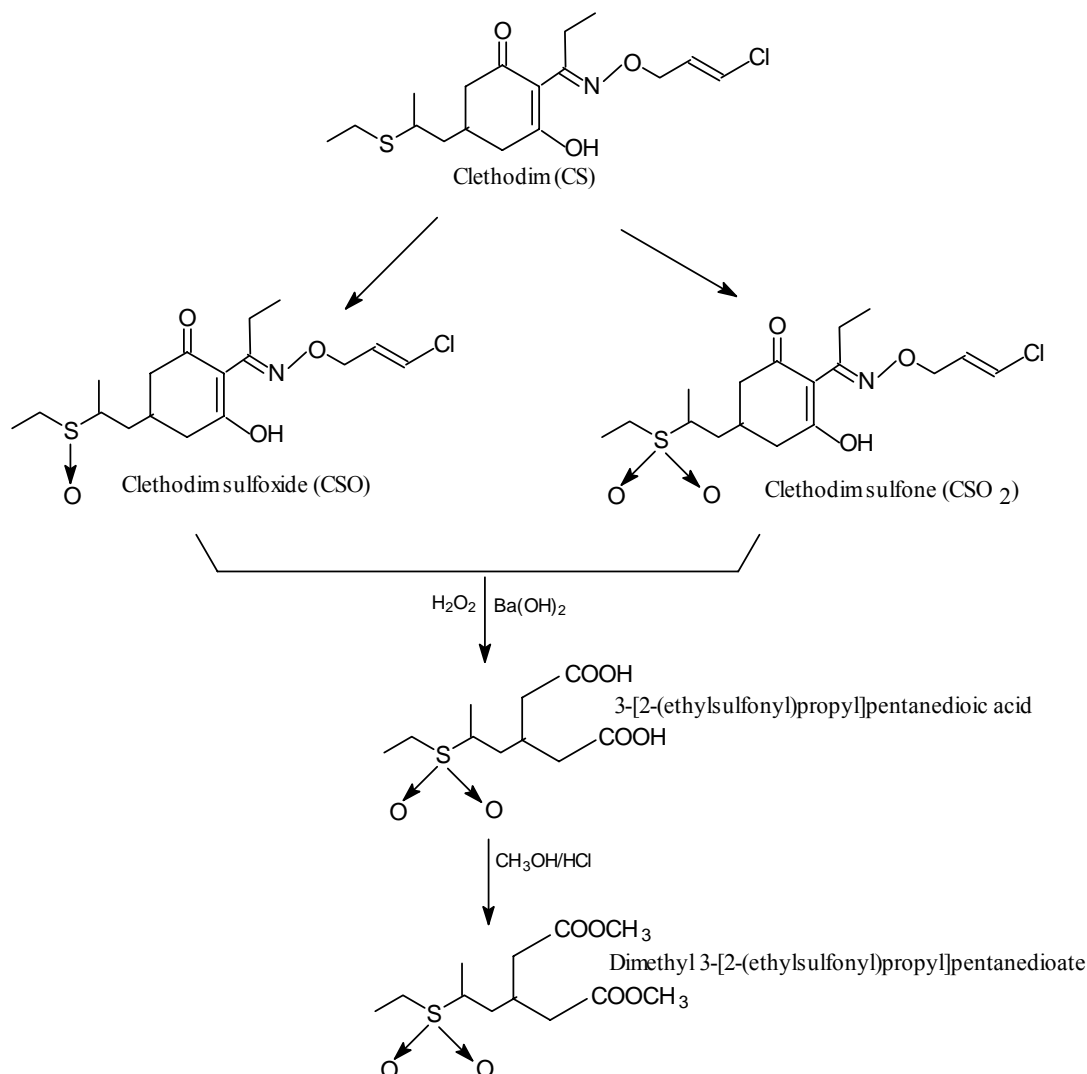
Sample	% of ¹⁴ C in sample as total radioactivity and as DME and DME-OH			
	¹⁴ C	DME	¹⁴ C	DME-OH
Soya bean leaves	67	62	2	3
Soya beans	46	56	18	18
Carrot leaves	48	56	3	4
Carrots	66	60	31	15
Cotton leaves	34	32	3	2
Cotton seeds	53	29	9	4

Soya beans	DME (expressed as mg/kg clethodim)	DME-OH (expressed as mg/kg clethodim)
Residue enforcement method	38.1	20.5
¹⁴ C as calculated*	39.9	19.3

* Calculated as sum of DME- and DME-OH-producing residues, *i.e.* sum of clethodim sulfoxide and sulfone, imine sulfoxide and sulfone, conjugates of clethodim sulfoxide and sulfone.

Figure 4. Reaction sequence in non-specific regulatory analytical method (POAST) to form DME.

(5-hydroxy-clethodim sulfoxide and sulfone are converted to the corresponding 3-hydroxy-substituted pentanedioate DME-OH).



The comparison between the calculated ¹⁴C residues expressed as clethodim and the residues determined by the enforcement method (sum of DME and DME-OH expressed as clethodim) shows that the enforcement method is capable of determining all the metabolites which are included in the residue as defined. The verification with soya beans using the standard enforcement method confirms this capability.

It was noted that the values for DME and DME-OH in the verification were reported as corrected for recovery. The recoveries of DME and DME-OH were 73% and 53% respectively, from fortification with clethodim and the 5-OH sulfone at 10 µg/g.

Environmental fate in soil

Several studies of degradation in or on soil previously submitted by the manufacturer were reviewed in the 1994 monograph. These included studies of aerobic and anaerobic degradation (Pack, 1988a,b, 1990) and photodegradation (Chen, 1988c,d). A new study of degradation and an investigation of the adsorption and desorption of clethodim are described below.

In a degradation study (Cosgrove, 1993), clethodim, clethodim sulfoxide and clethodim sulfone were added to sterilized and unsterilized loam soil and their degradation monitored for 60 days. Soil was collected from a test site in a canola-growing region in Canada and sterilized by autoclaving at 121°C for an hour. Unsterilized soil was refrigerated at 6°C until ready for use. The loam contained 42% sand, 47% silt and 11% clay, with pH 6.3, 9.5% organic carbon, and 68.6 meq/100 g cation exchange capacity. Test samples were fortified with about 1 mg/kg each of clethodim, clethodim sulfoxide and clethodim sulfone and maintained under aerobic conditions in the dark at temperatures of 6°C or 21°C. Samples were taken for chemical and microbial analysis at 0, 1, 3, 7, 14, 30 and 60 days after fortification. Clethodim and its derivatives were quantified by HPLC-MS; a limit of detection of 0.01 mg/kg was reported for each compound.

Clethodim was rapidly converted to clethodim sulfoxide in both sterile and non-sterile soils, and was detected only on day 0 in non-sterile soil, and on days 0 and 1 in sterile soil at both temperatures. The concentration of clethodim sulfoxide reached maximum levels after 7 days in sterile and non-sterile soils at 6°C and sterile soil at 21°C. In non-sterile soil at 21°C, maximum levels of clethodim sulfoxide were found 1 day after treatment. Maximum levels of clethodim sulfone in non-sterile soil were observed after 30 days at 6°C and 7 days at 21°C. Clethodim sulfone was not formed in the sterile soil at either temperature, indicating that microbial activity is responsible for its formation in loamy soil.

The calculated half-life of clethodim sulfoxide was 30 days in sterile soil and 17 days in non-sterile soil at 6°C, and 26 days and 8 days respectively at 21°C. Again, the degradation of clethodim sulfoxide was rapid in non-sterile soils at 21°C.

The calculated half-lives of clethodim sulfone were 45 and 18 days at 6°C and 18 and 12 days at 21°C in sterile and non-sterile soil respectively. Comparison of the half-lives and rate constants of the sulfoxide and sulfone indicated that both compounds are degraded at twice the rate in the non-sterile soil as in the sterile soil at both temperatures.

The recoveries of clethodim, clethodim sulfoxide and clethodim sulfone were 91-150%, 64-146% and 41-107% from soil fortified at 1, 0.96 and 0.88 mg/kg.

In a study of adsorption and desorption Pack (1988c) treated five soils with organic matter contents of 0.4-2.8% C with radiolabelled clethodim, clethodim sulfoxide, clethodim sulfone and clethodim oxazole sulfone. The soils were clay loam, loamy sand, silt loam, sand, and sandy clay loam. Clethodim and its sulfoxide and sulfone were labelled with ¹⁴C in the 4 and 6 ring positions and the oxazole sulfone in the 5 and 7 positions.

In the adsorption phase of the study aliquots of solutions at 0.1, 0.2, 0.5 and 1 µg/ml in 0.01 M CaCl₂ were added to weighed samples of soil, the mixtures were shaken for an hour, then centrifuged and the supernatants analysed by HPLC. In the desorption phase fresh 0.01 M CaCl₂ was added to each soil and shaken again for an hour. The resulting supernatants were analysed by HPLC and the soils combusted for measurement of ¹⁴C.

The calculated Freundlich adsorption and desorption constants (K_d) are given in Table 8.

Table 8. Adsorption and desorption constants of clethodim, clethodim sulfoxide, clethodim sulfone and clethodim oxazole sulfone.

Compound	Soil	K _d adsorption	K _d desorption
Clethodim	Clay loam	0.08	1.40
	Loamy sand	1.57	4.15
	Silt loam	0.15	380.0
	Sand	0.51	22.6
	Sandy clay loam	0.46	12.75
Clethodim sulfoxide	Clay loam	<0.2	
	Loamy sand	0.22	1.06
	Silt loam	<0.2	
	Sand	<0.2	
	Sandy clay loam	<0.2	
Clethodim sulfone	Clay loam	<0.1	
	Loamy sand	0.11	1.37
	Silt loam	<0.1	
	Sand	<0.1	
	Sandy clay loam	<0.1	
Clethodim oxazole sulfone	Clay loam	6.96	25.30
	Loamy sand	0.29	0.72
	Silt loam	1.79	3.30
	Sand	1.02	7.33
	Sandy clay loam	1.60	5.69

The results show that clethodim, clethodim sulfoxide and clethodim sulfone are weakly adsorbed and clethodim oxazole sulfone is weakly to moderately adsorbed by the soils tested.

Environmental fate in water/sediment systems

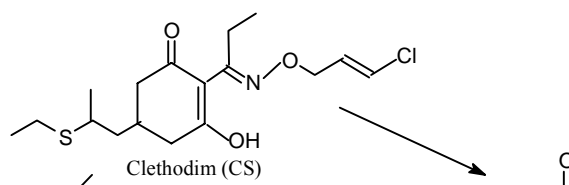
The photodegradation of clethodim in water was investigated in two studies by Chen (1988c,d). Buffered solutions at pH 5, 7 and 9 of [¹⁴C]clethodim (10 mg/l) labelled in the cyclohexene ring or the allyl group were exposed to natural sunlight for up to 30 days and analysed at regular intervals by HPLC-MS. Control samples were maintained at 25°C in the dark and the experimental samples were exposed to natural sunlight in the presence and absence of acetone which functioned as a photosensitizer.

Calculated photolysis half-lives of the ring-labelled compound were 1.71, 6.84 and 9.57 days at pH 5, 7 and 9 respectively without acetone and 0.94, 1.22 and 0.52 days with acetone. The detected photoproducts were clethodim sulfoxide, imine sulfoxide, oxazole sulfoxide, oxazole, imine and imine ketone, and DME sulfoxide. After 30 days, the main products remaining were the imine sulfoxide and DME sulfoxide.

Photolysis half-lives of the allyl-labelled compound were 1.49, 4.05 and 6.0 days at pH 5, 7 and 9 respectively in the absence of acetone, and 0.20, 0.61 and 0.33 days respectively in its presence. These half-lives are shorter than those found with the ring labels, apparently owing to higher light intensity.

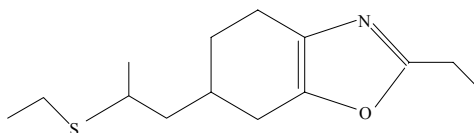
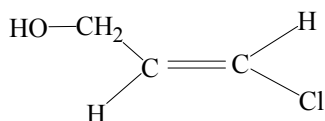
The photolytic mechanisms of transformation include oxidation at the ethylthio group, elimination of the chloroallyl side chain to form the imine and oxazole, with further oxidation to yield the DME sulfide and sulfoxide, and the oxazole sulfoxide. The allyl label showed chlorinated vinyl degradation products which decompose to CO₂

Figure 5. Proposed photolytic pathways of clethodim in water.



The hydrolysis of allyl- and propyl-labelled [^{14}C]clethodim was investigated in sterile water at pH 5, 7 and 9 at 25°C (Pack, 1988d). Solutions at 5 and 10 mg/l were incubated in the dark at 25°C and samples taken at 0, 1, 3, 7, 21 and 32 days were analysed by HPLC and GC-MS.

The HPLC chromatogram of clethodim showed two peaks. In solutions at pH 5 and 7 the ratio of the two peaks changed as a function of time. No significant change was observed at pH 9. The two peaks were interpreted as the (*E*)- and (*Z*)-oxime forms of clethodim, the (*E*)- form being less polar as it cannot form an internal H-bond between the oxime oxygen and the hydroxyl group of the cyclohexene ring. The rate of interconversion was fastest at pH 5, and not measurable in 30 days at pH 9. Two main degradation products were formed at pH 5, an oxazole and a hydroxyvinyl compound:



Cleavage of the vinyl group and ring closure to form the oxazole are the predominant mechanisms involved in the transformation of clethodim in sterile water.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Methods for the determination of clethodim and its metabolites in crops, chicken and beef tissues, milk, eggs, soil and aqueous solutions were provided. A non-specific method for the determination of clethodim residues in crops, chicken and beef tissues, milk and eggs reviewed in 1994 has since been revised (Lai, 1994a). The sample is extracted with MeOH and/or H₂O, and cleaned up by alkaline precipitation (Ca(OH)₂) and acidic back-extraction into CH₂Cl₂. Alkaline H₂O₂ oxidizes the ethylthio and sulfoxide groups to sulfone with oxidative cleavage to form dicarboxylic acids, which are converted to dimethyl esters (DME and DME-OH) with anhydrous MeOH and HCl and partitioned into CH₂Cl₂. After an optional clean-up on a silica gel column the esters are determined by GLC with a flame photometric detector in the sulfur mode. The total residues are expressed as clethodim. This method was used to determine the residues of clethodim and metabolites in the supervised residue trials detailed later.

In alfalfa trials in the USA (Lai, 1995a) reviewed in 1997 the original common moiety method (RM-26B-1) was used to determine total residues of clethodim, which were quantified as DME and DME-OH and summed as clethodim equivalents. The predominant component of the total residue was DME in most instances. Recoveries from forage and hay fortified with clethodim and 5-OH-clethodim sulfone at 0.05, 0.1, 0.2, 0.5, 1, 2 and 5 mg/kg of each compound were determined. Average recoveries from forage were 97% ± 23% (n = 57) for clethodim and 112% ± 20% (n = 57) for 5-OH-clethodim sulfone. Average recoveries from hay were 103 ± 33% (n = 51) for clethodim and 108% ± 29% (n = 52) for 5-OH-clethodim sulfone. Recoveries at the lowest fortifications of 0.05 mg/kg were 204 and 106% of clethodim and 5-OH-clethodim sulfone respectively from hay and 146 and 164 % from forage.

A compound-specific HPLC method, EPA-RM-26-D-3, for the determination of clethodim and its metabolites in crops, animal tissues, milk and eggs (Lai, 1996a) allows residues from the use of sethoxydim to be differentiated from those of clethodim. Residues of clethodim sulfoxide, clethodim sulfone, the 5-hydroxy sulfoxide and sulfone, and *S*-methyl-clethodim sulfoxide may be determined as enol methyl ethers. A chromatogram from a crop analysis was provided which showed the presence of clethodim, 5-hydroxy-clethodim sulfone, sethoxydim and 5-hydroxy-sethoxydim sulfone as four separate HPLC peaks. The method is a revised version of EPA-RM-26-D-1 (Lai and Ho, 1990) and its modification EPA-RM-26-D-2 (Lai and Fujie, 1993). These were reviewed in 1994 and 1997 respectively.

The method involves extraction with MeOH or MeOH/H₂O followed by alkaline precipitation. After partitioning with CH₂Cl₂, the residues are methylated with CH₂N₂, oxidized with *m*-chloroperbenzoic acid and cleaned up on a silica column. A base wash clean-up is included for crops and milk samples. The methylated sulfones of clethodim, 5-OH-clethodim and *S*-methyl-clethodim are determined by HPLC on a C-18 column with UV detection at λ = 266 or 254 nm. The limits of determination in various commodities ranged from 0.02 to 5 mg/kg, defined as the lowest fortification concentration giving acceptable recoveries. These are listed in Table 9.

Table 9. Limits of determination reported for the compound-specific method.

Commodity	Limit of determination (mg/kg)		
	CSO/CS	5-OH CSO ₂	S-MeCSO
Eggs	0.05		
Liver	0.20		
Milk	0.02		0.02

Commodity	Limit of determination (mg/kg)		
	CSO/CS	5-OH CSO ₂	S-MeCSO
Soya beans	0.05	0.05	
Onion	0.10	0.10	
Potato	0.20	0.20	
Tomato	0.20	0.02	
Alfalfa forage	1.0	1.0	
hay	5.0	5.0	
Sugar beet tops	0.25	0.10	
roots	0.10	0.10	
Peanut meat	0.20	0.20	
hay	0.20	2-3	
Dry bean seeds	0.20	0.20	

CSO clethodim sulfoxide CS clethodim
5-OH CSO₂ 5-hydroxy-clethodim sulfone S-MeCSO *S*-methyl-clethodim sulfoxide

The method allows recovery and quantification of the major metabolites likely to be present in crops, animal tissues, milk and eggs, and the limits of determination for clethodim and its sulfoxide in animal products were reported as 0.02 mg/kg in milk, 0.05 mg/kg in eggs and 0.2 mg/kg in hen liver. Representative chromatograms were provided for a crop and two chromatograms for animal extracts, one recorded before the method revision and the other after the revision.

A justification for the use of CH₂N₂ was provided, identical to that reported in 1997 (Rose, 1990).

Specialized methods for the determination of clethodim and its degradation products in soil and aqueous solutions were submitted. The method for aqueous solutions was reviewed in 1994.

The method reported by Ho (1989) describes the determination of clethodim, clethodim sulfoxide, clethodim sulfone, the oxazole sulfoxide and oxazole sulfone in soil. In brief, the analytical procedure involves extraction of soil with MeOH/H₂O, partitioning into hexane and CH₂Cl₂ and derivatization with CH₂N₂. After methylation the extract is washed with base, cleaned up on a silica column and analysed by HPLC with a UV detector at 254 nm. A C-18 column is used for clethodim and a C-4 column for the metabolites. The limit of detection for all the compounds is reported as 0.01 mg/kg.

The determination of clethodim and clethodim sulfoxide in aqueous solutions was described by Mitten (1990a,b). Samples are extracted with CH₂Cl₂, the solvent is evaporated and the remaining residue is dissolved in CH₃CN containing 2% v/v acetic acid. Clethodim is measured by HPLC with a UV detector at 247 nm. The limit of detection for clethodim and clethodim sulfoxide is reported as 0.01 mg/kg. The methods were reviewed in 1994 (referenced as Fujie,1990b).

Stability of pesticide residues in stored analytical samples

Data on the storage stability of clethodim and its metabolites in a number of crops and crop fractions were provided. These included alfalfa and its processed commodities, celery, clover, cotton, dry beans, dry onions and garlic, peanuts, soya beans, sunflowers, tomatoes, eggs, hen and cattle tissues, and milk.

The storage stability of clethodim, determined as the sum of DME and DME-OH, was investigated for up to 16 months in forage and 14 months in hay. The recoveries at each sampling are shown below.

Sample	Storage period, months	Recovery, %
Forage	15	69, 85, 92, 93
	16	75, 93

Sample	Storage period, months	Recovery, %
Hay	6.5	90, 141
	10.1	84, 109
	12.4	103, 136
	14.4	87, 118

The storage stability of clethodim residues in celery was reported by Lai (1996b) in connection with trials reported in Table 32 in the 1997 monograph. Samples of celery were fortified with clethodim, clethodim imine sulfone and 5-OH-clethodim sulfone at 2 mg/kg and stored as macerates for up to 739 days at -15°C to -25°C. The results are shown in Table 11. Analysis was by the revised non-specific enforcement method RM-26B-3 (Lai, 1994a); residues of clethodim and clethodim imine sulfone were determined as DME and residues of 5-OH-clethodim sulfone were determined as DME-OH.

Recoveries of clethodim and 5-OH-clethodim sulfone from celery fortified at 0.2, 0.5, 1.0, 2.0 and 5 mg/kg were acceptable, in the range 77-99% for clethodim and 62-107% for 5-OH-clethodim sulfone.

Table 10. Stability of clethodim and its metabolites in fortified celery macerates during frozen storage (Lai, 1996b).

Compounds added	Fortification level, mg/kg	Storage period, days	Recovery, %
Clethodim + clethodim imine sulfone	2 + 2	686	75, 77.0
		690	77, 79
		730	73, 67
		739	70, 74
5-OH-clethodim sulfone	2	686	26, 26
		690	40, 42
		730	54, 56
		739	55, 56

Recoveries of clethodim and clethodim imine sulfone from freshly fortified control samples of celery were unacceptably low (shaded areas in Table 10): 47.2 and 57.4% from the controls for 686 and 690 days storage and 30 and 39% from those for 730 days. The recovery of 5-OH-clethodim sulfone from freshly fortified samples was also low at 30, 47 and 57% for 686, 690 and 730-day controls. Only two recoveries of 88.2% for clethodim and 87.8% for 5-OH-clethodim sulfone can be considered within acceptable limits in freshly fortified samples. These were reference samples for the macerates stored for 739 days.

In a validation of a residue trial on clover (Lai, 1995/1996) macerated control samples were stored for 289-309 days at -15°C to -25°C after fortification with clethodim sulfoxide and 5-OH-clethodim sulfone. The results are shown in Table 11.

Table 11. Stability of clethodim metabolites in frozen fortified macerates of clover (Lai, 1995/1996).

Sample	Recovery, %		
	Storage period, days	Clethodim sulfoxide	5-OH-clethodim sulfone
Clover forage	289	84, 92	78, 87 ¹
	309	70, 80	71, 59
Clover hay	297	84, 93	77, 86

¹ A fresh control sample was not fortified with 5-OH-clethodim sulfone.

Recoveries from freshly fortified samples were 63-112% of clethodim and 56-123% of 5-OH-clethodim sulfone 56-123% from forage, and 84-105% of clethodim and 62-89% of 5-OH-clethodim sulfone from hay.

Since the samples in the residue trial (1997 monograph, Table 36) were analysed after 250-254 days, the results show that the residues would have remained stable during the period between sampling and analysis.

The stability of incurred clethodim residues in cotton seed was determined by Lai (1988c). Treated samples were analysed within two months of harvest and fuzzy seed macerates were analysed 55, 110 and 172 days after storage at -20°C. The recoveries are shown in Table 12.

Table 12. Stability of incurred residues in cotton seed stored at -20°C (Lai, 1988c).

Storage period, days	Initial residues, mg/kg	Recovery, %
55	0.44	110, 116
	1.37	95
110	0.33	83, 87
	1.15	80
172	0.44, 0.5	116, 128
	1.33	92

Total clethodim residues were quantified as the sum of DME and DME-OH by Method RM-26A-1. Recoveries from macerates freshly fortified at 0.5 mg/kg with clethodim and 5-OH-clethodim sulfone were 85-96% and 88-129% respectively.

Untreated dry beans, vines and hay from residue trials (Lai, 1994c) were fortified with clethodim and 5-hydroxy-clethodim sulfone, stored at -20°C, and periodically re-analysed. The results are shown in Table 13.

Table 13. Stability of residues in fortified dry beans, vines and hay stored at -20°C.

Sample	Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
		CS	5-OH CSO ₂	DME	DME-OH
Beans	0	89	106		
	135	73, 85	80, 89	102, 103	94, 114
	643	84	80	104, 119	81, 114
Vines, dry	0	79	81		
	126	83	104	83, 113	88, 106
	618	93	87	89, 95	94, 106
	637	85	81	156	97
	640	93	87	117	91
Hay	0	85	86		
	101	56	80	76, 78	86, 86
	430	76	89	99, 115	94, 110

CS: clethodim

5-OH CSO₂: 5-OH-clethodim sulfone

Recoveries of DME and DME-OH after storage are within acceptable limits and comparable to recoveries from freshly fortified samples analysed concurrently by Methods RM-26B-2 and RM-26B-3.

The storage stability in onions was investigated by Lai (1993). Untreated onion macerates were fortified with 0.5 mg/kg clethodim and 0.5 mg/kg 5-OH-clethodim sulfone, stored at -20°C, and analysed after 3, 6.6, 9.3 and 12.6 months of storage by the enforcement method RM-26B-1.

Table 14. Stability of clethodim and hydroxy-clethodim sulfone in fortified macerates of onions stored at -20°C.

Storage period, months	% recovery of clethodim	% recovery of sulfone
0	102, 110	108, 112
3	88, 90	98, 100
6.6	78, 82	94, 96
9.3	66, 80	82, 92
12.6	74, 80	92, 100

Recoveries from freshly fortified samples were 77-123% for clethodim and 89-112% for the sulfone. The results suggest a loss or degradation of clethodim of about 25% during the period of storage.

In connection with a processing study (Lai, 1994b), untreated macerates of peanut hay, vines and hulls were fortified with 0.5 mg/kg clethodim and 0.5 mg/kg 5-OH-clethodim sulfone and stored at -20°C for up to 390 days. Meal, presscake, crude oil, refined oil and soapstock were produced from field-treated nuts, and both fortified and treated samples were analysed at intervals after storage. Hydroxy-clethodim sulfoxide or sulfone residues were not initially present in peanut oil, so a laboratory-fortified sample was stored and analysed concurrently with the sample from treated nuts. The results are shown in Table 15.

Table 15. Stability of clethodim residues in macerates of peanuts and their processed commodities stored at -20°C .

Sample	Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
		CS	5-OH CSO ₂	DME	DME-OH
Kernels*	0	90	92		
	149	109	104	82, 85	147, 185
	255	120	95	129, 130	293, 300
	395	94	112	97, 113	244, 247
Hulls	0	94, 96	90, 98		
	104	107	92	66, 82	66, 92
	182	81	82	92, 104	70, 84
	282	72	79	82, 86	84, 86
Vines	0	106, 108	82, 86		
	107	115	95	94, 100	74, 80
	185	77	109	100, 102	82, 90
	277	95	114	94, 94	99, 99
Hay	0	105, 109	108, 111		
	104	**	107	98, 102	86, 92
	188	84	76	92, 102	80, 88
	286	93	102	90, 96	98, 104
Meal	0	113	115		
	448	94	79	90	113
Soapstock	0	67	91		
	429	76	99	69	146
Crude oil	0	98	112		
	433	74	64	76	
	530	65	97	76	
Refined oil	0	80	94		
	433	66	65	78, 81	
	530	65	97	84	
Laboratory sample	0		96, 100		
	99		97		98, 102

* Recoveries were reported as corrected.
CS clethodim

** Fortified with wrong concentration.
5-OH CSO₂ 5-OH-clethodim sulfone

The apparently higher recoveries from kernels after storage are explained as being due to the low initial levels of DME-OH.

Macerates of sugar beet roots and tops were fortified with clethodim and 5-OH-clethodim sulfone at 0.5 mg/kg and stored at -20°C for up to 11 months (Lai, 1991). Freshly fortified samples were analysed concurrently at each sampling. The results are shown in Table 16.

Table 16. Stability of clethodim and hydroxy-clethodim sulfone in fortified macerates of sugar beet tops and roots.

Sample	Storage period, days	% recovery of clethodim	% recovery of 5-hydroxy sulfone
Roots	0	103	114
	91	96, 98	104, 112
	200	74, 82	70, 92
	280	82, 92	90, 106
	346	76, 100	100, 100
Tops	0	80, 106	78, 98
	109	85, 88	98, 100
	189	66, 72	68, 76
	273	68, 70	76, 86

The residues in sugar beet roots were stable for 11 months but there was a slow loss from the tops of about 30% in 9 months. In the residue trial the samples of tops and roots were analysed within 9 and 10 months respectively. Recoveries from the freshly fortified samples were 73-106% for clethodim and 79-114% for the sulfone. The methods of analysis were RM-26A-1 and RM-26B-1.

Treated sunflower seeds were re-analysed after storage at -20°C for 97 days (Lai, 1996c); the results are shown in Table 17.

Table 17. Stability of incurred residues in sunflowers stored at -20°C.

Storage period, days	% recovery from fresh fortification		% recovery in stored sample	
	DME	DME-OH	DME	DME-OH
0	88	79		
97	104	74	93, 110	92, 81

The residues in the sunflower seeds were stable after storage for 97 days. In the residues trials the samples were extracted within 57 days after harvest.

Processed tomato commodities were either re-analysed after a period of storage at -20°C or fortified in the laboratory with clethodim and 5-OH-clethodim sulfone and re-analysed at intervals (Lai, 1995b). Freshly fortified samples were analysed concurrently with the stored samples. The results are shown in Tables 18 and 19.

Table 18. Stability of incurred residues in dry tomato pomace stored at -20°C.

Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
	DME	DME-OH	DME	DME-OH
0	85	108		
86	81	86	78, 78	158, 158
126	95	96	139	151
345	95	96	148	139

Table 19. Stability of clethodim and hydroxy-clethodim sulfone in fortified macerates of processed tomato commodities stored at -20°C.

Sample	Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
		CS	5-OH CSO ₂	CS	5-OH CSO ₂
Juice	0	90, 92	90, 92		
	153	84	86	52, 68	50, 58
	266	87	93	70, 72	66, 70
Paste	0	73, 74	70, 77		
	162	88	101	60, 66	78, 78
	274	75	87	64, 68	74, 78
Wet pomace	0	82, 96	93, 96		
	176	86	97	84, 86	80, 82
	266	83	92	84, 90	72, 78

There was a discernible loss of residues in tomato paste and juice after storage for 162 and 153 days. This loss was not apparent in the pomace. In the residue trials, samples of processed commodities were stored between 55 and 83 days before analysis by Method RM-26B-3.

Chicken tissues and eggs were fortified with clethodim, 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide at 1 and 2 mg/kg and stored up to 8 weeks at -13° to -29°C (Lear, 1989). The data were reviewed in the 1994 monograph and are shown in Table 20.

Table 20. Stability of clethodim and metabolites in fortified hen tissues and eggs at -13° to -29°C (Lear, 1989).

Sample	Storage period, weeks	Fortification level, mg/kg	Recovery, %		
			<i>S</i> -Me-CSO	CS	5-OH-CSO ₂
Eggs	0	1	77, 65	83, 69	90, 75
	4	1	100, 120, 110	113, 121, 103	94, 102, 91
	8	2	110, 111, 112	112, 111, 109	107, 99, 104
Fat	0	1	69, 76, 71	68, 83, 76	69, 88, 80
	3	1	98, 104, 95	100, 105, 96	105, 113, 101
	6	1	91, 94, 98	99, 103, 103	90, 96, 94
Gizzard	0	1	70, 76, 77	76, 80, 84	82, 84, 85
	3	1	91, 97, 101	88, 95, 97	92, 94, 98
	6	1	100, 104, 94	102, 106, 96	86, 89, 84
Liver	0	1	76, 77, 78	84, 84, 82	84, 83, 84
	3	1	99, 103, 99	96, 99, 99	100, 102, 96
	6	1	100, 95, 87	102, 96, 85	91, 85, 83
Muscle	0	1	67, 63, 70	71, 68, 75	72, 70, 77
	3	1	99, 106, 100	99, 105, 98	99, 105, 100
	6	1	101, 99, 112	104, 105, 116	88, 74, 101

S-Me-CSO: *S*-methyl clethodim sulfoxide

CS: clethodim

5-OH-CSO₂: 5-OH-clethodim sulfone

The three compounds were stable in chicken tissues and eggs after 6 or 8 weeks storage. Method RM-26A was employed to determine DME and DME-OH.

Samples of cattle tissues and milk from a feeding study were fortified with clethodim, 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide and stored at -20°C for up to 5 months (Weissenburger, 1989). Milk and tissue samples were fortified at 0.05 and 0.25 mg/kg respectively with each compound. Concurrent recoveries from freshly fortified samples were determined at each sampling. The results are shown in Table 21.

Table 21. Stability of clethodim and metabolites in fortified cattle tissues and milk at -20°C (Weissenburger, 1989).

Sample	Storage period, months	Fortification level, mg/kg	Recovery, % ¹		
			S-Me-CSO	CS	5-OH-CSO ₂
Milk	0	0.05	98, 92	94, 91	117, 109
	1	0.05	88 (83, 91)	80 (78, 84)	102 (99, 107)
	3	0.05	79, 82 (46, 46)	73, 75 (41, 39)	86, 97 (44, 44)
	3.5	0.05	84, 89 (82, 90)	79, 83 (86, 89)	90, 95 (101, 103)
	4	0.05	78, 92 (76, 80)	74, 80 (72, 76)	91, 107 (94, 98)
	5	0.05	72, 114 (65, 87)	70, 94 (64, 78)	80, 116 (75, 92)
Fat	0	0.25	83, 85	79, 79	99, 107
	1	0.25	93, 96 (91, 91)	82, 83 (89, 101)	101, 106 (101, 118)
	2	0.25	78, 82 (82, 92)	71, 82 (87, 95)	82, 82 (88, 94)
	3	0.25	75, 82 (83, 91)	75, 77 (80, 89)	83, 88 (83, 90)
	4	0.25	89, 92 (77, 86)	80, 83 (62, 79)	98, 100 (87, 96)
	5	0.25	85, 97 (84)	78, 90 (78)	89, 104 (83)
Kidney	0	0.25	77, 90	77, 88	94, 113
	1	0.25	82, 85 (79, 80)	80, 84 (79, 85)	98, 98 (101, 109)
	2	0.25	67, 74 (80, 87)	69, 71 (80, 87)	81, 81 (87, 98)
	3	0.25	83, 87 (74, 84)	78, 81 (74, 78)	85, 85 (71, 74)
	4	0.25	79, 84 (76, 81)	79, 84 (75, 79)	95, 95 (82, 95)
	5	0.25	86, 93 (81, 94)	80, 82 (77, 88)	86, 91 (77, 86)
Liver	0	0.25	78, 78	70, 70	72, 79
	1	0.25	70, 70 (74, 79)	69, 71 (78, 79)	80, 97 (102, 102)
	2	0.25	75, 81 (80, 81)	65, 71 (78, 78)	79, 84 (79, 84)
	3	0.25	77, 87 (86, 89)	68, 76 (79, 82)	91, 103 (83, 83)
	4	0.25	75, 95 (75, 82)	75, 90 (73, 80)	93, 113 (84, 97)
	5	0.25	74, 87 (79, 98)	72, 82 (81, 98)	85, 89 (81, 101)
Muscle	0	0.25	88, 88	80, 80	91, 98
	1	0.25	89, 90 (90, 93)	73, 76 (83, 88)	94, 100 (88, 94)
	2	0.25	86, 92 (80, 94)	76, 80 (71, 92)	92, 97 (87, 97)
	3	0.25	86, 106 (74, 84)	74, 94 (72, 77)	103, 111 (74, 78)
	4	0.25	90, 92 (86, 89)	78, 79 (81, 83)	103, 110 (99, 103)
	5	0.25	95, 99 (86, 95)	76 (82, 76)	98, 98 (91, 94)

S-Me-CSO: S-methyl-clethodim sulfoxide

CS: clethodim

5-OH-CSO₂: 5-OH-clethodim sulfone¹Values in parentheses are concurrent recoveries from freshly fortified samples

There was no discernible degradation of clethodim or the metabolites in the tissues or milk during the study.

Definition of the residue

The current definition is “sum of clethodim and its metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulfoxides and sulfones, expressed as clethodim”. Metabolism studies on carrots, cotton, soya beans, hens and a lactating goat confirm that the current definition is appropriate.

USE PATTERN

Registered uses on potatoes, cucumbers, dry beans, peppers and sunflowers are shown in Table 23. Use patterns on numerous crops were tabulated in the 1994 and 1997 monographs and are not repeated here. GAP for potatoes was reported by the Canadian government.

Table 22. Registered use patterns of clethodim on cucumbers, dry beans, peppers, potatoes and sunflowers.

Crop	Country	Form.	Application			PHI, days
			Method	Rate, kg ai/ha	No.	

Crop	Country	Form.	Application			PHI, days
			Method	Rate, kg ai/ha	No.	
Cucumbers	Chile	240 g/L	Spray	0.096-0.48	2	35
	Ecuador	240 EC	Spray	0.06-0.12		
	New Zealand	240 EC	Spray	0.06-0.72		
	Paraguay	2 EC	Spray	0.096-0.24		
	Poland	240 EC	Spray	0.096-0.24		
	USA ¹	2 EC	Spray	0.11-0.28		
	Venezuela	2 EC	Spray	0.12-0.24		
Dry beans	Belize	24 EC		0.072-0.24	7-10	
	Bolivia	240 EC		0.072-0.24		
	Brazil	240 EC		0.084-0.108		
	Bulgaria	240 EC		0.096-0.192		
	Costa Rica	24 EC		0.072-0.24		
	Dominican Republic	24 EC		0.06-0.12		
	El Salvador	24 EC		0.072-0.24		
	Guatemala	24 EC		0.072-0.24		
	Nicaragua	24 EC		0.072-0.24		
	Peru	240 EC		0.12-0.18		
	Turkey	240 EC		0.096-0.192		
	Uruguay ²	240 EC		0.084-0.168		
	USA	2 EC		0.11-0.28		
Peppers	Chile	240 g/L		0.096-0.48	20	
	Ecuador	240 EC		0.06-0.12		
	New Zealand	240 EC		0.06-0.72		
	Paraguay	2 EC		0.096-0.24		
	USA ¹	2 EC		0.11-0.28		
	Venezuela	2 EC		0.12-0.24		
Potatoes	Canada	240 EC		0.09	60	
Sunflowers	Argentina	240 EC		0.096-0.336	100	
	Bolivia	240 EC		0.072-0.24	65	
	Bulgaria	240 EC		0.096-0.192		
	Canada	240 EC		0.045-0.09	2	72
	Croatia	240 EC		0.096-0.24		
	France	240 EC		0.18-0.48		100
	Hungary	240 EC		0.072-0.288		
	Israel	240 EC		0.084-0.12		
	Paraguay	2 EC		0.096-0.24		
	Spain	240 EC		0.096-0.192	2	
	Ukraine	12.5 EC		0.048-0.216	1	
	Uruguay ²	240 EC		0.084-0.168	1	65
	USA ¹	2 EC		0.11-0.28		70
	Venezuela	2 EC		0.12-0.24		

¹ Pending

² Proposed label

RESIDUES RESULTING FROM SUPERVISED TRIALS

Data were provided from supervised trials on potatoes, cucumbers, beans, peppers (sweet and hot) and sunflowers. Some of the data were reviewed in 1994 and/or 1997 and are repeated here for convenience. The trials are reviewed in the crop sequence of the *Codex Alimentarius Classification of Foods and Animal Feeds*. GAP for each crop is tabulated with the residue data for ease of comparison.

Residues, application rates and spray concentrations have been rounded to 2 significant figures, or for residues near the limit of detection to 1 significant figure. Although the trials included control

plots, no residues in the untreated samples are reported unless they exceeded the limit of determination. Residues from trials according to GAP are underlined; those used to estimate STMRs are double-underlined. All residues, unless otherwise stated, are defined as *sum of clethodim and metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulfones, expressed as clethodim*. The analytical method used is included in the footnotes to each Table. The limit of determination is indicated at the bottom of each Table or in the text if reference is made to the validation of a specific method.

Potatoes. The results of supervised residue trials in Canada were reviewed in 1994 and 1997. Select 240 EC was applied at 15 cm height (flowering to early petal fall) to potato crops at the maximum label rate (0.09 kg ai/ha; 1% v/v adjuvant) and twice that rate. Samples were collected 45 and 60 days after treatment; the registered PHI is 60 days. The trials were conducted in 6 States in 12 representative growing areas of Canada. The results are shown in Table 23.

Table 23. Residues in potatoes from supervised field trials in Canada. Tubers analysed. Ref. 92-001.D.

Location year, (variety)	Application			PHI, days	Residues, mg/kg		Total, mg/kg
	Form	kg ai/ha	No.		DME	DME-OH	
Ontario, 1990, (Superior)	240 EC	0.09	1	46	<0.05	<0.05	<u><0.1</u>
Ontario, 1990 (Superior)	240 EC	0.09	1	46	<0.05	<0.05	<0.1
Ontario, 1990 (Kennebec)	240 EC	0.09	1	46	0.057	0.053	0.11
Nova Scotia, 1990, (Kennebec)	240EC	0.09	1	45	0.070	0.071	<u>0.141</u>
Ontario, 1990, (Superior)	240 EC	0.09	1	61	<0.05	<0.05	<u><0.1</u>
Ontario, 1990, (Superior)	240 EC	0.09	1	61	<0.05	<0.05	<0.1
Ontario, 1990, (Kennebec)	240 EC	0.09	1	60	0.066	0.071	0.137
Ontario, 1990, (Superior)	240 EC	0.18	1	46	0.059	0.062	0.121
Ontario, 1990, (Superior)	240 EC	0.18	1	46	<0.05	<0.05	<u><0.1</u>
Ontario, 1990, (Kennebec)	240 EC	0.18	1	46	<0.05	<0.05	<0.1
Ontario, 1990, (Superior)	240 EC	0.18	1	46	<0.05	<0.05	<0.1
Ontario, 1990, (Kennebec)	240 EC	0.18	1	46	0.127	0.126	0.253
Nova Scotia, 1990, (Kennebec)	240 EC	0.18	1	45	0.097	0.107	0.204
Ontario, 1991, (Sebago)	240 EC	0.09	1	45	0.109	0.095	0.204
Ontario, 1991, (Red Chieftain))	240 EC	0.09	1	45	0.073	0.101	0.174
PEI, 1991, (Russet Burbank)	240 EC	0.09	1	44	0.068	0.060	0.128
Quebec, 1991, (Kennebec)	240 EC	0.09	1	46	<0.05	<0.05	<0.1
Quebec, 1991, (Superior)	240 EC	0.09	1	46	<0.05	<0.05	<u><0.1</u>
Manitoba, 1991, (Norland)	240 EC	0.09	1	45	<0.05	<0.05	<0.1
Saskatchewan 1991, Norland)	240 EC	0.09	1	45	0.119	0.125	0.244
Alberta, 1991, (Shepody)	240 EC	0.09	1	44	0.242	0.221	<u>0.463</u>
Ontario, 1991,	240 EC	0.09	1	60	0.164	0.162	<u>0.326</u>
					0.1	0.108	0.208
					0.160	0.114	0.274
					0.199	0.149	<u>0.348</u>
					<0.05	<0.05	<u><0.1</u>
					<0.05	<0.05	<0.1
					<0.05	<0.05	<u><0.1</u>
					<0.05	<0.05	<0.1
					<0.05	<0.05	<u><0.1</u>

Location year, (variety)	Application			PHI, days	Residues, mg/kg		Total, mg/kg
	Form	kg ai/ha	No.		DME	DME-OH	
(Sebago)							
Ontario, 1991, (Red Chieftain)	240 EC	0.09	1	60	<0.05	<0.05	<0.1
PEI, 1991, (Russet Burbank)	240 EC	0.09	1	59	<0.05	<0.05	<0.1
Quebec, 1991, (Kennebec)	240EC	0.09	1	60	0.106	0.126	0.232
Quebec, 1991, (Superior)	240 EC	0.09	1	60	0.087	0.098	0.185
Manitoba, 1991, (Norland)	240 EC	0.09	1	60	0.127	0.127	0.254
Saskatchewan, 1991, (Norland)	240 EC	0.09	1	59	0.173	0.166	0.339
Alberta, 1991, (Shepody)	240 EC	0.09	1	60	0.109	0.081	0.190
Ontario, 1991, (Sebago)	240 EC	0.18	1	45	0.097	0.088	0.185
Ontario, 1991, (Red Chieftain)	240 EC	0.18	1	45	<0.05	<0.05	<0.1
PEI, 1991, (Russet Burbank)	240 EC	0.18	1	44	<0.05	<0.05	<0.1
Quebec, 1991, (Kennebec)	240 EC	0.18	1	46	0.069	0.062	0.131
Quebec, 1991, (Superior)	240 EC	0.18	1	46	0.054	0.051	0.105
Manitoba, 1991, (Norland)	240 EC	0.18	1	45	<0.05	<0.05	<0.1
Saskatchewan, 1991, (Norland)	240 EC	0.18	1	45	<0.05	0.05	<0.1
Alberta, 1991, (Shepody)	240 EC	0.18	1	44	0.065	0.073	0.138
(Shepody)					0.083	0.063	0.152
Ontario, 1991, (Sebago)	240 EC	0.18	1	60	<0.05	0.057	<0.17
Ontario, 1991, (Red Chieftain)	240 EC	0.18	1	60	<0.05	<0.05	<0.1
PEI, 1991, (Russet Burbank)	240 EC	0.18	1	59	<0.05	<0.05	<0.1
Quebec, 1991, (Kennebec)	240 EC	0.18	1	60	<0.05	0.05	<0.1
Quebec, 1991, (Superior)	240 EC	0.18	1	60	0.272	0.296	0.568
Manitoba, 1991, (Norland)	240EC	0.18	1	60	0.251	0.269	0.520
Saskatchewan, 1991, (Norland)	240EC	0.18	1	59	0.325	0.321	0.646
Alberta, 1991, (Shepody)	240 EC	0.18	1	60	0.396	0.349	0.745
GAP					0.163	0.110	0.273
Canada	240 EC	0.09	1	60	0.200	0.132	0.332
					<0.05	<0.05	<0.1
					<0.05	0.05	<0.1
					<0.05	<0.05	<0.1
					<0.05	0.05	<0.1

The common moiety method RM-26A-1 was used and recoveries of clethodim sulfoxide and 5-OH-clethodim sulfone were determined at 0.05, 0.1, 0.5 and 1 mg/kg. The range of recoveries at each concentration is shown below. The limit of detection of DME and DME-OH was 0.05 mg/kg.

Fortification level, mg/kg	Recovery, %	
	CSO	5-OH CSO ₂
0.05	66-105 (n = 11)	69-113 (n = 11)
0.1	66-86 (n = 3)	63-87 (n = 3)
0.5	61-77 (n = 4)	60-75 (n = 4)
1.0	66, 69	68, 69

Total clethodim residues ranged from <0.1 to 0.46 mg/kg in trials which were in accord with the registered use pattern.

Cucumbers. Supervised trials on cucumbers were conducted in Poland and the USA. The data were reviewed in 1997. The US data were generated as part of an IR-4 program[‡] and two sprays of clethodim were applied with a 14-day interval. In the Polish trial clethodim was applied at the 4-6 leaf stage of growth.

Table 24. Residues in cucumbers from trials in the USA and Poland.

Country, year, (variety)	Application			PHI, days	Residues, mg/kg		Reference
	Form.	kg ai/ha	No.		DME	DME-OH	
USA, (Florida), 1994		0.28	2	14	<0.14	<0.13	5219.94-FL47
USA, (New York), 1994		0.28	2	14	<0.14	<0.13	5219.94-NY10
USA, (Michigan), 1994		0.28	2	13	<0.14	<0.13	5219.94-MI15
USA, (Wisconsin), 1994		0.28	2	14	<0.14	<0.13	5219.94-WI13
USA, (Sth Carolina), 1994		0.28	2	13	<0.14	<0.13	5219.94-SC*08
USA, (Texas), 1994		0.28	2	14	<0.14	<0.13	5219.95-TX*21
Poland, 1995	240 EC	0.24 ¹	1	35 38	<0.05, <0.05, <0.05	<0.05, <0.05, <0.05	Report 1995
GAP	240 EC	0.1²	1	35			
Poland		0.24³	1	35			

¹Application at 4 to 6 leaf stage of growth.

²Annual monocotyledonous weeds.

³Couch grass.

Although the US results are listed, registration for the use of clethodim on cucumbers is pending.

Cucumbers were fortified with clethodim sulfoxide and 5-OH-clethodim sulfone at 1.12 and 0.99 mg/kg respectively and stored for 518 and 526 days at -12 to -22°C. Residues were determined as DME and DME-OH and expressed as clethodim. The recoveries are shown below.

Storage period, days	Recovery, %	
	Clethodim sulfoxide	5-OH clethodim sulfone
518	75, 91	89, 101
526	89, 93	96, 98

Recoveries in the US validation of the method were determined by fortification with clethodim sulfoxide and 5-OH-clethodim sulfone at 0.11 and 0.10 mg/kg respectively. Recoveries were 95-117% for clethodim sulfoxide and 87-94% for 5-OH-clethodim sulfone determined as DME and DME-OH.

Recoveries from cucumbers in the US trials were checked by fortification with clethodim sulfoxide at 0.116 and 1.16 mg/kg and 5-OH-clethodim sulfone at 0.09 and 0.92 mg/kg. Recoveries were 88-118% for clethodim sulfoxide and 89-116% for 5-OH-clethodim sulfone. In the Polish trials, the limit of detection was reported as 0.05 mg/kg, with recoveries at 0.1 and 1 mg/kg of 76-88% and 84-92% respectively.

Dry beans. The results of trials in Brazil and the USA are presented in Table 26. The Brazilian trials were reviewed in 1994 and 1997 and are tabulated for comparison with the new data. In the US trials two applications were made at 13-15 day intervals at rates of 0.28 or 0.29 kg ai/ha. Samples of dry

[‡] IR-4 = Interregional Research Project No. 4, which is the USDA Minor Use Program.

beans, vines and hay were collected at intervals after treatment. Recoveries in the US trials are reported in Table 13 as analyses at day 0.

Table 25. Residues in dry beans from trials in Brazil and the USA. The US trials were by Lai (1994c).

Country, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference	
	Form.	kg ai/ha	No.					
Brazil, 1989/1990	240 EC	0.108	2	45	bean	<0.5	61479 A/79119 ¹	
	240 EC	0.216	2	65	bean	<0.5		
Brazil, 1990	240 EC	0.084	1	25	bean	0.37	Chevron Brazil ²	
		0.108	1	45	bean	0.06		
		0.168		25	bean	<0.05		
				45	bean	<0.05		
		0.216		65	bean	<0.05		
				85	bean	<0.05		
		0.216		25	bean	0.48		
				45	bean	0.07		
		0.216		65	bean	<0.05		
				85	bean	<0.05		
Country, year (variety)	Application			PHI, days	Sample	Residues, mg/kg		Total, mg/kg
	Form	kg ai/ha	No.			DME	DME-OH	
USA (Michigan), 1993, (Sierra)	2 EC	0.28-0.29	2	30 + 5*	bean	0.76	0.22	0.98
					hay, dry	0.74	0.20	0.94
						0.81	0.49	1.3
					15	0.82	0.46	1.3
USA (Nth Dakota), 1993 (Pearl Navy)	2 EC	0.28	2	30 + 1*	bean	0.55	0.25	0.80
					hay	0.59	0.22	0.81
						1.8	0.32	2.1
					15	1.9	0.41	2.3
USA (California), 1993, (Henderson Bush Lima)	2 EC	0.28	2	30 + 7*	bean	0.55	0.25	0.80
					hay	0.59	0.22	0.81
						1.8	0.32	2.1
					15	1.9	0.41	2.3
USA (Idaho), 1993, (UI 537 Pink)	2 EC	0.28	2	30 + 15*	bean	0.40	0.24	0.64
					hay	0.39	0.25	0.64
						2.4	0.37	2.8
					15	2.9	0.39	3.3
USA (Michigan), 1992, (Albion)	0.94 EC	0.28	2	30 + 1*	bean	0.47	0.32	0.79
					hay	0.37	0.21	0.58
						0.67	0.59	1.3
					15	0.73	0.65	1.4
USA (Nth Dakota), 1992 (Upland)	0.94 EC	0.28	2	30 + 4*	bean	0.77	0.33	1.1
					hay	0.77	0.33	1.1
						1.2	0.33	1.5
						1.1	0.47	1.6
					hay	1.1	0.46	1.6
					hay	0.72	0.61	1.3

Country, year (variety)	Application			PHI, days	Sample	Residues, mg/kg		Total, mg/kg
	Form	kg ai/ha	No.			DME	DME-OH	
				24	vines, dry	1.1 0.88 1.0	0.91 0.46 0.48	<u>2.0</u> 1.3 <u>1.5</u>
USA (Colorado), 1992, (Pinto)	0.94 EC	0.28	2	30 + 9*	bean	0.69 0.44	0.45 0.28	<u>1.1</u> 0.72
					hay	3.7 2.7	1.8 1.3	<u>5.5</u> 4.0
				15	vines, dry	1.8 1.9	0.31 0.34	2.1 <u>2.2</u>
USA (California), 1992, (Dark Red Kidney)	0.94 EC	0.28	2	30 + 7*	bean	1.1 1.0	0.33 0.21	<u>1.4</u> 1.2
					hay	1.1 1.3	0.14 0.16	1.2 <u>1.5</u>
				30	vines, dry	0.22 0.23	<0.1 <0.1	0.22 <u>0.23</u>
USA (Nebraska), 1992, (Great Northerns Navy)	0.94 EC	0.28	2	30 + 2*	bean	0.79	0.25	1.0
					hay	0.86 1.3 1.5	0.26 0.26 0.28	<u>1.1</u> 1.6 <u>1.8</u>
				15	vines, dry	1.5 1.6	0.26 0.21	<u>1.8</u> 1.8
GAP	240 EC	0.084-		40				
Brazil		0.108						
USA	2 EC	0.105-	1-2	30				
		0.28						

* Drying time after harvest.

¹ Two sprays at the 4-7 leaf stage (10 cm plants) and at flowering (30-40 cm plants); plot size 9 m², soil pH 3.6, C 3.1%, 'argiloso' soil. Limit of detection 0.5 mg/kg; recovery of clethodim 93 and 52%, clethodim sulfoxide 90 and 69%, at 0.5 mg/kg. Method RM-26A.

² Post-emergent application with 0.5% v/v crop oil. Limit of detection 0.05 mg/kg. Recoveries of clethodim, clethodim sulfoxide and 5-OH-clethodim sulfone 110, 75%; 100, 78% and 100, 76% respectively.

Peppers (sweet and hot). Trials in Italy and the USA were reported (Table 27). The Italian trial was reviewed in 1994. Details are given as footnotes to Table 26. In the two US trials, two applications were made at 12- to 18-day intervals.

Table 26. Residues in peppers from trials in Italy and the USA.

Country, year (variety)	Application			PHI, days	DME	DME -OH	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.					
Italy (Latina), 1990, (Heldor)	240 EC	0.24	1	18 28 38			0.08, 0.116 0.03, 0.075 0.041, 0.049	0266-90 ¹
Bell peppers USA (Georgia), 1993	0.94 EC	0.28	2	20	0.11 0.14	<0.1 <0.1	0.11 0.14	Lai, 1995 ² 5226.93-GA802
USA (Texas), 1993	0.94 EC	0.28	2	21	0.17 0.20	0.12 0.14	0.29 0.34	5226.93-TX*02
USA (California), 1994	0.94 EC	0.28	2	NA	0.49 0.43	0.13 0.15	0.62 0.58	5226.94-CA*96
USA (Florida), 1993	0.94 EC	0.28	2	21	0.36 0.34	0.18 0.17	0.54 0.51	5226.93-FL17

Country, year (variety)	Application			PHI, days	DME	DME -OH	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.					
USA (Nth Carolina), 1993	0.94 EC	0.28	2	19	0.32 0.27	0.13 0.11	0.45 0.38	5226.93-NC01
USA (New York), 1993	0.94 EC	0.28	2	19	0.60 0.46	0.29 0.22	0.89 0.68	5226.93-NY01
Non-bell peppers USA (Georgia), 1993	0.94 EC	0.28	2	20	0.12 0.12	<0.1 <0.1	0.12 0.12	Lai, 1995 5335.93-GA*03
USA (Texas), 1993	0.94 EC	0.28	2	21	0.2 0.21	0.18 0.18	0.40 0.39	5355.93-TX*0.3
USA (California), 1993	0.94 EC	0.28	2	NA	0.62 0.56	0.29 0.26	0.91 0.82	5355.94-CA*95
USA (Florida), 1993	0.94 EC	0.28	2	21	0.25 0.28	0.18 0.20	0.43 0.48	5355.93-FL18
USA (New Jersey), 1993	0.94 EC	0.28	2	22	0.60 0.59	0.32 0.28	0.92 0.87	5355.93-NJ02
GAP USA (pending)		0.11- 0.28	1-2	20				

¹ Limit of detection 0.03 mg/kg. Residues determined as sum of DME and DME-OH, expressed as clethodim. Recoveries at 0.03 mg/kg 94, 94, 94%.

²Method RM-26B-3. Limit of detection 0.1 mg/kg. Recoveries at 0.1, 0.2 and 0.5 mg/kg: clethodim sulfoxide (as DME) 76-131% (n = 15), average 100%; 5-OH-clethodim sulfone (as DME-OH) 74-145% (n = 15), average 101%.

³Method RM-26-B-3. Limit of detection 0.1 mg/kg; recoveries of clethodim sulfoxide (as DME) at 0.2, 0.5 and 1mg/kg 69-102% (n = 9), average 92%; 5-OH-clethodim sulfone (as DME-OH) at 0.2, 0.5, 0.6 and 1.3 mg/kg 69-129% (n = 9), average 89%.

Data from the US trials are listed although registration is only pending.

Sunflowers. The trials were in Argentina, Canada, France, Italy and the USA. In the USA, Select Herbicide was applied twice at a rate of 0.28 kg ai/ha with a 14-day re-treatment interval, the first application 30-40 days after emergence and the second about 70 days before harvest. The samples collected were mature clean seed in the hull, dried to less than 14% moisture. In one trial in North Dakota, Select was applied at 5 times the pending maximum label rate and the seeds were processed into oil and meal; the results are shown in Table 45.

Data from one French trial were in summary form with no field details (Tomen, 1988). In two other French trials (Tomen France, 1997, 1998) Select 240 EC was applied at the maximum label rate of 0.5 kg ai/ha at the 6-8 leaf stage or before flowering. Only total residues were reported in two of the trials.

In the Canadian trials, clethodim was applied at 1 and 2 times the maximum label rate and the crops were harvested 72-96 days after treatment.

Table 27. Residues in sunflower seeds and products from supervised trials in Argentina, Canada, France, Italy and the USA.

Country, year, (variety)	Application			PHI, days	Sample	DME	DME- OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
Argentina, (Salto), 1987,	2 EC	0.12	1	108	seeds	0.06	<0.05	<u>0.06</u>	T7009 ¹
		0.24	1	108	seeds	<0.05	<0.05	<0.05	
Argentina, (Salto), 1986	2 EC	0.12	1	102	seeds	<0.05	<0.05	<0.05	T7010 ²
		0.24	1	102	seeds	0.085	<0.05	<u>0.085</u>	
Argentina, (Buenos Aires), 1987	2 EC	0.12	1	99	seeds	<0.05	<0.05	<0.05	T7011 ³
		0.24	1	99	seeds	0.16	<0.05	<u>0.16</u>	
					hulls	0.10	0.09	0.19	

Country, year, (variety)	Application			PHI, days	Sample	DME	DME- OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
					extracted presscake	0.17	0.17	0.34	
					expelled presscake	0.15	0.15	0.30	
					refined oil	<0.05	<0.05	<0.05	
					crude oil	<0.05	<0.05	<0.05	
					extracted crude oil	<0.05	<0.05	<0.05	
					processed seed	0.08	0.09	0.17	
Argentina, (Santa Fe), 1987	2 EC	0.12	1	106	seeds	<0.05	<0.05	<0.05	T7012 ⁴
		0.24	1	106	seeds	0.065	<0.05	0.065	
USA, (Illinois), 1995 (Pioneer)	0.94 EC	0.28	2	56	seeds	0.35	0.39	0.74	V-11186A ⁵
						0.33	0.40	0.73	
USA, (Minnesota), 1995 (Sigco 458)	0.94 EC	0.27- 0.28	2	66	seeds	2.8	1.2	4.0	V-11186-B
						3.1	1.3	4.4	
USA, (Nebraska), 1995 (974 lg)	0.94 EC	0.28	2	69	seeds	0.31	0.39	0.70	V-11186-C
						0.37	0.48	0.85	
USA, (Wyoming), 1995 (Mycogen 452)	0.94 EC	0.27- 0.28	2	70	seeds	0.63	0.46	1.1	V-11186-D
						0.74	0.68	1.4	
USA, (Nebraska), 1995 (s 3446)	0.94 EC	0.28	2	70	seeds	0.68	0.43	1.1	V-11186-E
						0.68	0.43	1.1	
USA, (Texas), 1995 (Mycogen 675)	0.94 EC	0.28	2	70	seeds	0.38	0.24	0.62	V-11186-F
						0.38	0.26	0.64	
USA, (Missouri), 1995 (Sunbred 256)	0.94 EC	0.27- 0.28	2	69	seeds	0.34	0.18	0.52	V-11186-G
		0.54- 0.57	2	69	seeds	0.31	0.15	0.46	
						0.55	0.25	0.80	
						0.74	0.26	1.0	
USA, (Nth Dakota), 1995 (Sicgo 458)	0.94 EC	0.27- 0.28	2	72	seeds	2.5	1.2	3.7	V-11186-H
		1.33- 1.45 ⁶	2	72	seeds	2.5	1.3	3.8	
						12	5.9	18	
						14	7.8	22	
Canada, (Saskatoon), 1994, (Aurora)	240 EC	0.045	1	72	seeds	0.026	0.025	0.051	Cosgrove
		0.09	1	72		<0.02	<0.02	<0.04	96-035 ⁷
		0.180	1	72		0.80	0.12	0.2	
						0.067	0.063	0.13	
						0.08	0.10	0.18	
						0.079	0.085	0.16	
		0.045	1	86	seeds	<0.02	<0.02	<0.04	
		0.09	1	86		<0.02	<0.02	<0.04	
		0.180	1	86		<0.02	<0.02	<0.04	
		0.09	1	81	seeds	<0.02	0.025	0.045	
						<0.02	<0.02	<0.04	
						0.076	0.060	0.14	
						0.054	0.071	0.13	
		0.18	1	81	seeds	0.16	0.28	0.44	
		0.09	1	96	seeds	0.058	0.061	0.12	
						0.048	0.037	0.085	
		0.18	1	96	seeds	0.11	0.05	0.16	

Country, year, (variety)	Application			PHI, days	Sample	DME	DME- OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
						0.066	0.053	0.12	
Canada, (Manitoba), 1995, (Dahlgren)	240 EC	0.09	1	88	seeds	<0.02	<0.02	<0.04	Cosgrove 96-035 ⁷
		0.18	1	88	seeds	<0.02	<0.02	<0.04	
Canada, (Manitoba), 1995, (Pioneer)	240 EC	0.09	1	94	seeds	<0.02	<0.02	<0.04	
		0.18	1	94	seeds	<0.02	<0.02	<0.04	
Canada, (Saskatoon), 1995, (Sierra)	240 EC	0.09	1	83	seeds	<0.02	<0.02	<0.04	
		0.18	1	83	seeds	<0.02	<0.02	<0.04, <0.04	
France, (Mongauzy), 1987, (Frankasol)		0.18	1	108	seeds	<0.03	<0.03	<0.06	Tomen, 1988, TE 2286 ⁸
France, (Veigne), 1987, (Viki)		0.48	1	111	seeds	<0.03	<0.03	<0.06	TE 2287 ⁹
France, (Esvres), 1987, (Mirasol)		0.48	1	123	seeds	<0.03	<0.03	<0.06	TE 2288 ¹⁰
France, (Vacquiers), 1996, (Albena)	240 EC	0.48	1	100	seeds			<0.03	Tomen France, 1997, BKA/620/9 6 ¹¹
France, (Mas Thibert), 1996, (Marko)	240 EC	0.48	1	101	seeds			<0.03	BKA/620/9 6 ¹²
France, (St Martin de Sanzay), 1997, (Alladin)	240 EC	0.52	1	100	seeds	0.07	0.06	0.13	Tomen France, 1998, F97017R ¹³
	2 EC	0.29	1	100	seeds	0.18	0.15	0.33	
France, (Sarrians), 1997, (Pistol)	240 EC	0.51	1	100	seeds	<0.03	<0.04	<0.07	F97018R ¹⁴
	2 EC	0.31	1	100	seeds	<0.03	<0.04	<0.07	
Italy, (Romauldo), 1989, (Pharaon)	240 EC	0.24	1	74	seeds			<0.03	0292-89 ¹⁵
				92				<0.03	
				110				<0.03	
				110	oil			<0.03	
Italy, (Ravenna), 1991, (Pharron)	240 EC	0.24	1	60	seeds	0.07	0.13	0.20	102660 ¹⁶
				75		0.06	0.13	0.19	
				90		0.05	0.10	0.15	
Italy, (Latina), 1991, (Montenuovo)	240 EC	0.24	1	60	seeds	0.04	0.12	0.18	103403 ¹⁷
				75		0.06	<0.03	<0.09	
				90		0.05	<0.03	<0.08	

Country, year, (variety)	Application			PHI, days	Sample	DME	DME- OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
GAP									
Argentina	240	0.16-		100					
	EC	0.24							
Canada	240	0.045	1-2	72					
	EC	-0.09							
Italy/France	240	0.18-		100					
	EC	0.48							
Italy/France	240	0.18-		100					
	EC	0.48							

¹ Applied at 8-leaf stage of growth. Limit of detection 0.05 mg/kg; recovery from seed at 0.1 mg/kg 81%.

² Applied at 10-leaf stage. Limit of detection 0.05 mg/kg; recovery at 0.1 mg/kg 55%.

³ Limit of detection 0.05 mg/kg; recovery at 0.1 mg/kg of clethodim and 5-OH-clethodim sulfone 76% and 104% respectively from hulls, 92% and 128% from solvent-extracted presscake, 63% and 132% from expelled presscake, 85% and 91% from refined oil, 88% and 136% from seeds.

⁴ Single application at flowering. Limit of detection 0.05 mg/kg; recovery of clethodim at 0.1 mg/kg 79% from seeds.

⁵ Limit of detection 0.1 mg/kg; recovery from seed at 0.2, 0.5 and 1 mg/kg 82-118% of clethodim sulfoxide, 71-107% of 5-OH-clethodim sulfone.

⁶ Processing study, with Select applied at fivefold rate. Seeds were processed into meal, crude oil and refined oil. Residues were 33 mg/kg in meal, 3.2 and 3.5 mg/kg in crude oil and <0.1 mg/kg in refined oil.

⁷ Limit of detection 0.02 mg/kg; recovery of clethodim sulfoxide at 0.02, 0.1 and 0.2 mg/kg from seed 65-119% (n = 10).

⁸ Limit of detection 0.03 mg/kg; recovery of clethodim at 0.06 and 0.1 mg/kg 72 and 82%.

⁹ Limit of detection 0.03 mg/kg; recovery of clethodim at 0.06 and 0.1 mg/kg 100 and 104%.

¹⁰ Limit of detection 0.03 mg/kg; recovery of clethodim at 0.06 and 0.1 mg/kg 95 and 65%.

¹¹ Single application 6-7 leaf stage. Limit of detection (total residues) 0.03 mg/kg; recovery at 0.03 mg/kg 87, 87 and 93%. Method RM 26B-2.

¹² Single application at 4 extended nodes stage of growth. Limit of detection 0.03 mg/kg; recovery at 0.03 mg/kg 87, 87 and 93%. Method RM 26B-2.

¹³ Single application at appearance of flower buds. Limit of detection 0.07 mg/kg (total residues), 0.03 mg/kg DME and 0.04 mg/kg DME-OH; recovery of clethodim 64, 81 and 89% at 0.07 mg/kg, 85% at 0.7 mg/kg. Method RM-26B-2.

¹⁴ Single application at 8-leaf stage. Limit of detection 0.07 mg/kg (total residues), 0.03 mg/kg DME and 0.04 mg/kg DME-OH; recovery of clethodim 64, 81 and 89% at 0.07 mg/kg, 85% at 0.7 mg/kg. Method RM-26B-2.

¹⁵ Single application by spraying. Limit of detection 0.03 mg/kg; recovery of clethodim at 0.03 mg/kg 79%. Plot size 1300 m², silt soil, pH 8, 1% C.

¹⁶ Single application at appearance of flowers. Plot size 90 m². Limit of detection 0.03 mg/kg DME and DME-OH; recovery 99, 112 and 116% at 0.03 mg/kg and 92 and 108% at 0.05 mg/kg.

¹⁷ Single application at flower development. Plot size 200 m². Limit of detection 0.03 mg/kg DME and DME-OH; recovery 99, 112 and 116% at 0.03 mg/kg and 92 and 108% at 0.05 mg/kg.

Animal feeding studies

Feeding studies on laying hens and dairy cattle which had been reviewed in 1994 were re-submitted by the manufacturer. Both studies are discussed here in relation to the estimation of the dietary exposure of livestock of treated feed items.

Groups of laying hens were dosed orally by gelatin capsule with a mixture of clethodim and clethodim sulfoxide (Fletcher and Pedersen, 1988). Doses were prepared daily and administered on day 1 and every day thereafter for 28 days. Each group consisted of 20 hens which were dosed according to the following regime.

Group	Dose, ppm in the diet		Dose, mg/kg body weight*	
	Clethodim	Clethodim sulfoxide	Clethodim	Clethodim sulfoxide
T-1	0.5	9.5	0.04-0.09	0.80-1.79
T-2	1.5	28.5	0.13-0.28	2.39-5.39
T-3	5.0	95.0	0.42-0.95	7.98-17.96

* Based on a maximum feed level of 151.3 g/bird/day and body weight range of 800-1800 g/bird.

Eggs were collected on days -1, 1, 2, 4, 7, 14, 21, 28, 29 and 30 and pooled from sub-groups of 10 birds within each treatment group. On day 29, ten hens from each group were killed and samples of muscle (thigh and breast), liver, gizzard and fat (subcutaneous and abdominal) were collected for analysis. The remaining hens in each group were killed on day 31, two days after the end of dosing.

The method of analysis was the common moiety method RM-26A, described in PAM, Vol. II, Pesticide Registration Section 180.412, with minor modifications to the gas-chromatographic conditions. A full description of the method was provided in the analytical phase of the report (Lear, 1989). Recoveries of clethodim, 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide from fortified eggs, fat, gizzard, liver and muscle were reported. The reported limit of detection was 0.05 mg/kg for each compound in all samples. The results are shown in Table 28.

Table 28. Recoveries from fortified hen tissues and eggs in a feeding study (Lear, 1989).

Sample	Fortification level, mg/kg	Recovery, %		
		Clethodim	5-OH-clethodim sulfone	S-Me-clethodim sulfoxide
Eggs	0.1	57-96	56-94	66-95
	0.5	61-75	66-70	56-67
Fat	0.1	63-98	48-166	47-93
	0.5	73, 83	73, 81	67, 76
	1.0	71-72	63-67	62-64
Gizzard	0.1	70-110	61-88	61-93
	0.5	85	82	75
	1.0	87	71	75
Liver	0.1	67-126	70-113	63-94
	0.5	83, 93	82, 85	74, 82
	1.0	78, 87	76, 76	72, 82
Muscle	0.1	82-120	71-110	71-90
	0.5	83, 93	79, 84	72, 79
	1.0	55, 79	68, 74	54, 73

The residues found in the eggs are shown in Table 29.

Table 29. Total clethodim residues in eggs after dosing at three levels.

Day	Residues, mg/kg, in group								
	T-1			T-2			T-3		
	C	5-OH CSO ₂	S-Me CSO	C	5-OH CSO ₂	S-Me CSO	C	5-OH CSO ₂	S-Me CSO
1	<0.05	<0.05	<0.05	0.06	<0.05	<0.05	0.21	<0.05	<0.05
2	<0.05	<0.05	<0.05	0.08	<0.05	<0.05	0.21	<0.05	<0.05
4	<0.05	<0.05	<0.05	0.08	<0.05	<0.05	0.19	<0.05	<0.05
7	<0.05	<0.05	<0.05	0.07	<0.05	<0.05	0.15	<0.05	<0.05
14	<0.05	<0.05	<0.05	0.08	<0.05	<0.05	0.17	<0.05	<0.05
21	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	0.14	<0.05	<0.05
28	<0.05	<0.05	<0.05	0.05	<0.05	<0.05	0.24	<0.05	<0.05
29	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
30	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

C: clethodim

5-OH CSO₂: 5-OH-clethodim sulfone

S-Me CSO: *S*-methyl-clethodim sulfoxide

The residues of clethodim during dosing were <0.05-0.09 mg/kg in the T-2 group and 0.14-0.24 mg/kg in T-3. One day after withdrawal of dosing, clethodim residues were below the limit of detection. The sulfone and sulfoxide were below the limit of detection in all the samples.

Clethodim, *S*-methyl-clethodim sulfoxide and 5-OH-clethodim sulfone were not detected above 0.05 mg/kg in any fat, muscle or gizzard samples. The only residue above this level was in one day 29 sample of liver in group T-3 (5 ppm clethodim + 95 ppm clethodim sulfoxide) which contained 0.06 mg/kg of DME; 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide were not detected above 0.05 mg/kg in any liver samples.

The results show that clethodim and clethodim sulfoxide do not accumulate in hen tissues.

Dairy cattle were dosed orally by capsule for 28 days with a mixture of clethodim and clethodim sulfoxide (Weissenburger *et al.*, 1989). Groups of four cows were treated according to the following regime.

Group	Dose equivalent, ppm in the diet		Dose, mg/kg body weight*	
	Clethodim	Clethodim sulfoxide	Clethodim	Clethodim sulfoxide
T-1	0.5	9.5	0.015-0.017	0.28-0.32
T-2	1.5	28.5	0.044-0.046	0.83-0.88
T-3	5.0	95.0	0.13	2.48-2.60

* Based on a maximum feed level of 17.65 kg/cow and body weight ranges of 518-594 kg (T-1); 566-603 kg (T-2); 644-676 kg (T-3).

Three cows from each group were slaughtered on day 29 (22-24 hours after the last dose) and samples of muscle, fat (peritoneal and subcutaneous), liver and kidney were taken for analysis.

The animals were milked in the morning and evening and the milk from each treatment group was composited for analysis. Milk samples taken on days 1, 2, 4, 7, 12, 16, 20, 24, 28, 29, 30 and 31 were analysed, those from days 29, 30 and 31 being from a cow which had been withdrawn from dosing for 1, 2 and 3 days. Milk samples from the T-3 group on days 25, 26 and 27 were composited for processing into skimmed milk, cream and acid whey for comparison of the residues in the processed commodities with the levels in whole pasteurised milk.

The residues were quantified as *S*-methyl-DME, DME or DME-OH and reported as clethodim (Weissenburger and Krupiak, 1988a,b). Recoveries from milk were determined by fortification with clethodim, *S*-methyl-clethodim sulfoxide and 5-OH-clethodim sulfone at 0.0125, 0.025, 0.05 and 0.1 mg/kg. Tissues were fortified with 0.05 and 0.1 mg/kg. The limits of determination were reported as 0.0125 mg/kg in milk and 0.05 mg/kg in liver, kidney, muscle and fat.

The maximum residues found in milk, processed milk products and tissues are shown in Tables 30, 31 and 32.

Table 30. Maximum residues in milk of cows dosed at three levels.

Group	Maximum residues, expressed as mg/kg clethodim		
	DME	<i>S</i> -methyl DME	DME-OH
T-1	<0.0125	<0.0125	<0.0125
T-2	0.0334	<0.0125	<0.0125
T-3	0.0812	0.0316	<0.0125

Table 31. Total clethodim residues in processed milk products from cows dosed at the equivalent of 100 ppm in the diet (T-3).

Commodity	Maximum residues expressed as mg/kg clethodim		
	DME	<i>S</i> -methyl DME	DME-OH
Pasteurised whole milk	0.0606	0.0139	<0.0125

Skimmed milk	0.0269	<0.0125	<0.0125
Cream*	0.1096	<0.0125	<0.0125
Acid whey	0.0265	<0.0125	<0.0125

*Butterfat content ranged from 2.8 to 4.5% in the whole milk.

Table 32. Maximum clethodim residues in cattle tissues.

Group	Sample	Residues expressed as mg/kg clethodim		
		DME	S-methyl DME	DME-OH
T-1	Liver	0.059	<0.05	<0.05
	Kidney	0.051	<0.05	<0.05
	Muscle	<0.05	<0.05	<0.05
	Fat	<0.05	<0.05	<0.05
T-2	Liver	0.119	<0.05	<0.05
	Kidney	0.170	<0.05	<0.05
	Muscle	<0.05	<0.05	<0.05
	Fat	0.052	<0.05	<0.05
T-3	Liver	0.445	0.087	<0.05
	Kidney	0.538	0.078	<0.05
	Muscle	0.070	<0.05	<0.05
	Fat	0.153	<0.05	<0.05

Recoveries from tissues and milk are shown in Table 33.

Table 33. Recoveries from fortified cattle tissues, milk, and processed milk products.

Sample	Fortification level, mg/kg	Recovery, %		
		Clethodim	S-methyl-clethodim sulfoxide	5-OH-clethodim sulfone
Liver	0.05	79	91	78
	0.1	72	80	78
Kidney	0.05	83, 86	100, 100	90, 109
	0.1	77	78	89
Muscle	0.05	79	91	96
	0.10	88	86	104
Fat	0.05	86	90	85
	0.10	70	71	76
Whole milk	0.10	87	95	106
Cream	0.10	70	78	94
Skimmed milk	0.05	80	80	105
Acid whey	0.05	71	80	74
Milk	0.0125	103, 106	95	96, 115
	0.025	78, 96	67, 97	65, 110
	0.05	78, 80, 82, 85, 85, 87, 98	80, 83, 103, 77	70, 80, 84, 86, 86, 91, 93
	0.10	70, 72, 73, 75, 79, 80, 83, 85, 92, 99	74, 78, 83, 85, 86, 88, 96	72, 73, 74, 83, 87, 94, 96, 97, 98, 109

The residues in the tissues of animals slaughtered 2 days after the withdrawal of dosing were <0.05 mg/kg in all groups. Similarly, the levels of each component of the residue in the milk after withdrawal of dosing for 1, 2 and 3 days were <0.0125 mg/kg.

Estimation of dietary burden of livestock

Estimates of the exposure of cattle and hens to clethodim residues in treated feed items are shown in Tables 35 and 36. Maximum and median residues in animal feed commodities are shown for comparison. All median residues have been estimated from the results of trials which were considered to conform to GAP. Data from the 1994 and 1997 monographs have been included where relevant and processing factors derived where possible. Where the dry matter content is 85% or higher no

adjustment for moisture has been made. Items for which intake figures were not available have been included as they may be used in animal feed.

An intake of 15 kg dry matter/day was assumed for cattle, with an average body weight of 500 kg.

Table 34. Estimated dietary intake of clethodim residues from treated feed by cattle. The items contributing mainly to the intake are shown bold.

Crop or Commodity	Maximum residue, mg/kg	Median residue, mg/kg	Maximum % in diet	% DM	Intake, mg/animal/day	Reference
Alfalfa hay	8.9	1.6	70		16.80	JMPR 1997 ¹
Bean hay	5.5	1.8	25 ²	88	6.75	Table 26
Bean vines	2.8 (dry wt)	1.5 (dry wt)	25 ²	25	5.62	
Clover forage	0.07		30	30	1.03	JMPR 1997
Cotton seed	0.48	0.15	25	88	0.56	JMPR 1994
Cotton hulls		0.18	20		0.54	
Cotton meal		0.25	15		0.56	
Field peas	2.0	0.08	20	90	0.24	JMPR 1997
Fodder beet	<0.03	0.03	20 ³		0.09	JMPR 1997
Lupins		<0.1	20	88	0.3	JMPR 1997
Pea straw		<0.1	25	88	0.38	JMPR 1997
Peanut vines	12	1.13	25	85	4.23	
Peanut hay	2.6	0.57	25		2.13	
Peanut meal		3.1	15	85	6.97	JMPR 1997
Rape seed meal	1.5		15	88	3.37	JMPR 1994
Soya bean meal	10		15	92	22.50	JMPR 1994
Sugar beet tops		<0.03	20	23	0.39	JMPR 1997
Sunflower meal	1.4	0.38	15	92	0.85	Tables 47, 28,
Tomato pomace		1.2	10		1.80	JMPR 1997

¹Residue evaluation, Table 35

²Taken from OPPTS 860.1000 (USEPA)

³Figure for sugar beet used

The highest contributions come from soya bean meal, alfalfa hay, peanut meal and rape seed (canola) meal. The total exposure is calculated to be 46.3 mg clethodim/animal/day or 3.1 ppm in the diet from a diet of alfalfa hay, soya bean meal and peanut meal. The lowest dose in the cow feeding study was equivalent to 10 ppm clethodim (0.5 mg/kg clethodim and 9.5 mg/kg clethodim sulfoxide). At this dose level, each component of the residue in the whole milk, muscle and fat was below the limit of determination. In the milk the total residues were equivalent to <0.0375 mg/kg and in muscle and fat to <0.15 mg/kg. Residues of 0.059 and 0.051 mg/kg DME were found in liver and kidney respectively, with corresponding total residues of <0.16 and <0.151 mg/kg.

Hens were assumed to have a body weight of 2 kg and a feed intake of 150 g dry matter/day. The estimated intake of clethodim residues is shown in Table 35.

Table 35. Estimated dietary intake of clethodim residues from treated feed by hens. The items contributing mainly to the intake are shown bold.

Commodity	Maximum residue, mg/kg	Median residue, mg/kg	Maximum % in feed	% DM	Intake, mg/hen/day
Cotton meal		0.25	20	89	0.0075
Field peas		0.08	20	90	0.0024
Lupins		<0.01	15	88	0.0003
Peanut meal		3.1	25	85	0.1163
Rape seed meal	1.5		15	88	0.0338
Soya beans	10		20	89	0.3

Commodity	Maximum residue, mg/kg	Median residue, mg/kg	Maximum % in feed	% DM	Intake, mg/hen/day
Soya bean meal	10		40	92	0.6
Sunflower meal		0.38	30	92	0.017

The highest possible exposure in the hen diet is calculated to be 1.05 mg/bird/day or 7 ppm in a diet composed of peanut meal, rape seed meal, soya beans and soya bean meal. The lowest dose in the hen feeding study was equivalent to 10 ppm clethodim (0.5 mg/kg clethodim and 9.5 mg/kg clethodim sulfoxide). At that level each component of the residue in all tissues and eggs was <0.05 mg/kg and the total clethodim residues <0.15 mg/kg.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were available.

In processing

Processing studies on oilseed crops (cotton seed, canola, peanuts, soya beans and sunflowers), tomatoes and sugar beet were reported. The stability of residues in processed fractions of peanuts and tomatoes was discussed in the section on methods of residue analysis.

Canola. Crops at two sites in Canada were treated with Select 240 EC herbicide at about twice the maximum label rate (Cosgrove, 1990a,b). The single application was made at the 2-3 leaf stage of growth and the crops were harvested 67 and 75 days after treatment. The residues in the seed are shown in Table 36 and details of the trials are given as footnotes. The seed from the Saskatchewan trials was processed into meal, crude oil, hydrogenated oil, deodorised hydrogenated oil and deodorised oil. Residues in crude oil and desolventized meal were reported (Table 37).

Table 36. Residues in canola seed from an exaggerated treatment with clethodim in Canada, 1989.

Location, (variety)	Application			PHI, days	Residues, mg/kg			Reference
	Form.	kg ai/ha	No.		DME	DME-OH	Total	
Manitoba (Tobin)	240 EC	0.24	1	75	0.078 0.065	0.119 0.122	0.197 0.187	Cosgrove 1990 ¹
Saskatchewan (Westar)	240 EC	0.21	1	66	0.077 0.099 0.067	0.205 0.230 0.224	0.282 0.329 0.291	Cosgrove 1990 ²

¹ Single application with 1%v/v corn oil using tractor-mounted pump. Plot size 1 ha, sandy loam soil.

² Single application with 1 % corn oil using tractor-mounted pump. Plot size 1 ha, silty clay soil.

Table 37. Residues in canola and its processed commodities, with processing factors.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Canola seed	0.081 (average)	0.220 (average)	0.301 (average)	-
Crude oil	<0.05	<0.05	<0.1	<0.3
Meal # 1	0.242	0.051	0.29	0.96
# 2	0.106	0.66	0.766	2.54

The meal samples were re-analysed and the second analysis (meal #2) showed total residues of 0.77 mg/kg in the meal, giving a concentration factor of 2.54. As residues above the limit of determination were not found in the crude oil, the remaining oil samples were not analysed. Recoveries were checked by fortification with clethodim sulfoxide and 5-OH-clethodim sulfone at

0.05 and 2 mg/kg. Recoveries of clethodim sulfoxide at 0.05 and 0.2 mg/kg were 76 and 86% in crude oil and 127 and 131% in meal; the corresponding recoveries of 5-OH-clethodim sulfone were 78 and 95% in crude oil and 125 and 98% in meal.

Cotton. Select 2 EC was applied to cotton at 8 times the maximum recommended seasonal rate in Mississippi (Lai, 1988a). The crop was treated with two applications (30-day interval) at a rate equivalent to 2.24 kg ai/ha, and harvested 40 days after the last application. The seed was processed into meal, hulls, crude oil, refined oil, soapstock, delinted seed, linters and linter motes (Table 38).

Table 38. Residues in cotton seed and its processed commodities from 2 x 2.24 kg ai/ha of 2 EC¹. USA, 1987 (Lai, 1998a).

Location (variety)	Application			PHI, days	Sample	Residues, mg/kg			Processing factor
	Form.	kg ai/ha	No.			DME	DME-OH	Total	
Mississippi (DPL 41)	2 EC	2.24	2	40	fuzzy seed	0.58	<0.1	<0.68	-
						0.65	0.30	0.95	
						0.60	0.18	0.78	
					mean	0.61	0.19	0.80	
					meal	0.94	0.41	1.35	1.69
					hulls	0.78	<0.2	<0.98	1.22
					crude oil	0.14	<0.04	<0.18	0.22
					refined oil	<0.04	<0.04	<0.08	0.1
					soapstock	0.65	<0.2	<0.85	1.06
delinted seed	0.67	0.21	0.88	1.1					

¹ Applied by tractor-mounted sprayer with 1 qt/acre crop oil; plot size 4 rows of 61 m. Cotton stored for 24 hours before ginning, then frozen.

Recoveries were determined by fortification with clethodim sulfoxide and 5-OH-clethodim sulfone at 0.2, 0.5 or 1 mg/kg. Methods RM-26A and RM-26A-1 were used. The results are shown in Table 39.

Table 39. Recoveries from fortified cotton seed and processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO ₂	CSO	5-OH CSO ₂
Fuzzy seed	0.5	0.5	77, 82, 91	90, 109, 110
Meal	1.0	1.0	86	86
Hulls	1.0	1.0	85	78
Crude oil	0.2	0.2	77	57
Refined oil	0.2	0.2	75	57
Soapstock	1.0	1.0	82	56
Delinted seed	0.5	0.5	90	64

All recoveries of clethodim sulfoxide were acceptable. Recoveries of the sulfone were low from crude and refined oils, soapstock, and delinted seed.

Peanuts were treated twice with Select 2 EC at a rate equivalent to 1.4 kg ai/ha, 5 times the maximum recommended US rate, with a 14-day interval at the 'pegging' stage of crop growth (Lai, 1994b). The peanuts were harvested 40 days after treatment with an additional 3 days allowed for drying. The results and processing factors are shown in Table 40.

Table 40. Residues in peanuts and their processed commodities.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Kernels	3.6	0.32	3.9	-

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
	3.6	0.39	4.0 (average 4.0)	-
Meal	9.2	0.42	9.6	2.4
Crude oil	1.7	<0.04	1.7	0.4
Refined oil	0.32	<0.04	0.36	0.09
Soapstock	10	0.13	10.1	2.5

The results show a concentration of residues in peanut meal and soapstock. Analytical recoveries from the individual processed fractions are shown in Table 15.

Soya beans were treated twice with post emergent applications of Select 2 EC at 2.2 kg ai/ha (27 day re-treatment), equivalent to 8 times the maximum recommended US rate, and harvested after 40 days (Lai, 1988b). The beans were separated from the hulls and processed into meal, crude oil, refined oil, soapstock, degummed oil and crude lecithin. The residues are shown in Table 41.

Table 41. Residues in soya beans and their processed commodities.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Dry shelled bean	18, 21	8.7, 9.0	27. 30 (average 28.5)	-
Meal	22	5.2	27	0.95
Hulls	17	9.1	26	0.91
Crude oil	2.6	0.17	2.8	0.1
Refined oil	<0.04	<0.04	<0.08	<0.003
Soapstock	32, 32	1.3, 1.6	33, 34	1.2
Degummed oil	1.5	0.1	1.6	0.06
Crude lecithin	36	6.1	42	1.5

There was a slight concentration of clethodim residues in soapstock and crude lecithin. Recoveries were measured at 0.2 and 1 mg/kg by Methods RM-26A and RM-26A-1 (Table 43).

Table 42. Recoveries from fortified soya beans and processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO ₂	CSO	5-OH CSO ₂
Soya beans	1.0	1.0	88	102
Meal	1.0	1.0	76	64
Hulls	1.0	1.0	89	113
Crude oil	0.2	0.2	73	73
Refined oil	0.2	0.2	70	55
Soapstock	1.0	1.0	80, 85	90,, 120
Degummed oil	0.1	0.1	82	90
Crude lecithin	1.0	1.0	82	99

Sugar beets were treated at the fivefold rate of 1.4 kg ai/ha at the 5th and 12th leaf stages of growth (Lai, 1991) with an interval of 16 days between applications. The crops were harvested 99 days after treatment. The individual residues in the roots were below the limit of determination of 0.1 mg/kg (total <0.2 mg/kg). The roots were processed into sliced beets, dehydrated pulp, refined sugar and molasses. The residues are shown in Table 43.

Table 43. Residues in sugar beets and their processed commodities.

Sample	Residues, mg/kg		
	DME	DME-OH	Total
Sugar beets	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2
Sliced beets	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2

Sample	Residues, mg/kg		
	DME	DME-OH	Total
Dehydrated pulp	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2
Refined sugar	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2
Molasses	0.24	<0.1	0.24

The results show a concentration in molasses, but processing factors could not be calculated as the residues in the raw beets were below the level of determination. Recoveries are shown in Table 44.

Table 44. Recoveries from fortified sugar beet and processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO ₂	CSO	5-OH CSO ₂
Sliced beets	0.2	0.2	74	76
Dehydrated pulp	0.2	0.2	83	72
Molasses	0.2	0.2	68	102
	0.5	0.5	74	100
Refined sugar	0.1	0.1	96	118
	0.2	0.2	63	64
	0.5	0.5	79	78

Sunflowers were treated twice at an interval of 15 days at 1.33-1.45 kg ai/ha, about 5 times the maximum recommended rate, with the last application at 50% flowering and harvested after 72 days (Lai, 1996c). The seed was processed into meal and crude and refined oil. The residues and processing factors are shown in Table 45.

Table 45. Residues in sunflower seeds and their processed commodities.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Seeds	10, 12	4.3, 5.9	14, 18 (average 16)	-
Hulls	16, 12	7.6, 5.8	18, 24 (average 21)	1.3
Meal	23, 23	10, 9.9	33, 33	2
Crude oil	2.8, 3.1	0.38, 0.40	3.2, 3.5 (average 3.3)	0.2
Refined oil	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.006

There was some concentration of residues in the meal and hulls. Recoveries of clethodim sulfoxide and 5-OH-clethodim sulfone were determined at concentrations of 0.2, 0.5, 2.5 or 5 mg/kg with the results shown in Table 46.

Table 46. Recoveries from fortified sunflower seeds and their processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO ₂	CSO	5-OH CSO ₂
Seeds	5	5	94	89
Hulls	0.5	0.5	84	120
Meal	0.5	0.5	120	113
Crude oil	2.5	2.5	67	69
Refined oil	0.2	0.2	65	73

Tomatoes were treated twice with Select 0.94 EC at 1.4 kg ai/ha or 5 times the maximum recommended rate (Lai, 1995b). The applications were made at blooming or fruit set and immature fruit stages at an interval of 16 days. Fruit were harvested 20 days after the last application and processed into wet pomace, dry pomace, paste and juice. Two studies were conducted in consecutive years, with the results shown in Table 47.

Table 47. Residues in tomatoes and their processed commodities.

Sample	Total residues, mg/kg		Processing factor
	1993	1994	
Fruit	0.84	1.2	
Wet pomace	0.79	1.0	0.94, 0.83
Dry pomace	2.6	4.0	3.1, 3.3
Purée	–	2.6	2.2
Paste	2.9	3.6	3.5, 3.0
Juice	0.76	0.92	0.90, 0.77

There was a concentration of clethodim residues in purée, paste and dry pomace. Recoveries from juice, paste and pomace were within acceptable limits and are given in Tables 18 and 19.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was provided.

NATIONAL MAXIMUM RESIDUE LIMITS

The information provided is given below. The residue is considered to be defined as “sum of clethodim and metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulfones, expressed as clethodim”, unless otherwise stated.

Country	MRL, mg/kg	Commodity
Argentina	0.5	Cotton seed, peanut, soya bean, sunflower seed
	3.0	Soya bean straw, sunflower straw
	10	Alfalfa forage
	15	Alfalfa hay
Australia ¹	0.01*	Fennel (bulb)
	0.05*	Edible offal (mammalian), eggs, meat (mammalian), milk, poultry offal, poultry meat,
	0.05	Endive
	0.1*	Beans (except broad beans and soya beans), broad beans, cucurbits, peas, pulses (except lupins), spinach, sunflower seed
	0.1	Celery, lettuce (leaf and head), strawberry, tomato
	0.2	Flowerhead brassicas, cotton seed, lupins, poppy seed,
	0.3	Garlic, onion (bulb), leeks (T)
	1	Asparagus, root and tuber vegetables
Belgium	0.05	Fodder beet, onions, sugar beet
	0.1	Beans, peas, potatoes
Brazil	0.05	Garlic, onion, tomato, dry beans, potato, carrot, cotton seed
	1.0	Soya beans
Canada	0.1	Canola, seedling alfalfa, sunflower (including sunola)
	0.3	Flax
	0.4	Mustard seed
	0.5	Field peas, lentils, potatoes, desi and kabuli chickpeas
Czech Republic	0.03	Fodder beet (root and leaves), horse bean, oil seed rape, sugar beet (root and leaves)
	0.1	Potato
	0.3	Peas
France	0.05	Sugar beet
	0.1	Proteaginous peas, sunflower
Hungary	0.1	Forestry, mustard, potato, soya bean, sugar beet, sunflower, tomato
	0.2	Peas
Italy	0.2	Sugar beet, fodder beet, tomato
	1	Soya bean
Japan	0.1	Carrot, sweet potato, onion
	0.2	Sugar beet, kidney bean
	0.3	Azuki

Country	MRL, mg/kg	Commodity
Mexico	10	Soya bean
New Zealand	<0.1	White clover, seed crops, peas, lentils, oil seed rape, orchards, vegetables
Peru	1	Alfalfa
	5	Orange, apple, cotton seed
	10	Bean
Russia	0.1	Carrot, sugar beet, fodder beet, red beet, onion, soya bean, flax seed, flax
	0.2	Potato
Spain	0.05	Sunflower, onion, garlic, potato
	0.1	Beans, field peas, tomato, flaxseed
	0.3	Soya bean
Switzerland	0.05	Sugar beet, fodder beet
	0.1	Potato, vegetables
Ukraine	0.1	Carrot, sugar beet, fodder beet, red beet, onion, soya bean, flax seed
	0.2	Potato
USA	0.05	Milk
	0.2	Dry onions, garlic, shallots, sugar beet (roots), cattle fat, cattle meat, cattle meat by-products, eggs, goat fat, goat meat, goat meat by-products, hog fat, hog meat, hog meat by-products, horse fat, horse meat, horse by-products, poultry fat, poultry meat, poultry meat by-products, sheep fat, sheep meat, sheep by-products
	0.5	Potato, sugar beet (tops)
	1.0	Cotton seed, tomato
	2.0	Cotton seed meal, sugar beet (molasses), dry beans, tomato (purée)
	3.0	Peanut (nutmeat), peanut hay, tomato (paste)
	5.0	Peanut meal
	6.0	Alfalfa (forage)
	10	Soya bean, alfalfa (hay)
Uzbekistan	0.1	Onion, carrot, soya bean, beet
	0.2	Potato

¹ Listed with sethoxydim.

APPRAISAL

Clethodim was evaluated by the JMPR in 1994 and 1997. In the first evaluation MRLs were recommended for several crops and animal feed commodities. At the 1996 CCPR (28th Session), several matters were referred to the JMPR for further consideration. These included the characterization and quantification of metabolites in plant metabolism studies and a lactating goat study, methods of analysis for clethodim and sethoxydim, and the lowest reported limit of determination in animal commodities.

In the 1997 evaluation some of the above issues were discussed, including a compound-specific method which allowed residues arising from the use of clethodim to be distinguished from those from sethoxydim. Additional studies on alfalfa, artichokes, cabbage, field peas, lupins, carrots, cauliflower, clover, celery, flax, garlic, cucumbers, leeks, lentils, lettuce, onions, peaches, peppers, spinach, summer squash (zucchini) and tomatoes were reviewed. MRLs for beans, sunflower seed and sunflower seed oil (crude and edible) were recommended for withdrawal.

At the 1999 CCPR, comments were made in relation to the MRLs recommended for cattle meat and cattle offal and the corresponding limits of determination for the two commodities. Moreover, it was noted that no justification was provided for the animal commodity MRLs on the basis of the levels of clethodim found in treated feed items. It was suggested that the JMPR should provide an estimate of the exposure of livestock through the feeding of treated commodities.

For the present evaluation, new trials on cucumbers, dry beans, peppers and sunflowers were reported, together with processing data for canola (rape seed), cotton seed, peanuts, soya beans, sugar beet, sunflowers and tomatoes. Data from previously reviewed Canadian trials on potatoes were also submitted with new data to allow a review of the MRL for potato. Data on photodegradation,

adsorption and fate in water/sediment systems were also submitted for evaluation. In order to respond to some of the issues raised by the CCPR, some metabolism and feeding studies reviewed in 1994 and 1997 were re-examined.

The predominant metabolites formed by the biochemical transformation of clethodim in hens and goats are clethodim sulfoxide, clethodim sulfone and *S*-methyl-clethodim sulfoxide. In plants, the main metabolites are clethodim sulfoxide and imine sulfoxide. In the metabolism studies, a comparison between the method used to determine the total radioactivity and a non-specific enforcement method in goat liver and kidney, hen muscle and soya beans was reported. The comparison shows that total residues determined by the routine methods of enforcement are very similar to the total radioactive residues found in the tissues and soya beans, and confirms that the residue definition for routine enforcement is appropriate. The routine method is not compound-specific however, and does not differentiate between residues originating from the use of clethodim and those arising from the use of sethoxydim.

The rates of degradation of clethodim, clethodim sulfoxide and clethodim sulfone were investigated in sterile and non-sterile soils. The calculated half-lives for the degradation of all the compounds were higher in sterile than in non-sterile soils, indicating that degradation is a function of microbial activity as well as temperature.

The adsorption and desorption of clethodim, clethodim sulfoxide and clethodim sulfone in five different soils were investigated. The results showed that all three compounds are weakly adsorbed to the soils tested, with K_d values ranging from <0.2 to 1.6.

Clethodim is degraded rapidly by photolysis in water in the presence of a photosensitiser such as acetone. Calculated half-lives were 0.94, 1.22 and 0.52 days, respectively, in solutions at pH 5, 7 and 9 which were exposed to natural sunlight for up to 30 days. Photolytic mechanisms of transformation include oxidation at the thioethyl function, elimination of the chloroallyl side chain to form clethodim imine and clethodim oxazole, and further oxidation to the oxazole sulfoxide and the sulfide and sulfoxide of dimethyl 3-[2-(ethylsulfonyl)propyl]pentanedioate (DME).

The hydrolysis of clethodim was investigated in sterile water at pH 5, 7 and 9 in the dark. HPLC analysis of the solutions at intervals up to 32 days showed that at pH 5 and 7, clethodim was an equilibrium mixture of two oxime forms, *anti* and *syn* conformations caused by H-bond formation between the oxyimino oxygen and the hydroxyl group on the hydroxy-cyclohexenone ring. Interconversion was fastest at pH 5. The resulting degradation products included an oxazole and a hydroxyvinyl compound.

In response to questions raised by the CCPR regarding a compound-specific method of analysis, new validation experiments were reported with milk, eggs and hen liver. A limit of 0.02 mg/kg was reported for clethodim, clethodim sulfoxide and *S*-methyl-clethodim sulfoxide in milk. In the goat metabolism study, the radioactivity in milk was predominantly due to clethodim sulfoxide, *S*-methyl-clethodim sulfoxide and lactose derivatives at levels of 20%, 5.5% and 30-50% respectively, so the method has been validated and recoveries determined with the appropriate metabolites. The limit of determination of total residues in milk was <0.04 mg/kg.

In tissues, the limit of determination was reported as 0.2 mg/kg with recoveries of clethodim sulfoxide at that level reported for hen tissues, beef liver and beef muscle. Results from the hen and goat metabolism studies showed that clethodim sulfoxide and *S*-methyl sulfoxide were the predominant sources of the radioactivity in tissues. The compound-specific method has therefore been validated for one of the main metabolites, with acceptable recoveries reported in hen and cattle tissues. The limit of determination for total residues by the non-specific common moiety method would be 0.04 mg/kg in tissues or thereabouts. This is comparable to the limit of determination found in the cow and hen feeding studies, where the common moiety method was employed.

In eggs, the compound-specific method was validated at 0.05 mg/kg and recoveries were determined at this level with clethodim sulfoxide. In the hen metabolism study, clethodim sulfoxide was the main source of the radioactivity in egg white and egg yolk during the 5-day dosing period. The method is therefore capable of quantifying clethodim residues in eggs down to a limit of 0.05 mg/kg.

Specialised methods were reported for soil and water where total clethodim residues included clethodim sulfoxide, clethodim sulfone, and the oxazole sulfoxide and oxazole sulfone. These compounds were characterized in studies of degradation in soil and water.

Studies of the storage stability of clethodim residues in alfalfa (forage and hay), celery, clover, cotton seed, beans (seeds, vines and hay), onions, peanuts and their processed commodities, sugar beet (tops and roots), sunflower seeds, tomatoes and their processed commodities, chicken tissues and eggs, and bovine tissues and milk were reported. In all the studies, clethodim residues were adequately stable during the period of storage. Discernible losses ($\leq 20\%$) occurred in peanut soapstock at 429 days and in tomato paste and juice after 153-162 days. Freshly fortified samples were analysed concurrently with the stored samples. The Meeting agreed that $<20\%$ decrease in stored samples did not constitute degradation.

Residue data were submitted for cucumbers, dry beans, peppers (sweet and chilli), potatoes and sunflowers. Registered use patterns were reported only for these crops; further information on GAP is reported in the 1994 and 1997 monographs.

Data on residues in potatoes were submitted in response to questions raised at the 1999 CCPR on the registered use pattern in Canada and the establishment of an import tolerance in the USA. In the 1994 evaluation, data from France, Italy and the Ukraine were reviewed and an MRL of 0.2 mg/kg was recommended. The new data from Canada show that residues above 0.2 mg/kg were found in potatoes treated in accordance with Canadian GAP (single application at 0.09 kg ai/ha and a PHI of 60 days). The residues in the tubers were <0.1 -0.46 mg/kg at PHIs of 45 or 46 days and <0.1 -0.34 mg/kg at PHIs of 59 or 60 days. The residues in rank order were <0.1 (15), 0.137, 0.141, 0.19, 0.232, 0.326, 0.339, 0.348 and 0.463 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg. An STMR could not be estimated as the previously reviewed data from France, Italy and the Ukraine were not re-submitted.

Data on cucumbers were reported from trials in the USA and a trial in Poland. The trials in the USA are indicated as being in accordance with GAP, but the use pattern is not yet registered with the USEPA. The Meeting did not estimate a maximum residue level or an STMR as the registration was only pending.

Residue data on dry beans were generated in Brazil and the USA. In the 1994 evaluation data from Brazil only were the basis of the recommended MRL of 0.1 mg/kg. In 1997 an STMR of 0.05 mg/kg was estimated. The manufacturer resubmitted data previously reviewed in 1994 and 1997. The registered use pattern in Brazil allows application of clethodim at rates of 0.084-0.11 kg ai/ha with a PHI of 40 days. The registered use pattern in the USA allows 1 or 2 applications at rates equivalent to 0.11-0.28 kg ai/ha and a PHI of 30 days. The new data from the USA include residues in the whole seeds, hay and dry vines. The residues in the dry beans in rank order were <0.1 , <0.5 , 0.64, 0.79, 0.81, 0.98, 1.1, 1.41 and 1.6 mg/kg. On the basis of the combined Brazilian and US data, the Meeting recommended an MRL of 2 mg/kg and estimated an STMR of 0.81 mg/kg for dry beans. The 1997 Meeting recommended the withdrawal of the draft MRL of 0.1 mg/kg.

The residues in bean hay in rank order were <0.1 , 1.3, 1.4, 1.5, 1.8, 2.0, 2.3, 3.3 and 5.5 mg/kg. The Meeting recommended an MRL of 10 mg/kg for bean fodder (hay) and estimated an

STMR of 1.8 mg/kg for animal feed purposes. The residues were not corrected for dry matter content (88%).

The residues in dry bean vines in rank order were <0.1, 0.23, 1.2, 1.5 (2), 1.8 (2), 2.2 and 2.8 mg/kg. The Meeting recommended an MRL of 5 mg/kg for bean forage and estimated an STMR of 1.5 mg/kg for animal feed purposes. As the residues in vines were expressed on a dry weight basis, a correction for dry matter content is not required for the calculation of the dietary burden for livestock.

Supervised residues trials on peppers were conducted in Italy and the USA. No registered use pattern or label was provided from Italy so the data could not be compared to relevant GAP. In the USA the registration of clethodim for use on peppers is pending. The proposed GAP is given as 1 or 2 applications at rates of 0.14-0.28 kg ai/ha with a PHI of 20 days. The residues in bell peppers (capsicums) and chilli peppers in trials which corresponded with the proposed GAP were 0.11-0.89 mg/kg. As the registration for peppers is pending, the Meeting did not estimate a maximum residue level or STMR.

Trials on sunflowers were carried out in Argentina, Canada, France, Italy and the USA. The Argentinian data were reviewed in 1994 and an MRL of 0.2 mg/kg was recommended. In the following review in 1997, the recommendation was withdrawn as there were too few results from trials according to GAP. The registered use pattern in Argentina allows single applications at rates of 0.16-0.24 kg ai/ha and a PHI of 100 days. GAP in Canada allows 1 or 2 applications at rates of 0.045-0.09 kg ai/ha with a PHI of 72 days and in France rates of 0.18-0.48 kg ai/ha with a PHI of 100 days. As a label from Italy was not provided, the Italian data were evaluated against French GAP. In the USA there is a pending use pattern of 0.11-0.28 kg ai/ha and a PHI of 70 days; the number of applications is not specified. As the registration is pending the US data were not used in the estimation of the STMR or maximum residue level. The residues in sunflower seed in rank order were <0.03 (3), <0.04 (5), <0.05, 0.051, <0.06 (3), 0.065, <0.07 (2), <0.08, 0.085, 0.12, 0.13 (2), 0.14, 0.15, 0.16, 0.20 and 0.33 mg/kg. The Meeting recommended an MRL of 0.5 mg/kg and estimated an STMR of 0.06 mg/kg. The draft MRL of 0.2 mg/kg was recommended for withdrawal by the 1997 JMPR.

A processing factor of 0.2 for crude sunflower seed oil was derived from a processing study on sunflowers. This processing factor may be applied to the recommended MRL to estimate a maximum residue level for crude sunflower seed oil. The STMR is calculated as 0.012 mg/kg for intake estimation. In the 1997 evaluation the draft MRLs for crude and edible sunflower seed oil were recommended for withdrawal owing to insufficient data. The Meeting recommended an MRL of 0.1* mg/kg for crude sunflower seed oil.

Feeding studies with laying hens and dairy cattle were reviewed in 1994 and 1997. The studies are repeated here for completeness. Doses in both studies were composed of a mixture of clethodim and clethodim sulfoxide (5:95), to simulate the exposure that may occur from feeding treated crops and processed commodities. At the 1999 CCPR, the JMPR was requested to justify the recommended MRLs for animal commodities by estimating the dietary exposure to livestock from feeding treated crops. Tables listing various treated feed commodity items and the residues likely to be found in them were constructed for a hen and dairy cow diet, and estimates of the composition of the diets were based on figures given in the FAO Manual and listed in USEPA guideline OPPTS 860.1000. Estimates of the likely dietary exposure of dairy cattle and hens were 2.9 and 7 ppm in the diet respectively, or 43.4 and 1.05 mg/animal/day.

The lowest feeding levels in both studies were 10 ppm in the diet. Continuous feeding at 10 ppm in the diet of dairy cattle led to total clethodim residues of <0.15 mg/kg in muscle and fat. The residues in liver and kidney were <0.16 and <0.151 mg/kg respectively. In milk the total residues were <0.0375 mg/kg over the 28-day period of the feeding study. As the highest exposure of dairy cattle is estimated as one third of the lowest level in the feeding study, it is expected that residues

above the limit of determination would not be found in milk or cattle tissues. The method of analysis for the determination of clethodim and metabolites in milk and bovine tissues is a common moiety or non-specific method, and the limits of determination in tissues and milk would be 0.2* and 0.05* mg/kg respectively. In the compound-specific method, the limit of determination was reported as 0.04 mg/kg in milk and 0.2 mg/kg in tissues. Therefore on the basis of the limits of determination in both specific and non-specific methods, MRLs of 0.05* mg/kg can be recommended for milk and 0.2* mg/kg for cattle tissues and offal; STMRs of 0 were estimated for both tissues and milk. Withdrawal of dosing at the 10 ppm level for 2-3 days led to residues below the limit of determination in all tissues.

Similarly in hens, the lowest residue level in the feed was 10 ppm. Continuous feeding at that level for 28 days resulted in residues below the limit of determination in all tissues and eggs. In the compound-specific method, the limit determination in eggs was reported as 0.05 mg/kg and in tissues as 0.2 mg/kg. However in the non-specific common moiety method used in the feeding study, the limits of determination were 0.15 mg/kg in both eggs and tissues. On the basis of the specific method, MRLs of 0.05* mg/kg are recommended for eggs and 0.2* mg/kg for poultry meat and offal. STMRs of 0 were estimated for eggs, poultry meat and poultry offal.

Processing studies on canola (rape seed), cotton, peanuts, soya beans, sugar beet, sunflowers and tomatoes were reported. Calculated processing factors were 0.22 and 0.1 for crude and edible cotton seed oil respectively, 0.4 and 0.09 for crude and refined peanut oil 0.32, for crude rape seed oil, and 0.09 and 0.002 for crude and refined soya bean oil respectively. STMRs for cotton seed, rape seed and soya beans had not previously been estimated, so STMRs for the processed products could not be calculated.

An STMR of 0.35 mg/kg was estimated for tomatoes in the 1997 review of clethodim. STMRs of 0.27, 1.2 and 0.77 were calculated for tomato juice, paste and purée respectively from the corresponding processing factors.

An STMR of 1.3 was estimated for peanuts in 1997. STMRs of 0.52 and 0.12 respectively were calculated for crude and edible peanut oil.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: sum of clethodim and metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulfoxides and sulfones, expressed as clethodim.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
VD 0071	Beans (dry)	2	0.1 ¹	0.81
AL 0061	Bean fodder (hay)	10	–	1.8
AL 1030	Bean forage (green)	5	–	1.5
MO 1280	Cattle, kidney	W	0.2*	–
MO 1281	Cattle, liver	W	0.2*	–
MM 0812	Cattle meat	W	0.5*	–
ML 0812	Cattle milk	W	0.1*	–
PE 0840	Chicken eggs	W	0.5*	–
PM 0840	Chicken meat	W	0.5*	–

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
MO 0105	Edible offal (mammalian)	0.2*	–	0
PE 0112	Eggs	0.05*	–	0
MM 0095	Meat (from mammals other than marine mammals)	0.2*	–	0
ML 0106	Milks	0.05*	–	0
OC 0697	Peanut oil, crude			0.52
OR 0697	Peanut oil, edible			0.12
VR 0589	Potato ²	0.5	0.2	
PO 0111	Poultry, edible offal of	0.2*	–	0
PM 0110	Poultry meat	0.2*	–	0
SO 0702	Sunflower seed	0.5	0.2 ¹	0.06
OC 0702	Sunflower seed oil, crude	0.1*	0.05 ¹	0.012
JF 0448	Tomato juice			0.27
	Tomato paste			1.2
	Tomato purée			0.77

¹ Withdrawal was recommended by the 1997 JMPR

² STMR could not be estimated as previously received data were not re-submitted

Note. Previous recommendations for cattle milk, meat and offal have been changed to general recommendations for mammalian commodities as it is unlikely that residues would be detectable in other livestock which are exposed to treated feed items. The highest exposure to treated feed items is for beef and dairy cattle; exposure of pigs and goats is lower.

FURTHER WORK OR INFORMATION

Desirable

Data on residues occurring in commerce and/or at consumption (from 1994 and 1997 Meetings).

DIETARY RISK ASSESSMENT

Chronic intake

In the current evaluation, STMRs for 16 commodities have been estimated. Where consumption data were available these STMRs were used in the estimates of dietary intake together with existing STMRs and a revised estimated maximum residue level for potato.

Estimated Dietary Intakes for the five GEMS/Food regional diets, based on new and existing STMRs and a proposed MRL, were in the range of 3-30% of the ADI (Annex III). The Meeting concluded that the intake of residues of clethodim resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The Meeting concluded that an acute RfD for clethodim is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard, and residues are therefore unlikely to present an acute risk to consumers.

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