CLETHODIM (187)

IDENTITY

ISO common name: clethodim

Chemical name:

IUPAC: (±)-2-[(*E*)-1-[(*E*)-3-chloroallyloxyimino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxycyclohex-2-enone

CA: (*E*,*E*)-(±)-2-[1[[(3-chloro-2-propenyl)oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one

CAS No.: 99129-21-2

Synonyms: Select[R], Centurion[R], RE-45 601

Structural formula:

Molecular formula: $C_{17}H_{26}ClNO_3S$
Molecular weight: 359.92

Physical and chemical properties

Pure active ingredient

Vapour pressure: <0.01 mPa (<10^{-7} torr) at 25°C

Melting point: Clethodim is a pale yellow viscous oil at ambient temperatures

Octanol/water
partition coefficient: 1.5×10^4

Solubility: Soluble in most organic solvents (>90 g/100 ml)
Solubility in water, 0.54 g/100 ml at pH 7

Specific gravity: 1.1395 g/ml at 20°C

Dissociation constant: $pK_a = 4.47$

pH: 4.1

Technical material

Purity: 91.2% (typical technical material)
37% (manufacturing use product)

Formulations

Clethodim is available commercially as an emulsifiable concentrate containing 26.4% of the technical material, equivalent to 24% ai.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Rats. A metabolic study in rats was undertaken with the objectives of determining the absorption, distribution, excretion and metabolic fate, including metabolic characterisation, of [*propyl*-1-^{14}C]clethodim administered orally to male and female rats at two different doses. Clethodim was not sufficiently soluble in saline or water to permit intravenous dosing (Rose and Griffis, 1988).

The rats were divided into three groups, Low Dose (4.4 mg/kg bw), Repeated Dose (4.8 mg/kg bw) and High Dose (468 mg/kg bw) and treated with a single oral dose of [*propyl*-1-^{14}C]clethodim. Before radiolabelled dosing, the Repeated Dose group was given a single daily oral dose of unlabelled clethodim (4.5 mg/kg bw) for 14 consecutive days. Excreta were collected for seven days (except CO_2 which was collected for 48 hours), at which time the animals were killed. Tissues were analysed for the distribution of [^{14}C]clethodim and in all treatment groups the recovery of the radiolabelled dose was 103-110%. After 7 days, the total amount of the radiolabel recovered from the organs and tissues from each dose group, male or female, was less than 1% of the applied dose. There was no difference in the concentration of radiocarbon in the tissues of the Repeated Dose and Low Dose groups, indicating that there was no change in the distribution of radioactivity in the tissues as a result of repeated low dose exposure.

Nearly all of the administered dose was eliminated from all treatment groups in the urine (87.2-93.2%), faeces (9.3-17.0%) and as carbon dioxide (0.5-1.0%). Elimination was rapid, most of the dose being recovered within 48 hours. The Low Dose group eliminated clethodim slightly faster (98% in about 40 hours) than did the High Dose group (98% in about 50 hours) but there was no difference in the rate of elimination between the Low Dose group and the Repeated Dose group. Repeated exposure to low doses of clethodim did not alter the rate of elimination and there were no sex differences in the elimination rate.

Autoradiogram TLC profiles of urinary metabolites were very similar for males and females within a dose group and also between dose groups. Clethodim, clethodim sulphoxide, clethodim sulphone, imine sulphoxide, *S*-methyl sulphoxide and 5-hydroxy sulphone were isolated from urine and positively identified by chemical ionisation and electron-impact mass spectrometry, TLC co-chromatography with reference standards in two solvent systems, and HPLC co-chromatography with reference standards. Further evidence for the presence of these metabolites and of 5-hydroxy sulphoxide was obtained by LC-MS. Using LC-MS, imine sulphoxide, oxazole sulphoxide, oxazole sulphone, *S*-methyl sulphoxide, trione sulphoxide, 5-hydroxy sulphoxide, and clethodim sulphoxide were detected in the 12-hour urine collection from the High Dose group males and females. Apart from trione sulphoxide, these were confirmed by TLC co-chromatography as above.

Clethodim is rapidly absorbed and then (a) oxidized to clethodim sulphoxide (dominant) and thence to clethodim sulphone; (b) converted to *S*-methyl via a sulphonium cation intermediate; (c) converted to imine; or (d) hydroxylated at the 5 position. The proposed *S*-methyl would follow the dominant metabolic process and form the observed *S*-methyl sulphoxide and smaller amounts of *S*-methyl sulphone. Similarly, imine would rapidly be oxidized to imine sulphoxide and imine sulphone. Any 5-hydroxy-clethodim formed (this was not detected) would be rapidly oxidized to the observed 5-hydroxy sulphoxide and corresponding sulphone.

Goats. A metabolism study was carried out on a lactating goat treated with 1.16 mg/kg bw/day, equivalent to 24 ppm of [*propyl*-1-^{14}C]clethodim in the diet, divided into 3 equal doses (14.2 mg/dose) for three days and a final dose of 14.2 mg on the morning of the fourth day. A control goat received the same number of empty gelatine capsules. Milk was collected twice daily and excreta daily. The goat was slaughtered about 4 hours after the last dose and samples of muscle, fat, liver, kidneys, heart and blood were collected (Rose and Suzuki, 1988).

Clethodim was rapidly absorbed and excreted. Most of the dose was found in the urine (56.4%) and faeces (34.4%). The concentration of radiocarbon in the milk reached a plateau of about 0.035 mg/l by day 2. Radiocarbon in the blood (0.17 mg/l) was higher than that in muscle (0.033, 0.034 mg/kg) or fat (subcutaneous 0.079 mg/kg; peritoneal 0.047 mg/kg) and therefore there appeared to be little potential for accumulation. Somewhat higher amounts of radiocarbon were found in the liver (0.42 mg/kg) and kidney (0.38 mg/kg); the heart contained 0.058 mg/kg clethodim equivalents.

Chickens. A poultry metabolism study was carried out with [*cyclohexene*-4,6-^{14}C]clethodim. Young laying hens were assigned to one of two test groups or to the control group. The Low Dose group (2.1 mg/kg bw) was used for radioanalysis and metabolite determination while the High Dose group (51.3 mg/kg bw) was reserved for use to isolate quantities of metabolites for spectroscopic identification. Each bird received a single oral dose in a gelatine capsule filled with commercial poultry feed on each of 5 consecutive days. At the end of the dosing period the birds were slaughtered and tissues were collected for analysis. Most of the administered radioactivity was excreted and tissue accumulation was not apparent (Lee, 1988).

Identification of the metabolites was focused on the edible tissues and eggs using TLC and HPLC. Three major metabolites were identified, in order of increasing amounts clethodim, clethodim sulphone and clethodim sulphoxide. In some cases clethodim sulphoxide accounted for up to 57% of the radioactivity in the tissue, while the proportion of the sulphone ranged from 10.2 to 31.2%. On average, the parent clethodim amounted to only a few per cent of the radioactivity, although a much higher percentage was observed in the fat.

This metabolic pathway was simpler than that observed in other animal studies. None of the

imine analogues, 5-hydroxy analogues or *S*-methyl analogues that have been found in the rat and goat were seen in the chicken. Small amounts of unidentified materials were also seen on the TLC plates. Table 1 shows the relative amounts of radioactivity found in various tissues from the Low Dose feeding trial.

Table 1. Distribution of metabolites in tissues of chickens treated with [^{14}C]clethodim at 2.1 mg/kg bw for five consecutive days.

	% Tissue radioactivity			
Tissue	Clethodim	Sulphoxide	Sulphone	Unidentified
Kidney	2.7	42.5	27.8	10.1
Liver	7.5	33.2	21.1	13.2
Skin	4.6	56.9	16.7	13.1
Heart	1.6	48.0	21.6	10.7
Fat	64.9	14.5	10.2	7.1
Gizzard	12.9	44.8	21.3	8.9
Thigh	2.4	50.5	26.7	9.1
Breast	4.1	36.8	31.2	12.4

Similar results were obtained with the High Dose group, 33.5% of the tissue radioactivity being found in the chicken fat. In eggs, a similar distribution was observed in the whites but higher proportions of parent clethodim appeared in the yolks, as Table 2 illustrates.

Table 2. Distribution of metabolites in eggs of chickens treated with [14C]-clethodim at 2.1 mg/kg bw for five consecutive days.

	% of tissue radioactivity			
Egg sample	Clethodim	Sulphoxide	Sulphone	Unidentified
White				
Day 0	2.3	82.2	11.2	1.9
Day 1	5.7	38.7	37.1	15.5
Day 2	6.3	45.8	34.2	9.3
Day 3	6.4	25.9	38.2	24.4
Day 4	4.7	25.8	14.8	27.8
Yolk				
Day 0	insufficient yolk for metabolite identification			
Day 1	34.4	36.9	10.6	7.2
Day 2	18.8	31.7	26.7	6.0
Day 3	24.2	25.1	10.8	19.9
Day 4	16.5	36.7	14.6	3.2

Again, the High Dose group gave similar results.

Plant metabolism

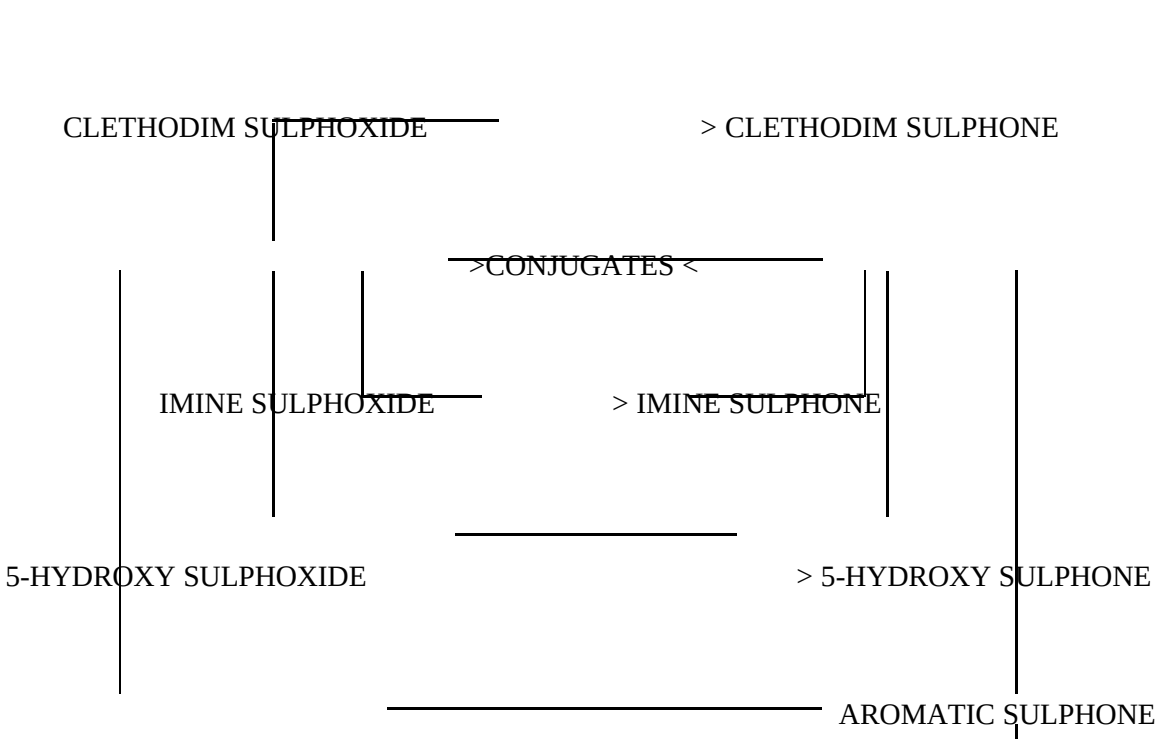
Metabolism studies were carried out using ^{14}C-labelled clethodim on carrots, soya beans and cotton. These showed that clethodim is readily metabolized, little or no parent compound being found in the mature plants. The major metabolites found were the sulphoxide and sulphone, together with their conjugates, 5-hydroxy sulphoxide and 5-hydroxy sulphone.

Using [*cyclohexene*-4,6-^{14}C]clethodim, carrot, cotton and soya bean plants were treated twice with a 14-day interval at 0.29 kg ai/ha as a post-emergence foliar spray. Crops were harvested at maturity, PHIs from 20 to 70 days. The harvested plants were separated into leaves, stems, roots, beans, pods, seeds, fibre and shells, as appropriate. Most of the radio-carbon was in the leaves and therefore both leaves and edible fractions were taken for metabolite characterisation by TLC and HPLC co-chromatography with authentic standards. Major metabolites were confirmed by LC-MS (Chen, 1988).

The main metabolic pathway of clethodim in the plants studied was initial sulphoxidation to

clethodim sulphoxide, followed by further oxidation to clethodim sulphone, elimination of the chloroallyloxy side chain to give the imine sulphoxide and sulphone, and hydroxylation to form the 5-hydroxy sulphoxide and sulphone. Clethodim sulphoxide and sulphone conjugates were also detected as major or minor metabolites depending on the plant and the subfractions examined. Total residues were low in the edible seeds, beans and roots.

The proposed metabolic pathway is shown below.



A similar study was carried out using [*chloroallyl*-2-^{14}C]clethodim, giving closely similar results. It was shown that the chloroallyloxy moiety was eliminated in the plant leaves, undergoing extensive metabolism with loss of the chlorine atom, while the three-carbon moiety was incorporated into the plant constituents (Chen, 1988b). The total ^{14}C residue was low in cotton seeds and carrot roots but was significantly higher in soya beans.

Environmental fate in soil

Results from four studies on the fate of clethodim in soils showed that metabolism by micro-organisms dominated the degradation process with no photoproducts being formed. The half-life was 1 to 3 days under aerobic conditions, the major metabolite being the sulphoxide and the only volatile metabolite CO_2. Under anaerobic conditions the sulphoxide was again the major product.

Aerobic fate. In two photolysis studies [*cyclohexene*-4,6-^{14}C]clethodim on a sandy loam soil was exposed to natural sunlight for 0, 1, 2, 3, 4 and 7 days at soil surface temperatures of 11 to 18°C and 2 to 17°C. Volatile ^{14}C compounds were collected in a xylene scrubber and $^{14}CO_2$ was collected in NaOH. No ^{14}C was volatilised as organic material and very little as $^{14}CO_2$. No photoproducts were detected in the systems, all substances found being products of metabolism, thus showing that

photodegradation did not occur on the soil (Chen, 1988c).

When the aerobic metabolism of [*propyl*-1-^{14}C]clethodim was studied at 10 mg/kg in a sandy soil, the clethodim was degraded rapidly, with a half-life of about 3 days. Clethodim sulphoxide was the major metabolite and this was also degraded rapidly. The most stable metabolite found was clethodim oxazole sulphone whose concentration remained fairly constant, but low, for 6 to 12 months. The only volatile metabolite was CO_2 (Pack, 1988a). The proposed metabolic pathways are shown below.

CLETHODIM IMINE SULPHOXIDE

CLETHODIM → CLETHODIM SULPHOXIDE → CLETHODIM SULPHONE → CO_2

CLETHODIM OXAZOLE → CLETHODIM OXAZOLE SULPHOXIDE → CLETHODIM OXAZOLE SULPHONE

A further study was carried out using [*cyclohexene*-4,6-^{14}C]clethodim and [*chloroallyl*-2-^{14}C]clethodim on a similar sandy soil at about 10 mg/kg. Clethodim was again degraded rapidly, half-life about 1 day, and $^{14}CO_2$ was the only volatile metabolite, containing 45 to 57% of the initial ^{14}C application after 4 months. The major non-volatile product was clethodim sulphoxide, which was further metabolized to clethodim sulphone. These compounds underwent rearrangement to form clethodim oxazole sulphoxide and clethodim oxazole sulphone respectively, cleaving off the chloroallyl side chain. The latter was degraded via formylacetic acid to CO_2 and chloride ion. The cyclohexene ring moiety was metabolized to smaller fragments that yielded CO_2. At two months after application all of the metabolites in the soil constituted less than 10% of the initial ^{14}C (Pack, 1990). The results were in good agreement with the earlier experiment (Pack, 1988a).

Anaerobic fate. The anaerobic metabolism of clethodim in soil was also studied by Pack (1988b). [*cyclohexene*-4,6-^{14}C]clethodim was applied at 9.8 mg/kg to a sandy loam soil in the dark at 25°C. Test samples were kept under aerobic conditions for one half-life, 1 day after application, and they were then made anaerobic by flushing through with nitrogen; samples were taken 30 and 62 days after anaerobic conditions were started.

The only volatile metabolite found during the aerobic phase was CO_2, the liberation of which essentially ceased under anaerobic conditions. At 1 day, clethodim sulphoxide was the only major aerobic metabolite. After 30 days of anaerobic conditions most of the remaining clethodim and clethodim sulphoxide had been degraded, only two significant anaerobic metabolites, clethodim imine and clethodim imine sulphoxide, being formed. In the aerobic studies reported above, clethodim imine was not detected and clethodim imine sulphoxide was only a minor metabolite.

After 30 days under anaerobic conditions, about 12% of the initial ^{14}C was not extractable with methanol or aqueous $CaSO_4$, while at 62 days the unextractable ^{14}C had increased to about 22% of the initial amount. It appeared that the ^{14}C fragments were becoming increasingly incorporated into the soil matrix and, under anaerobic conditions, were not oxidized to CO_2 but continued to build up in the soil.

Under these anaerobic conditions clethodim was metabolized primarily to clethodim imine which appeared to be relatively stable, being present at 33% of the initial ^{14}C treatment after 62 days. Clethodim sulphoxide formed aerobically is transformed to clethodim imine sulphoxide under anaerobic conditions. The proposed major anaerobic metabolic pathways are shown below.

CLETHODIM IMINE

(anaerobic)

CLETHODIM

(aerobic)

(anaerobic)

CLETHODIM SULPHOXIDE CLETHODIM IMINE SULPHOXIDE

Environmental fate in water/sediment systems

Under anaerobic conditions the half-lives of clethodim were 177 days at 25°C and 559 days at 5°C, the degradation being primarily microbiological with the metabolites being degraded at the same rate as they were formed. Under aerobic conditions the pattern was similar but degradation was quicker, with half-lives of clethodim of 5 days at 25°C and 23 days at 5°C, the only volatile metabolite again being CO_2.

Anaerobic fate. The anaerobic aquatic metabolism of clethodim was studied using [*cyclohexene*-4,6-^{14}C]clethodim in a Canadian slough water/sediment system fortified at about 1 mg/l. Treated materials were kept in the dark at 5°C and 25°C and samples for analysis were taken at intervals up to 6 months, followed by two further samples at 9 months and 1 year (Tucker, 1990a, 1991).

The 25°C samples were monitored for the generation of volatile organic products and $^{14}CO_2$ in addition to the ^{14}C remaining in the water and sediment. Total ^{14}C accountability ranged from 90 to 107%, with a mean of 97.5% over 6 months, at which time 55.8% of the original ^{14}C was in the aqueous supernatant, 28.3% and 1.3% were extractable with methanol and 10mM CaSO4 respectively, and 10.7% was unextracted from the sediment. The half-lives of clethodim were 177 days at 25°C and 559 days at 5°C.

The aqueous supernatants and methanol extracts of the sediment were analysed qualitatively and quantitatively by HPLC with a UV detector and a radioactivity detector in series. Representative samples were examined by LC-MS and TLC/autoradiography to confirm the identity of the metabolites. The major metabolites were clethodim imine in the sediment and clethodim sulphoxide in the aqueous supernatant liquid.

These results are in accordance with the findings of the anaerobic soil metabolism study described above.

Aerobic fate. The aerobic aquatic metabolism of clethodim was studied using [*cyclohexene*-4,6-^{14}C]clethodim in a Canadian slough water/sediment system fortified at about 1 mg/l. Treated materials were maintained at 25°C in the light and at 5°C in the dark. Samples for analysis were taken at intervals up to 6 months (Tucker, 1990b).

The 25°C samples were monitored for the generation of volatile organic products and $^{14}CO_2$ in addition to the ^{14}C remaining in the water and sediment.
Total ^{14}C accountability ranged from 80 to 99%, with a mean of 90% over 6 months. The only volatile metabolite was $^{14}CO_2$, which accounted for 39% of the original ^{14}C after 6 months in the dark. After 6

months in the light, only 4.4% of the initial ^{14}C was released as $^{14}CO_2$ because the green algae and aquatic plants in the supernatant utilized the $^{14}CO_2$ in photosynthesis, producing ^{14}C materials that became incorporated into the soil matrix. After 6 months, 85% of the initial ^{14}C was in the sediment and 2% was in the aqueous supernatant. After 6 months in the dark, 36% of the initial ^{14}C treatment was in the sediment and 14% in the aqueous supernatant.

The aqueous supernatants and methanol extracts of the sediment were analysed qualitatively and quantitatively by HPLC with a UV detector and a radioactivity detector in series. Representative samples were examined by LC-MS and TLC/autoradiography to confirm the identity of the metabolites. The major metabolites were clethodim imine in the sediment and clethodim sulphoxide in the aqueous supernatant liquid, which were further oxidized to their sulphones. A minor metabolic pathway was the formation of clethodim oxazole, which was oxidized to its sulphoxide and sulphone. These metabolites were readily degraded in the water/sediment system and at 6 weeks were each less than 10% of the initial ^{14}C treatment. The clethodim was degraded with half-lives of 5 days at 25°C in the light or in the dark and 23 days at 5°C in the dark.

The results are in agreement with those found in the degradation studies in aerobic soil systems.

METHODS OF RESIDUE ANALYSIS

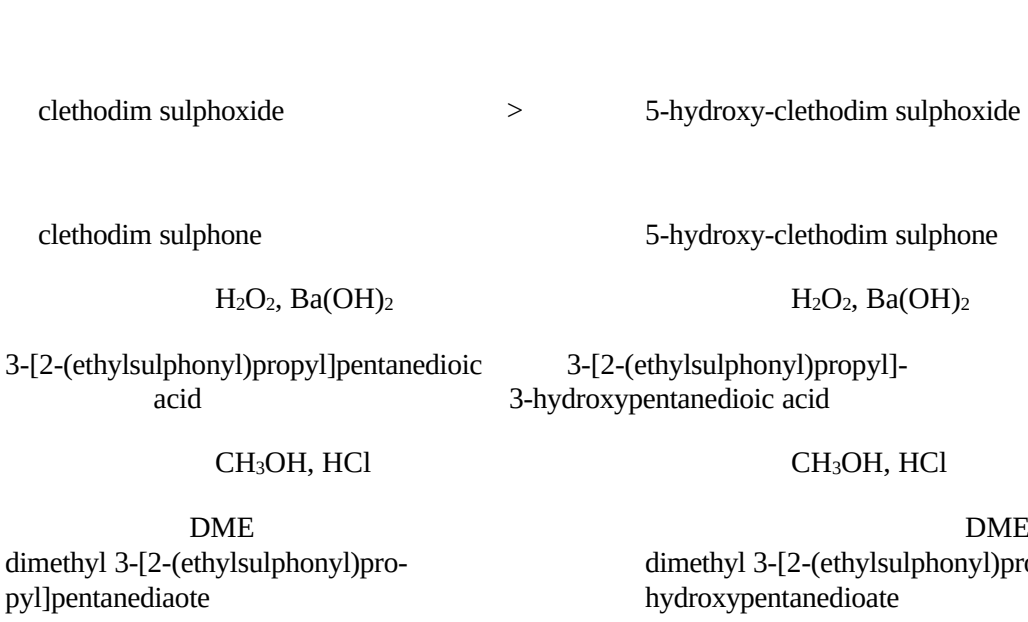
Analytical methods

The analytical methods used in the studies reported here are modifications of that used for residues of sethoxydim as given in PAM (King, 1984). In the procedure, all clethodim-related metabolites which retain the cyclohexene-1-one structure are oxidized to two common compounds.

Clethodim and its metabolites are extracted from plant material with water and methanol and the extract is partitioned into dichloromethane. After clean-up by alkaline precipitation and acidic back-extraction, oxidation with hydrogen peroxide at pH 9-10 yields dicarboxylic acids which are methylated with methanol to yield the common compounds DME, dimethyl 3-[2-(ethylsulphonyl)propyl]pentanedioate, and DME-OH, dimethyl 3-[2-(ethylsulphonyl)propyl]-3-hydroxypentanedioate. After a silica gel or methylene chloride partition clean-up step, these are then determined by gas chromatography using a flame photometric detector in the sulphur mode. The limit of determination is of the order of 0.05 mg/kg.

The total residue of DME + DME-OH is then expressed as clethodim i.e. mg/kg clethodim = mg/kg DME x 1.22 + mg/kg DME-OH x 1.16. The procedure has proved to be adaptable to the many food commodities so far examined (Fujie, 1990a). An outline of it is given in Figure 1.

Figure 1. Reaction sequence for the residue analysis method.



A procedure is also available for the determination of clethodim sulphoxide in aqueous solutions. Samples are extracted with methylene chloride, the solvent is removed by rotary evaporation and the residue taken up in acetonitrile containing 2% v/v acetic acid for measurement by HPLC using a UV detector at 247 nm. When a 50 ml sample is extracted as described and diluted to 1 ml the limit of determination is 0.01 mg/l; recoveries ranged from 70 to 120% (Fujie, 1990b).

However, these methods will not distinguish residues of clethodim from those of similar herbicides, such as sethoxydim, for which the procedures were devised. A method for the confirmation of the presence of clethodim residues has been provided that is applicable to crops, animal tissues, milk and eggs (Lai and Ho, 1990). Residues are extracted with methanol/water and cleaned up by an alkaline precipitation step. Cloproxydim sulphoxide is added as an internal standard and, after partitioning into dichloromethane, methylation with diazomethane, oxidation with metachlorobenzoic acid and silica Sep-Pak clean-up, analysis for the methylated sulphones of clethodim, 5-hydroxy-clethodim and cloproxydim is conducted by HPLC on a C-18 column with UV detection. This procedure is claimed to be specific for the determination of clethodim and its metabolites.

Isomerism of clethodim and related compounds

Clethodim and related metabolic compounds show three types of isomerism, geometric, tautomeric and enantiomeric, and as a result some chromatograms can show multiple peaks or spots owing to the resolution of some of these isomers. Care in analytical interpretation is therefore necessary (Reynolds, 1988).

Geometric isomerism. Clethodim and related oximes have the alkoxy group orientated syn- or anti- to the cyclohexanedione ring. In general, both isomers are present and can be separated. The two forms equilibrate to a fixed ratio that is solvent-dependent, although the rate may be slow enough at ambient temperatures for resolution to occur during HPLC or TLC.

Tautomerism. Clethodim is an oxime of a 2-acyl-cyclohexane-1,3-dione system and is an equilibrium mixture of tautomers at NMR concentrations (0.1 molar). Four keto-enol tautomers are possible and their presence explains the syn-/anti- isomerization and optical isomer racemization reactions.

Optical isomerism. Clethodim and its related compounds have at least one asymmetric centre. Those with two or more such centres can often be resolved as diastereoisomeric pairs on chromatographic columns.

Stability of pesticide residues in stored analytical samples

Residue levels (0.05 to 0.25 mg/kg) of clethodim, *S*-methyl clethodim sulphoxide and 5-hydroxy clethodim sulphone in bovine tissues (fat, kidney, liver and muscle) and milk showed no degradation when stored at -20°C for 5 months (Weissenburger, 1989).

In similar studies on residues in chicken eggs and tissues (fat, gizzard, liver and muscle), all residue components were stable for at least 8 weeks at -18 ± 3°C, although 5-hydroxy clethodim sulphone appeared to be slightly less stable in the gizzard, liver and muscle samples for the 6-week period, when less than 90% of the added material was recovered; it was stable in the other matrices studied and over 3 to 4-week periods (Lear, 1989).

When fuzzy cotton seed containing residues of clethodim ranging from 0.38 to 1.44 mg/kg was stored for periods up to six months at -20°C, analyses showed 80 to 128% of the initial residues (Lai, 1988a).

The storage stability of clethodim residues in frozen soya bean macerates has been studied, with the results shown in Table 3.

Table 3. Stability of clethodim residues in frozen soya bean macerates.

	Residue as clethodim (mg/kg)					
Day	DME		DME-OH		Total Clethodim	
Sample No.	5	6	5	6	5	6
0	9.1	9.3	4.7	4.4	13.8	13.7
86	8.1	7.9	3.8	4.8	11.9	12.7
141	6.9	7.2	3.0	3.4	9.9	10.6
208	8.9	9.0	5.6	5.8	14.5	14.8

Thus, the combined residues represented between 71.7 and 108% of the initially found residue from 86 to 208 days later (Lai, 1988b).

USE PATTERN

Clethodim is a post-emergence herbicide, active against annual and perennial grasses and similar narrow-leaved weeds, including "volunteer" cereals. It belongs to the class of acetyl coenzyme-A carboxylase inhibitors which includes the compounds sethoxydim and cycloxydim. It is currently registered in some 35 countries on over 20 crops. The rate of application varies from 0.06 to 0.36 kg ai/ha, the higher rates being needed for stubborn weeds such as Bermuda grass (*Cynodon dactylon*) , Quackgrass (*Agropyron repens*) and Rhizome Johnson grass (*Sorghum halepense*), and also when grasses are at maximum height or crops are under heavy grass pressure.

Clethodim is available as a 24% emulsifiable concentrate and registered uses are listed in Table

4. There are no authorised uses in Germany (Germany, 1993) and products based on clethodim are not authorised for use on agricultural crops in The Netherlands (Netherlands, 1994). From the crops on which uses are registered, and the extent of the residue data provided, it appears that the major uses of clethodim are on beans (dry), field peas, soya beans, potatoes, sugar beet, cotton seed, rape seed and sunflower.

Table 4. Registered uses of clethodim. All formulations are 24% EC.

Crop	Country	Applications		PHI, days
		No.	kg ai/ha	
Fruits				
Fruit trees or orchards	Ecuador	1-2	0.12-0.18	--
	Morocco	1-2	0.10-0.34	50-75
	New Zealand	1-2	0.06-0.72	35
	Peru	1-2	0.12-0.18	15
Citrus	Paraguay	1-2	0.12-0.24	5
Berries	Paraguay	1-2	0.12-0.24	5
Strawberry	Paraguay	1-2	0.12-0.24	5
Vegetables				
Vegetables	Ecuador	1-2	0.06-0.12	--
	New Zealand	1-2	0.06-0.72	35
Garlic	Spain	1-2	0.10-0.20	--
Onions	Israel	1-2	0.10-0.34	50
	Spain	1-2	0.10-0.20	--
Cucurbits	Paraguay	1-2	0.12-0.24	5
Tomato	Israel	1-2	0.10-0.34	50
	Spain	1-2	0.10-0.20	--
Beans	Belgium	1-2	0.07-0.36	90
	Bolivia	1-2	0.08-0.24	65
	Ecuador	1-2	0.06-0.12	--
	Guatemala	1-2	0.2	50
	Paraguay	1-2	0.12-0.24	5
	Peru	1-2	0.12-0.18	15
	Spain	1-2	0.10-0.20	--
Peas	Belgium	1-2	0.07-0.36	90
	Israel	1-2	0.10-0.34	50
	New Zealand	1-2	0.06-0.72	35
	Spain	1-2	0.10-0.20	--
Broad beans	Australia	1-2	0.06	--
	Spain	1-2	0.10-0.20	--
Chick peas	Australia	1-2	0.06	--
	Spain	1-2	0.10-0.20	--
Field peas	Australia	1-2	0.06	--
Lentils	New Zealand	1-2	0.06-0.72	35
	Spain	1-2	0.10-0.20	--
Lupins	Australia	1-2	0.06	--
Soya beans	Argentina	1-2	0.10-0.34	65
	Australia	1-2	0.06-0.09	--
	Bolivia	1-2	0.08-0.24	65
	Brazil	1-2	0.07-0.12	90
	Colombia	1-2	0.18-0.24	--
	Costa Rica	1-2	0.07-0.12	--
	Ecuador	1-2	0.06-0.12	--
	Guatemala	1-2	0.2	50
	Korea	1	0.14	--
	Mexico	1-2	0.06-0.18	60
	Morocco	1-2	0.10-0.34	50-75

Crop	Country	Applications		PHI, days
		No.	kg ai/ha	
	Nicaragua	1-2	0.08-0.24	60
	Paraguay	1-2	0.12-0.24	5
	Peru	1-2	0.12-0.18	15
	USA	1-2	0.10-0.28	60
Beetroot	Israel	1-2	0.10-0.34	50
Carrot	Israel	1-2	0.10-0.34	50
Potato	Belgium	1-2	0.07-0.36	90
	Ecuador	1-2	0.06-0.12	--
	Peru	1-2	0.12-0.18	15
	Switzerland	1-2	0.12-0.24	56
Sugar beet	Belgium	1-2	0.07-0.36	90
	Morocco	1-2	0.10-0.34	50-75
	Spain	1-2	0.10-0.20	--
	Switzerland	1-2	0.12-0.24	56
Oilseed				
Palm	Ecuador	1-2	0.06-0.12	--
Cotton	Argentina	1-2	0.10-0.34	100
	Bolivia	1-2	0.08-0.24	65
	Colombia	1-2	0.18-0.24	--
	Costa Rica	1-2	0.07-0.12	--
	Ecuador	1-2	0.06-0.12	--
	Israel	1-2	0.10-0.34	50
	Morocco	1-2	0.10-0.34	50-75
	Spain	1-2	0.10-0.20	--
	USA	1-2	0.10-0.28	60
Linseed	Canada	1-2	0.05-0.10	60
Peanut	Argentina	1-2	0.10-0.34	70
	Bolivia	1-2	0.08-0.24	65
Rape seed	Canada	1-2	0.05-0.10	60
	New Zealand	1-2	0.06-0.72	35
	Spain	1-2	0.10-0.20	--
Sunflower	Argentina	1-2	0.10-0.34	60
	Bolivia	1-2	0.08-0.24	65
	Ecuador	1-2	0.06-0.12	--
	Israel	1-2	0.10-0.34	50
	Morocco	1-2	0.10-0.34	50-75
	Paraguay	1-2	0.12-0.24	5
	Spain	1-2	0.10-0.20	--
Animal feed				
Alfalfa	Ecuador	1-2	0.12-0.18	--
	Peru	1-2	0.12-0.18	15
Clover	Israel	1-2	0.10-0.34	50
Fodder beet	Belgium	1-2	0.07-0.36	90

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data obtained from trials on about 30 crops in several countries were provided, although there were only very limited, or summary, data in many cases.

Peach. In six trials in Spain in 1989 (1) and 1992 (5), peach orchards were treated twice with clethodim at 0.18 kg ai/ha at periods ranging from green-fruit stage to harvest, with PHIs from 0 to 60 days. No residues were above the limit of determination of 0.03 mg/kg (Bayer Spain, 1990/93).

Garlic. One trial in Spain in 1989, when garlic was treated with clethodim at 0.24 kg ai/ha, showed a residue of 0.12 mg/kg on the treatment day but <0.03 mg/kg 21 days later (Bayer Spain, 1990a).

Leek. Treatment of leeks in France in 1987 with 0.12, 0.18, 0.18 and 0.48 kg ai/ha gave residues up to 0.06, 0.10, 0.13 and 0.34 mg/kg respectively at 28 days and 0.09, 0.16, 0.11 and 0.17 mg/kg respectively at 56 days (Tomen France, 1988a).

Onion. Onions treated in New Zealand in 1988/89 with clethodim at 0.24 or 0.48 kg ai/ha showed no residues above the limit of determination (0.03 mg/kg) 42 or 84 days later (Nufarm [New Zealand], 1988/89). Similarly, onions treated in Italy in 1989 at 0.24 kg ai/ha showed no residues at 20, 30 or 40 days PHI (Bayer Italy, 1990a). In Moldavia, trace amounts of clethodim, <0.1 mg/kg, were reported 55 days after application at 1.2 kg ai/ha, but only summary data were available (Tomen Ukraine, 1993).

Cauliflower. One trial in New Zealand in 1988/89 gave a residue of 0.28 mg/kg 42 days after treatment at 0.24 kg ai/ha, but <0.03 mg/kg after 84 days (Nufarm [New Zealand], 1989).

Squash, Summer. Treatment of zucchini in a trial in Italy in 1989 showed residues below 0.03 mg/kg at 28, 33 and 42 days after application at 0.24 kg ai/ha (Bayer Italy, 1990b).

Peppers, Sweet. Residues of 0.1, 0.05 and 0.05 mg/kg of clethodim were found 18, 28 and 38 days respectively after treating sweet peppers in Italy in 1990 at a rate of 0.24 kg ai/ha (Bayer Italy, 1992a).

Tomato. Treatment of tomatoes in Italy in 1988 at 0.24 kg ai/ha gave residues of 0.06 mg/kg at 30 days but <0.03 mg/kg after 51 days (Bayer Italy, 1989a). In six trials in Spain from 1989 to 1992, using applications of 0.24 kg ai/ha, a maximum residue of 0.05 mg/kg was found once at day 0 but all other results were at or below the limit of determination (0.03 mg/kg) at 0, 21, 22 or 60 days after application (Bayer Spain, 1990/92).

Lettuce, Head. Lettuces were treated in France in 1987 with clethodim at rates of 0.12, 0.18, 0.18 and 0.48 kg ai/ha; the corresponding residues were 0.19, 0.13, 0.27 and 0.34 mg/kg at 28 days PHI (Tomen France, 1988b). Trials in Italy in 1990 at 0.24 kg ai/ha yielded residues of 0.31, 0.16, 0.05 and 0.07 mg/kg at 0, 10, 15 and 20 days after treatment (Bayer Italy, 1992b).

Spinach. In France in 1987, spinach was treated with clethodim at 0.12, 0.18, 0.18 and 0.48 kg ai/ha; residues were respectively 0.14, 0.19, 0.10 and 0.15 mg/kg at 15 days and 0.04, 0.08, 0.03 and 0.08 mg/kg at 30 days (Tomen France, 1988c).

Peas. Marrowfat peas treated in New Zealand in 1988 with 0.24 kg ai/ha showed residues in the podded peas of 0.29 mg/kg after 43 days. The pea silage contained 0.47 mg/kg at the same time (Nufarm [New Zealand], 1988a). Broad bean. In one trial on broad beans in Spain in 1988, treatment at 0.14 kg ai/ha led to residues below the limit of determination (0.03 mg/kg) in the bean and in the husk (Bayer Spain, 1990b).

Common bean. Green beans treated in Belgium in 1992 with clethodim at 0.09 kg ai/ha showed no residues in the pods above the limit of determination of 0.025 mg/kg (Bayer Belgium, 1993).

French beans were treated in France with 0.18 kg ai/ha; at harvest, 32 days later, residues in the beans were below 0.03 mg/kg (Tomen, 1987a).

Green beans were treated in Italy in 1988 with clethodim at 0.24 kg ai/ha, yielding residues of

0.11 and 0.09 mg/kg after 20 and 24 days respectively (Bayer Italy, 1989b).

However, none of these treatments were within the accepted GAP of the countries concerned.

Beans (dry). In Brazil in 1989, beans were treated with clethodim at rates of 0.084, 0.108, 0.168 and 0.216 kg ai/ha. At PHIs of 65 and 85 days, the dry beans showed no residues above the limit of determination of 0.05 mg/kg. At 25 and 45 days after application, residues in the beans ranged from 0.37 to 0.93 and 0.06 to 0.14 mg/kg respectively (Chevron Brazil, 1990).

Field peas (dry). Field peas were treated in Australia in 1987 with clethodim at 0.06, 0.12 and 0.24 kg ai/ha. At harvest, 110 days after application, residues in the dry pea seeds and in the straw were all below the limit of determination of 0.03 mg/kg (Shell Australia, 1987a).

Four trials of field pea (Maro) treatments in the UK in 1988 were at rates of 0.36 and 0.72 kg ai/ha. At the lower treatment rate, residues in the pea seed and the husk were not above 0.03 mg/kg at PHIs of 53 and 85 days. At the higher rate residues of 0.04 and 0.05 mg/kg were found in the peas at 53 days, and <0.03 and 0.08 mg/kg at 85 days (Bayer UK, 1988).

When protein peas were treated in Belgium in 1992 at 0.09 and 0.18 kg ai/ha, the residues in the seeds 41 days later were below 0.025 mg/kg (Bayer Belgium, 1992).

Protein peas were treated at six sites in France in 1987 with single applications of clethodim at rates of 0.18, 0.48 and 0.96 kg ai/ha; residues obtained are detailed in Table 5 (Tomen France, 1988d).

Table 5. Residues of clethodim in protein peas in France.

PHI (days)	Residue (mg/kg) from treatment at 0.18 kg/ha	0.48 kg/ha	0.96 kg/ha
67	0.05	0.11	0.29
72	0.03	0.08	0.15
72	<0.03	0.13	0.17
80	0.04	0.08	--
80	<0.03	0.04	0.14
82	0.06	0.28	0.75

Lentil (dry). Lentils were treated in Spain in 1990 with clethodim at 0.18 kg ai/ha. On the day of treatment, residues in the husk were 2.2 mg/kg; 21 days later they were 1.1 and 1.4 mg/kg (Bayer Spain, 1992).

Lupin (dry). Clethodim was applied at 0.06, 0.12 and 0.24 kg ai/ha to lupins in Australia in 1987. No residues above the limit of determination of 0.1 mg/kg were found in the dried seed or in the straw at harvest, 167 days later (Shell Australia, 1987b).

Soya bean (dry). In three trials in Australia in 1988, soya beans were treated with clethodim at 0.06, 0.12 and 0.24 kg ai/ha. No residues above the limit of determination of 0.1 mg/kg were found in either the dried seed or the straw after 109 days (Shell Australia, 1988).

In Brazil in 1989, a soya bean plantation was treated with clethodim at 0.084, 0.108, 0.168 and 0.216 kg ai/ha. Both the plant and dry beans were sampled at 13, 27, 52 and 91 days after application. At 91 days PHI, residues in both plant and beans were below the limit of determination of 0.05 mg/kg at all treatment rates. However, residues were found at up to 2.4 mg/kg in both sets of samples at the other PHIs, as Table 6 shows.

Table 6. Residues of clethodim in soya beans in Brazil in 1989.

Application kg ai/ha	Residue, mg/kg					
	Dry beans			Plant		
	PHI, days			PHI, days		
	13	27	52	13	27	52
0.084	0.44-0.58	0.77-0.78	0.12-0.13	0.23-0.45	0.31-0.340.	07-0.19
0.108	0.57-0.58	1.2 -1.3	0.11-0.17	0.50-0.55	0.47-0.53	0.14-0.17
0.168	0.81-0.88	1.6 -2.4	0.19-0.21	0.56-0.89	0.55-0.66	0.16-0.31
0.216	1.1 -1.3	2.4 -2.4	0.26-0.29	0.69-0.82	0.75-0.76	0.23-0.33

From these results it would appear that clethodim can be absorbed and translocated in soya bean plants. In addition, it seems that the amount of clethodim residue in the beans is dependent on the growth stage of the crop at the time of application (Chevron Brazil, 1989).

Small plot trials were carried out at three sites in Ontario, Canada in 1990 using the maximum proposed label rate of application of 0.09 kg ai/ha. In addition, in order to simulate field overlap conditions, a second set of samples was collected following a second application of clethodim at the same rate immediately after the first application. No residues above the limit of determination of 0.05 mg/kg were found following the single application, although one result from nine was at that level. From the double application trials, residues of 0.05, 0.06, 0.11, 0.11, 0.13 and 0.18 mg/kg were observed (Rhône-Poulenc Canada, 1991a).

Two trials in France in 1987 at a rate of 0.18 kg ai/ha showed residues of 0.07 mg/kg in the mature beans after 87 days but <0.03 mg/kg in the dry seeds after 105 days (Tomen France, 1987a).

From a trial in Italy in 1988 using one application at 0.24 kg ai/ha, residues of 0.58, 0.23 and 0.35 mg/kg were found after 30, 50 and 69 days PHI respectively. In 1991, three similar trials were carried out using two applications at 0.18 kg ai/ha when residues in the seed were 0.38 and 0.29 mg/kg at 30 days; 0.15 and 0.15 mg/kg at 45 days; <0.03 and 0.05 mg/kg at 60 days (Bayer Italy, 1988/91a).

Summary data from applications of 0.12, 0.17, 0.24 and 0.29 kg ai/ha to soya beans in the Ukraine indicated that no residues were detected in the beans at harvest time (Tomen Ukraine, 1993).

Supervised trials of clethodim on soya beans were carried out at 12 sites in 10 States in the USA in 1988. Table 7 shows the results obtained (Lai, 1988b).

Table 7. Residues of clethodim in soya beans in the USA in 1988. All treatments were at 0.28 kg ai/ha, using two applications 14 days apart.

State	PHI, days	Residue, mg/kg
Arkansas	69	1.4, 1.5
Iowa	60	2.9, 6.4
Iowa	61	5.6, 6.1
Illinois	60	6.1, 7.3
Indiana	62	<0.04, <0.04
Louisiana	60	0.99, 1.1
Minnesota	53	10, 16
Mississippi	40	8.4, 9.2
Mississippi	60	0.94, 0.97
Mississippi	80	<0.04, <0.04
Missouri	61	4.3, 4.5
Nebraska	60	0.83, 0.94
Ohio	58	2.1, 2.3

In addition, in order to determine the effect of application rate on residues, at one Iowa site two applications at 0.45 kg ai/ha were also used; residues from these treatments gave 8.0 and 10.1 mg/kg at 61 days. The ratio between the mean results of these two trials (5.85:9.05 mg/kg) was 1.55, very close to the ratio between the applied doses (0.4:0.25 = 1.6), thus indicating that the residue levels were proportional to the applied rate. Aerial and ground applications were compared in two States, Iowa and Mississippi; the residues found in the dry shelled soya beans were not significantly different, aerial spraying showing 4.6 and 0.73 mg/kg as compared with the 5.8 and 0.96 mg/kg found from ground spraying.

Beetroot. Summary data from trials of clethodim on beetroot treated at 0.1 to 0.24 kg ai/ha in the Ukraine gave residues up to 0.9 mg/kg at 44 days but were below 0.04 mg/kg at harvest time (Tomen Ukraine, 1993).

Carrot. Application at 0.07 to 0.28 kg ai/ha to carrots in Moldavia and Russia showed no residues above the limit of determination (0.1 mg/kg) at harvest [summary data only] (Tomen Ukraine, 1993).

Fodder beet. Three trials of clethodim on fodder beet were carried out in France in 1986 and 1987 at rates of 0.18 to 0.96 kg ai/ha. Residues were always below the limit of determination (0.03 mg/kg) in both the roots and tops at PHIs of 102 to 129 days (Tomen France, 1986/87).

Potato. Summary data from a trial in Belgium in 1990 showed residues of clethodim to be below 0.025 mg/kg following treatment at 0.09 or 0.36 kg ai/ha (Bayer Belgium, 1993b).

In 1990, potatoes were treated with clethodim at three sites in Ontario and one in Nova Scotia, Canada, using the maximum proposed label rate of application of 0.09 kg ai/ha. In addition, in order to simulate field overlap conditions, another set of samples was collected following a second application of clethodim at the same rate immediately after the first. From the single application, only one of the sites in Ontario yielded residues above 0.05 mg/kg, these being 0.11 and 0.14 mg/kg as clethodim at

PHIs of 46 and 61 days. After the double application, residues were found in five of the eight samples examined, ranging from 0.13 to 0.25 mg/kg at PHIs of 45 or 46 days (Rhône-Poulenc Canada, 1991b). This use is not registered in Canada.

Potatoes were treated in France with clethodim at 0.18 kg ai/ha in two trials. Residues in the tubers were <0.03 and 0.08 mg/kg at 47 days PHI and <0.03 and <0.03 at 80 days (Tomen France, 1987b).

Trials were carried out at three sites in Italy in 1990-91 using clethodim at 0.24 kg ai/ha. Apart from one result at 0.07 mg/kg, all residues were at or below the limit of determination of 0.03 mg/kg at PHIs from 30 to 80 days (Bayer Italy, 1992c).

One trial in Morocco in 1992 at 0.14 kg ai/ha showed no residue after 91 days (Bayer Italy, 1992d).

Summary data from trials in the Ukraine using applications of clethodim from 0.7 to 1.2 kg ai/ha showed no residues in the tubers above the high limit of determination of 0.2 mg/kg (Tomen Ukraine, 1993).

Sugar beet. Eleven trials of clethodim on sugar beet were carried out in France in 1986 (6 trials) and 1987 (5 trials). After application at rates of 0.18, 0.36, 0.48 or 0.96 kg ai/ha, residues in the roots at PHIs from 112 to 136 days were always below the limit of determination (0.03 mg/kg). In the beet tops, only in two samples treated at the highest rate were residues found, at 0.03 and 0.04 mg/kg (Tomen France, 1986/87).

Sugar beet treated in Germany in 1986 with 0.14 kg ai/ha gave no residues above 0.05 mg/kg in either the roots or the tops at 92 or 132 days PHI (Bayer Germany, 1986).

Two trials were carried out in Italy in 1991 at 0.24 kg ai/ha and the results obtained are shown in Table 8 (Bayer Italy, 1993).

Table 8. Residues of clethodim in sugar beet in Italy, 1991.

Commodity	Clethodim residue (mg/kg)		
PHI (days)	30	45	59/60
Root	0.08	0.08	0.17
Tops	0.23	0.07	0.07
Root	0.11	0.04	0.06
Tops	0.06	0.07	<0.03

In one trial in Morocco in 1993, sugar beet was treated with clethodim at 0.6 kg ai/ha; residues were below 0.03 mg/kg in the root after 153 days (Bayer Italy, 1994).

Artichoke, Globe. Globe artichokes were treated in Italy in 1990 with clethodim at a rate of 0.24 kg ai/ha. Residues of 0.5, 0.29 and 0.21 mg/kg were found after 20, 25 and 30 days respectively (Bayer Italy, 1990c).

Cotton seed. Cotton was treated in seven States in the USA with clethodim, using two applications at 0.28 kg ai/ha from 13 to 83 days apart. Fuzzy cotton seed samples were taken 60 days after the last application. The analytical results are given in Table 9.

Table 9. Residues of clethodim in fuzzy cotton seed in the USA in 1988.

State	PHI (days)	Residues as clethodim (mg/kg)		
		DME	DME-OH	Total
Arkansas	60	0.09, 0.10	<0.05, <0.05	<0.14, <0.15
California	60	0.09, 0.09	<0.05, <0.05	<0.14, <0.14
California	40	0.26, 0.33	0.16, 0.17	0.33, 0.40
	60	0.17, 0.18	<0.05, <0.05	<0.22, <0.23
	74	0.11, 0.22	<0.05, <0.05	<0.16, <0.17
Louisiana	60	0.13, 0.13	<0.05, <0.05	<0.18, <0.18
Mississippi	60	0.06, 0.07	<0.05, <0.05	<0.11, <0.12
Tennessee	60	0.23, 0.24	0.16, 0.17	0.39, 0.41
Texas	60	0.31, 0.38	<0.05, 0.10	<0.36, 0.48
Texas	60	0.08, 0.10	<0.05, <0.05	<0.13, <0.15

The second California trial was conducted to study the effect of timing of the application on residues in cotton seed. The data showed that the residue levels decreased as the interval from the last application increased from 40 to 74 days, dropping from a maximum of 0.4 mg/kg to a minimum of <0.16 mg/kg; however, this difference may not be significant at those residue levels. Similarly, differences between residues found after aerial and ground spraying were not significant (aerial 0.14, 0.12 mg/kg; ground 0.22, 0.14 mg/kg) (Lai, 1988e).

Linseed. Summary data were provided from trials on linseed in Canada in 1988 and 1990. Residues in the seed after treatment with 0.105 kg ai/ha were 0.07, <0.05, 0.08 and <0.05 mg/kg, 67, 84, 95 and 108 days later (Rhône-Poulenc Canada, 1988/90).

Summary data indicated that residues were not detected (<0.03 mg/kg) in linseed from flax treated in the Ukraine at 0.072, 0.12, 0.17, 0.24 or 0.29 kg ai/ha (Tomen Ukraine, 1993).

Peanut. Trials in Argentina in 1991 gave residues of <0.1 and 0.6 mg/kg 70 days after treatment with clethodim at 0.12 and 0.24 kg ai/ha respectively (Tomen, 1991).

Rape seed. Oilseed rape (two varieties of canola) was treated at four sites in Canada in 1988 with clethodim, either once or twice at 0.105 kg ai/ha. Similar trials were conducted in 1989, using rates of 0.06 and 0.105 kg ai/ha. Results obtained from the two experiments are detailed in Table 10.

Table 10. Residues of clethodim in oilseed rape in Canada.

Site/year	Applic. rate (kg ai/ha)	No. of applic.	PHI, days	Residue as clethodim (mg/kg) in whole seed
Ontario/88	0.105	1	58	<0.05, 0.07, 0.09, 0.09
		2	58	<0.05, <0.05
Saskatchewan/88	0.105	1	70	<0.05, <0.05, <0.05, <0.05, <0.05, <0.05
		2	70	<0.05, <0.05, <0.05, 0.07, 0.09, 0.14
Manitoba/88	0.105	1	78	<0.05, <0.05, <0.05, <0.05
		2	78	<0.05, <0.05
Alberta/88	0.105	1	87	<0.05, <0.05, <0.05, 0.06, 0.14, 0.14
		2	87	<0.05, <0.05, <0.05, 0.13
Saskatchewan/89	0.06	1	70	0.10, 0.11

Site/year	Applic. rate (kg ai/ha)	No. of applic.	PHI, days	Residue as clethodim (mg/kg) in whole seed
		2	70	0.10, 0.32
	0.105	1	70	0.21, 0.29
		2	70	0.10, 0.15
Saskatchewan/89	0.06	1	70	0.20, 0.31
		2	70	0.30, 0.35
	0.105	1	70	0.16, 0.20
		2	70	0.47, 0.54
Alberta/89	0.06	1	103	<0.05, <0.05
		2	103	<0.05, <0.05
	0.105	1	103	<0.05, <0.05
		2	103	<0.05, <0.05
Alberta/89	0.06	1	86	<0.05, 0.06
		2	86	0.06, 0.06
	0.105	1	86	0.05, 0.07
		2	86	<0.05, <0.05

Thus, there was little difference in the residues arising from either single or double applications at either rate; there was more difference between the results from Saskatchewan and those from Alberta in the 1989 than the 1988 trials (Rhône-Poulenc, 1989).

Eleven trials of clethodim on oilseed rape were conducted in France in 1985/6 and 1986/7. Applications at rates from 0.18 to 0.96 kg ai/ha were made either in the autumn on young plants or in the spring as vigorous growth began. The results obtained are given in Table 11.

Table 11. Residues of clethodim in oilseed rape in France, 1985-87.

Month/year of applic.	Applic. rate (kg ai/ha)	PHI, days	Residue as clethodim (mg/kg)		
			DME	DME-OH	Total
April/86	0.36	98	nd	0.05	0.05
Nov./85	0.18	253	nd	nd	nd
	0.36	253	nd	nd	nd
Sept./85*	0.18	305	nd	0.06	0.06
March/86*	0.18	126	nd	0.05	0.05
Nov./85	0.18	248	nd	nd	nd
	0.36	248	0.03	0.05	0.08
Oct./85*	0.18	299	nd	0.09	0.09
April/86*	0.18	117	nd	0.10	0.10
Nov./85	0.18	253	nd	nd	nd
	0.36	253	nd	nd	nd
Oct./86	0.18	283	nd	nd	nd
	0.36	283	nd	nd	nd
	0.48	283	nd	nd	nd
April/87	0.18	108	nd	nd	nd
	0.36	108	nd	0.09	0.09
*	0.48	108	nd	0.08	0.08
Oct./86	0.18	267	nd	nd	nd
	0.36	267	nd	0.05	0.05
	0.48	267	nd	nd	nd
April/87	0.18	106	nd	nd	nd
	0.36	106	nd	0.11	0.11
*	0.48	106	nd	0.10	0.10
	0.96	106	0.07	0.12	0.19
Oct./86	0.18	268	nd	nd	nd
	0.36	268	0.05	0.08	0.13

Month/year of applic.	Applic. rate (kg ai/ha)	PHI, days	Residue as clethodim (mg/kg)		
			DME	DME-OH	Total
	0.48	268	nd	nd	nd
April/87*	0.18	107	nd	0.05	0.05
	0.36	107	0.04	0.07	0.11
*	0.48	107	nd	0.04	0.04
	0.96	107	0.07	0.04	0.11
Oct./86	0.18	288	nd	nd	nd
	0.36	288	nd	nd	nd
	0.48	288	nd	nd	nd
Oct./86	0.18	268	nd	nd	nd
	0.36	268	nd	nd	nd
	0.48	268	nd	nd	nd

[nd = below the limit of determination of 0.03 mg/kg]

In the trials marked * in the Table, rape seed oil was prepared from the treated seed. In all cases the residues in the oil were below the limit of determination of 0.03 mg/kg (Tomen, 1985-87).

Similar trials were also carried out in France in 1987/88; results are given in Table 12. Again, nearly all of the residues were below the limit of determination, the highest level found being 0.07 mg/kg (Tomen France, 1988e).

Table 12. Residues of clethodim in oilseed rape in France, 1987-88.

Month/year of applic.	Applic. rate (kg ai/ha)	PHI, days	Residue as clethodim (mg/kg)		
			DME	DME-OH	Total
Oct./87	0.18	267	nd	0.03	0.03
	0.48	267	nd	nd	nd
March/88	0.18	132	nd	nd	nd
	0.48	132	nd	nd	nd
March/88	0.18	119	nd	nd	nd
	0.48	119	nd	0.07	0.07
Nov./87	0.18	259	nd	nd	nd
	0.48	259	nd	nd	nd
Nov./87	0.18	235	nd	nd	nd
March/88	0.18	115	nd	nd	nd
March/88	0.18	117	nd	nd	nd
Oct./87	0.18	267	nd	nd	nd
	0.48	267	nd	nd	nd

[nd = below the limit of determination of 0.03 mg/kg]

From three trials of clethodim on oilseed rape in the UK in 1987, using either 0.36 or 0.72 kg ai/ha, residues at harvest after 258 to 294 days were below the limit of determination of 0.03 mg/kg (Bayer UK, 1989).

Sunflower seed. Trials of clethodim on sunflowers were carried out in Argentina in 1986/87, using 0.12 or 0.24 kg ai/ha. The results obtained are shown in Table 13 (Tomen, 1987c).

Table 13. Residues of clethodim in sunflower seeds in Argentina.

Month/year of applic.	Applic. rate (kg ai/ha)	PHI, days	Residue as clethodim (mg/kg)

			DME	DME-OH	Total
Dec./86	0.12	108	0.06	<0.05	<0.11
	0.24	108	<0.05	<0.05	<0.1
Dec./86	0.12	102	<0.05	<0.05	<0.1
	0.24	102	0.09	<0.05	<0.14
Jan./87	0.12	106	<0.05	<0.05	<0.1
	0.24	106	0.07	<0.05	<0.12

Residues of clethodim in sunflower seeds treated in France in 1988 at either 0.18 or 0.48 kg ai/ha were below the limit of determination (0.03 mg/kg) 108, 112 and 123 days later (Tomen, 1988b).

Two trials were conducted in Italy in 1989, using clethodim at a rate of 0.24 kg ai/ha. Residues in the seeds did not exceed the limit of determination (0.03 mg/kg) 74, 92 or 110 days later; residues were also not observed in the raw oil or refined oil prepared from the crop. From one trial in Italy in 1991, the same treatment gave residues of 0.07, 0.06 and 0.06 mg/kg, 60, 75 and 90 days later respectively (Bayer Italy, 1989/91).

Clover. In one trial in New Zealand in 1988, white clover was treated with clethodim at 0.24 kg ai/ha. After 62 days, the silage prepared from the clover showed residues of 0.26 mg/kg; after 71 days the regrowth showed 0.07 mg/kg
(Nufarm [New Zealand], 1988b).

Animal feeding studies

Chickens. White Leghorn laying hens were fed doses of clethodim (5%) and clethodim sulphoxide (95%) as follows, 20 chickens being in each dosage group.

Nominal ppm in the diet			
Dose level	Clethodim	Clethodim sulphoxide	Total
0	0	0	0
1x	0.5	9.5	10
3x	1.5	28.5	30
10x	5.0	95.0	100

The hens were fed with gelatine capsules containing the clethodim daily for 28 days. Egg samples were taken from test days -1, 1, 2, 4, 7, 14, 21, 28, 29 and 30. The amounts of DME (as clethodim) found in eggs from hens treated at 10 ppm were all less than 0.05 mg/kg. At 30 ppm, DME in eggs ranged from 0.05 to 0.09 mg/kg during the feeding period and declined to less than 0.05 mg/kg by day 29. The DME found in eggs from the 100 ppm treatment ranged from 0.14 to 0.24 mg/kg during the feeding period and declined to less than 0.05 mg/kg by day 29. Neither DME-OH nor *S*-methyl DME were found above the limit of determination (0.05 mg/kg) in any of the egg samples.

Ten chickens from each group were killed on day 29 and the rest on day 31; from each batch samples of thigh and breast muscle, liver, gizzard, and subcutaneous and abdominal fat were taken for analysis. The only tissue fraction found to contain any clethodim-related residues was the liver from the 100 mg/kg dose level which showed 0.06 mg/kg of DME. All other results were below the limit of determination of 0.05 mg/kg (Fletcher and Pederson, 1988).

Cows. Fourteen dairy cows were used in a study of the distribution of clethodim residues in bovine tissues. Two were used as controls and the others were split into three groups of four cows each for treatment daily for 28 days with capsules containing clethodim (5%) and clethodim sulphoxide (95%), as follows:

Nominal ppm in the diet				
Group	Dose level	Clethodim	Clethodim sulphoxide	Total
Control	0	0	0	0
T-1	1x	0.5	9.5	10
T-2	3x	1.5	28.5	30
T-3	10x	5.0	95.0	100

Duplicate samples of whole milk were collected from all cows on days -1, 1, 2, 4, 7, 12, 16, 20 and 28 of the treatment period and on test days 29, 30 and 31 from the available animals. Three cows from each tested group and one control cow were killed on test day 29, within 24 hours of the last dose; the remaining cow in each group was killed on the morning of test day 31.

Analysis of the milk samples from treated cows showed no residues corresponding to clethodim or its metabolites for the control or 1x feeding levels. The 3x feeding level showed only "clethodim-type" residues, with a maximum of 0.033 mg/kg clethodim equivalents and a plateau by test day 1. The 10x feeding level showed a maximum of 0.081 mg/kg of "clethodim-type" residues with a plateau by day 1, and a maximum residue of 0.032 mg/kg clethodim equivalents for the *S*-methylated metabolite residues with a plateau by day 2. No 5-hydroxy-metabolite residues were found at any feeding level.

One cow at each feeding level was held for a two-day withdrawal period and in all cases any residue present during the treatment declined to below 0.0125 mg/kg by the end of the withdrawal period. Table 14 gives details of the residues observed (Weissenburger *et al*., 1989).

Table 14. Residues of clethodim in bovine tissues and milk commodities.

Commodity	Feeding level	Maximum residue as clethodim (mg/kg)		
		DME	S-Me-DME	DME-OH
Liver	0	<0.05	<0.05	<0.05
	1x	0.06	<0.05	<0.05
	3x	0.12	<0.05	<0.05
	10x	0.45	0.09	<0.05
Kidney	0	<0.05	<0.05	<0.05
	1x	0.05	<0.05	<0.05
	3x	0.17	<0.05	<0.05
	10x	0.54	0.08	<0.05
Muscle	0	<0.05	<0.05	<0.05
	1x	<0.05	<0.05	<0.05
	3x	<0.05	<0.05	<0.05

Commodity	Feeding level	Maximum residue as clethodim (mg/kg)		
		DME	S-Me-DME	DME-OH
	10x	0.07	<0.05	<0.05
Fat	0	<0.05	<0.05	<0.05
	1x	<0.05	<0.05	<0.05
	3x	0.05	<0.05	<0.05
	10x	0.15	<0.05	<0.05
Whole milk	0	<0.0125	<0.0125	<0.0125
	1x	<0.0125	<0.0125	<0.0125
	3x	0.033	<0.0125	<0.0125
	10x	0.081	0.032	<0.0125
Milk (pasteurised)	10x	0.06	0.14	<0.0125
Cream (fat solids)	10x	0.11	<0.0125	<0.0125
Skim milk (non-fat solids)	10x	0.03	<0.0125	<0.0125
Acid whey (lactose)	10x	0.03	<0.0125	<0.0125

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information was available on the fate of residues of clethodim in stored produce.

In processing

Data were available on the fate of residues of clethodim when cotton seed, rape seed, soya beans and sunflower seed were processed to yield the respective oils. Apart from soya bean soapstock and crude lecithin there was virtually no transfer of clethodim from the treated raw agricultural commodity to the processed items.

Soya bean. Soya beans were treated at eight times the normal rate (in order to ensure that residues were high enough for the study to be effective) in Iowa in 1987 and the samples were processed in Texas, all processed fractions being sampled and analysed. Results are given in Table 15.

Table 15. Effects of processing on residues of clethodim in soya beans.

Material	Clethodim (mg/kg)
Unprocessed beans	27
Meal	27
Hulls	26
Crude oil	2.8
Refined oil	<0.08
Soapstock	34

Degummed oil	1.6
Crude lecithin	42

Thus, when the soya beans were processed, clethodim residues were reduced in crude oil (90%), degummed oil (94%) and refined oil (>99%), while residue levels in the hulls and meal were unchanged from those in the unprocessed beans; residues were somewhat concentrated in soapstock (126%) and crude lecithin (156%) (Lai, 1988d).

Cotton seed. Cotton was treated at eight times the normal rate (in order to ensure that residues were high enough for the study to be effective) in Mississippi in 1987 and the samples were processed in Texas. All processed fractions, except linter and linter motes, were collected and analysed for clethodim residues. The results are shown in Table 16.

Table 16. Effect of processing on residues of clethodim in cotton seed.

Material	Residues as clethodim (mg/kg)		
	DME	DME-OH	TOTAL
Fuzzy cotton seed	0.61	0.19	0.80
(from processor)		(means of three results)	
Meal	0.94	0.41	1.35
Hulls	0.78	<0.20	<0.98
Crude oil	0.14	<0.04	<0.18
Soapstock	0.65	<0.20	<0.85
Delinted cotton seed	0.67	0.21	0.88

Thus, the processing reduced the combined clethodim residues in crude and refined oil to about 20% and 10% respectively, of the amounts in the raw agricultural commodity. Residues remained essentially the same in soapstock, delinted cotton seed and hulls but were slightly concentrated (1.7 times) in the meal (Lai, 1988c).

Rape seed. Rape seed (canola) was treated with clethodim at twice the normal rate at two sites in Western Canada in 1989. The seed was then processed to oil and meal using standard commercial techniques and specific fractions from the process were sampled and analysed for clethodim residues. From rape seed containing 0.2 and 0.3 mg/kg of clethodim, no residues could be detected in the crude oil fraction. Initial analyses of the desolventized meal fractions yielded non-reproducible results with poor recoveries but re-analysis gave acceptable recovery and showed a total residue of 0.77 mg/kg as clethodim. A mass balance showed that virtually all of the initial residue was retained in the meal (Cosgrove, 1990a,b).

In trials in France in 1985 to 1987, rape seed oil was prepared from treated seed. In all cases the residues in the oil, as in the seed, were below the limit of determination of 0.03 mg/kg (Tomen, 1985-87).

Sunflower seed. Sunflower seeds from clethodim-treated crops in Argentina were processed to the oil. While residues remained in the presscakes, those in the oils were below the limit of determination (Tomen, 1987b). The results obtained are detailed in Table 17.

Table 17. Effects of processing on residues of clethodim in sunflower seeds.

Material	Residues as clethodim, mg/kg		
	DME	DME-OH	TOTAL
Seeds	0.09	0.07	0.16
Hulls	0.10	0.09	0.19
Seeds (from processor)	0.08	0.09	0.17
Solvent-extracted presscake	0.17	0.17	0.34
Expelled presscake	0.15	0.15	0.30
Expelled crude oil	<0.05	<0.05	<0.05
Solvent-extracted crude oil	<0.05	<0.05	<0.05
Refined oil	<0.05	<0.05	<0.05

From two trials in Italy in 1989, residues in the seeds did not exceed the limit of determination (0.03 mg/kg) and residues were also not observed in the raw oil or refined oil prepared from the crop (Bayer Italy, 1989/91).

Residues in the edible portions of food commodities

No data were provided on residues in the edible portions of food commodities, except as included with the supervised trials or in the processing data given above.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was provided on residues of clethodim occurring in commerce or at consumption.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national Maximum Residue Limits (MRLs) were brought to the attention of the Meeting.

Residue: expressed as clethodim

Country	Commodity	MRL, mg/kg	Ref.
Argentina	Cotton seed	0.51	
	Peanut	0.5[1]	
	Soya straw	3[1]	
	Sunflower seed	0.5[1]	
Australia (combined MRLs for clethodim and	Asparagus	1	Australia 1994

Country	Commodity	MRL, mg/kg	Ref.
sethoxydim)			
	Beans (except broad beans and soya beans)	0.1	
	Broad beans	0.1	
	Brassica (cole or cabbage) vegetables	0.1	
	Celery	0.05	
	Cotton seed	0.2	
	Edible offal (mammalian)	0.05	
	Eggs	0.05	
	Endive	0.05	
	Fennel, bulb	0.01	
	Fruiting veg., cucurbits	0.1	
	Leeks	0.01	
	Lettuce, head	0.05	
	Lettuce, leaf	0.05	
	Lupin, dry	0.2	
	Meat (mammalian)	0.05	
	Milks	0.05	
	Onion, bulb	0.3	
	Peanut	2	
	Peanut oil, crude	2	
	Peas	0.1	
	Poppy seeds	0.2	
	Poultry, edible offal of	0.05	
	Poultry meat	0.05	
	Pulses (except lupin), dry	0.1	
	Rape seed	0.1	
	Root and tuber vegetables	1	
	Spinach	0.1	
	Strawberry	0.1	
	Sunflower seed	0.1	
	Tomato	0.1	
Belgium	Beans	0.1	
	Fodder beet	0.03*	
	Peas	0.1	
	Onions	0.03*	
	Potato	0.1	
	Sugar beet	0.03*	
Canada	Linseed	0.3	Canada 1994
	Linseed oil	0.1	
	Potato	0.5	

Country	Commodity	MRL, mg/kg	Ref.
	Rape seed (Canola) oil	0.1	
	Soya bean	10	
Netherlands	Food commodities[3]	0*	
New Zealand	Vegetables[4]	1	
Peru	Alfalfa	1	
	Apple	5	
	Beans	10	
	Cotton seed	5	
	Orange	5	
Spain	Cotton seed	0.1	Spain 1994
	Garlic	0.05	
	Legume (pulses)[5]	0.05	
	Onion	0.05	
	Rape seed	0.1	
	Sugar beet	0.05	
	Sunflower seed	0.05	
	Tomato[6]	0.1	
Switzerland	Potato	0.1	
	Sugar beet	0.05	
	Vegetables	1	
Ukraine	Beetroot	0.1	
	Carrot	0.1	
	Fodder beet	0.1	
	Linseed	0.1	
	Onion	0.1	
	Potato	0.2	
	Soya bean	0.1	
	Sugar beet	0.1	
USA	Cotton seed	1	
	Cotton seed meal	2	
	Soya bean	10	
	Soya bean soapstock	15	

[1] Temporary MRL - until July 1994
[2] Includes broad beans, chick peas, field peas, soya beans
[3] MRL not established, therefore zero tolerance applies; analytical detection limit between 0.03 and 0.05 mg/kg (Netherlands, 1994)
[4] Includes peas, lentils and "all" vegetables. All other crops on the New Zealand label have residues at <0.1 mg/kg and require no MRL.
[5] Includes beans, broad beans, chick peas, lentils, peas, all dry.
[6] Field or greenhouse.
* Limit of determination.

APPRAISAL

Metabolic studies using radiolabelled clethodim were carried out on rats, a lactating goat and chickens. In all cases, most (>90%) of the radioactivity was rapidly excreted in the urine and faeces.

The metabolic study in rats was undertaken with the objectives of determining the absorption, distribution, excretion and metabolic fate, including metabolic characterization, of propyl[1-^{14}C]clethodim administered orally to male and female rats at different dose rates, Low Dose (4.4 mg/kg bw), Repeated Dose (4.8 mg/kg bw) and High Dose (468 mg/kg bw) and treated with a single oral dose of propyl[1-^{14}C]clethodim. The autoradiogram TLC profiles of urinary metabolites were very similar for males and females within a dose group and also between dose groups. Clethodim, clethodim sulphoxide, clethodim sulphone, clethodim imine sulphoxide, *S*-methyl sulphoxide and 5-hydroxy sulphone were isolated from urine and positively identified by chemical ionization and electron-impact mass spectrometry, TLC co-chromatography and HPLC co-chromatography. Further evidence for the presence of these metabolites and of the 5-hydroxy sulphoxide was obtained by LC-MS, whereby the imine sulphoxide, oxazole sulphoxide, oxazole sulphone, *S*-methyl sulphoxide, trione sulphoxide, 5-hydroxy sulphoxide, and clethodim sulphoxide were detected in the 12-hour urine collection from the High Dose group males and females. Thus, it appears that clethodim is rapidly absorbed and then (a) oxidized to clethodim sulphoxide (dominant) and thence to clethodim sulphone; (b) converted to the *S*-methyl analogue via a sulphonium cation intermediate; (c) converted to imine, or (d) hydroxylated at the 5 position. The proposed *S*-methyl-clethodim would follow the dominant metabolic process and form the observed *S*-methyl sulphoxide and smaller amounts of *S*-methyl sulphone. Similarly, the imine would rapidly be oxidised to imine sulphoxide and imine sulphone. Any 5-hydroxy-clethodim formed (this was not detected) would be rapidly oxidized to the observed 5-hydroxy sulphoxide and sulphone.

In goats, 91% of the radioactive dose was excreted in the faeces and urine; the concentration in the milk reached a plateau of 0.035 mg/l by the second day. There was little evidence of accumulation in tissues, although some radiocarbon was observed in the liver (0.41 mg/kg) and kidney (0.38 mg/kg).

In the chicken study, identification of the metabolites was focused on the edible tissues and eggs, using TLC and HPLC. Three major compounds were identified: in order of increasing amounts clethodim, clethodim sulphone and clethodim sulphoxide. In the skin clethodim sulphoxide accounted for as much as 57% of the radioactivity, while the proportions of the sulphone in the tissues ranged from 10.2 to 31.2%. On average, the parent clethodim amounted to only a few per cent of the radioactivity, although a higher percentage was observed in the fat. The metabolic pathway was simpler than that observed in other animals. None of the imine analogues, 5-hydroxy analogues or *S*-methyl analogues that were found in the rat and goat were seen in the chicken.

Results from four studies on the fate of clethodim in soils showed that metabolism by micro-organisms dominated the degradation process, with no photoproducts being formed. The half-life of clethodim was 1 to 3 days under aerobic conditions, the major product being the sulphoxide and the only volatile product CO_2. Under anaerobic conditions the sulphoxide was again the major product.

Under anaerobic conditions the half-lives of clethodim were 177 days at 25°C and 559 days at 5°C, the degradation being primarily microbiological with the metabolites being degraded at the same rate as they were formed. Under aerobic conditions the degradation pattern was similar but quicker, with half-lives of clethodim of 5 days at 25°C and 23 days at 5°C, the only volatile metabolite again being CO_2.

In the analytical methods used in the reported studies, all clethodim-related metabolites which

retain the 2-cyclohexene-1-one structure are oxidized to one of two compounds, depending upon whether 5-hydroxylation has occurred. Clethodim and its metabolites are extracted from plant material with water and methanol and the extract is partitioned into dichloromethane. After clean-up by alkaline precipitation and acidic back-extraction, oxidation with hydrogen peroxide at Ph 9-10 yields dicarboxylic acids which are methylated with methanol to yield the two esters DME, dimethyl 3-[2-(ethylsuphonyl)propyl]pentanedioate, and DME-OH, dimethyl 3-[2-(ethylsulphonyl)propyl]-3-hydroxypentanedioate. After a silica gel or methylene chloride partition clean-up step, these are then determined by gas chromatography using a flame-photometric detector in the sulphur mode. The limit of determination is of the order of 0.05 mg/kg. The total residue of DME + DME-OH is then expressed as clethodim equivalents: mg/kg clethodim = (mg/kg DME x 1.22) + (mg/kg DME-OH x 1.16). The procedure has proved to be adaptable to the many food commodities so far examined and should be suitable for regulatory use. However, it is essential also to use the confirmatory HPLC procedure to show that the residues found are from clethodim and not some other similar herbicide such as sethoxydim.

Clethodim and related metabolic compounds show three types of isomerism, geometric, tautomeric and enantiomeric, and as a result some chromatograms can show multiple peaks or spots owing to the resolution of some of these isomers. Care in analytical interpretation is therefore necessary.

Residue levels (0.05 to 0.25 mg/kg) of clethodim, *S*-methyl-clethodim sulphoxide and 5-hydroxy-clethodim sulphone in bovine tissues (fat, kidney, liver and muscle) and milk showed no degradation when stored at -20°C up to 5 months. In similar studies on residues in chicken eggs and tissues (fat, gizzard, liver and muscle), all components were stable up to 8 weeks at -18 ± 3°C, although 5-hydroxy-clethodim sulphone appeared to be slightly less stable in the gizzard, liver and muscle samples for the 6-week period, when less than 90% of the added material was recovered; it was stable in the other matrices studied and over 3- to 4-week periods. When fuzzy cotton seed containing residues of clethodim ranging from 0.38 to 1.44 mg/kg was stored up to six months at -20°C, analysis showed 80 to 128% of the initial residues.

Clethodim is available as a 24% emulsifiable concentrate. Residue data obtained from trials on about 30 crops in several countries were provided, although there were only very limited or summary data in many cases. Of the crops on which its use is registered, it appears that the major uses of clethodim are on beans, field peas, soya beans, potatoes, cotton, rape seed, sugar beet and sunflower.

Insufficient or inadequate data were provided for recommendations to be made in respect of artichoke, beetroot, broad beans, carrot, cauliflower, clover, common bean, fodder beet, garden peas, garlic, leek, lentil, lettuce, linseed, lupin, onion, peach, peanut, peppers (sweet), spinach, summer squash or tomato.

Peach. In six trials in Spain no residues were above the limit of determination of 0.03 mg/kg.

Garlic. One trial in Spain showed no residue above 0.03 mg/kg, 21 days after treatment.

Leek. Treatment of leeks in France gave residues up to 0.34 mg/kg at a 28-day PHI and 0.17 mg/kg at 56 days.

Onion. Onions treated in New Zealand showed no residues above the limit of determination (0.03 mg/kg) 42 or 84 days later. Similarly, onions treated in Italy gave no residues at 20, 30 or 40 days PHI. In Moldavia, trace amounts of clethodim, <0.1 mg/kg, were reported, 55 days after application.

Cauliflower. One trial in New Zealand gave a residue of 0.28 mg/kg 42 days after treatment but <0.03 mg/kg after 84 days.

Squash, Summer. Treatment of zucchini in a trial in Italy gave residues below 0.03 mg/kg at 28, 33 and 42 days PHI.

Peppers, Sweet. Residues of 0.1, 0.05 and 0.05 mg/kg were found 18, 28 and 38 days (respectively) after treating sweet peppers in Italy.

Tomato. Treatment of tomatoes in Italy gave residues of 0.06 mg/kg at 30 days but <0.03 mg/kg after 51 days. In six trials in Spain from 1989 to 1992, a maximum residue of 0.05 mg/kg was found once at day 0 but all other results were at or below 0.03 mg/kg at 0, 21, 22 or 60 days after application.

Lettuce, Head. Lettuces were treated in France with clethodim at rates of 0.12, 0.18, 0.18 and 0.48 kg ai/ha; the corresponding residues were 0.19, 0.13, 0.27 and 0.34 mg/kg at 28 days PHI. Trials in Italy in 1990 at 0.24 kg ai/ha yielded residues of 0.31, 0.16, 0.05 and 0.07 mg/kg at 0, 10, 15 and 20 days after treatment.

Spinach. In France, spinach was treated with clethodim at 0.12, 0.18, 0.18 and 0.48 kg ai/ha; residues were respectively 0.14, 0.19, 0.10 and 0.15 mg/kg at 15 days and 0.04, 0.08, 0.03 and 0.08 mg/kg at 30 days.

Peas. Marrowfat peas treated in New Zealand showed residues in the podded peas of 0.29 mg/kg after 43 days. The pea silage contained 0.47 mg/kg at the same time.

Broad bean. One trial on broad beans in Spain gave residues below the limit of determination (0.03 mg/kg) in the bean and in the husk.

Common bean. Green beans treated in Belgium showed no residues in the pods above the limit of determination of 0.025 mg/kg. French beans treated in France also gave no residues in the beans above 0.03 mg/kg. Green beans treated in Italy with clethodim yielded residues of 0.11 and 0.09 mg/kg at 20 and 24 days PHI respectively. However, none of these treatments were in accordance with the GAP of the countries concerned.

Beans (dry). In Brazil, beans were treated with clethodim at rates of 0.084, 0.108, 0.168 and 0.216 kg ai/ha. At PHIs of 65 and 85 days, the dry beans showed no residues above the limit of determination of 0.05 mg/kg, although at 25 and 45 days PHI residues in the beans ranged from 0.37 to 0.93 and 0.06 to 0.14 mg/kg respectively. The Meeting estimated a maximum residue level of 0.1 mg/kg for beans,dry.

Field peas (dry). Field peas were treated in Australia with clethodim at rates up to 0.24 kg ai/ha. At harvest, 110 days after application, residues in the dry pea seeds and in the straw were all below the limit of determination of 0.03 mg/kg. Four trials were made on field peas in the UK at rates of 0.36 and 0.72 kg ai/ha. At the lower rate, residues in the pea seed and the husk were not above 0.03 mg/kg at PHIs of 53 and 85 days. At the higher application rate, residues of 0.04 and 0.05 mg/kg were found in the peas at 53 days, and <0.03 and 0.08 mg/kg at 85 days.

When protein peas were treated in Belgium the residues in the seeds 41 days later were below 0.025 mg/kg. Protein peas were treated at six sites in France with clethodim at rates of 0.18, 0.48 and 0.96 kg ai/ha; residues were below 0.06 mg/kg at the lowest rate, up to 0.28 mg/kg at the middle rate and up to 0.75 mg/kg at the top rate, all at 82 days PHI.

The Meeting estimated a maximum residue level of 0.1 mg/kg for field pea (dry).

Lentil (dry). Lentils were treated in Spain with clethodim at 0.18 kg ai/ha. On the day of treatment, residues in the husk were 2.2 mg/kg; 21 days later they were 1.1 and 1.4 mg/kg.

Lupin (dry). When clethodim was applied at rates up to 0.24 kg ai/ha to lupins in Australia no residues were above the limit of determination of 0.1 mg/kg in the dried seed or in the straw at 167 days PHI.

Soya bean (dry). In three trials in Australia, soya beans were treated with clethodim at rates up to 0.24 kg ai/ha. No residues above the limit of determination of 0.1 mg/kg were found in either the dried seed or the straw at 109 days PHI.

In Brazil, a soya bean plantation was treated with clethodim at 0.084, 0.108, 0.168 and 0.216 kg ai/ha. Both the plant and dry beans were sampled at 13, 27, 52 and 91 days after application. At 91 days PHI, residues in both plant and beans were below the limit of determination of 0.05 mg/kg at all treatment rates. However, residues were found in both sets of samples at the other PHIs, reaching maxima of 1.3 mg/kg at 13 days, 2.4 mg/kg at 27 days and 0.29 mg/kg at 52 days in the dry beans. From these results, it appears that clethodim can be absorbed and translocated in soya bean plants and that the amount of clethodim residue in the beans is dependant on the growth stage of the crop at the time of application.

Trials were carried out on soya beans at three sites in Ontario, Canada using the maximum proposed label rate of application of 0.09 kg ai/ha. No residues were above the limit of determination of 0.05 mg/kg, although one result from nine was at that level. When a second application was made at the same rate immediately after the first, residues of 0.05, 0.06, 0.11, 0.11, 0.13 and 0.18 mg/kg were observed.

Two trials in France showed residues of 0.07 mg/kg in the mature beans after 87 days but <0.03 mg/kg in the dry seeds after 105 days.

From a trial in Italy using one application at 0.24 kg ai/ha, residues of 0.58, 0.23 and 0.35 mg/kg were found after 30, 50 and 69 days PHI respectively. Three similar trials were carried out using two applications at 0.18 kg ai/ha which gave residues in the seed of 0.38, 0.29 mg/kg at 30 days, 0.15, 0.15 mg/kg at 45 days and <0.03, 0.05 mg/kg at 60 days PHI.

Summary data from applications up to 0.29 kg ai/ha to soya beans in the Ukraine indicated that no residues were detected in the beans at harvest.

Supervised trials of clethodim on soya beans were carried out at 12 sites in 10 States in the USA, all treatments being at 0.28 kg ai/ha, with two applications 14 days apart. At PHIs from 40 to 80 days, residues ranged from <0.04 to 10 mg/kg, apart from one result of 16 mg/kg at 53 days PHI for which the corresponding duplicate determination was 10 mg/kg. In addition, in order to determine the effect of the application rate on residues, at one site two applications at 0.45 kg ai/ha were also used; residues from these treatments gave 8.0 and 10.1 mg/kg at 61 days. The ratio between the mean results of these two trials (5.85:9.05 mg/kg) was 1.55, very close to the ratio between the applied doses (0.4:0.25 = 1.6), indicating that the residue levels were proportional to the applied rate. Aerial and ground applications were compared in two States; the residues found in the dry shelled soya beans were not significantly different, aerial spraying showing 4.6 and 0.73 mg/kg as compared with the 5.8 and 0.96 mg/kg found from ground spraying.

The Meeting estimated a maximum residue level of 10 mg/kg for soya bean, dry, 1 mg/kg for soya bean oil, crude and 0.1 mg/kg for soya bean oil, edible.

Beetroot. Summary data from trials of clethodim on beetroot treated in the Ukraine gave residues up to 0.9 mg/kg at 44 days but below 0.04 mg/kg at harvest.

Carrot. Application at 0.07 to 0.28 kg ai/ha to carrots in Moldavia and Russia showed no residues above the limit of determination (0.1 mg/kg) at harvest.

Fodder beet. Three trials of clethodim on fodder beet were carried out in France at rates up to 0.96 kg ai/ha. Residues were always below the limit of determination (0.03 mg/kg) in both the roots and tops at PHIs of 102 to 129 days.

Potato. Summary data from a trial in Belgium in 1990 showed residues of clethodim to be below 0.025 mg/kg.

When potatoes were treated with clethodim at three sites in Ontario and one in Nova Scotia, using the maximum proposed label rate of application of 0.09 kg ai/ha, only one of the sites in Ontario yielded residues above 0.05 mg/kg, these being 0.11 and 0.14 mg/kg as clethodim at PHIs of 46 and 61 days. When another set of samples was collected following a second application of clethodim at the same rate immediately after the first, residues were found in five of the eight samples examined, ranging from 0.13 to 0.25 mg/kg at PHIs of 45 or 46 days.

Potatoes treated in France in two trials gave residues in the tubers of <0.03, 0.08 mg/kg at 47 days PHI and <0.03, <0.03 at 80 days.

From trials carried out at three sites in Italy, apart from one result at 0.07 mg/kg, all residues were at or below the limit of determination of 0.03 mg/kg at PHIs of from 30 to 80 days. One trial in Morocco showed no residue after 91 days.

Summary data from trials in the Ukraine using applications of clethodim up to 1.2 kg ai/ha showed no residues in the tubers above the somewhat high limit of determination of 0.2 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg for potato.

Sugar beet. Eleven trials of clethodim on sugar beet were carried out in France, using application rates of 0.18, 0.36, 0.48 or 0.96 kg ai/ha. Residues in the roots at PHIs from 112 to 136 days were always below the limit of determination (0.03 mg/kg), while in the beet tops residues were found in only two samples treated at the highest rate at 0.03 and 0.04 mg/kg.

Sugar beet treated in Germany gave no residues above 0.05 mg/kg in either the roots or the tops at 92 or 132 days PHI.

In two trials carried out in Italy, residues in the roots were 0.08, 0.11; 0.04, 0.08; and 0.06, 0.17 mg/kg at PHIs of 30, 45 and 59/60 days respectively. Corresponding residues in the tops were 0.06, 0.23; 0.07, 0.07; and <0.03, 0.07 mg/kg.

In one trial in Morocco residues were below 0.03 mg/kg in the root after 153 days.

The Meeting estimated a maximum residue level of 0.2 mg/kg for sugar beet.

Artichoke, Globe. Globe artichokes treated in Italy gave residues of 0.5, 0.29 and 0.21 mg/kg after 20, 25 and 30 days respectively.

Cotton seed. Cotton was treated in seven States in the USA with clethodim, using two applications at 0.28 kg ai/ha from 13 to 83 days apart, fuzzy cotton seed samples being taken 60 days after the last application. Total clethodim residues ranged from <0.11 to 0.48 mg/kg at 40 to 74 days PHI.

A second trial was conducted in California to study the effect of timing of the application on residues in cotton seed. The data showed that the residue levels decreased as the interval from the last application increased from 40 to 74 days, dropping from a maximum of 0.4 mg/kg to a minimum of <0.16 mg/kg; however, this difference may not be significant at those residue levels. Similarly, differences between residues found after aerial and ground spraying were not significant (aerial, 0.14, 0.12 mg/kg; ground, 0.22, 0.14 mg/kg).

The Meeting estimated a maximum residue level of 0.5 mg/kg for cotton seed, 0.1 mg/kg for cotton seed oil, crude and 0.05 mg/kg for cotton seed oil, edible.

Linseed. Summary data were provided from trials on linseed in Canada. Residues in the seed after treatment with 0.105 kg ai/ha were 0.07, <0.05, 0.08 and <0.05 mg/kg, at 67, 84, 95 and 108 days PHI. Summary data also indicated that residues were not detected (<0.03 mg/kg) in linseed from flax treated in the Ukraine at rates up to 0.29 kg ai/ha.

Peanut. Trials in Argentina gave residues of <0.1 and 0.6 mg/kg 70 days after treatment with clethodim at 0.12 and 0.24 kg ai/ha respectively.

Rape seed. Oilseed rape (two varieties of canola) was treated at four sites in Canada in 1988 with clethodim, either once or twice at 0.105 kg ai/ha. Similar trials were performed in 1989, using rates of 0.06 and 0.105 kg ai/ha. Residues in the whole seed ranged from <0.05 to 0.54 mg/kg at PHIs from 58 to 103 days; there was little difference between the residues arising from single and double applications at either rate, but there was more difference between results from Saskatchewan and those from Alberta in the 1989 trials.

Eleven trials of clethodim on oilseed rape were conducted in France using rates from 0.18 to 0.96 kg ai/ha either in the autumn on young plants or in the spring as vigorous growth began. The majority of the results were below the limit of determination of 0.03 mg/kg, the highest being 0.19 mg/kg from the highest treatment rate with several others around 0.1 mg/kg. In some trials rape seed oil was prepared from the treated seed, and in all cases the residues in the oil were below the limit of determination of 0.03 mg/kg. In similar trials in France, nearly all of the residues were below the limit of determination, the highest being 0.07 mg/kg.

From three trials of clethodim on oilseed rape in the UK, using either
0.36 or 0.72 kg ai/ha, residues at harvest after 258 to 294 days were below the limit of determination of 0.03 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg for rape seed, and 0.05 mg/kg for rape seed oil, both crude and edible.

Sunflower seed. Trials of clethodim on sunflowers were carried out in Argentina using 0.12 or 0.24 kg ai/ha. Residues in the seeds did not exceed 0.14 mg/kg at 102 to 108 days PHI. Residues of clethodim in sunflower seeds treated in France at either 0.18 or 0.48 kg ai/ha were below the limit of determination, 0.03 mg/kg, at 108, 112 and 123 days later.

Two trials were conducted in Italy, using clethodim at a rate of 0.24 kg ai/ha. Residues in the seeds did not exceed the limit of determination (0.03 mg/kg) after 74, 92 or 110 days; residues were also not observed in the raw or refined oil prepared from the crop. From another trial in Italy the same treatment gave residues of 0.07, 0.06 and 0.06 mg/kg, at 60, 75 and 90 days PHI respectively.

The Meeting estimated a maximum residue level of 0.2 mg/kg for sunflower seed and 0.05 mg/kg for sunflower seed oil, crude and edible.

Clover. In one trial in New Zealand, white clover was treated with clethodim at 0.24 kg ai/ha. After 62 days, the silage prepared from the clover showed residues of 0.26 mg/kg, while 71 days later the regrowth showed 0.07 mg/kg.

Chickens. Laying hens were fed doses of clethodim (5%) and clethodim sulphoxide (95%), at nominal doses of 0, 10, 30, and 100 ppm of total clethodim in the diet, for 28 days. Egg samples were taken on 10 test days from days -1 to 30. The levels of DME (as clethodim) found in eggs from hens treated at 10 ppm were all less than 0.05 mg/kg. The levels of DME found in eggs from the 30 ppm and 100 ppm treatments ranged from 0.05 to 0.09 mg/kg and from 0.14 to 0.24 mg/kg respectively, during the feeding period; in both cases they declined to less than 0.05 mg/kg by day 29. Neither DME-OH nor S-MeDME were above the limit of determination (0.05 mg/kg) in any of the egg samples.

Ten chickens from each group were killed on day 29 and the rest on day 31; from each batch, samples of thigh and breast muscle, liver, gizzard, and subcutaneous and abdominal fat were taken for analysis. The only tissue fraction found to contain any clethodim-related residues was the liver from the 100 ppm dose level which showed 0.06 mg/kg of DME. All other results were below the limit of determination of 0.05 mg/kg.

The Meeting estimated a maximum residue level of 0.05* mg/kg for chicken meat and chicken eggs.

Cows. Fourteen dairy cows were used in a study of the distribution of clethodim residues in bovine tissues. Two were used as controls and the others were split into three groups of four cows each for treatment daily for 28 days with capsules containing clethodim (5%) and clethodim sulphoxide (95%), the nominal doses being 0, 10, 30, and 100 ppm of total clethodim in the diet.

Duplicate samples of whole milk were collected from all cows on days -1, 1, 2, 4, 7, 12, 16, 20, and 28 of the treatment period and on test days 29, 30 and 31 from the available animals. Three cows from each treated group and one control cow were killed on test day 29, within 24 hours of the last dose; the remaining cow in each group was killed on the morning of test day 31.

Analysis of the milk samples from treated cows showed no residues corresponding to clethodim or its metabolites for the control or 10 mg/kg feeding levels. The 30 ppm feeding level showed only "clethodim-type" residues, with a maximum of 0.033 mg/kg clethodim equivalents and a plateau by test day 1. The 100 ppm feeding level showed a maximum of 0.081 mg/kg of "clethodim-type" residues with a plateau by day 1, and a maximum residue of 0.032 mg/kg clethodim equivalents for the *S*-methyl metabolite residues with a plateau by day 2. No 5-hydroxy metabolite residues were found at any feeding level. One cow at each feeding level was held for a two-day withdrawal period and in all cases any residue present during the treatment declined to below 0.0125 mg/kg by the end of the withdrawal period.

The Meeting estimated a maximum residue level of 0.05* mg/kg for cattle milk and cattle meat

and 0.1 mg/kg for cattle kidney and cattle liver.

No information was available on the fate of residues of clethodim in stored produce.

Data were provided on the fate of residues of clethodim when soya beans, cotton seed, rape seed and sunflower seed were processed to yield the respective oils. Apart from soya bean soapstock and crude lecithin there was virtually no transfer of clethodim from the treated raw agricultural commodity to the processed fractions.

Soya bean. Soya beans were treated at eight times the normal rate, in order to ensure that residues were high enough for the study to be effective, and the samples were processed in the usual way, all processed fractions being sampled and analysed. When the soya beans were processed, clethodim residues were reduced in crude oil (by 90%), degummed oil (94%) and refined oil (>99%), while residue levels in the hulls and meal were unchanged from those in the unprocessed beans; residues were concentrated somewhat in soapstock (126%) and crude lecithin (156%).

Cotton seed. Cotton was similarly treated at eight times the normal rate and the samples were processed. All processed fractions except linter and linter motes were collected and analysed for clethodim residues. The processing reduced the combined clethodim residues in crude and refined oil to about 20% and 10% respectively, of the amounts in the raw agricultural commodity. Residues remained essentially the same in soapstock, delinted cotton seed and hulls but were concentrated slightly (1.7 times) in the meal.

Rape seed. Rape seed was treated with clethodim at twice the normal rate at two sites in western Canada. The rape seed was then processed to oil and meal using standard commercial techniques, and specific fractions from the process were sampled and analysed for clethodim residues. From rape seed containing 0.2 and 0.3 mg/kg of clethodim, no residues could be detected in the crude oil fraction. Final analyses of the solvent-free meal fractions showed a total residue of 0.77 mg/kg as clethodim. A mass balance showed that virtually all of the initial residue was retained in the meal.

Sunflower seed. Sunflower seeds from clethodim-treated crops in Argentina were processed to the oil. While residues remained in the press cakes, those in the oils were below the limit of determination. From two trials in Italy, residues in the seeds, raw oil or refined oil did not exceed the limit of determination (0.03 mg/kg).

No data were provided on residues in the edible portions of food commodities other than those included with the supervised trials or processing data reported above.

No information was provided on residues of clethodim occurring in commerce or at consumption.

RECOMMENDATIONS

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

Definition of the residue: sum of clethodim and its metabolites containing the 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim.

Commodity		Recommended MRL (mg/kg)	PHI on which based, days
CCN	Name		
VD 0071	Beans (dry)	0.1	65
MO 1280	Cattle, kidney	0.1	--
MO 1281	Cattle, liver	0.1	--
MM 0812	Cattle meat	0.05*	--
ML 0812	Cattle milk	0.05*	--
PE 0840	Chicken eggs	0.05*	--
PE 0840	Chicken meat	0.05*	--
SO 0691	Cotton seed	0.5	60
OC 0691	Cotton seed oil, crude	0.1	--
OR 0691	Cotton seed oil, edible	0.05	--
VD 0561	Field pea (dry)	0.1	50-110
VR 0589	Potato	0.2	30-61
SO 0495	Rape seed	0.5	70-106
OC 0495	Rape seed oil, crude	0.05	--
OR 0495	Rape seed oil, edible	0.05	--
VD 0541	Soya bean (dry)	10	50
OC 0541	Soya bean oil, crude	1	--
OR 0541	Soya bean oil, edible	0.1	--
VR 0596	Sugar beet	0.2	60-112
SO 0702	Sunflower seed	0.2	106
OC 0702	Sunflower seed oil, crude	0.05	--
OR 5702	Sunflower seed oil, edible	0.05	--

FURTHER WORK OR INFORMATION

Desirable

Data on residues occurring in food in commerce and/or at consumption.

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