TOLCLOFOS-METHYL

IDENTITY

ISO common name: tolclofos-methyl

Chemical name
IUPAC: *O*-2,6-dichloro-*p*-tolyl *O*,*O*-dimethyl phosphorothioate
CA: *O*-(2,6-dichloro-4-methylphenyl) *O*,*O*-dimethyl phosphorothioate

CAS No: 57018-04-9

Synonyms: Rizolex, Risolex, Grancer, Basilex, S-3349

Structural formula:

Molecular formula: $C_9H_{11}Cl_2O_3PS$

Molecular weight: 301.12

Physical and chemical properties

Technical material

Physical form:	white crystalline solid
Purity:	94.0% minimum
Odour:	Faint characteristic odour
Density:	0.838
Melting point:	78-80°C
Vapour pressure: (24.8°C)	1.38×10^{-5} mm Hg (1.84×10^{-3} Pa)
Solubility in water: (25°C)	1.10 ± 0.08 mg/litre

Solubility, common solvents (25°C):	% w/w
Acetone	50.2
Methyl isobutyl ketone	36.5
Cyclohexanone	36.0
Methanol	5.9
Ethyl cellosolve	11.8
Ethylene glycol	0.3
Ethyl acetate	38.9
Hexane	3.8
Xylene	36.0
Petroleum ether	2.3
Acetonitrile	33.1
Chloroform	49.0
Dimethyl formamide	48.7

Octanol-water partition coefficient ($LogP_{ow}$ at 24.8°C):	4.56
Stability:	Stable for 6 months in storage at 60°C. Indefinitely stable under normal storage conditions.

Formulations

Tolclofos-methyl is formulated as a 50% SC, and various concentrations of WPs and dusts.

METABOLISM AND ENVIRONMENTAL FATE

The fate of tolclofos-methyl has been studied in animals (mice, rats, goats and laying hens), plants (cotton, peanut and sugar beet), soil and water. The chemical names, abbreviated designations, and structures of the compounds identified are shown in Table 1.

Animal metabolism

Five SD rats of each sex were given a single dose of a corn oil solution of 5 mg/kg bw of [U-^{14}C-*phenyl*]tolclofos-methyl by oral intubation. A second group of animals was dosed in the same way with 200 mg/kg. A third group was pre-treated with unlabelled tolclofos-methyl, administered daily for 14 consecutive days at 5 mg/kg bw/day, prior to the administration of a single dose of the labelled compound at the same level. Radiocarbon in the urine and faeces and $^{14}CO_2$ in the expired air were monitored from 30 minutes after administration of the labelled compound for a period of 7 days at which time the animals were killed for assay of radioactivity in various tissues.

Metabolites in the faeces, urine, bile and major tissues were isolated by chromatography and identified by co-chromatography with authentic standards and/or spectroscopic analysis.

In all three treated groups over 95% of the administered radiocarbon was excreted with the urine and faeces within 48 hours. Four major metabolites (DM-TMO, DM-TM-CH_2OH, DM-TM-COOH and DM-TM: see Table 1) and 6 minor metabolites were identified in the excreta. The unidentified residues amounted to about 5% of the total radioactivity. The concentration of total residues in the high-dose animals amounted to 0.1-1.3 mg/kg in the kidneys, 1.08-1.75 mg/kg in the liver, 0.38-0.45 mg/kg in muscle and <0.01-1.33 mg/kg in blood, expressed as tolclofos-methyl. The

total ^{14}C in all tissues analysed accounted for less than 1.0% of the administered dose. The overall recovery of radiocarbon was 103.8% after 7 days (Krautter *et al.*, 1987, 1988).

A similar study was carried out with [^{14}C]phenyl-labelled tolclofos-methyl at 5 mg/kg bw. Rats were killed at intervals up to 72 hours after administration to determine the changes in tissue residues with time after administration. In a parallel study with bile-cannulated male and female rats bile, urine and faeces were monitored over a 48-hour period after administration. The ^{14}C was distributed in various organs and reached its peak in almost all tissues within 2 hours after administration. The total residues expressed as tolclofos-methyl amounted to 1.14-1.27 mg/kg in plasma, 3.45-4.67 mg/kg in the kidneys, 1.22-1.24 mg/kg in the liver and 0.74-0.84 mg/kg in blood. Thereafter the concentration of total radioactivity in the plasma and in most tissues decreased. The cumulative excretion of ^{14}C in the bile, urine and faeces for 48 hours after administration was 5.8-11.7%, 46.7-59.4% and 23.7-42.3% of the oral dose, respectively. Two hours after administration at least 7 metabolites were detected in the blood, liver and kidneys. The main products were TM-COOH, PH-COOH, DM-TM and DM-TM-CH_2OH. Only a small amount of the parent compound was detected in the liver. Most of the ^{14}C excreted into the bile within 24 hours was found to be in polar metabolites consisting mainly of the glucuronides of TM-CH_2OH and PH-CH_3. Radiocarbon excreted into the faeces from 0 to 24 hours after administration was found to be from the parent compound only (Esumi *et al.*, 1989)

Further studies were carried out with tolclofos-methyl labelled in the tolyl methyl group. Male and female SD rats and RC mice received single doses by oral intubation of the test compound in corn oil at the rate of 5 mg/kg bw. Again, urinary and faecal elimination was monitored over a 7-day period and the animals then killed. Whole-body autoradiograms of male rats 1, 6 and 24 hours after administration showed that the highest radioactivity was located in the digestive organs including the stomach and intestines 1 h and 6 h after treatment, followed by the kidneys and liver. Seven days after dosing, 27 tissues of the rats were examined for ^{14}C residues, which were below 6 ì g/kg tolclofos-methyl equivalents. The hair contained 52-60 ì g/kg.

Approximately 87-91% of the administered radiocarbon was excreted in the urine and faeces within a week and less than 1% in the expired air. The total ^{14}C residues in the animals' bodies were less than 1% of the dose. The residues in tissues were low, but somewhat higher residues were found in the hair. 13 metabolites were identified in both rats and mice. The major metabolites detected in the excreta of mice were PH-CH_3 (9% of the dosed ^{14}C), TMO-COOH (11%), DM-TM-COOH (12%), PH-COOH (12%) and PH-CO-glyc (13%). (Mihara *et al.*, 1981).

Table 1. Identified metabolites of tolclofos-methyl and their designation.

Chemical names and designation of compounds	Structural formula
O-(2,6-dichloro-4-methylphenyl) *O,O*-dimethyl phosphorothioate TM	
O-(2,6-dichloro-4-formylphenyl) *O,O*-dimethyl phosphorothioate TM-CHO	
3,5-dichloro-4-hydroxybenzaldehyde	

Chemical names and designation of compounds	Structural formula
PH-CHO	
3,5-dichloro-4-hydroxybenzoic acid PH-COOH	
2,6-dichloro-4-methylphenyl dimethyl phosphate TMO	
3,5-dichloro-4-hydroxybenzyl alcohol PH-CH_2OH	
2,6-dichloro-4-methylphenol PH-CH_3	
O-(4-carboxy-2,6-dichlorophenyl) *O*,*O*-dimethyl phosphorothioate TM-COOH	
O-(2,6-dichloro-4-methylphenyl) *O*-methyl *S*-methyl phosphorothioate SM-TM	
O-(2,6-dichloro-4-hydroxymethylphenyl) *O*,*O*-dimethyl phosphorothioate TM-CH_2OH	
2,6-dichloro-4-formylphenyl dimethyl phosphate TMO-CHO	

Chemical names and designation of compounds	Structural formula
4-carboxy-2,6-dichlorophenyl dimethyl phosphate TMO-COOH	
2,6-dichloro-4-(hydroxymethyl)phenyl dimethyl phosphate TMO-CH_2OH	
N-(3,5-dichloro-4-hydroxybenzoyl)glycine PH-CO-gly	
O-(2,6-dichloro-4-methylphenyl) *O*-methyl *O*-hydrogen phosphorothioate DM-TM	
O-(2,6-dichloro-4-methylphenyl) *S*-methyl *O*-hydrogen phosphorothioate DM-SM-TM	
O-(4-carboxy-2,6-dichlorophenyl) *O*-methyl O-hydrogen phosphorothioate DM-TM-COOH	
2,6-dichloro-4-methylphenyl methyl hydrogen phosphate DM-TMO	
4-carboxy-2,6-dichlorophenyl methyl hydrogen phosphate DM-TMO-COOH	
O-[2,6-dichloro-4-(hydroxymethyl)phenyl] *O*-methyl *O*-hydrogen phosphorothioate DM-TM-CH_2OH	

Chemical names and designation of compounds	Structural formula
2,6-dichloro-4-(hydroxymethyl)phenyl methyl hydrogen phosphate DM-TMO-CH_2OH	

[U-^{14}C]Phenyl-labelled tolclofos-methyl was administered orally at 10 mg/kg bw/day to a lactating goat of approximately 40 kg weight for four consecutive days. This was equivalent to approximately 250 ppm in the diet but was administered by capsule. Urine and faeces were collected separately at 7, 24, 48, 72 and 79 hours after the start of the study. Milk was collected twice daily and the animal was slaughtered 7 hours after the last of the four doses.

The urine samples were acidified to pH 1 and extracted with diethyl ether to give "free metabolites". The remaining liquid was neutralized to pH 7, lyophilised and extracted with methanol/water. The total radioactivity in the various substrates was determined by combustion analysis and the radioactive components fractionated by a series of solvent extractions. Milk was extracted with ether and the extracted residues dissolved in acetonitrile after removal of the fat fraction. Tissues and faeces were acidified to pH 1 and extracted with ether. The residual material was refluxed and re-extracted with ether to give "acid-released metabolites". This was followed by pH adjustment to 12, reflux for 1 hour and subsequent extraction to give a "base-released fraction". The fractions were analysed for total radioactivity, and where there was sufficient material the metabolites were separated by TLC (Nelson *et al*., 1987). The residues identified in various samples are shown in Table 2.

Urine was the principal route of elimination and accounted for 26% of the total applied dose by the end of the study at 79 hours, when the total radioactivity amounted to 485 mg/kg TM equivalent. Faecal elimination accounted for only 0.6% of the dose. The concentration of radioactivity in the faeces increased continuously during the study, the TM equivalents being 4, 24, 44, 81 and 143 mg/kg at 7, 24, 48, 72 and 79 hours. This implied that if the study had been prolonged the faeces could have become a much more important route of elimination.

There was very little elimination of radioactivity in the milk, accounting for 0.001% or less of the applied dose. The concentration in whole milk reached 0.87 mg/kg tolclofos-methyl equivalent by the end of the study. Just under 0.6% of the applied dose was retained in the tissues with the highest concentrations in the liver and kidneys (3.0 and 4.3 mg/kg respectively). The muscle contained 0.2 mg/kg of total residue.

In the milk, 65% of the total radioactivity was in the acetonitrile fraction from the sample taken at 48 hours. The rest of the radioactivity in the milk was either extractable in hexane (9.3%), remained in the aqueous phase (3.1%), or remained unextracted in the solids (18.3%). The radioactivity in the acetonitrile was fractionated and various metabolites were identified. The most important were the oxon TMO (42.4%), the carboxylic acid derivative DM-TM-COOH (6.8%) and the phenolic carboxylic acid (PH-COOH) (9%). These, together with an unknown (7%) accounted for 65% of the total radioactivity in the milk.

Radioactivity in the fat and muscle was too low for further identification (Nelson *et al*., 1987). The proposed metabolic pathways of tolclofos-methyl are shown in Figure 1.

[U-^{14}C]Phenyl-labelled tolclofos-methyl was administered orally for four consecutive days at 10 mg/kg bw/day to 3 laying hens which were killed 7 hours after the last dose. Three more hens were treated with the vehicle only. The dosage was equivalent to approximately 167 ppm in the diet but was administered each day as a single dose. All eggs laid during the study were collected and excreta were collected daily. The excreta and tissues were extracted by procedures broadly similar to those used in the goat study above.

Over 71% of the first dose was eliminated in the first 7 hours and 87% within 24 hours. During the following days the excreted proportion of the administered pesticide varied around 85%. Residues in eggs were 0.37 mg/kg tolclofos-methyl equivalents in the yolk at 72 hours and 0.27 mg/kg at 79 hours. The corresponding levels in the albumin rose to a maximum of 0.07 mg/kg. The highest residues occurred in the fat, kidneys and liver (1.0, 6.0 and 3.4 mg/kg respectively). Those in other tissues were heart 0.18, muscle 0.11, lung 0.44, spleen 0.12 and ovary 0.47 mg/kg.

Most of the residues in the excreta were readily extracted with ether. Acid hydrolysis released another 4% whilst the aqueous and unextracted residues from the residual solids were 6 and 4% respectively. Unchanged tolclofos-methyl accounted for 36% of the residues and the major metabolites in decreasing order were PH-COOH (23%), TM-CHO (9%), TMO-COOH (7%) and TM-COOH (3%). DM-TMO-CH_2OH, PH-CH_2OH, PH-CH_3, PH-CHO, TMO, DM-TM and DM-TMO were identified as only minor metabolites.

In the liver about 20% of the radioactivity was in the form of free metabolites with a further 8% liberated by acid and base hydrolysis. Water-soluble and unextractable radioactivity accounted for about 30 and 41% respectively. The unchanged parent was not detected in the liver and the only identified metabolite was TM-CHO. There were other compounds in the extract but they could not be identified.

In the kidneys 40% of the radioactivity was directly extracted, with a further 18% released by acid and base hydrolysis. The rest of the radioactivity was made up of 15 and 25% in the aqueous and unextracted fractions. The only metabolite identified was PH-COOH which accounted for 9% of the total radioactivity. There were 8 other metabolites but further identification was not possible owing to the small amounts present.

Figure 1. Proposed metabolic pathways of tolclofos-methyl in goats.

Table 2. Distribution of residues in a goat dosed orally with [^{14}C]tolclofos-methyl for four consecutive days.

Residues	Radioactivity, mg/kg TM equivalent or % of total in sample						
	Urine[1], %[2]	Faeces[1], %[3]	Liver[4], mg/kg	Kidneys, mg/kg	Muscle, mg/kg	Fat, mg/kg	Milk[5], mg/kg
TM	ND	28.16					
TMO	0.7	ND					0.17
TM-CHO	ND	0.69					
TM-COOH	0.21	5.73					
TM-CH_2OH		12.86					
PH-CHO	2.76		0.026				
PH-COOH	8.90		0.55	0.9			0.036
PH-CH_2OH	14.21		0.16				
PH-CH_3	1.47						
PH-CO-Gly	1.8						
TMO-CHO		3.24					
TMO-COOH		8.08		0.91			
TMO-CH_2OH	0.14			0.47			
DM-TM	0.08						
DM-TM-CH_2OH	2.94						
DM-SM-TM	0.02						
DM-TM-COOH	1.85						0.027
DM-TMO	44.77			0.13			
DM-TMO-COOH	2.16						
DM-TMO-CH_2OH	7.94	0.94		0.16			
Unknowns	1.5		0.32	0.32			0.028
Organoextractable					0.076	1.3	0.31
Water soluble			0.62	1.87	0.11		0.013
Unextractable solid			0.89	0.16	0.016	0.09	0.075
Total			3.0	4.3	0.2	1.1	0.041

[1] Average of samples taken at 24 h and 79 h
[2] Combined residues in the free and methanol fractions expressed as percentage of the total activity measured in urine
[3] Combined residues in the free and acid-released fractions expressed as percentage of the total activity measured in faeces
[4] Sum of free and acid- and base-released organoextractable fractions
[5] The identified metabolites were in the acetonitrile extract

In eggs and muscle, levels of radioactivity were too low to permit the identification of individual components (Yu and Guirguis, 1987)

Plant metabolism

Phenyl-labelled tolclofos-methyl was applied to the leaves of six-month-old sugar beet plants in pots in a greenhouse. The product was applied in methanol solution to the upper surface of the third leaves at the rate of 2 mg per leaf of approximate surface area 60 cm². Two plants were withdrawn at intervals and separated into treated leaves, untreated leaves and roots. The treated leaves were subjected to a surface wash with methanol and then homogenized with methanol/chloroform. Untreated shoots and roots were processed in the same way. The residual radioactivity in the extracted material was determined by combustion analysis.

Three days after the treatment, only 40% of the applied radioactivity was recovered from the treated leaves, 15% in the surface wash and 23.2% in the extract from the macerated leaves. The methanol/chloroform extract contained several metabolites in proportions which varied with time. The distribution of radioactivity and residues in treated leaves, untreated shoots and roots is shown in Table 3.

A parallel study was also carried out where sugar beet plants were grown in pots to the age of six months. At that time the top 5 cm of soil was removed and treated with labelled tolclofos-methyl at the rate of 20 mg/kg on a dry weight basis. The treated soil was replaced in the pots, and two beets were removed at intervals and the roots and leaves analysed for residues. The results are shown in Table 4. (Mikami *et al.*, 1980a).

Cotton plants were grown in field conditions in soils which had been treated at the rate of either 5.24 or 15.7 kg/ha with labelled tolclofos-methyl. Cylinders of soil, surrounded by a casing, were treated to a depth of 5 cm. Cotton seeds were planted shortly afterwards and the plants were grown to maturity (150 days). Various plant parts were separated and analysed.

In plants grown on the soils treated with 5.24 kg/ha, no radioactivity was detected in bolls, squares, seed or leaves. The limits of determination were 0.004, 0.004, 0.003 and 0.008 mg/kg TM equivalents respectively. Minor amounts were found in the stems (0.008-0.01 mg/kg). In plants from soils treated at the higher rate the levels of total radioactivity in bolls, squares and seed were still below the limits of determination but trace amounts were found in the leaves (0.015 mg/kg) and stems, ranging from 0.015 to 0.026 mg/kg at different heights. The levels were too low to allow the identification of any metabolites (Savidge *et al.*, 1987).

A study on peanuts was carried out in parallel with the study on cotton except that in this case the treatments included a foliar application (4.24 or 22.25 mg ai/plant) 75 days after the soil treatment. Samples were taken of leaves, stems, hulls and nuts from the mature plants. All samples were solvent-extracted, but the extraction of the leaves was preceded by a solvent wash to determine surface deposits. The radioactive residues are shown in Table 5.

The radioactivity on the surface of the leaves at maturity from the high treatment rate in duplicate samples amounted to 2.6-3.7% of the ^{14}C. It was from TM (2.3-3.2%), TM-CH_2-OH (6.9-7.0%), PH-CH_2-OH (14.6-18.6%) and polar conjugates (50.2-69.6%). The parent compound was not detected in the leaf extracts, where the main identified residues were PH-CHO (15.7-22.7%), TM-CH_2OH (5.2-17.4%), PH-CH_3 and TMO (both ND-3.7%). There were three unidentified components (8.9-10.6%). Between 10 and 18% of the extracted residue remained at the origin in the TLC separation and this was hydrolysed with cellulase to liberate mainly PH-CH_2OH (51.2-58.1%) and TM-CH_2OH (26.7-31.4%) with smaller amounts of TMO, PH-CHO and TMO-CH_2OH. The level of radioactivity in the nuts was too low to fractionate (Savidge *et al.*, 1987). The residues in the hulls were TM (5.8%), DM-TMO (9.8%), and two unknowns (12.1 and 5.5%). 66.8% of the radioactivity remained at the origin on the TLC plate.

Metabolic pathways of tolclofos-methyl in plants are shown in Figure 2 (page 1250).

Table 3. Distribution of radiocarbon and residues in sugar beets after foliar treatment.

Sample, Fraction, Metabolite	% of applied radiocarbon after interval, days

	3	7	14	21	28	35	50
Treated leaves	39.5	22.9	20.2	8.0	7.7	7.6	7.1
Surface wash	15.0	2.8	0.5	0.4	0.3	0.3	0.3
Tolclofos-methyl	14.7	2.6	0.4	0.2	0.2	0.2	0.1
TMO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Others CH_3	0.3	0.2	0.1	0.2	0.1	0.1	0.2
MeOH/$CHCl_3$ extract	23.2	17.8	17.4	5.6	5.4	5.2	4.5
Tolclofos-methyl	19.7	3.9	1.1	1.4	0.5	0.5	0.5
TMO	0.2	1.4	0.3	0.1	0.1	0.1	0.1
TM-CH_2OH	<0.1	<0.1	<0.1	0.1	0.2	<0.1	<0.1
TMO-CH_2OH	<0.1	2.3	3.7	<0.1	<0.1	<0.1	<0.1
TMO-COOH	<0.5	0.4	0.5	1.1	0.5	0.3	0.4
DM-TM	0.6	0.9	1.4	0.6	0.3	0.3	0.2
DM-TMO	1.4	1.9	7.8	1.9	2.9	3.2	2.8
PH-CH_3	0.2	4.6	1.3	<0.1	<0.1	<0.1	<0.1
PH-CH_2OH	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	<0.1
Others	0.6	2.0	1.3	0.4	0.9	0.8	0.5
Shoots	0.3	1.3	1.3	1.6	1.5	1.5	1.0
Tolclofos-methyl	0.2	0.7	0.5	0.7	0.7	0.7	0.4
TMO	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
TMO-COOH	<0.1	<0.1	<0.1	0.3	0.2	0.2	<0.1
Others	<0.1	0.3	0.5	0.3	0.3	0.2	0.2
Roots	0.5	0.4	0.5	0.6	0.6	0.6	0.3
Tolclofos-methyl	0.1	<0.1	<0.1	0.1	0.1	0.1	0.1
TMO-COOH	<0.1	0.1	<0.1	0.1	0.2	0.1	<0.1
Others	0.3	0.3	0.4	0.3	0.2	0.3	0.1
Total	40.3	24.6	22.0	10.2	9.8	9.7	9.4

Table 4. Distribution of radiocarbon and residues in sugar beets and soil after soil treatment.

Sample, fraction or metabolite	% of applied radiocarbon or residues as tolclofos-methyl equivalent, mg/kg, after interval, days						
	3	7	14	21	28	35	75
Whole beets, total residue %	0.2	0.6	2.5	1.0	0.7	0.9	1.2
Roots, total residue %	0.1	0.4	1.5	0.5	0.4	0.5	0.6
mg/kg	0.11	0.38	1.75	0.50	0.49	0.48	0.44
TM %	<0.1	0.2	1.0	0.2	0.2	0.2	0.1
mg/kg	0.03	0.22	1.16	0.19	0.18	0.17	0.07
TMO %	<0.1	0.1	0.2	0.1	0.1	0.1	0.1
PH-CH_3 %	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Others %	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Sample, fraction or metabolite		% of applied radiocarbon or residues as tolclofos-methyl equivalent, mg/kg, after interval, days						
		3	7	14	21	28	35	75
Unextracted residues	%	<0.1	0.1	0.2	0.2	0.1	0.2	0.4
Shoots, total residue	% mg/kg	0.1 0.12	0.2 0.13	1.0 0.82	0.5 0.46	0.3 0.33	0.4 0.27	0.6 0.24
TM	% mg/kg	<0.1 0.02	<0.1 0.03	0.7 0.6	0.2 0.2	0.1 0.07	0.1 0.07	0.1 0.05
TMO	%	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
PH-CH_3	%	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Others	%	<0.1	0.1	0.1	0.1	0.1	0.1	0.1
Unextracted residues	%	0.1	0.1	0.2	0.2	0.1	0.2	0.4
Soil, total residue	% mg/kg	62.7 2.3	61.4 2.13	57.5 1.85	49.9 1.64	50.4 1.62	47.2 1.62	46.5 1.54
TM	% mg/kg	34.0 1.25	31.5 1.09	29.1 0.94	24.1 0.79	20.7 0.69	19.0 0.65	15.3 0.51
TMO	%	1.2	0.9	0.8	0.5	<0.1	<0.1	<0.1
PH-CH_3	%	3.9	3.9	3.6	0.9	2.3	1.4	4.4
Others	%	5.5	4.5	4.2	2.6	5.4	4.1	3.3
Unextracted residues	%	18.1	20.6	19.8	21.8	22.0	22.7	23.5

Table 5. Total radioactivity in mature treated peanuts.

Treatment	Radioactivity as mg/kg tolclofos-methyl equivalents				
	Nuts	Hulls	Leaves, surface	Leaves, internal	Stems
5.2 kg ai/ha soil + 4.2 foliar	0.01	0.016	0.030	1.37	0.04-0.08
15.7 kg ai/ha soil + 22 foliar	0.01	0.05	0.18	3.64	0.09-0.38

Field studies were carried out in Japan with soya beans and wheat for the determination of the oxon TMO and the alcohol TM-CH_2OH, the two metabolites that had been considered most likely to occur in plant material. In both cases studies were at two locations. In the case of wheat tolclofos-methyl was applied as a 50% wettable powder at a concentration of 0.1% ai in the spray, giving an application rate of 1.5 kg ai/ha. It was applied to soya beans either as a 50% wettable powder or as a 20% dust, at rates of 15 kg ai/ha and 60 kg ai/ha respectively. The applications were made to both crops at three different times before harvest. The results obtained for grain and beans at normal harvest time are summarized in Table 6. Residues of both metabolites were below the LOD in all samples.

Table 6. Residues of tolclofos-methyl and its metabolites in wheat and soya beans treated with unlabelled pesticide (Ref. Ohnishi, 1982a,b)

Crop	Treatment	PHI, days	Residues, mg/kg in grain or beans		
			TM	TMO	TM-CH_2OH
Wheat	WP 1.5 kg ai/ha	275	<0.005	<0.005	<0.01
Wheat	WP	287	<0.005	<0.005	<0.01
Soya	WP 15 kg ai/ha	14	0.009	<0.005	<0.0
Soya	WP	30	0.035	<0.005	<0.01
Soya	Dust 60 kg ai/ha	14	0.060	<0.005	<0.01
Soya	Dust	30	0.036	<0.005	<0.01
Soya	WP 15 kg ai/ha	14	<0.005	<0.005	<0.01
Soya	WP	28	0.006	<0.005	<0.01
Soya	Dust 60 kg ai/ha	14	0.019	<0.005	<0.01
Soya	Dust	28	0.023	<0.005	<0.01

Environmental fate in soil and soil/water systems

The fate of tolclofos-methyl in various soils was extensively studied under aerobic and partially or completely anaerobic conditions in the laboratory and under natural field conditions, with the labelled and unlabelled compound.

The methods in all the laboratory studies were similar. The parent compound, labelled uniformly in the phenyl ring, was incubated with the soils. The soils were fresh and the test material was added at the rates ranging from 0.38 mg/kg to 26 mg/kg. The soils were placed in containers fitted for aspiration with CO_2-free air and trapping systems including polyurethane filters for organic materials and NaOH solution for CO_2. The soil moisture was kept at the same level during incubation which took place in the dark at temperatures from 15°C to 25°C for 30 to 365 days. Soils were withdrawn periodically and analysed for extractable metabolites, bound residues and liberated volatiles, including those trapped by polyurethane. The radioactivity present in the humic or fulvic acid fractions of the soils was determined separately in some studies. The unextracted radioactivity was determined by combustion analysis. The total recovery of radiocarbon was generally above 90%.

The details of the experiments were as follows.

A. Takarazuka soil: OM 2.28%, pH 6.19, clay 14%, sand 78%. Aerobic incubation at 25°C for 90 days (Mikami *et al.*, 1980b).

B. Azuchi soil: OM 2.5%, pH 6.3, clay 17%, sand 65%. Aerobic incubation at 25°C for 90 days (Mikami *et al.*, 1980b).

C. Takarazuka soil: aerobic incubation at 25°C for 180 days (Mikami *et al.*, 1984).

D. Takarazuka soil: aerobic incubation at 15°C for 240 days (Mikami *et al.*, 1984).

Figure 2. Metabolic and abiotic degradation of tolclofos-methyl in plants, soil and water

E. Sapporo soil: OM 11.6%, pH 5.34, clay 24%, sand 48%. Aerobic incubation at 25°C for 90 days (Mikami *et al.,* 1980b).

F. Sapporo soil: aerobic incubation at 25°C for 180 days (Mikami *et al.,* 1984).

G. Sapporo soil: aerobic incubation at 15°C for 240 days (Mikami *et al.,* 1984).

H. Kodaira soil: OM 15.3%, pH 5.5, Clay 29%, sand 31%. Aerobic incubation at 25°C for 90 days (Mikami *et al.,* 1980b).

I. Sapporo soil: aerobic incubation at 25°C for 180 days. Results in Table are from 30 days (Yoshimura, *et al.* 1985).

J. Sapporo soil: anaerobic incubation at 25°C for 60 days. Results in Table are from 30 days (Yoshimura *et al.,* 1985).

K. Sapporo soil: sterile incubation at 25°C for 30 days, (Yoshimura *et al.,* 1985).

L. Azuchi soil: aerobic incubation at 25°C for 180 days. Results in Table are from 30 days (Yoshimura *et al.,* 1985).

M. Azuchi soil: anaerobic incubation at 25°C for 60 days. Results in Table are from 30 days (Yoshimura *et al.,* 1985).

N. Azuchi soil: sterile incubation at 25°C for 30 days (Yoshimura *et al.,* 1985).

O. California Tulare sandy loam soil: OM 0.8%, pH 7.1, clay 12%, sand 70%. Aerobic incubation at 25°C for 365 days according to EPA Subdivision N Guidelines, Section 162-1. (Itoh *et al.*, 1993).

P. California Tulare sandy loam soil: incubation at 25°C for 32 days under aerobic conditions and continued for additional 60 days under anaerobic conditions by covering the soil with oxygen-free water. The study was according to EPA Subdivision N Guidelines, Section 162-1. (Kono and Mikami, 1993).

R. California Tulare sandy loam soil: incubation under anaerobic conditions under water for 1 month, test material incorporated and incubated for a year at 25°C. Soil and water phases analysed separately. (Mikami and Itoh, 1993).

S. Sandy loam from Germany: OM 1.42%, pH (KCl) 5.24, clay 18.9%, sand 31.4%. Aerobic incubation at 20°C for 100 days with unlabelled compound according to BBA Guidelines IV.4.1 (Römbke, 1989).

T. Silt loam from Germany, OM 1.24%, pH (KCl) 5.52, clay 19.3%, sand 5.6%. Aerobic incubation at 20°C for 100 days with unlabelled compound according to BBA GL IV.4.1 (Römbke, 1989).

U. Sandy loam in North Carolina: treatment in tin cylinders of 10 cm diameter with 15.7 kg ai/ha nominal rate of an EC formulation containing phenyl-labelled tolclofos-methyl. After treatment the pesticide was incorporated into the top 5 cm of the soil, the soil surface was sprinkled with water and cotton and peanut seeds were planted within 15-30 minutes (Savidge *et al.,* 1987). This is also the study of metabolism by cotton and peanut plants described above.

The distribution of radioactivity among volatile, extractable and bound residues at the end of the incubation periods and the estimated half-lives in various soils are summarized in Table 7.

The pattern of degradation did not differ greatly among the soils in spite of their widely differing compositions. Altogether 27 degradation products were detected and 12 were identified in the extracts of soils under aerobic conditions. TMO (highest concentration range 0.1-1.2%), DM-TMO (0.1-1.8%), PH-CH_3 (0.1-6.3%) and DM-TM (0.3-18%) were the major compounds. In addition, TM-CH_2OH, TMO-CH_2OH, TM-COOH, TMO-COOH, DM-TM-COOH, PH-CH_2OH, SM-TM and PH-COOH were detected at less than 1% of the added dose. The bound ^{14}C was mostly found in the fulvic and humic acid fractions, in proportions which changed with time.

Most of the volatile material in the polyurethane traps was the parent compound, while virtually all of that in the caustic soda traps was CO_2. The main volatile compounds apart from the parent and CO_2 were 2,6-dichloro-4-methylphenol (PH-CH_3) and the corresponding free phenol. Their maximum proportions were 5.6 and 1.7% of the applied radioactivity respectively.

Under anaerobic conditions *p*-cresol (4-methylphenol), 2-chloro-4-methylphenol and four minor unknowns were found which were not detected under aerobic conditions. DM-TM, DM-TMO and PH-CH_3 were present as major products reaching maxima of 4.8-31.2%, 1-2.6% and 2.6-3.7% of the added dose respectively. The other identified compounds were the same as under aerobic conditions.

The distribution of radioactivity in an anaerobic soil/water system (experiment R) is shown in Table 8. This experiment revealed that under anaerobic condition methane was formed and was not absorbed by the gas trapping system employed, with a consequent decrease in the total recovery. However, in a separate study with a similar anaerobic soil/water system the headspace gases were analysed and found to contain appreciable amounts of methane as well as carbon dioxide.

The proportions of the parent compound and the major degradation products in the water and soil phases at various times during the study are shown in Tables 9 and 10.

Table 7. Distribution of radioactivity and estimated half-lives of TM after incubation of tolclofos-methyl in various soils.

Experiment	% of added radioactivity						Estimated half-life (days)
	Volatile			Extractable from soil		Bound in soil	
	TM	Other	CO_2	TM	Others		
A	10.2	1.7	26.1	11.9	3.8	38.0	14-28
B	7.3	1.8	27.9	13.9	3.4	38.1	1-28
C	1.6		33	2.4	2.8	42	20
D	0.4		27	6.5	5.4	42	46
E	5.5	2.6	34.4	9.7	2.6	33.9	7-14
F	1.0		27	6.2	9	47	28
G	0.7		18.4	15	18	36	67
H	6.9	0.9	38	8.9	2.6	43.2	7-14
I	0.6		1.9	41.5	11.2	33.8	
J	0.1		0.4	50.2	16.9	26.6	
K	0.1		<0.1	65.4	7.1	19.1	
L	1.5		3.7	41.8	8.4	32.5	
M	0.1		0.4	64.1	8.9	23	
N	0.2		<0.1	76.3	7.7	11	

Experiment	% of added radioactivity						Estimated half-life (days)
	Volatile			Extractable from soil		Bound in soil	
	TM	Other	CO_2	TM	Others		
O	18	7.9	33.3	5.3	15.4	19.6	60
P (32 d. aerobic + 60 d. anaerobic)	2.1 2.7	0.4 0.6	4.1 5.1	66.6 39.8	20.2 42.6	2.5 4.1	53 80
S							9.6*
T							9.3*

* DT-90 values were 110 and 107 days for studies S and T respectively.

Table 8. Distribution of radioactivity in a soil-water system under anaerobic conditions.

Days	% of added radioactivity					
	Water	Extracted from soil	Bound to soil	NaOH solution	Other volatiles	Total recovery
0	48.3	50.3	0.1			98.7
3	39.1	56.8	0.2	<0.01	0.1	96.1
30	47.9	49.8	0.4	0.4	0.1	98.6
62	63.6	23.8	2.1	1.8	0.3	91.6
120	40.1	10.2	4.4	8.4	0.7	63.7
182	22.4	6.3	14.7	16.8	1.2	55.2
364	13.3	8.3	8.7	23.5	1.5	55.2

Table 9. Compounds found in the aqueous phase of the soil-water system of Table 8.

Days	% of added ^{14}C						
	Tolclofos-methyl	DM-TM	4-Methyl-phenol	2-chloro-4-methylphenol	PH-CH_3	Others	Total in water
0	47.8	0.2	<0.06	<0.06	0.1	0.2	48.3
3	35.2	3.4	<0.06	<0.06	0.3	0.2	39.1
30	18.3	18.6	2.1	8.2	0.4	0.3	47.9
62	6.8	51.8	3.1	0.4	0.7	0.8	63.6
120	0.4	32.9	1.5	1.3	0.5	3.5	40.1
182	<0.06	14.0	0.4	1.6	2.5	3.9	22.4
364	<0.06	1.2	<0.06	1.3	6.8	4.0	13.3

Table 10. Compounds found in the soil phase of the soil-water system of Table 8.

Days	% of added ^{14}C				
	Tolclofos-methyl	DM-TM	Other extracted including humic substances	Bound	Total in soil
0	50.0	<0.06	0.3	0.1	50.4
3	55.3	1.0	0.5	0.2	57.0
30	44.4	2.7	2.7	0.4	50.2
62	18.3	4.6	0.9	2.1	25.9
120	4.8	3.6	1.8	4.4	14.6
182	2.2	1.6	2.5	8.4	14.7

364	1.0	1.2	6.1	8.7	17.0

In studies in Germany with unlabelled tolclofos-methyl, the parent compound (96.8% pure) was added to the fresh soils to give an initial nominal concentration of 0.375 mg/kg on a dry soil basis. The soil samples taken from plots P and R after 0, 32, 64 and 100 days incubation contained parent residues of 0.41 and 0.36, 0.08 and 0.12, 0.05 and 0.05, and 4.0 and 3.1 mg/kg respectively.

As part of the study U on metabolism in cotton and peanut plants, the residues in the soil were also determined periodically in samples taken at 0-7.5, 7.5-15 and 15-23 cm depths. The total residues decreased to 17% and 7% of the initial concentration in 75 and 150 days after application. The total residues found at different depths after treatment at 15.7 kg ai/ha with incorporation into the top 5 cm are shown in Table 11. The individual residues in the top 7.5 cm layer of the soil are shown in Table 12.

Table 11. Distribution of the total ^{14}C in the soil (Study U).

Depth zone, cm	Total residues, mg/kg TM equivalents, at interval, days		
	0	40	75
0-7.5	21.3	4.82	3.64
7.5-15	0	0.18	0.31
15-23	0	0.04	0.09

Table 12. Nature of the residues in the top 7.5 cm soil layer after incorporation of tolclofos-methyl at 15.7 kg ai/ha into the top 5 cm (Study U).

Residue	% of total extracted radiocarbon, range		
	75 days	120 days	150 days
TM	91.0-93.6	82.2-89.1	80.6-91.1
PH-CH_3	ND-2.6	ND	ND-3.6
TM-CH_2OH	0.5- 1.4	ND-0.9	ND-1.7
TMO	0.8-1.6	0.6-2.4	1.3-3.8
Unidentified 1	ND	ND-1.2	ND-1.4
Unidentified 2		ND	ND
Unidentified 3	ND-0.8	ND-1.2	ND-0.8
Unidentified 4	ND	ND-6.2	ND-6.0
Unidentified 5	ND-2.6	ND-0.8	ND-1.2
Unidentified 6	ND-3.0	ND-4.1	ND-6.0
Unidentified 7, 8*	ND ND		
Origin	1.1-4.3	4.1-9.2	3.4-7.3

ND Not detected. Detection limit 0.1-0.2%
* Two unidentified metabolites which occurred only in samples taken 75 days after soil treatment

In three Italian supervised field trials on crops, soil samples were analysed after applications of tolclofos-methyl.

In the first trial, with lettuce, the product was applied as a 30% WP at 4.8, 9.9 and 19.8 kg ai/ha onto the surface of the soil and lightly incorporated shortly before planting. Soil samples were taken to a depth of 20 cm 58 days afterwards. The residues of parent tolclofos-methyl were 0.14, 0.21 and 1.8 mg/kg respectively. Collina *et al.*, 1993a).

In the second study, carried out at two different sites, the product was sprayed on to the soil as either a 50% or 30% WP at rates of 13.5, 30 or 45 kg ai/ha. The plots were then planted with lettuce and subjected to normal cultivation and irrigation. Approximately 34 days after the first planting, the plots were cultivated and replanted with lettuce. The soils were sampled at intervals after application. The results at 3 of the 5 sampling intervals are shown in Table 13. The half-lives of the compound in the soils ranged between 7.4 and 11.2 days (Collina *et al.*, 1993b).

Table 13. Average residues in soil (0-20 cm depth) following soil treatments in Italy.

Application rate, kg ai/ha	Formulation	Tolclofos-methyl residues (mg/kg) at days after treatment					
		Site 1			Site 2		
		2	23	99	4	40	85
13.5	50% WP	1.1	0.29	<0.01	0.98	0.19	0.01
13.5	30% WP	1.2	0.24	0.03	0.83	0.04	0.02
30	50% WP	2.6	1.4	<0.01	2.5	1.0	0.03
30	30% WP	2.5	0.82	<0.01	2.1	0.37	0.02
45	30% WP	4.0	1.8	<0.01	3.8	2.2	0.06

In the third study, a 50% WP formulation was sprayed on to soils at rates of 5 and 10 kg ai/ha in June shortly before planting beans. The soils were sampled to a depth of 20 cm after application and then at 52 and 92 days. Initial residue levels of 1.6 and 2.7 mg/kg from the low and high rates respectively fell to 0.15 and 0.21 mg/kg at 52 days and 0.10 and 0.21 mg/kg at 92 days (Maini and Boni, 1985b).

To study photodegradation soil thin-layer plates were prepared from Kodaira, Azuchi, Takarazuka and Sapporo the soils. Labelled tolclofos-methyl was applied to give a rate of 7 µg/cm² and the plates were exposed to natural sunlight for 16 days during the month of August in Japan. A parallel series was kept in the dark. There was no provision for maintaining the moisture content of the soils, which dried out during the course of the study. A further series of plates was exposed in quartz flasks to allow the determination of volatile products. Soil samples were withdrawn periodically, extracted with ethyl acetate/N HCl and analysed by TLC. Half-lives ranged from 1.0 to 2.0 days (the latter in the Azuchi soil). The soils in the dark showed half-lives of 10 to >15 days with the exception of the Kodaira soil where the half-life was only 2 days. Volatilization played an important role in the loss. The distribution of residues after 16 days exposure is shown in Table 14.

Degradation on the soil surfaces also occurred in the dark. Extractable and bound residues amounted to 68-75% and 10-14% of the total residues in soils of low organic matter content (Takarazuka and Azuchi), while 15-18% was probably lost by volatilization. The soils of high organic matter content (Sapporo and Kodaira) contained a higher proportion of bound residues (27-34% of the applied ^{14}C), and the extractable residues were around 48-49%. TMO and DM-TMO were formed in small quantities (Mikami *et al*., 1980c; Takahashi *et al.*, 1985a).

A further thin-layer soil study was carried out in the USA according to EPA Pesticide Assessment Guidelines, Subsection N-161-3 Chemistry, 1982. The soil was a neutral sandy loam with 1.3% organic matter. Labelled tolclofos-methyl was applied to the plates at a rate of 17.9 kg ai/ha, equivalent to 0.18 mg/cm², some 26 times that in the previous study in Japan. The plates were exposed to natural sunlight for a period of 30 days with a parallel series kept in the dark. Exposures were in quartz-covered vessels to allow volatiles to be collected and estimated. The temperature of the soil surfaces rose during the course of each day, usually to maxima somewhat above 30°C for the exposed plates and 2-3°C lower for the dark controls. The moisture content of the soils was adjusted to 75% of field capacity and the vessels aerated with humidified air so that the soils presumably remained reasonably moist throughout the study. The exhausted air was passed through ethylene glycol and caustic soda traps. The soils were extracted with acetone/water and analysed by HPLC. The identities of the residues were confirmed by GC-MS.

Table 14. ^{14}C residues volatilized from and remaining in Japanese soils incubated with [^{14}C]tolclofos-methyl after 16 days of exposure to sunlight.

Residue	% of initial ^{14}C			
	Takarazuka	Azuchi	Sapporo	Kodaira
Volatile ^{14}C	58.7	37.3	20.1	34.6
TM	50.1	32.0	15.6	30.3
PH-CH_3	4.4	2.9	1.5	1.9
DM-TM	1.5	0.9	0.9	1.1
Others - vapour	1.0	0.5	0.9	0.7
CO_2	1.7	1.0	1.2	0.6
Extracted ^{14}C	31.3	35.1	42.7	33.0
TM	22.1	31.8	38.4	29.8
TMO	0.1	0.1	0.7	0.4
TM-SCH_3	0.3	0.1	<0.1	<0.1
TM-CH_2-OH	0.3	0.3	0.5	0.6
PH-CH_3	1.4	0.5	0.9	0.5
DM-TM	<0.1	<0.1	<0.1	<0.1
DM-TMO	5.6	0.8	0.6	0.5
Others	1.5	1.5	1.6	1.2
Bound ^{14}C	12.3	14.3	26.7	31.1
Total	102.3	86.6	89.5	98.6

Exposure to sunlight under the conditions of this study did not cause appreciable decomposition. In fact the half-life of the tolclofos-methyl on the irradiated plates was 113 days compared with 72 days in the dark. By the end of the study 83% of the tolclofos-methyl remained intact in the irradiated soil compared with only 75% in the dark control. Less than 10% was recovered as metabolites, there was no evidence of volatilization of the parent in either the light or dark, and in both cases only about 1% of the radioactivity was recovered as CO_2. The main differences between the light and dark plates were that the light contained a higher proportion of unextracted residues (3.8% compared with 1.1% of the applied radioactivity), an increased amount of SM-TM (6.2% compared with 2.5% and a smaller amount of DM-SM-TM (0.2% light, 7.6% dark) (Concha *et al.*, 1992).

A study of adsorption by soils was carried out according to EPA Guideline Subdivision N, section 163-1, on four soils from the USA. All were near neutral in pH. They were a sandy loam, a loamy sand, a silty clay loam and a clay, in the order California, Kentucky 3, 4, and 5. Their organic carbon contents were 0.46, 0.41, 1.37 and 0.69% respectively.

The soils were shaken for 2 hours with 0.01 M calcium chloride solution containing 0.02, 0.04, 0.20 and 0.39 mg/kg of labelled tolclofos-methyl. Adsorption was determined by analysis of the supernatant liquid. No correction for adsorption onto the glass vessels was needed. Desorption was studied by equilibrating the soils first with the TM solutions for 2 hours and then partially replacing the supernatant liquid with tolclofos-methyl-free solution and determining the amount desorbed into the diluted supernatant. The stability of tolclofos-methyl within the period of the study was determined by analysis of extracts from both the soils and the supernatant after the desorption procedure but there was practically no evidence of degradation.

The compound showed low to slight mobility in these soils. The adsorption followed the

Freundlich adsorption equation. The results are shown in Table 15 (Mikami *et al*., 1991).

Table 15. Adsorption and desorption constants of four soils in the USA.

Soil	Adsorption		Desorption	
	K_d	K_{oc}	K_d	K_{oc}
California	7.59	1650	11.8	2570
Kentucky 3	25.2	6140	27.0	6580
Kentucky 4	44.0	3210	59.0	4300
Kentucky 5	24.0	3480	29.3	4240

A further study of adsorption was carried out on 13 soils from Japan ranging in pH from 4.6 to 7.0, in organic matter from 0.9 to 15.3% and in texture from sand to light clay. The procedures employed were basically the same as those in the preceding study. Similar concentrations of tolclofos-methyl and similar equilibration times were used. The adsorption process in each soil could be described by the Freundlich equation and the constants shown in Table 16 were obtained.

Table 16. Adsorption of tolclofos-methyl by Japanese soils.

Soil	% Organic carbon[1]	Adsorption	
		K_d	K_{oc}
Sapporo	6.4	60.3	940
Takarazuka	1.6	30.6	1910
Kodaira	8.9	37.2	420
Azuchi	1.5	26.0	1730
Gunma	2.3	52.4	2280
Kagoshima	1.3	69.6	5350
Nagano	1.2	39.3	3280
Gifu	0.5	6.4	1280
Kasai	1.6	51.8	3240
Katano	1.1	43.6	3960
Hyogo	1.7	47.6	2800
Tochigi	6.3	62.5	990
Iwate	3.6	43.2	1200

[1] 1% organic matter ÷ 1.724

A laboratory column leaching study was carried out with Azuchi, Kodaira, Sapporo (used also in the experiments referred to previously as B, H and E respectively) and Muko soils from Japan. The Muko consisted of 99% sand with less than 0.1% organic matter and it had very low retention. The air-dried soils (300 g) were packed into glass columns to a depth of 25 cm. The corresponding soils (30 g) were treated with 10 mg/kg labelled tolclofos-methyl and added to the tops of the columns either immediately before leaching or after incubation for 4 weeks at 25°C under aerobic conditions. Provision was made for trapping volatile degradation products during both the incubation and the subsequent leaching. Leaching was carried out at 25°C in the dark with a total of 1050 ml water at a rate of 1.5 ml/hour so that the duration of the study was about a month. At the end of the period, the

columns were extruded and segmented into 5 cm lengths. The total radioactivity was determined by combustion analysis. Portions were also extracted with ethyl acetate/HCl for the determination of extractable radioactivity and characterization of degradation products. The eluate was also analysed for trapped CO_2.

It was found that in the three "normal" soils most of the applied radioactivity remained in the top 5 cm of the columns with comparatively little difference between the incubated and unincubated soils. Between 1.7 and 6.9 % of the applied radioactivity reached the eluate and most was associated with degradation products, including CO_2. Most of the radioactivity in the initially treated soils and the top 5 cm column sections was in the form of bound and extractable parent material. In the Muko soil there was very little retention or degradation, as would be expected from its comparatively inert nature (Mikami *et al.*, 1981b).

A study was also carried out with three German soils according to the BBA Guidelines in Technical Brochure 37 using 98% technical grade tolclofos-methyl, a 10% dust and a 50% wettable powder formulation. Soil columns were prepared and the products were applied to the tops of the columns at rates of 3.39, 0.98 and 3.02 mg ai/column respectively, equivalent to 17.3, 5.0 and 15.4 kg ai/ha. Leaching proceeded for 2 days with the equivalent of 20 cm water. The leachates were extracted with dichloromethane and analysed for tolclofos-methyl, which was not detected in any of the eluates (<0.01 mg/kg, which was less than 1% of the applied tolclofos-methyl) (Anon, 1980a,b,c).

An aged column leaching study was carried out according to EPA Pesticide Assessment Guidelines Subdivision N Section 163-1. A Californian sandy loam soil (described under experiment O) was treated with labelled tolclofos-methyl at the rate of 4 mg/kg and incubated for 30 days at 75% water-holding capacity. Twenty g portions of the incubated soil were added to the tops of two 30 cm columns prepared from the same but untreated soil. The flasks receiving the eluate were equipped with ethylene glycol and sodium hydroxide traps for trapping volatiles. The columns were leached at 25°C with 260 ml 0.01 M calcium chloride solution, equivalent to 50 cm of water, over a period of about 13 hours. At the end of the study the columns were separated into 5 cm segments which were analysed together with the trap solutions and the eluates.

At the beginning of the leaching phase of the study about 75% of the radioactivity in the soil could be extracted and about 8.7% was bound. Volatile parent and small amounts of volatile degradation products accounted for 4.25% and CO_2 for 6.6%, making a total of 94.6% of the applied radioactivity. At the end of the leaching period, 60.4% of the applied ^{14}C was retained in the soil columns and 20.3% appeared in the leachate. No CO_2 or other volatiles were recovered during the leaching phase. Of the 20.3% of radioactivity in the leachate 19.9% was in the form of DM-TM. No parent compound was detected. The soil radioactivity was practically confined to the treated soil and the top 15 cm of the columns. Table 17 shows the average amounts of ^{14}C found in the two columns, expressed as percentages of that originally added. The overall average recovery was 91.6% (Mikami *et al.*, 1992).

Table 17. Distribution of residues in leached columns of a Californian soil.

Soil	% of radioactivity found as				
	TM	DM-TM	PH-CH_3	Humus	Bound
Treated soil					
Before leaching	48.0	17.1	2.73		8.7
After leaching	25.0	0.5	1.6	2.7	7.9
0-5 cm depth	14.1	nd	nd	na	1.5
5-10 cm depth	3.7	nd	nd	na	0.3

10-15 cm depth	nd	nd	nd	na	0.2

nd not detected
na not analysed

The volatilization of tolclofos-methyl was measured as part of the photodegradation study of Mikami *et al*., (1980) described above. Unchanged tolclofos-methyl liberated in the vapour phase after 16 days ranged from 15.6 to 50.1% of applied amount (Table 14).

The sandy soil from Muko (previously described) was treated with labelled tolclofos-methyl in the form of a 5% granule at a rate equivalent to 5.6 kg ai/ha. However, in contrast to the photodegradation study, the product was mixed into a 5 mm depth of the soil and not applied solely to the surface. The soil moisture level was adjusted to 75% of field moisture capacity. Moistened air was passed over the treated soil and volatile material was trapped in polyurethane plugs which were periodically replaced and extracted with methanol. The trapping efficiency was around 96%.

The volatility was slight over the 30-day period of the study: 99.1% of the applied tolclofos-methyl remained in the soil (Katagi *et al*., 1988).

Environmental fate in water/sediment systems

A study of hydrolysis was carried out in buffer solutions at pH 5, 7 and 9 at temperatures of 22, 40 and 60°C using tolclofos-methyl labelled in the phenyl ring. At intervals, solutions were acidified to pH 1, extracted with ethyl acetate, and the extracts fractionated by TLC. Half-lives of tolclofos-methyl are shown in Table 18.

The two major hydrolysis products were identified as DM-TM (the demethyl derivative) and PH-CH_3 (2,6-dichloro-4-methylphenol). The rate of formation of DM-TM was 2-3.4 times that of PH-CH_3, indicating that the P-O-methyl linkage is more susceptible to neutral hydrolysis than the P-O-aryl (Takahashi *et al*., 1983, 1985b).

A further hydrolysis study was carried out to meet EPA Guidelines (EPA Pesticide Assessment Guidelines, Subdivision N, Environmental fate, Chemistry Series 161-1, 1982). Labelled tolclofos-methyl was added to buffer solutions at pH 5, 7 and 9 prepared in accordance with the Federal Register 45 (no. 277) 77351, 1980. The solutions were autoclaved before the start of the study to ensure sterility. The test material was added to the buffers to give a concentration of 0.11 mg/kg and maintained at 25°C in the dark for 30 days. Samples of the solutions were acidified to pH 2 and extracted with ethyl acetate. The extracted material was fractionated by TLC. Half-lives are shown in Table 18 and the distribution of radioactivity at 30 days in Table 19.

Table 18. Half-lives (days) of tolclofos-methyl in buffer solutions.

pH	Temperature			
	22°C[1]	25°C[2]	40°C[1]	60°C[1]
	139	51	12.7	1.43
7	417	61	21.4	1.87
9	238	62	19.3	1.32

[1] Takahashi *et al*., 1983, 1985b
[2] Ekdawi and Yu, 1990

Table 19. Products of hydrolysis of tolclofos-methyl found after 30 days in three buffer solutions.

Residue	% of initial ^{14}C		
	pH 5	pH 7	pH 9
TM	63.6	63.1	72.9
PH-CH_3	0.5	0.4	0.6
TMO	8.2	12.0	7.7
DM-TM	23.1	16.1	11.2
Unidentified	4.6	8.4	5.2
Aqueous unextracted	0.8	1.0	0.7
Total recovery	100.8	101.0	98.3

The main difference between the results of this and the earlier study was the greater prominence of TMO among the degradation products (Ekdawi and Yu, 1990).

The sediments of a river or pond were suspended in natural water, filtered through a coarse filter and the filtrate treated with labelled tolclofos-methyl to give a concentration of 0.3 mg/kg. The water was then incubated at 20°C for 4 weeks, with a parallel control with sterilized water. Air, free of CO_2, was passed over the surface of the water at weekly intervals and the volatile products trapped first in a polyurethane plug and then in caustic soda. Water samples were taken weekly and extracted with ethyl acetate/HCl. The BOD was measured periodically to determine whether or not the test compound affected the biological activity of the water.

It was found that tolclofos-methyl did not inhibit the respiration or number of the biological flora in the water, which consisted primarily of bacteria with relatively few actinomycetes and fungi. The sterilized water was practically free of organisms (<4 per ml).

In the sterilized water the total recovery of radioactivity (volatile plus extracted) remained essentially complete (101.6-103.1% after 4 weeks), whereas in the unsterilized water the recovery gradually fell from 91 to 80%, presumably owing to incorporation of radioactivity into the organisms. After 4 weeks the parent was still the main source of radioactivity but DM-TM was also important, followed in order by TMO, PH-CH_3 and DM-TMO. The general pattern of degradation in natural water was reflected to some extent in the sterilized waters but in these degradation was slower and very little of the volatile radioactivity was attributable to CO_2. The results are shown in Table 20 (Mikami *et al*., 1981a).

Table 20. Distribution of radioactivity after incubation of tolclofos-methyl with two natural waters.

Residue	% of initial radioactivity after 4 weeks			
	River water		Pond water	
	Natural	Sterilized	Natural	Sterilized
Volatiles except CO_2	3.1	5.4	1.4	5.1
CO_2	4.0	0.2	2.7	0.3
TM	42.3	75.5	52.0	80.9

Residue	% of initial radioactivity after 4 weeks			
	River water		Pond water	
	Natural	Sterilized	Natural	Sterilized
TMO	3.7	1.1	3.1	0.1
DM-TM	16.2	11.7	25.4	11.6
DM-TMO	1.5	1.2	1.0	1.3
PH-CH_3	2.9	1.2	1.6	1.8
Others	6.1	5.3	4.1	2.1
Total recovery	79.8	101.6	91.3	103.2

In view of the occurrence of DM-TM as an important product, a further study was carried out to investigate its further degradation (Nambu *et al.*, 1984). The conditions were comparable to those of the previous one. The DM-TM, labelled with ^{14}C in the phenyl ring, was added to the waters at 0.1 mg/kg and incubated for an 8-week period in the dark at 20°C. The distribution of radioactivity after 8 weeks is shown in Table 21.

Table 21. Distribution of radioactivity after incubation of DM-TM with two natural waters.

Residue	% of initial radioactivity after 8 weeks			
	River water		Pond water	
	Natural	Sterilized	Natural	Sterilized
CO_2	2.8	1.9	2.6	0.5
DM-TM	77.1	82.7	75.8	84.2
DM-TMO	3.4	2.1	7.5	2.2
PH-CH_3	2.2	2.1	1.2	1.6
Others	5.7	4.3	4.5	4.4
Dissolved CO_2	0.5	0.4	0.6	0.4
Total recovery	91.7	93.5	92.2	103.1

Labelled tolclofos-methyl was added to distilled water, 2% aqueous acetone (as a triplet sensitizer) and water from the river and pond used in the above study, but filtered through a micropore filter to give essentially sterile solutions. The concentration of test material was 0.2 mg/kg and the solutions were exposed to natural sunlight in quartz flasks for 8 hours/day for 8 weeks. Air was passed over the acetone solution and volatiles were collected. The estimated half-lives are given in Table 22.

Table 22. Half-lives of tolclofos-methyl in aqueous media in sunlight and in the dark.

Medium	Half-life, days	
	Irradiated	Dark
Distilled water (pH 6.0)	44	90
2% aqueous acetone (pH 6.0)	2	105
River water (pH 7.8)	25	60
Pond water (pH 6.8)	28	56

Identification of the degradation products showed that DM-TM and DM-TMO were predominant in distilled water but in the two natural waters (which presumably contained photosensitizers) by far the most important degradation product was DM-TMO, which accounted for around 50% of the radioactivity at 56 days. In the acetone solution, where there was provision for collecting volatiles, one third of the radioactivity was volatile after 32 days of irradiation and was mainly labelled CO_2. In the other three studies, in which the volatiles were not trapped, the total recoveries of radioactivity fell considerably by the end of the study, presumably owing to the escape of radioactivity as CO_2. Recoveries from the dark controls were nearly all close to 100% although considerable amounts of DM-TM and DM-TMO were produced, presumably by simple hydrolysis (Mikami *et al*., 1980; Takahashi *et al*., 1985a).

An additional study of photolysis was carried to comply with EPA Guidelines (EPA Pesticide Assessment Guidelines, Subdivision N, Environmental fate, Chemistry Series 161-2). Irradiation was provided by a xenon arc lamp with a spectrum similar to sunlight. The labelled tolclofos-methyl was dissolved (0.2 mg/kg) in a buffer solution at pH 7 and exposed to light continuously for 30 days at 25°C. A parallel study was carried out in the dark. Air was passed over the solutions to collect volatiles and the solutions were analysed at intervals. The samples were extracted with ethyl acetate/HCl and individual components separated by TLC. Volatiles were separated into those trapped by polyurethane and by caustic soda. TM and DM-TM on the plates were estimated by HPLC.

The half-lives in irradiated and "dark" solutions were estimated to be 38 and 77 days respectively. The radioactivity in the volatile fractions amounted to less than 0.1% of that added. Small amounts were not extracted: up to 7% in the irradiated solution by the end of the study. In both the irradiated and dark solutions the main compounds were the parent and DM-TM, amounting to 60% and 80%, and 12.6% and 5% respectively. Small amounts of $PH\text{-}CH_3$ and DM-TMO were also reported, together with a series of "others" which reached 11% in the irradiated solution and 4% in the dark (Katagi and Takahashi, 1988).

The proposed degradation pathways of Tolclofos-methyl in water are shown in Figure 2 above.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The principles of the analytical methods used in the supervised trials are shown below. The typical recoveries (R, %) and limits of determination (LOD, mg/kg) are given in parentheses.

Potatoes. Extraction with methanol/acetonitrile (4:1), clean-up on a silica gel column with

hexane/acetone as eluant and determination by GLC with a thermionic detector (R 93, LOD 0.001) (Ohnishi *et al.*, 1980).

Extraction with aqueous methanol/acetonitrile (4:1), partitioning into dichloromethane and clean-up on a Florisil column with 1% ethyl acetate in toluene as eluant. Determination by GLC with an electron capture detector (ECD), (R 86, LOD 0.01) (Macdonald and Richardson, 1987).

Extraction with 1:4:0.3 methanol/acetonitrile/water, partitioning into dichloromethane and clean-up on a silica column with toluene as eluant. Residue redissolved in acetone and analysed by GLC with flame-photometric detection (R 75, LOD 0.001) (Smith & Brunt, 1989).

Milk, liver and fat of cows. Extraction of fat and milk samples with ethyl acetate, and liver with acetone. Clean-up by hexane/acetonitrile partition followed by Florisil column with hexane/acetone as eluant. Determination by GLC with FPD, (R 94 for liver, 98 for fat and 95 for milk, LOD 0.01) (Ohnishi *et al.*, 1985a).

Eggs and skin of hens. Extraction of eggs with ethyl acetate and skin with acetone. Clean-up and determination as for cow samples (R 92 for skin, 98 for yolk, 93 for white of egg, LOD 0.01), (Ohnishi *et al.*, 1985b).

Soil (TM, TMO and PH-CH_3). Extraction with methyl alcohol/0.1N hydrochloric acid (2:1), partition into ethyl acetate. Evaporation to dryness, dissolution of residue in acetone, determination by GLC with FPD. To determine PH-CH_3 the filtrate is re-extracted with hexane and cleaned up on silica gel with hexane/acetone (3:1) as eluant. Detection with ECD. (R 99 for TM, 83 for TMO and 88 for PH-CH_3, LOD 0.002 for TM and TMO and 0.01 for PH-CH_3) (Ohnishi *et al.*, 1985c, 1988).

Water. Extraction with dichloromethane, evaporation to dryness, dissolution in acetone. (If interference is excessive, the residue may be dissolved in hexane/acetone and cleaned up on a Florisil column before evaporation and transfer to acetone) determination by GLC with FPD, (R 99, LOD 0.05 ì g/l) (Hirota *et al.*, 1992).

Peanuts (TM, TMO and PH-CH_3). Vines are homogenized with water and homogenate extracted with methanol. Pulverized kernels and shells are extracted with methanol. After addition of 10% NaCl solution to methanolic extract, residues are partitioned into dichloromethane (to determine PH-CH_3, aliquot of solution is acidified and partitioned into n-hexane). Clean-up on silica gel column with n-hexane/ethyl acetate (3:2) eluant. The concentrated eluate is analysed by GLC with thermionic or ECD (average R for TM, TMO and PH-CH_3 85 for vine, 89 for nut-meat, and 86 for shell, LOD 0.01 for TM and TMO, 0.05 for PH-CH_3) (Ohnishi *et al.*, 1982).

Wheat grain and soya bean seeds (TM, TMO and TM-CH_2-OH). Extraction with methanol with overnight soaking. Addition of 10% NaCl solution, partitioning into dichloromethane, clean-up by column chromatography on activated silica gel, eluting with 9:1 hexane/acetone followed by 3:1 hexane/acetone. The eluate contains both metabolites. Concentration under reduced pressure, dissolution in acetone, analysis by GLC with thermionic detector (average R for TM 83, for TMO 101 and for TM-CH_2OH 91, LOD for TM 0.005, for TMO and TM-CH_2OH 0.010) (Ohnishi, 1982a,b).

Stability of residues in stored analytical samples

The stability of residues in potatoes during deep-frozen storage was reported for a three-month period. The initial residues of 0.5 mg/kg did not show any decrease (Burden, 1994d).

USE PATTERN

Potatoes. Tolclofos-methyl is very widely used for the control of seed-borne diseases in potatoes. The product may be applied to the tubers at planting as a solid formulation or as a dip treatment. In some cases it is applied to the soil before planting, either as an overall incorporated treatment or in the furrow. In the method of use in most countries, pre-harvest intervals are fixed by the growth period of the crop. Approved uses expressed in terms of g ai/t seed are shown in Table 23. With applications directly to the soil, rates may be expressed as g ai/100 m row in the case of furrow applications or as kg ai/ha for overall soil treatment. Corresponding recommendations are shown in Table 24.

Table 23. Recommended uses of tolclofos-methyl for treatment of seed potatoes.

Country	Formulation	Rate, g ai/t seed
Argentina	10% or 5% dust	160
Australia	10% dust	200
Austria	10% dust or 25% SC	200-208
Costa Rica	50% WP	200
Czech Rep/Slovakia	50% SC	150
Denmark	50% SC or 10% dust	100-150
Dominican Rep.	50% WP	100-300
France	25% SC	50-62.5
France	9% dust	180
Germany	10% dust	200
Germany	25% SC	150
Honduras	50% WP	100
New Zealand	10% dust	200-250
Norway	10% dust or 50% SC	100-150
Paraguay	50% WP	100-300
Poland	50% WP	250
Poland	10% dust	200
Romania	10% dust	200
El Salvador	50% WP	75-125
Sweden	10% dust	125-150
Sweden	50% SC	100-150
UK	10% dust	125-250
UK	50% SC	125

Table 24. Recommended uses of tolclofos-methyl for soil treatment before planting potatoes.

Country	Formulation	Application rate, ai
Algeria	50% WP	2-3 kg/ha (overall)
Costa Rica	50% WP	3 kg/ha (overall)
Dominican Republic	50% WP	10 kg/ha (overall)
Dominican Republic	50% WP	25-50 g/100 m row
Mexico	75% WP	3.75-5.25 kg/ha (overall)
Netherlands	50% WP or 50% SC	10-15 kg/ha (overall)
Oman	30% WP (with thiram)	9 kg/ha (overall)
Oman	30% WP (with thiram)	42-60 g/100 m row
Paraguay	50% WP	10 kg/ha (overall)
Paraguay	50% WP	40-60 g/100 m row
El Salvador	50% WP	0.5-1.0 kg/ha (overall)
Spain	50% WP	15-25 kg/ha (overall)
Spain	20% with Thiram	10-20 kg/ha (overall)
UAE	30% WP (with thiram)	9 kg/ha (overall)
UAE	30% WP (with thiram)	42-60 g/100 m row

It is theoretically possible to convert rates used in furrow applications to overall soil application rates on the assumption that the rows are 50 cm apart. Since treatment in the row gives a higher concentration around the plant than the equivalent rate distributed throughout the soil, the soil rates are only meaningful if the mode of application is described.

In addition to the protection of potatoes just before planting, tolclofos-methyl may also be used in some countries for the protection of seed potatoes in store. The following countries have approved uses.

Costa Rica. Dip in a suspension of 50% WP to give a deposit of 200 g ai/t seed.
Japan. Dip in a suspension of 50% WP at 5-10 g ai/l.

Lettuce. The product is applied as a spray either to the surface of the soil shortly before planting or to the established plants so that the growing plants are exposed. In some countries multiple post-planting applications are allowed and in such cases a PHI is sometimes in force. Current recommendations are shown in Table 25.

Table 25. Recommended uses of tolclofos-methyl on lettuce.

Country	Formulation	Type of treatment	Rate, kg ai/ha, (typical no. of treatments)	PHI, days
Austria	50% WP	Spray at seeding or planting, then every 7-14 days	3 (3-4)	
Belgium	50% WP	One spray after transplanting	2 (1)	
Italy	50% WP	Pre-plant soil treatment	10-40 (1)	
Italy	50% WP	One spray after transplanting and then every 15 days	0.5-1.0 (2-3)	30
Japan	50% WP	One spray at seeding followed by 1-2 foliar sprays at 0.05%	15 (at seeding, 1) Foliar spray (1-2)	7

Country	Formulation	Type of treatment	Rate, kg ai/ha, (typical no. of treatments)	PHI, days
Netherlands	50% SC or WP	One spray up to a week after trans-planting	2.0 (1-2)	28 (summer) 56 (winter)
Spain	50% WP	One spray at transplanting	15-25 (1)	90
UK	50% WP	One spray at transplanting	10 (1)	

Radishes. Treatments are confined to soil applications at or just before planting and are shown in Table 26. The growing plants are not normally exposed.

Other crops. Australia, The Netherlands and Spain reported registered uses on some additional crops which are summarized in Table 26.

Table 26. Registered or approved uses on other crops. All single applications.

Crop	Country	Application			PHI, days
		Formulation	Method	Rate (ai)	
Broccoli, cauliflower, Brussels sprouts, cabbage (head), chinese cabbage, savoy cabbage and kohlrabi	Netherlands	50 WP	spray at sowing	5 kg /ha	
Cotton	Australia	100 D	seed dressing	4 g/kg	
Pepper	Spain	50 WP	spray at sowing	15-25 kg/ha	90
Radish	Belgium	50 WP	spray at sowing	2 kg/ha	
	Netherlands	50 WP	spray at sowing	2.5 kg/ha	
Tomato	Spain	50 WP	spray at sowing	15-25 kg/ha	90
Sugar beet	Spain	50 WP	spray at sowing	15-25 kg/ha	90

RESIDUES RESULTING FROM SUPERVISED TRIALS

Potatoes. Numerous field trials have been reported from Australia, Germany, Greece, Denmark, Poland and the UK. Tolclofos-methyl was applied as dust, SC and WP formulations for the seed treatment of potatoes at recommended and higher rates. The results are shown in Table 29. The frequency distribution of residues in daughter potatoes from trials at maximum recommended rates is shown in Table 27.

Data from treatments applied to the soils shortly before planting are shown in Table 30.

Table 27. Distribution of tolclofos-methyl residues in daughter potatoes from seed treatments at maximum recommended rates.

Residue range, mg/kg	No. of values	Cumulative %
≤0.01	43	59
≤0.05	21	88
≤0.1	6	96
≤0.2	2	99
≤0.25	1	100

Lettuce. Supervised trials were carried out in Italy, The Netherlands and the UK applying EC, WP and dust formulations at recommended and higher rates. The treatments were carried out before and after planting. Samples were also collected from the second crop grown after soil treatment. The results are shown in Table 31. The distribution of residues from treatments according to GAP is shown in Table 28. The high residues were from pre-emergence summer applications in the UK with dust, granule and SC formulations.

Table 28. Distribution of tolclofos-methyl residues in lettuce.

Residue range, mg/kg	No. of values	Cumulative %
≤0.01	20	38
≤0.05	18	73
≤0.1	5	83
≤0.2	4	90
≤0.5	2	94
≤1	2	98
≤2	1	100

Residues arising from foliar applications decline fairly rapidly. Thus in Italy (Maini & Boni, 1985), where three sprays had been applied, the residue of 54 mg/kg nine days after the last application fell to 0.07 mg/kg after a further 21 days. Where there had been only one application, a residue of 0.8 mg/kg 34 days after the application fell to 0.01 mg/kg after a further 21 days.

Radishes. Supervised trials were conducted in France and The Netherlands. The results are given in Table 32.

Table 29. Residues of tolclofos-methyl in potato tubers grown from treated seed. Underlined residues are from treatments according to GAP.

Country	Formulation	Rate, g ai/t	PHI, days	Residues, mg/kg	Reference
Australia	10% dust	300	120	0.03	Perrett, 1986
Australia	10% dust	400	120	0.02	Perrett, 1986
Australia	10% dust	100	180	0.003	Perrett, 1985
Australia	10% dust	200	180	0.008	Perrett, 1985
Australia	10% dust	400	180	0.003	Perrett, 1985
Germany	10% dust	200	135	<0.01	Almond, 1980
Germany	10% dust	200	145	<0.01	Almond, 1980
Germany	10% dust	200	147	<0.01	Almond, 1980
Germany	10% dust	200	138	<0.01	Almond, 1981
Germany	10% dust	200	106	<0.01	Almond, 1981
Germany	10% dust	200	142	<0.01	Almond, 1981
Germany	10% dust	200	147	<0.01	Almond, 1981
Germany	10% dust	200	168	<0.01	Almond, 1981
Germany	25% SC	150	125	<0.002	Anon 1986b
Germany	25% SC	150	139	<0.002	Anon 1986b
Germany	10% dust	200	144	0.06	Anon 1986c
Germany	10% dust	200	162	0.008	Anon 1986c
Germany	25% SC	150	147	<0.002	Anon 1986d
Germany	25% SC	150	165	<0.002	Anon 1986d
Germany	10% dust	200	147	0.009	Anon 1986e
Germany	10% dust	200	162	<0.002	Anon 1986e
Germany	25% SC	150	123	<0.002	Anon 1986f
Germany	25% SC	150	136	<0.002	Anon 1986f
Germany	10% dust	200	147	0.04	Anon 1986g
Germany	10% dust	200	162	0.002	Anon 1986g
Germany	25% SC	150	136	0.007	Anon 1986h
Germany	25% SC	150	147	<0.002	Anon 1986h
Germany	10% dust	200	136	0.013	Anon 1986j
Germany	10% dust	200	147	0.002	Anon 1986j
Germany	25% SC	150	150	0.002	Anon 1986k
Germany	25% SC	150	165	<0.002	Anon 1986k
Greece	10% dust	200	76	<0.01	Macdonald & Proctor, 1985
Greece	10% dust	200	92	<0.01	Macdonald & Proctor, 1985
Greece	10% dust	200	111	<0.01	Macdonald & Proctor, 1985
Denmark	10% dust	100	74	0.01	Macdonald *et al*., 1984
Denmark	10% dust	100	101	<0.01	Macdonald *et al*., 1984
Denmark	10% dust	100	129	<0.01	Macdonald *et al*., 1984
Poland	10% dust	200	130	0.03	Ambrus, 1993
Poland	10% dust	200	130	0.02	Ambrus, 1993
Poland	50% WP	250	130	0.01	Ambrus, 1993
Poland	50% WP	250	130	0.01	Ambrus, 1993

Country	Formulation	Rate, g ai/t	PHI, days	Residues, mg/kg	Reference
UK	50% WP	125	153	<0.01	Cron, 1982
UK	50% WP	250	153	0.01	Cron, 1982
UK	50% WP	500	153	0.01	Cron, 1982
UK	50% WP	125	155	<0.01	Cron, 1982
UK	50% WP	250	155	<0.01	Cron, 1982
UK	50% WP	500	155	0.04	Cron, 1982
UK	50% WP	125	162	0.07	Cron, 1982
UK	50% WP	250	162	0.08	Cron, 1982
UK	50% WP	500	162	0.62	Cron, 1982
UK	50% WP	125	167	0.01	Cron, 1982
UK	50% WP	250	167	0.01	Cron, 1982
UK	50% WP	500	167	0.02	Cron, 1982
UK	50% WP	125	196	0.03	Cron, 1982
UK	50% WP	250	196	0.01	Cron, 1982
UK	50% WP	500	196	0.05	Cron, 1982
UK	50% WP	250	110	0.06	Cron, 1982
UK	50% WP	500	110	0.20	Cron, 1982
UK	25% SC	250	110	0.21	Cron, 1982
UK	50% WP	60	132	0.02	Cron, 1982
UK	50% WP	500	132	0.04	Cron, 1982
UK	25% SC	250	132	0.04	Cron, 1982
UK	50% WP	60	183	<0.01	Cron, 1982
UK	50% WP	500	183	0.05	Cron, 1982
UK	25% SC	250	183	0.01	Cron, 1982
UK	50% WP	250	189	0.02	Cron, 1982
UK	50% WP	500	189	0.12	Cron, 1982
UK	25% SC	250	189	0.04	Cron, 1982
UK	10% dust	250	-	0.02	Cron, 1982
UK	10% dust	250	145	0.03	Cron, 1982
UK	5% dust	125	134	0.01	Longland & Churchill, 1983
UK	10% dust	250	134	0.02	Longland & Churchill, 1983
UK	5% dust	125	99	0.02	Longland & Churchill, 1983
UK	10% dust	250	99	0.08	Longland & Churchill, 1983
UK	5% dust	125	119	0.02	Longland & Churchill, 1983
UK	10% dust	250	196	0.02	Longland & Churchill, 1983
UK	5% dust	125	98	0.02	Longland & Churchill, 1983
UK	10% dust	250	98	0.03	Longland & Churchill, 1983
UK	5% dust	125	89	0.01	Longland & Churchill, 1983
UK	10% dust	250	89	0.18	Longland & Churchill, 1983
UK	20% EC	250	153	<0.01	Cron, 1982
UK	20% EC	250	155	0.12	Cron, 1982
UK	20% EC	250	162	0.04	Cron, 1982
UK	20% EC	250	167	0.01	Cron, 1982
UK	20% EC	250	196	<0.01	Cron, 1982
UK	20% EC	250	110	0.07	Cron, 1982

Country	Formulation	Rate, g ai/t	PHI, days	Residues, mg/kg	Reference
UK	20% EC	400	110	0.05	Cron, 1982
UK	20% EC	60	132	<0.01	Cron, 1982
UK	20% EC	250	132	0.05	Cron, 1982
UK	20% EC	400	132	0.05	Cron, 1982
UK	20% EC	60	183	<0.01	Cron, 1982
UK	20% EC	250	183	0.01	Cron, 1982
UK	20% EC	400	183	0.02	Cron, 1982
UK	20% EC	250	189	0.03	Cron, 1982
UK	20% EC	250	189	0.03	Cron, 1982
UK	20% EC	250	189	0.03	Cron, 1982
UK	20% EC	400	189	0.04	Cron, 1982
UK	10% dust	125	110	0.08	Burden, 1994a
			124	<0.05	
UK	10% dust	250	149	<0.05	Burden, 1994a
UK	10% dust	250	83	<0.05	Burden, 1994a
			111	<0.05	
			156	<0.05	
UK	10% dust	125	96	<0.05	Burden, 1994a
			115	<0.05	
UK	50 SC	125	0[1]	100-140	Burden, 1994b
			141[2]	0.2	
			155	0.06	
UK	50SC	62.5	0[1]	13-19	Burden, 1994b
			120[2]	<0.05	
			139	<0.05	
UK	50 SC	125	0[1]	46	Burden, 1994c
			84[2]	0.06, 0.07 0.16, 0.13	
UK	50 SC	125	0[1]	41	Burden, 1994c
			84[2]	0.07	

[1] Seed potatoes treated directly with tolclofos-methyl
[2] Daughter potatoes. Samples taken at 84-98 days were new potatoes, while mature tubers were taken beyond 110 days.

Table 30. Residues in potato tubers grown in treated soil. Underlined residues are from treatments according to GAP.

Country	Formulation	Rate, kg ai/ha	PHI, days	Residues, mg/kg	Reference
Australia	20% dust	1	180	0.003	Perrett, 1985
Australia	20% dust	5	180	0.03	Perrett, 1985
Netherlands		20	106	0.02	Jonsgstra *et al*., 1980
Netherlands		20	113	0.01	Jonsgstra *et al*., 1980
Netherlands		20	84	0.01	Jonsgstra *et al*., 1980
Netherlands	50% WP	15	120	0.07	Banks *et al*., 1985b
Netherlands	50% WP	15	120	0.01	Banks *et al*., 1985b

Country	Formulation	Rate, kg ai/ha	PHI, days	Residues, mg/kg	Reference
Netherlands	50% WP	15	harvest	0.03	Smith & Brunt, 1989
Netherlands	50% WP	30	harvest	0.13	Smith & Brunt, 1989
Netherlands	50% WP	15	harvest	0.01	Smith & Brunt, 1989
Netherlands	50% WP	30	harvest	0.03	Smith & Brunt, 1989
Netherlands	50% WP	3.75	harvest	0.01	Smith & Brunt, 1989
Netherlands	50% WP	7.5	harvest	0.02	Smith & Brunt, 1989
Netherlands	50% WP	15	harvest	0.07	Smith & Brunt, 1989
Netherlands	50% WP	7.5	harvest	0.02	Smith & Brunt, 1989
Netherlands	50% WP	15	harvest	0.03	Smith & Brunt, 1989
Netherlands	50% WP	30	harvest	0.09	Smith & Brunt, 1989

FATE OF RESIDUES IN STORAGE AND PROCESSING

The distribution of residues in potato tubers was studied in The Netherlands where potatoes had been planted in soils treated at a rate of 10 kg ai/ha, incorporated to a depth of 15 cm. Residues in whole washed potatoes ranged from 0.004 to 0.038 mg/kg but none of the peeled potatoes contained residues above the limit of determination of 0.002 mg/kg. (Jongstra *et al.*, 1980).

Table 31. Residues of tolclofos-methyl in lettuce from soil and foliar treatments. Underlined residues are from treatments according to GAP.

Country	Formulation	Rate, kg ai/ha	Application method[1]	PHI, days	Residues, mg/kg	Reference
Italy (1)	50%WP	13.5	PP	99	<0.001	Collina *et al.*, 1993a
Italy (1)	30%WP	13.5	PP	99	<0.001	Collina *et al.*, 1993a
Italy (1)	50%WP	30	PP	99	<0.001	Collina *et al.*, 1993a
Italy (1)	30%WP	30	PP	99	<0.001	Collina *et al.*, 1993a
Italy (1)	30%WP	45	PP	99	<0.001	Collina *et al.*, 1993a
Italy (2)	50%WP	13.5	PP	39	<0.001	Collina *et al.*, 1993a
Italy (2)	30%WP	13.5	PP	39	0.002	Collina *et al.*, 1993a
Italy (2)	50%WP	30	PP	39	0.003	Collina *et al.*, 1993a
Italy (2)	30%WP	30	PP	39	0.008	Collina *et al.*, 1993a
Italy (2)	30%WP	45	PP	39	<0.001	Collina *et al.*, 1993a
Italy (3)	50%WP	13.5	PP	84	0.004	Collina *et al.*, 1993a
Italy (3)	30%WP	13.5	PP	84	0.007	Collina *et al.*, 1993a
Italy (3)	50%WP	30	PP	84	0.009	Collina *et al.*, 1993a
Italy (3)	30%WP	30	PP	84	0.005	Collina *et al.*, 1993a
Italy (3)	30%WP	45	PP	84	0.007	Collina *et al.*, 1993a
Italy	30%WP	5.4	PP	45	0.009	Collina *et al.*, 1993b
Italy	30%WP	11	PP	45	0.02	Collina *et al.*, 1993b
Italy	30%WP	22	PP	45	0.02	Collina *et al.*, 1993b
Italy	50% WP	10	PS	34	0.63	Maini & Boni, 1985a
Italy	50% WP	10	PS	55	0.01	Maini & Boni, 1985a
Italy	50%WP	5	3 x PS	9	54.2	Maini & Boni, 1985a
Italy	50%WP	5	3 x PS	30	0.07	Maini & Boni, 1985a
Netherlands	50% WP	1.0	PS + 10	51	0.11	Churchill & Longland, 1984a

Country	Formulation	Rate, kg ai/ha	Application method[1]	PHI, days	Residues, mg/kg	Reference
Netherlands	50% WP	2.0	PS + 10	51	0.04	Churchill & Longland, 1984a
Netherlands	50% WP	1.0	PS + 42	99	0.02	Churchill & Longland, 1984a
Netherlands	50% WP	1.0	PS + 42	99	0.03	Churchill & Longland, 1984a
Netherlands	50% WP	2.0	PS + 42	99	0.03	Churchill & Longland, 1984a
Netherlands	50% WP	1.0	PS + 6	60	<0.02 (3)	Banks *et al*., 1985a
Netherlands	50% WP	2.0	PS + 6	60	0.02 (2) 0.04	Banks *et al*., 1985a
Netherlands	50% WP	1.0	PS + 6	62	0.06 0.07 0.1	Banks *et al*., 1985a
Netherlands	50% WP	2.0	PS + 6	62	0.08	Banks *et al*., 1985a
UK	10% dust	5.0	PP	38	<0.01	Churchill & Longland, 1984b
UK	20% EC	5.0	PP	38	0.02	Churchill & Longland, 1984b
UK	10% dust	5.0	PP	41	0.11	Churchill & Longland, 1984b
UK	20% EC	5.0	PP	41	0.15	Churchill & Longland, 1984b
UK	50% WP	5.0	PP	41	0.11	Churchill & Longland, 1984b
UK	10% dust	5.0	PP	42	0.01	Churchill & Longland, 1984b
UK	10% dust	5.0	PP	42	0.01	Churchill & Longland, 1984b
UK	10% dust	10.0	PP	42	0.05	Churchill & Longland, 1984b
UK	10% dust	10.0	PPI	42	0.06	Churchill & Longland, 1984b
UK	10% dust	5.0	PPI	77	<0.01	Churchill & Longland, 1984b
UK	20% EC	5.0	PPI	77	0.02	Churchill & Longland, 1984b
UK	10% dust	5.0	PPI	77	0.02	Churchill & Longland, 1984b
UK	20% EC	5.0	PPI	77	0.04	Churchill & Longland, 1984b
UK	10% dust	5.0	PP	45	<0.01	Churchill & Longland, 1984b
UK	10% dust	5.0	PP	45	<0.01	Churchill & Longland, 1984b
UK	10% dust	7.5 x 1	SS	138	<0.01	Churchill & Longland, 1984b
UK	10% dust	7.5 x 2	PP + SS	76	0.08	Churchill & Longland, 1984b
UK	50% WP	20 x 1	SS	138	0.03	Churchill & Longland, 1984b
UK	50% WP	20 x 2	PP + SS	76	0.11	Churchill & Longland, 1984b
UK	10% dust	5.0	PPI	28	0.02	Churchill & Longland, 1984b
UK	10% dust	10.0	PPI	57	0.03	Churchill & Longland, 1984b
UK	10% dust	15.0	PPI	28	0.06	Churchill & Longland, 1984b
UK	20% EC	15.0	PPI	57	0.02	Churchill & Longland, 1984b
UK	20% EC	15.0	PPI	57	0.08	Churchill & Longland, 1984b
UK	25% SC	5.0 + 12	PPI + PS	14	4.2	Churchill & Longland, 1984b
UK	10% dust	10.0	PPI	40	0.28	Churchill & Longland, 1984b
UK	10% dust	10.0	PPI	35	0.40	Churchill & Longland, 1984b
UK	25% SC	10.0	PPI	35	1.56	Churchill & Longland, 1984b
UK	10% dust	5.0	PP	84	0.78	Longland & Stalley, 1985
UK	20% EC	5.0	PP	84	0.97	Longland & Stalley, 1985
UK	5% gran	5.0	PP	54	0.41	Longland & Stalley, 1985
UK	25% EC	5.0	PP	54	0.47	Longland & Stalley, 1985
UK	50% WP	10.0	PP	62	<0.01	Last, 1986

[1] PP pre-plant soil treatment; PPI pre-plant, incorporated; SS application at seeding; PS applications to the growing crop; PS + number application at indicated days after planting

(1) the crop was planted 37 days after the application

(2) & (3) Two successive crops were planted. The first was harvested 39 days after seeding and application. The second

planting was made at approximately 40 days after the application.

Table 32. Residues of tolclofos-methyl in treated radishes. Underlined residues are from treatments according to GAP.

Country	Formulation	Rate, kg ai/ha	No. of applications	PHI, days	Residues, mg/kg	Reference
France	25% EC	0.25	1	79	<0.02	Massenot & Culoto, 1988
Netherlands	50% WP	5	2	19	0.07	Jongstra & Lanenga, 1984
Netherlands	50% WP	2.5	2	13	0.03	Jongstra & Lanenga, 1984
Netherlands	50% WP	5	2	13	0.1	Jongstra & Lanenga, 1984
Netherlands	50% WP	2.5	1	19	0.03	Jongstra & Lanenga, 1984
Netherlands	50% WP	5	1	19	0.11	Jongstra & Lanenga, 1984
Netherlands	50% WP	1.25	1	78	0.03	Jongstra & Lanenga, 1984
Netherlands	50% WP	2.5	1	78	0.06	Jongstra & Lanenga, 1984
Netherlands	50% WP	5	1	78	0.18	Jongstra & Lanenga, 1984
Netherlands	50% WP	1.25	1	68	<0.01	Jongstra & Lanenga, 1984
Netherlands	50% WP	2.5	1	68	0.01	Jongstra & Lanenga, 1984
Netherlands	50% WP	5	1	68	0.02	Jongstra & Lanenga, 1984
Netherlands	50% WP	1.25	1	37	<0.01	Churchill & Longland, 1984a
Netherlands	50% WP	2.5	1	37	<0.01	Churchill & Longland, 1984a
Netherlands	50% WP	1.25	1	33	<0.01	Churchill & Longland, 1984a
Netherlands	50% WP	2.5	1	33	0.02	Churchill & Longland, 1984a

In the UK, residues were determined in potatoes where the seed had been treated at the rate of either 0.125 or 0.25 kg ai/t. In these studies the peel constituted about 30% of the total tuber (Longland and Churchill, 1983). The residues in the whole potatoes and the peel are given in Table 33.

Table 33. Residues in whole potatoes and peel from supervised trials in the UK.

Treatment rate, kg ai/t	Residues, mg/kg	
	Whole potatoes	Peel
0.125	0.02	0.04
0.25	0.01	0.05
0.25	0.02	0.08
0.25	0.06	0.09
0.125	0.01	0.06
0.25	0.18	1.19
	Peeled potato: 0.01	

In a further study in The Netherlands, potatoes were planted in soils that had been treated with different rates of tolclofos-methyl and the tubers were analysed for residues. Table 34 shows the residues measured in the peel and whole tubers and calculated values for whole tubers based on the residues in the peel and the ratio of the weight of the peel to that of the tuber.

Table 34. Residues in whole potatoes and their peel.

Treatment rate, kg ai/ha	% peel in whole potatoes	Residues, mg/kg		
		Peel	Whole tubers (found)	Whole tubers (calc. from peel)
15	18.7	0.083	0.019	0.016
30	21.1	0.152	0.029	0.032
60	20.9	0.383	0.086	0.080

The calculated results support the findings of previous trials which indicated that residues in potatoes were essentially concentrated in the peel.

The peel was fractionated into starch, juice and fibre. The residues measured are shown in Table 35. (Smith and Brunt, 1989).

Table 35. Distribution of residues in processed fractions of potato peel.

Treatment rate, kg ai/ha	Distribution of residues, %			
	Starch	Juice	Fibre	Total recovery
15	<1	20	68	88
30	<1	20	64	84
60	<1	20	73	93

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Data on residues of tolclofos-methyl in commodities moving in commerce were reported from The Netherlands and Sweden (Andersson, 1991). The results are shown in Tables 36 and 37.

Table 36. Residues of tolclofos-methyl in imported foods in Sweden (1990).

Crop	No. of samples analysed	No. of samples with residues in given ranges, mg/kg						Max. residue mg/kg
		<0.06	0.06-0.10	0.11-0.20	0.21-0.30	0.31-0.50	0.51-1.0	
Cucumber	180			1				0.17
Lettuce (head)	15	1		1		1		0.41
Lettuce	61	4	2	8	3	2	1	0.61
Potato	146		1					0.07
Radish	12		1					0.08

Table 37. Residues of tolclofos-methyl in foods in The Netherlands (1984-85).

Crop	No. of samples analysed	No. of samples with residues in given ranges, mg/kg							
		≤0.02	≤0.05	≤0.10	≤0.2	≤0.50	≤1.0	≤2.0	>10
Endive	31	7	8	10	4	2			
Beans, French	4	3			1				
Carrots	3			3					
Celeriac	7	2	1	1		2		1	
Chinese cabbage	3	2		1					
Cucumber	3	1	1			1			
Lettuce	140	38	35	34	16	9	7		1
Radish	87	35	27	9	12	4			
Spinach	9	4	3			2			

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported to the Meeting.

Country	Crop	MRL mg/kg
Australia	Cotton seed	0.01
	Potatoes	0.1
Austria	Lettuce	1.0
	Potatoes	0.05
	Radish	0.1
Belgium	Lettuce	0.1
	Radish	0.02
Germany	Potatoes	0.05

Country	Crop	MRL mg/kg
Italy	Lettuce	1.0
	Potatoes	0.1
Netherlands	Lettuce	1.0
	Potatoes	0.05
	Radish	0.1
Spain	Lettuce	0.05
	Peppers	0.05
	Potatoes	0.01
	Sugar beet	0.05
	Tomatoes	0.05

APPRAISAL

Tolclofos-methyl is an organophosphorus fungicide that is effective in the control of soil-borne fungus diseases caused by infection with Basidiomycete fungi such as *Rhizoctonia solani* and *Corticium rolfsii*. It is registered in a number of countries around the world mainly for the control of soil-borne diseases of potatoes but may also be used for the treatment of lettuce and certain other crops. It is usually applied as a seed-dressing and soil treatment shortly before sowing or planting. In the case of lettuce 2 or 3 post-planting applications may also be made.

The metabolism of tolclofos-methyl has been studied in rats, mice, goats and hens, as well as in cotton, peanut and sugar beet plants.

The identified residues are indicated as follows.

Parent compound: TM.
Oxidation products of 4-methyl group of parent:
alcohol TM-CH_2OH, aldehyde TM-CHO, acid TM-COOH.

Oxon: TMO.
Oxidation products of 4-methyl group:
alcohol TMO-CH_2OH, aldehyde TMO-CHO, acid TMO-COOH.

Demethyl-tolclofos-methyl (*O*-(2,6-dichloro-4-methylphenyl) *O*-methyl *O*-hydrogen phosphorothioate): DM-TM.
Oxidation products of 4-methyl group:
alcohol DM-TM-CH_2OH, aldehyde DM-TM-CHO, acid DM-TM-COOH.

Demethyl-oxon: DM-TMO.
Oxidation products of 4-methyl group:
alcohol DM-TMO-CH_2OH, aldehyde DM-TMO-CHO, acid DM-TMO-COOH.

Phosphorothiolate isomer of TM: SM-TM.
Phosphorothiolate isomer of DM-TM: DM-SM-TM.

Products from cleavage of P-O-aryl bond:
2,6-dichloro-4-methylphenol: PH-CH_3
2-chloro-4-methylphenol: DC-PH-CH_3

3,5-dichloro-4-hydroxybenzyl alcohol: PH-CH_2OH
3,5-dichloro-4-hydroxybenzaldehyde: PH-CHO
3,5-dichloro-4-hydroxybenzoic acid: PH-COOH

Rats of both sexes were given a single dose by oral intubation of a corn oil solution of 5 mg/kg bw of tolclofos-methyl labelled with ^{14}C uniformly in the phenyl ring. A second group of animals was dosed in the same way with 200 mg/kg bw. A third group was pre-treated with unlabelled tolclofos-methyl, administered daily for 14 consecutive days at 5 mg/kg bw/day before administration of a single dose of the labelled compound 5 mg/kg/bw. In one experiment mice were given by oral intubation a single dose of a corn oil solution of 5 mg/kg bw of tolclofos-methyl labelled with ^{14}C in the 4-methyl group. Radiocarbon in the urine and faeces as well as $^{14}CO_2$ were monitored from 30 minutes after administration of labelled parent compound for a period of 7 days. Animals were slaughtered periodically for assay of the radioactivity in various tissues.

These studies gave similar results which indicated that the main routes of elimination of the residues were via the urine and faeces. More than 95% of the dosed radioactivity was excreted within 48 hours of administration. Within 7 days, 80-91% of the dose was excreted in the urine, 9-20% in the faeces and less than 1% in the expired air.

In a study of bile-cannulated rats, 6-12% of the dose was excreted in the bile, 47-60% in the urine and 24-42% in the faeces within 24 hours.

Total ^{14}C levels in most of the tissues reached maxima 2 hours after administration. They rapidly decreased, in proportion to the decline of residues in the blood, to less than 5% of the maximum level in each tissue 72 hours after administration.

Whole-body autoradiography showed that the radioactivity was primarily in the gastrointestinal tract, including the stomach, intestine, kidney and liver, in that order, 1 and 6 hours after administration. Only a low level of radioactivity was detected in the whole body 24 hours after administration. The tissue residues were less than 1% of the administered dose 7 days after administration. The small amounts of radioactivity remaining in the animals were primarily in the hair, fat, skin, red blood cells, liver and kidney.

No qualitative differences were observed between the sexes or the doses. The following major metabolites were found in the excreta of rats: DM-TMO (10-26% of the dosed ^{14}C), DM-TM-CH_2OH (12-25%), DM-TM-COOH (11-35%) and DM-TM (12-44%). In addition 10 minor metabolites were detected. Of these at least seven, including TM-COOH, PH-COOH, DM-TM and DM-TM-CH_2OH, were already present 2 hours after oral administration in the blood, liver and kidney.

In the study of bile-cannulated rats, most of the radioactivity excreted into the bile within 24 hours after administration was in the form of polar metabolites, the major ones being DM-TM-CH_2OH and PH-CH_3 glucuronide. Except for the formation of conjugates (glucuronic acids in rats and conjugation of the resulting acid with glycine in mice), the metabolites in rats and mice were essentially the same.

[^{14}C]Phenyl-labelled tolclofos-methyl was administered daily by capsule to a lactating goat of approximately 40 kg weight for four consecutive days. The dosage was equivalent to approximately 250 ppm in the diet. Urine and faeces were collected separately at 7, 24, 48, 72 and 79 hours after the start of the study. Milk was collected twice daily and the animal was slaughtered 7 hours after the last of the four doses.

The urine was the principal pathway of elimination and accounted for 26% of the total applied dose by the end of the study at 79 hours, when the total radioactivity amounted to 485 mg/kg TM equivalent. Faecal elimination accounted for only 0.6% of the dose. The concentration of radioactivity in the faeces continuously increased during the study up to 143 mg/kg at 79 hours. The results indicated that passage of the administered material through the gut was slow and that the low recovery of administered radioactivity was probably due to retention in the gut contents.

In the urine (average of 24 and 79 hour samples) no parent material was found and the various fractions identified in the extracts, including some minor unknowns, accounted for 95.5% of the total radioactivity. The most important metabolite was the demethylated oxon DM-TMO (44.8%), which, together with its alcohol and acid derivatives, accounted for 55% of the total. The next most important group comprised the phenolic alcohol, aldehyde and acid (14.2, 2.8 and 8.9% respectively), which together accounted for nearly 26%. The remaining radioactivity was distributed among 14 other products of which 5 were not identified.

In the faeces (average of 24 and 79 hour samples) 60% of the extracted radioactivity was identified. More than 28% was accounted for by unchanged parent. Otherwise, the metabolite pattern was similar to that in the urine.

There was very little elimination of radioactivity in the milk, which accounted for 0.001% or less of the applied dose. Concentrations in whole milk reached 0.87 mg/kg tolclofos-methyl equivalent by the end of the study. In the milk sample taken at 48 hours, 65% of the total radioactivity was in the acetonitrile fraction. The rest of it was either extractable in hexane (9.3%), remained in the aqueous phase (3.1%) or remained unextracted in the solids (18.3%). The radioactivity in the acetonitrile was fractionated. The most important metabolites found were the oxon, TMO (42.4%) the carboxylic acid derivative, DM-TM-COOH (6.8%), and the *p*-hydroxybenzoic acid (PH-COOH) (9%).

Just under 0.6% of the applied dose was retained in the tissues with the highest levels in liver and kidney (3.0 and 4.3 mg/kg respectively). The muscle contained 0.2 mg/kg total residue. The major metabolites and their percentage of the total radioactivity in the kidney were TMO-CH_2OH (11%), TMO-COOH (21.2%), PH-COOH (21.1%). Two unknowns and two demethylated metabolites made up the rest of the organo-extractable radioactivity which amounted to 67.4% of the total. The rest of the radioactivity in the kidney consisted of methanol- and water-extracted material (37.5 and 6.3% respectively) and unextracted matter (3.8%), giving a total recovery of 114.9%. In the liver, just over 50% of the total radioactivity was in the extracted fractions. The four phenyl derivatives, (PH-CH_3, PH-Ch_2OH, PH-CHO, and PH-COOH) together accounted for 39.5% of the total radioactivity with a further 11% attributed to an unknown. The rest of the liver radioactivity consisted of methanol- and water-extractable residues (20.6%) and unextractable material (29.8%) in the solids. Radioactivity in the other tissues (fat and muscle) was too low for separation and identification.

[U-^{14}C]Phenyl-labelled tolclofos-methyl was administered orally for four consecutive days to 3 laying hens which were killed 7 hours after the last dose. This dosage was equivalent to approximately 167 ppm in the diet but was administered each day as a single dose.

The administered radioactivity was eliminated rapidly in the excreta. Over 71% of the first dose was eliminated in the first 7 hours and 87% within 24 hours. Equilibrium between excretion and intake was reached within 3 days. Unchanged tolclofos-methyl accounted for 36% of the residues in the excreta. The major metabolites identified were PH-COOH (23%), TM-CHO (9%), TMO-COOH (7%) and TM-COOH (3%). DM-TMO-CH_2OH, PH-CH_2OH, PH-CH_3, PH-CHO, TMO, DM-TM and DM-TMO were identified as only minor metabolites.

Residues in egg yolks were 0.37 mg/kg tolclofos-methyl equivalents at 72 hours and 0.27 mg/kg at 79 hours. Corresponding levels in the white rose to a maximum of 0.07 mg/kg. The retention of residues in body tissues was low. The highest residues occurred in the fat, kidney and liver (0.23%, 0.11% and 0.2% of the total administered dose or 1.0, 6.0 and 3.4 mg/kg respectively). The levels expressed as mg/kg total residue in other tissues were heart 0.18, muscle 0.11, lung 0.44, spleen 0.12 and ovary 0.47.

In the liver, about 20% of the radioactivity was in the form of free metabolites with a further 8% liberated by acid and base hydrolysis. The unchanged parent was not detected, and the only identified metabolite was TM-CHO (3.4% of the total radioactivity in the liver). In the kidney the only metabolite identified was PH-COOH, which accounted for 9% of the total radioactivity. There were 8 other metabolites but further identification was not possible owing to the small amounts present.

In eggs and muscle the levels of radioactivity were too low to permit the identification of individual components.

The pattern of metabolism in rats, mice, goats and hens was essentially similar, the identified metabolites were the same and the parent compound was metabolized and excreted rapidly with less than 1% of the administered dose retained in various tissues after 3-7 days. The identified and quantified metabolites show that the major biotransformation reactions in animals are oxidation to the oxon and related derivatives, oxidation of the 4-methyl group to the alcohol and acid, cleavage of the P-O-aryl and P-O-methyl linkages, and conjugation of the resulting acids and phenols.

Phenyl-labelled tolclofos-methyl was applied to the leaves of six-month old sugar beet plants in pots in a greenhouse. Three days after the treatment only 40% of the applied radioactivity was recovered in the treated leaves, and of this 15% was in the surface wash and 23% in the extract from the macerated leaves. The radiocarbon on and in the treated leaves gradually decreased thereafter, accounting for 0.3% and 4.5% of the applied ^{14}C, respectively, 50 days after treatment. TM accounted for 98%, 66% and 33% of the surface residue at 3, 35 and 50 days. TMO was not present above 0.1% during the study period. The methanol/chloroform extract contained several metabolites in varying proportions at various intervals after treatment. After 2 weeks and later DM-TMO was the major metabolite, reaching a maximum of 7.8% of the applied dose after 14 days. DM-TMO represented 4.5% and 62% of the total extractable residue at 14 and 50 days respectively. In addition TM, TMO-COOH and DM-TM were present at 11%, 8.8% and 4.4% of the total extractable residue at 50 days. Other metabolites (TMO, TM-CH_2OH, TMO-CH_2OH, PH-CH_3, PH-CH_2OH were present in amounts of $\leq$0.1%. The radiocarbon in the untreated shoots amounted to 0.3%, 1.3%, 1.6% 1.5% and 1.0% of the applied dose 3, 7, 21, 35 and 50 days after application, indicating that there was little translocation within the plant.

The uptake of residues by sugar beet plants following soil treatment was very small, reaching a maximum of 2.5% of the radioactivity applied to the soil after 14 days. Of this, 1.5% was in the roots and 1.0% in the tops and most of the residue (1.7%) was the parent compound. By the end of the study, the total radioactivity recovered from the plants had fallen to 1.2% of that applied. Residues in the soil fell from 62.7% of the applied radioactivity at 3 days to 46.5% by the end of the study at 75 days.

Cotton plants were grown in field conditions in soils which had been treated at 5.2 or 15.7 kg/ha with labelled tolclofos-methyl. In plants grown on the soils treated with 5.2 kg/ha no radioactivity was detected in the bolls, squares, seed or leaves above the limits of determination which were 0.004, 0.004, 0.003 and 0.008 mg/kg respectively. Small amounts were found in the stems (0.008-0.01 mg/kg). In plants from soils treated at the higher rate, the levels of total radioactivity in the bolls, squares and seed were still below the limits of determination but trace amounts were found in the leaves

(0.015 mg/kg) and stems (0.015-0.026 mg/kg at different heights). The residue levels were too low to allow the identification of any metabolites.

A study on peanuts was carried out in parallel with the study on cotton. The treatments included a foliar application (4.2 and 22 mg ai/plant) 75 days after soil treatment. The extraction of the leaves was preceded by a solvent wash to determine surface deposits. The radioactive residues on the surface of the leaves at maturity from the high treatment rate amounted to 2.6-3.7% of the ^{14}C. Its average composition[1] was TM 2.8%, TM-CH_2OH 7.0%, PH-CH_2OH 16.6%, and polar conjugates 59.9%. In the leaves the main residues were PH-CHO 18.2%, TM-CH_2OH 11.3%, PH-CH_3 3.7%, TMO 1.9% and three unidentified components 9.8%. The parent compound was not detected. Between 10 and 18% of the extracted residue remained at the origin on TLC separation and this was hydrolysed with cellulase to liberate PH-CH_2OH (55%) and TM-CH_2OH (29%) with smaller amounts of TMO, PH-CHO and TMO-CH_2OH. The level of radioactivity in the nuts was too small to identify the residues. The residues in the hulls included TM (5.8%), DM-TMO (9.8%) and two unknowns (12.1 and 5.5%). About 67% of the radioactivity remained at the origin on the TLC plate.

The TMO and TM-CH_2OH residues were determined in wheat and soya grown at two locations in Japan. In wheat the product was applied as a 50% wettable powder at 1.5 kg ai/ha, while the soya beans were treated with either a 50% wettable powder at 15 kg ai/ha or a 20% dust at 60 kg ai/ha. The PHIs were 275-287 days for wheat and 14-30 days for soya beans. No residues of TMO (<0.005 mg/kg) or TM-CH_2OH (<0.01 mg/kg) could be detected in any of the samples. The parent compound was not detectable in wheat (<0.005 mg/kg), but in soya beans its concentration ranged from <0.005 to 0.06 mg/kg at 14 days and from 0.006 to 0.036 mg/kg at 30 days.

In summary, the plant metabolism studies indicated that the uptake of residues from soil and their translocation within the plants were limited, the same metabolites were formed in plants as in animals, the parent tolclofos-methyl was a major residue component, the residues decreased rapidly, and volatilization was an important factor in the loss of surface residues.

The environmental fate of tolclofos-methyl was extensively studied in various soils under aerobic and partially or completely anaerobic conditions in the laboratory, and under natural field conditions with the labelled and unlabelled compound.

Tolclofos-methyl labelled in the aryl ring was incubated with several soils of widely varying composition. The soils were fresh and the test material was added at rates ranging from 0.38 mg/kg to 26 mg/kg. The soil moisture was kept at the same level during incubation which was in the dark at temperatures from 15°C to 25°C for 30 to 365 days. Samples were taken periodically and analysed for extractable metabolites, bound residues and liberated volatiles. The unextracted radioactivity was determined by combustion analysis. The total radiocarbon recovered was generally above 90%.

The estimated half-lives were between 9.3 and 60 days under aerobic and up to 80 days under anaerobic laboratory conditions. In field studies the total residue level in the top 7.5 cm layer of the soils decreased to about 17% and 7% of the initial concentration within 75 and 150 days after application. Under field conditions the calculated half-lives in the soil ranged from about 7 to 39 days.

The pattern of degradation did not differ greatly between the soils in spite of their widely differing compositions. Altogether 27 degradation products were detected and 12 identified in the extracts of soils incubated under aerobic conditions. Of these TMO (0.1-1.2%), DM-TMO (0.1-1.8%), PH-CH_3 (0.1-6.3%) and DM-TM (0.3-18%) were the major products. In addition, TM-CH_2OH, TMO-

[1] The figures in this paragraph should be substituted for those in the report of the Meeting, p.195

CH_2OH, TM-COOH, TMO-COOH, DM-TM-COOH, PH-CH_2OH, SM-TM and PH-COOH were detected at less than 1% of the added dose. They were present in such small amounts as to be regarded as only intermediates in the mineralization of the residues. It is significant that the degradation products and the total residues reached a maximum at some point during the study and were all decreasing in the later stages.

In summary, the main reactions in the degradation of residues under aerobic conditions were oxidation of the phosphorothioate to phosphate, de-esterification with the loss of either a methyl or the aryl group and oxidation of the *p*-methyl on the aryl ring to CH_2OH and eventually to COOH.

The bound ^{14}C amounted to over 33% of the applied dose 60 days or more after the soil treatment. The bound residues were mainly in the fulvic and humic acid fractions, in proportions which changed with time.

Volatilization played an important role in the dissipation of residues. In most of the studies the volatile products accounted for over 35% of the initial activity. The parent compound, CO_2 and other volatile products continued to be liberated up to the end of the studies. The main volatile products, apart from CO_2 and the parent compound, were 2,6-dichloro-4-methylanisole and the corresponding free phenol which accounted for 5.6 and 1.7% of the applied radioactivity respectively. When the compound was incorporated into the soil the loss by volatilization decreased below 10%.

The results indicated that mineralization and volatilization were the main routes of loss, with some of the unextractable radioactivity probably incorporated into the carbon pool of the soil organic matter.

Sterile conditions reduced the rates of degradation of the parent compound in the soil and the mineralization of the metabolites, which suggests that biochemical processes play an important part in the degradation process. Since oxidation reactions are responsible for some of the steps in the pathway, degradation is also slowed by anaerobic conditions although less so than by sterilization.

Under anaerobic conditions 4-methylphenol, 2-chloro-4-methylphenol and four minor unknowns were found in the soil, they were not detected under aerobic conditions. DM-TM, DM-TMO and PH-CH_3 were the major compounds of the 26 products detected, reaching maximum ranges of 4.8-31%, 1-2.6% and 2.6-3.7% of the added doses respectively. The other compounds identified were the same as under aerobic conditions.

In a soil/water system under anaerobic conditions the main products identified in the aqueous phase, apart from tolclofos-methyl itself, were DM-TM and smaller amounts of 2-chloro-4-methylphenol (DC-PH-CH_3), 4-methylphenol and PH-CH_3. DM-TM and DC-PH-CH_3 reached a maximum at about 60 days but their subsequent rapid decline showed them to be only transient. The total radioactivity in the aqueous phase increased until day 62 and the fact that this increase was approximately parallel to the increase of DM-TM suggested that the migration of DM-TM from the soil to water accounted for much of the increased radioactivity in the aqueous phase.

The appearance of 4-methylphenol is of special interest as it indicates a dechlorination pathway in the degradation of the aromatic moiety. It rose to a maximum after 50-60 days and decreased thereafter to undetectable levels over a year. 4-Methylphenol was degraded under these conditions to carbon dioxide and methane.

In field trials the degradation was qualitatively similar to that observed under laboratory conditions. Practically all of the extractable radioactivity in the soil (82-94%) was still in the form of

the parent at both 75 and 150 days. The rest was mainly TMO with some TM-CH_2OH and small amounts of unknowns. Extractable radioactivity constituted between 60 and 70% of the total during the sampling period of 75 to 150 days.

Photodegradation was studied with thin layers of various soils. Exposure to sunlight increased the dissipation of residues on dry soil surfaces, but had no effect when the soil was wet. Volatilization played an important role in the loss. The products detected in soils exposed to sunlight and in those kept in the dark were the same. The main differences between the light and dark series were the greater production of TMO and DM-TMO and greater volatilization in the light series.

Studies on adsorption to the soil indicated that tolclofos-methyl is strongly adsorbed by typical agricultural soils.

The leaching behaviour of the parent compound and aged residues was studied in several soils. The residues generally remained in the top layer of the soil columns. In a detailed study on a sandy loam soil with low organic matter content, about 75% of the aged radioactivity in the soil could be extracted before leaching. Of this, some 48% was unchanged parent and 17% was DM-TM with eight other components accounting for a further 9.6%. An additional 8.7% was accounted for by bound residues. About 20.3% of the applied radioactivity was found in the eluate, in which no parent compound was detectable and DM-TM amounted to about 99.5% of the residue. Only 0.3% of the DM-TM originally in the treated soil remained in the column. Only about 6% of the parent and other residues moved below the top 5 cm of the untreated soil, even under the intensive leaching conditions of the study.

In field trials only trace levels of residues reached a depth of 15-20 cm, and it was calculated that after 75 days, 90% of the radioactivity remained in the treated top 7.5 cm. Radioactivity was not detected outside the treated disc, indicating that lateral migration was also negligible.

In summary, it may be concluded from these studies that tolclofos-methyl is strongly adsorbed to the soil and the majority of the residues remain in the top soil. It is degraded readily in typical agricultural soils, and although a number of degradation products have been identified the ultimate fate is complete mineralization without accumulation of either the parent or any of its identified degradation products. It is unlikely that either parent or degradation products would be present in soil in subsequent years or would reach ground water when tolclofos-methyl has been applied according to GAP.

The environmental fate in water/sediment systems was studied in sterile and natural waters and sediments. The Ph ranged between 5 and 9 at temperatures from 20°C to 60°C. Half-lives (days) in buffer solutions at the three pH values of 5, 7 and 9 were 139 and 12.7, 417 and 21.4 and 238 and 19.3 at 22°C and 40°C respectively. At 25°C in the pH range 5-9, the parent compound amounted to about 63-73% of the total residue, while the main degradation products and their proportions were DM-TM (11.2-23.1%), TMO (7.7-12.0%), and PH-CH_3 (0.4-0.6%). The effect of pH on both the rate of hydrolysis and the products formed was very limited. In natural water and sediments the degradation pattern was the same but the rate of degradation was faster. About 42-52% of the applied dose was present as the parent compound and the proportion of degradation products was higher following 4 weeks incubation at 20°C. A study on the further degradation of DM-TM under similar conditions indicated that although degradation was slower than in the case of the parent compound, mineralization occurred as shown by the production of CO_2.

The degradation of the parent compound as well as DM-TM was much slower in sterile water.

Photodegradation studies in sterile natural waters and buffer solutions revealed that tolclofos-

methyl is not particularly light-sensitive. Although it has a weak absorption band around 290 nm, its main absorption occurs at about 215 nm, beyond the range of natural sunlight. Under exposure to sunlight the half-lives decreased to about half the values obtained in the dark. However in aqueous acetone solution (the acetone acting as a photosensitizer) the half-life of tolclofos-methyl was decreased about fifty-fold by irradiation.

The analytical methods for the parent compound are based on extraction with solvent mixtures and clean-up by passage through either a silica gel or Florisil column, or less frequently by repeated partitioning. The residues are determined by GLC using either a flame-thermionic or an electron-capture detector. Recoveries were generally above 90%, and the limits of determination ≤0.01 mg/kg. The methods for TMO, TM-CH_2OH and PH-CH_3 are basically similar to those for the parent compound except that GLC conditions are modified and some differences in solvent treatment are needed for PH-CH_3.

The residues of the parent compound did not show any degradation in potatoes stored in a deep-freeze for 3 months.

Numerous field trials have been conducted in Australia, Germany, Greece, Denmark, Poland and the UK. Tolclofos-methyl was applied as a dust, SC and WP formulations for the seed treatment of potatoes within recommended and at higher rates. In 73 seed treatments at maximum recommended rates 95% of the residues were at or below 0.1 mg/kg and 98% at or below 0.2 mg/kg, with only one value of 0.21 mg/kg above 0.2 mg/kg. This residue was found in a study in the UK where seed was treated with 25% SC at the maximum rate of 250 g/t. The residues from soil treatments before planting were lower.

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

Supervised trials with lettuce were performed in Italy, The Netherlands and the UK, applying EC, WP and dust formulations within recommended and at higher rates. The treatments, in 52 trials, were carried out before and after planting. 90% of the residues were below 0.2 mg/kg and 98% below 1 mg/kg. A single higher value (1.56 mg/kg) was obtained from pre-emergence soil treatments with recommended rates in the UK.

In view of the continuous distribution of residues from 0.28 to 1.56 mg/kg in the UK trials, the Meeting estimated a maximum residue level of 2 mg/kg for lettuce.

Radishes were grown in soil treated at recommended and higher rates in France and The Netherlands. The residues from the trials according to GAP ranged from <0.01 to 0.06 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg for radish.

In supervised trials reported from Norway on cauliflower, Chinese cabbage, kohlrabi, onions and turnips the residues were below the limit of determination (0.05 mg/kg) in the harvested crops. In carrots residues ranged from <0.02 to 1.6 mg/kg. As no GAP has been established in Norway and the reports did not specify the mode of application, the results could not be evaluated.

Several potato samples were analysed whole and after peeling. The residues were concentrated essentially in the peel. Starch prepared from potato peel contained less than 1% of the residues.

Analysis of food commodities moving in commerce in The Netherlands and Sweden indicated that measurable residues occurred in beans, carrots, celeriac, cabbages, cucumbers, potatoes, radishes and spinach. Detectable residues in lettuce occurred in 102 of 140 samples analysed in The Netherlands

and 20 of 76 samples in Sweden. With one exception in The Netherlands where >10 mg/kg was measured in one sample, the residues in lettuce were below 1 mg/kg.

In view of the recommended uses of the compound and the low residues in treated crops, the Meeting concluded that no residues would occur in food of animal origin when tolclofos-methyl is used according to GAP.

RECOMMENDATIONS

On the basis of the residues resulting from supervised trials the Meeting concluded that the residue levels listed below are suitable for use as MRLs.

Definition of the residue: tolclofos-methyl

Commodity		Recommended MRL, mg/kg	PHI on which based, days
CCN	Name		
VL 0482	Lettuce, Head	2	30
VL 0483	Lettuce, Leaf	2	30
VR 0589	Potato	0.2	>80
VR 0494	Radish	0.1	>30

FURTHER WORK OR INFORMATION

Desirable

A metabolism study on potatoes.

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