

THIOPHANATE-METHYL (077)

[See also BENOMYL (069) and CARBENDAZIM (072)]

EXPLANATION

Thiophanate-methyl was first evaluated in 1973 (T,R), and the last evaluations are from 1994 (R) and 1995 (T,E). The 1994 evaluation considered desirable further information on residue in fruits and vegetables arriving from post-harvest treatment, as well as residue data on lettuce, peppers, tomatoes and sugar beets, and supporting data on crops for which CXLs are listed. The CCPR in 1994 noted that the data base for residue data was not complete (ALINORM 95/24, para 194). The periodic re-evaluation by the 1998 JMPR was confirmed by the 1997 CCPR. The main manufacture, and the government of The Netherlands and Poland (analytical method and national limits) provided data.

IDENTITY

ISO common name: thiophanate-methyl

Chemical name: dimethyl 4,4'-(*o*-phenylene)bis(3-thioallophanate) (IUPAC)
dimethyl [1,2-phenylenebis(iminocarbonothioyl)]bis[carbamate] (CAS)

CAS registry No.: 23564-05-8

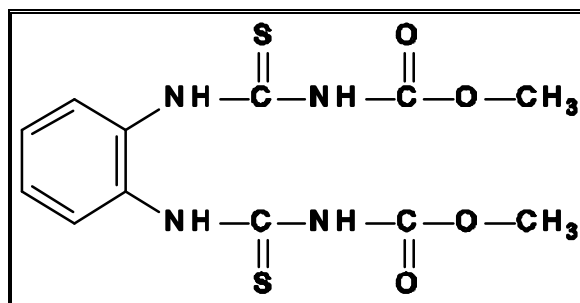
CIPAC No.: 262

Synonyms: NF-44

Molecular formula: C₁₂H₁₄N₄O₄S₂

Molecular weight: 342.4

Chemical structure:

**Physical and chemical properties**Pure substance

Appearance: white powder

Odour: none

Vapour pressure: <math> < 1.3 \times 10^{-2} \text{ mPa at } 25^{\circ}\text{C} \text{ (OECD No104)} </math>

Melting point: decomposition at 165.0°C(CIPAC MT-2)

Octanol/water partition coefficient:
 P_{ow} 25.3 (log P_{ow} 1.40) (Shiotani, 1992a)

Solubility: water 24.6 mg/l at 25°C
 40 mg/l at 25°C

Organic solvents (g/100 ml solvent at 25°C)
 acetone 2.9
 methanol 0.6
 acetonitrile 1.3 g/100 ml
 toluene 0.04
 n-Hexane 0.6×10^{-4}

Specific gravity: 1.45 at 20°C (CIPAC MT-3.2.1 iii)

Hydrolysis: half-life at 25°C 867 days (pH 5), 36 days (pH 7), 0.7 days (pH 9)

Dissociation constant, pKa: 7.28 at 25°C (OECD No112)

Technical grade

Melting point: decomposition 162.6 °C(CIPAC MT-2)

Stability: stable for 14 days at 54°C; for 3 years at room temperature

Formulations

Table 1 shows the formulations registered for use internationally for thiophanate-methyl. WP: wettable powder, WG: wettable granule, SC: suspension concentrate, PA: paste, OS: oily suspension, OD: oil dispersible powder, D: dustable powder

Table 1. Formulations of thiophanate-methyl.

Product	Formulation	Active ingredient	Concentration, %
ARNOS	SC	thiophanate-methyl	34.7
BOTORIRAM B	WP	Copper folpet thiophanate-methyl	10 20 10
BOTRIRAM	SC	copper folpet thiophanate-methyl	15 30 14
CASTAWAY PLUS	SC	lindane thiophanate-methyl	6 50
CERCOBIN FL	SC	thiophanate-methyl	50
CERCOBIN LIQUID	SC	thiophanate-methyl	50
CERCOBIN M	WP	thiophanate-methyl	70
COMPASS	SC	iprodione thiophanate-methyl	16.7 16.7
ENOCUPROL	D	copper thiophanate-methyl sulfur	5.0 2.5 40
ENOCUR	WP	copper thiophanate-methyl zineb	15 14 32

Product	Formulation	Active ingredient	Concentration, %
ENOCUR B	WP	copper thiophanate-methyl	23 7
ENOCUR C	WP	copper thiophanate-methyl	40 7
ENOSED TM	D	thiram thiophanate-methyl	40 40
ENOVIT F	WP	fenarimol thiophanate-methyl	4 50
ENOVIT METIL	WP	thiophanate-methyl	70
ENOVIT METIL FL	SC	thiophanate-methyl	38.3
ENOVIT METIL P	D	thiophanate-methyl	3.0
ENOVIT PZ	D	thiophanate-methyl sulfur	2.5 50
FENADOR MIX	WP	fenarimol mancozeb thiophanate-methyl	1.6 60 14
FRUMIDOR	WP	maneb thiophanate-methyl	60 14
FRUMIDOR CP	WG	clorotalonil thiophanate-methyl	50 20
FRUMIDOR-C	WP	mancozeb thiophanate-methyl	50 70
FRUMIDOR-M	WP	mancozeb thiophanate-methyl	60 14
Konker R	SC	thiophanate-methyl vinclozolin	25 25
MELPREX COMBI	WP	dodine thiophanate-methyl	32.5 35
MICEVIT P	D	maneb thiophanate-methyl zineb	3.0 2.5 2.7
MICEVIT PZ	D	maneb thiophanate-methyl sulfur	4.0 2.5 40
MILDOTHANE LIQUID	SC	thiophanate-methyl	50
NEOPTAN	WP	captan thiophanate-methyl	62 17.5
NEOTOPSIN	WP	thiophanate-methyl	70
ORGANIL 648	WP	folpet thiophanate-methyl	30 7
PELT 44 LIQUIDE	SC	thiophanate-methyl	45
PELTAR FLO	SC	maneb thiophanate-methyl	30 15
PELTIS 40	OS	thiophanate-methyl white petroleum	40 50
ROVER COMBI	SC	clorotalonil thiophanate-methyl	30 12
RUMILITE	WP	thiophanate-methyl triflumizol	45 15
RUMILITE-EX	WP	thiophanate-methyl triflumizol	45 15
SIPCAPLANT	WP	captan thiophanate-methyl	45 16
SIPCAPLANT OF	WP	captan dinocap thiophanate-methyl	32 12 10.5
SIPCASAN	WP	dodine thiophanate-methyl	35 35
SIPCASAN B	WP	dodine thiophanate-methyl	39 28

Product	Formulation	Active ingredient	Concentration, %
SIPCAVIT	SC	folpet thiophanate-methyl	45 16
SIPCAVIT Z	WP	forpet thiophanate-methyl sulfur	30 10 40
SIPCAVIT-L	SC	folpet thiophanate-methyl	40 14
SPOT	SC	cyproconazole thiophanate-methyl	5.3 30
TOCSIN	WP	thiophanate-methyl	70
TOPSIN	SC	thiophanate-methyl	45
TOPSIN COMBI	WP	mancozeb thiophanate-methyl	68 10.5
TOPSIN M PASTA	PA	thiophanate-methyl	3.0
TOPSIN M 500	SC	thiophanate-methyl	50
TOPSIN M 70	WG	thiophanate-methyl	70
Topsin M spuitpoeder	WP	thiophanate-methyl	70
Topsin M vloeibaar	SC	thiophanate-methyl	50
TOPSIN-M	WP	thiophanate-methyl	70
TOPSIN-M 70%	WP	thiophanate-methyl	70
TOPSIN-M 70%OD	OD	thiophanate-methyl	70
TOPSIN-M FL	SC	thiophanate-methyl	50
TOPSIN-M ULV	SC	thiophanate-methyl	50
TORAM	WP	thiophanate-methyl thiram	17.5 60
Valsa wax	PA	thiophanate-methyl	3.5

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Mice. An unspecified number of male dd-Y strain mice were given single doses of radiolabelled thiophanate-methyl. The mice were killed 3, 24, and 96 h after dosing, and the tissue samples analysed for the radiolabel. The faeces, urine and expired gas were analysed 3, 6, 12, 24, 48, 60, 72, 84 and 96 h after dosing, and blood samples after 3, 6, 12, 24, 48 and 72 h. The radioactivity in the blood and urine decreased steadily from peak levels within 3 h, and faecal excretion peaked at about 12 h in all cases, decreasing significantly by 48 h. The rate of excretion varied slightly between labels but the total excretion reached a plateau by about 24 h (Table 2).

Table 2. Percentage of radiolabel excreted by male dd-Y mice after 96 h.

Compound	Radiolabel excreted, % of dose			Total recovery of radiolabel by day 4, %
	Urine	Faeces	Expired gas	
[methyl- ¹⁴ C]thiophanate-methyl	78	17.5	nd	95.5
[thioureido- ¹⁴ C]thiophanate-methyl	66	21	nd	87
[thioureido- ³⁵ S]thiophanate-methyl	66	16	1.1	83.1
[phenyl- ¹⁴ C]thiophanate-methyl	78	27	nd	105

nd = not detected

None of the labels accumulated in any organ or tissue, and they disappeared relatively rapidly within the 96-h investigation period. [thioureido-³⁵S] was the only label found in bone after 96 h,

suggesting that the labelled sulfur might be cleaved and hence behave differently (Fujino *et al.*, 1973).

Rats. An unspecified number of male Wistar rats were given single doses of ^{14}C -labelled thiophanate-methyl by gavage. 84% of the total administered radiolabel was excreted within 24 h, 56% in the faeces and 28% in urine, and 89% by 72 h. Table 3 shows the 24-h faecal and urinary compounds identified. Of 56% of the administered radiolabel detected in the faeces, 1% in the water-soluble phase was uncharacterized and >4% remained in the residue; of 28% of the radiolabel in the urine, 14% was not characterized because it was not extractable.

Table 3. Identified ^{14}C compounds in rat urine and faeces 24h after administration of ^{14}C -labelled thiophanate-methyl (Fujino *et al.*, 1973).

Compound	Recovery of administered ^{14}C , %	
	Faeces	Urine
Thiophanate-methyl	38	1
4-hydroxy-thiophanate-methyl (4-OH-TM)	6	3
5-hydroxy-carbendazim (5-HBC)	2	6
dimethyl 4,4'-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	1	2
dimethyl 4,4'-(o-phenylene)bisallophanate (FH-432)	1	2
Carbendazim	1	1

Fifteen female Wistar rats were treated with [*phenyl*- ^{14}C]thiophanate-methyl by gavage for 20 days at a dose level equivalent to 45 ppm in a daily diet of 10 g. After the last dose, the animals were fed on a normal diet for 7 days, and the faeces and urine analysed daily or every other day from the initial dose to the time of death. The rats were killed 3 h and 1, 3 and 7 days after the last dose and tissue samples analysed for the radiolabel.

An average of 89.60% of the administered radioactivity was excreted every day (urine 54.22% and faeces 35.38%). As well as the gastro-intestinal tract, some radioactivity remained temporarily in the thyroid, adrenals and liver. Table 4 shows the 24-h faecal and urinary identified metabolites.

Table 4. Recovery of ^{14}C -labelled compounds in rat urine and faeces 24h after administration of [*phenyl*- ^{14}C]thiophanate-methyl (Kosaka *et al.*, 1975).

Compound	Recovery of administered ^{14}C , %	
	Faeces	Urine
thiophanate-methyl	2.2	0.7
4-hydroxy-thiophanate-methyl (4-OH-TM)	2.7	3.1
5-hydroxy-carbendazim (5-HBC)	11.8	28.4
dimethyl 4,4'-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	1.6	4.6
dimethyl 4,4'-(o-phenylene)bisallophanate (FH-432)	1.1	0.6
carbendazim	1.7	3.6

Groups of five Fisher strain F344 rats of each sex were given [*phenyl*- ^{14}C]thiophanate-methyl by gavage. Group A received single doses of 13 mg/kg bw and group B single doses of 10 mg/kg bw after 14 days of preconditioning with unradiolabelled thiophanate-methyl at 14 mg/kg bw per day; group D received single doses of 130 mg/kg bw and group C 173 mg/kg bw for males and 220 mg/kg bw for females. Blood and excreta were collected for 4 days. In all groups, >99% of the recovered radioactivity had been excreted in the urine or faeces at the time of death 4 days after treatment. Urinary excretion accounted for 52-60% of the dose in males given the low dose or preconditioned, and 31% in animals given the high dose. The average maximum concentrations of 1.7-4.2 $\mu\text{g/g}$ in groups A and B were attained in blood within 1-3 h, and of 17-22 $\mu\text{g/g}$ in group D within 2-4 h. The initial elimination half-lives of radioactivity in the blood were calculated to be 2.5-

2.8 h in group A, 1.6-2.2 h in group B and 2.4-4.8 h in group D. Among the tissues examined, the level of thiophanate-methyl equivalents was highest in the thyroid and liver. The 0-1 day samples of urine and faeces were combined within each group and sex for analysis. The results are shown in Table 5 (Tanoue, 1992a,b). Proposed metabolic pathways in rats are shown in Figure 1.

Table 5. Recovery of ^{14}C from rat urine and faeces 24h after administration of [*phenyl*- ^{14}C]thiophanate-methyl.

Compound	Total recovery in faeces and urine, % of administered ^{14}C		
	group B male	group C male	group D male
thiophanate-methyl	24.2	52.4	10.0
4-hydroxy-thiophanate-methyl (4-OH-TM)	8.0	5.1	10.6
5-hydroxy-carbendazim (5-HBC)	3.3	2.0	7.0
dimethyl 4,4'-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	0.3	0.1	0.4
dimethyl 4,4'-(<i>o</i> -phenylene)bisallophanate (FH-432)	0.1	0.1	0.1
carbendazim	2.3	1.6	2.9
5-hydroxy-carbendazim sulfate (5-HBC-S)	27.3	18.9	36.0

Dogs. An unspecified number of male beagle dogs were given single doses of [*thioureido*- ^{14}C]thiophanate-methyl by capsule. Blood, urine and faeces were collected 8, 15, and 30 min and 1, 2, 3, 6, 12, 24, 35, 48, 60, 72 and 96 h after administration. The urine contained 74% of the total radiolabel and the faeces 14%. Maximal total excretion occurred after about 24 h by both routes (Fujino *et al.*, 1973).

Poultry. Thirty white leghorn laying hens were dosed daily for 10 days by capsule with the equivalent of 40–50 ppm of [*phenyl*- ^{14}C]thiophanate-methyl. Excreta and eggs were collected daily. The hens were killed within 25 h after the last dose. No effects were observed on the vital parameters of any of the birds. Thiophanate-methyl was mainly eliminated through the excreta (up to 94%), with only a small percentage of total dose found in the tissues and eggs. The target tissues were the liver (1.66 mg/kg as thiophanate-methyl) and kidneys (1.23 mg/kg). Significant residues were also found in the egg yolks (0.54 mg/kg), and in the other tissues ranged from 0.061 to 0.145 mg/kg. The excreta contained 42.5 mg/kg at day 7.

The results indicate that thiophanate-methyl is mainly metabolized in laying hens by hydroxylation of the phenyl ring at the 3 or 4 position, followed by oxidation, cleavage and cyclization of the side chains to form 4- or 5-HBC (Figure 2). Table 6 shows the identified tissue metabolites (Wright, 1992).

Figure 1. Proposed metabolic pathways of thiophanate-methyl in rats.

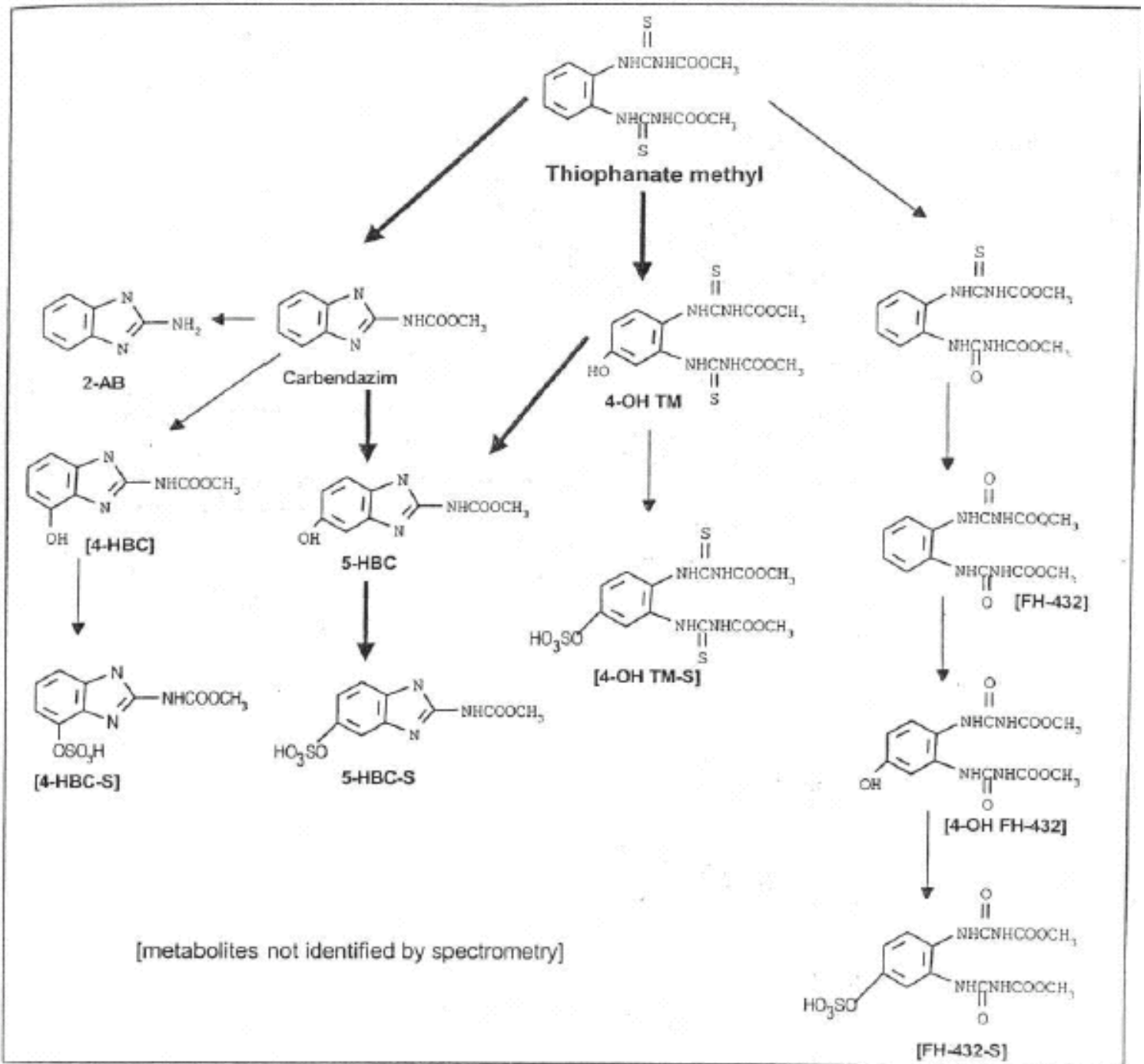
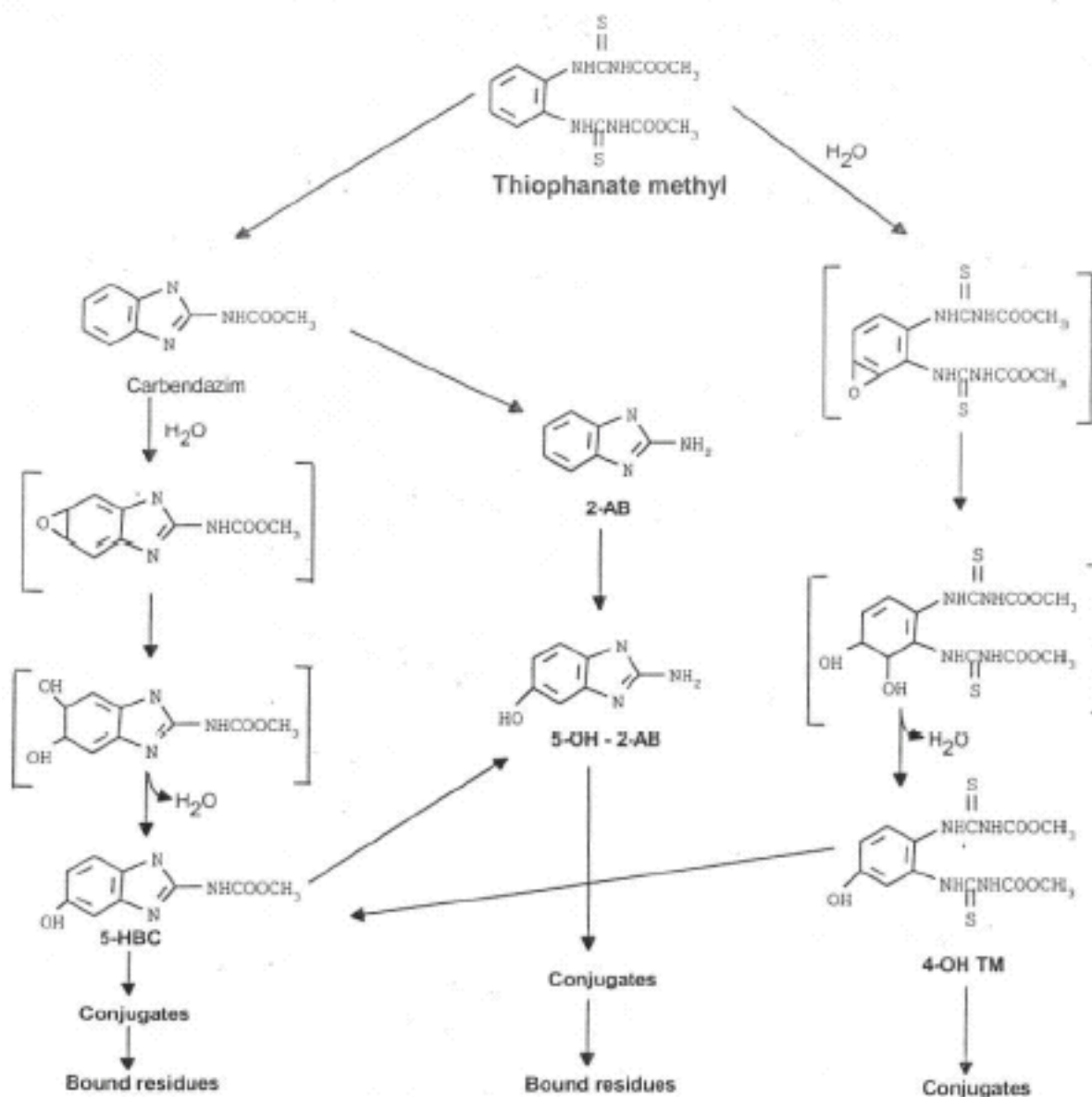


Figure 2. Proposed metabolic pathways of thiophanate-methyl in hens.

Table 6. Compounds found in hen tissues 25 h after administration of [phenyl-U-¹⁴C]thiophanate-methyl.

Compound	¹⁴ C, mg/kg as thiophanate-methyl		
	Liver	Kidney	Egg Yolk
Total ¹⁴ C	1.663	1.233	0.537
Thiophanate-methyl	0.106	0.045	0.243
4-hydroxy-thiophanate-methyl (4-OH-TM)	0.026	nd	0.012
5-hydroxy-carbendazim (5-HBC)	0.105	0.179	0.056
dimethyl 4,4'-(4-hydroxy-1,2-phenylene)bisallophanate (4-OH FH-432)	nd	nd	nd
dimethyl 4,4'-(o-phenylene)bisallophanate (FH-432)	nd	nd	nd
carbendazim	0.028	0.073	0.054
5-(2-methoxycarbonylamino)benzimidazolyl sulfate (5-HBC-S)	nd	0.143	0.014
Conjugates of 4-OH-TM	0.053	0.014	nd

nd: not detected

Goats. Two lactating goats were dosed twice daily for 5 consecutive days at rates equivalent to 52.4 and 57.3 ppm of [*phenyl*-U-¹⁴C]thiophanate-methyl in the diet, using a balling gun. Milk, urine and faeces were collected during the dosing period and the goats were killed approximately 14 hours after the last dose.

Thiophanate-methyl was rapidly metabolized. About 56.4% and 14.1% of the total administered dose was excreted in the urine and faeces respectively over the five days. Residues in the liver, kidney, muscle and fat constituted 2.1% of the administered dose, with maximum levels of 5.25 mg/kg, 1.3 mg/kg, 0.2 mg/kg and 0.12 mg/kg as thiophanate-methyl respectively. The milk contained 1.5% of the total dose and the residue reached 1.59 mg/kg at day 4. Table 7 shows the identified tissue metabolites (Hanlon and Norris, 1992a,b). Proposed metabolic pathways in goats are shown in Figure 3.

Table 7. Residues of thiophanate-methyl in goat tissues.

Compound	¹⁴ C, mg/kg as thiophanate-methyl		
	Liver	Kidney	Milk
Total ¹⁴ C, mean	4.72	1.21	0.847
thiophanate-methyl	0.04	0.01	0.003
4-hydroxy-thiophanate-methyl (4-OH-TM)	nd	0.04	0.008
3-hydroxy-thiophanate-methyl (3-OH-TM)	0.02	nd	nd
5-hydroxy-carbendazim (5-HBC)	0.32	0.02	0.023
4-hydroxy-carbendazim (4-HBC)	0.27	0.23	ND
carbendazim	0.19	0.27	0.085
5-hydroxy-carbendazim sulfate (5-HBC-S)	ND	0.45	0.623
UNK18'00	2.41	nd	nd

nd: not detected

On further characterization, it was concluded that UNK18'00 was the glucose conjugate of a dihydroxy-2-aminobenzimidazole (Eldeib *et al.*, 1993).

Figure 3. Proposed metabolic pathways of thiophanate-methyl in goats.

Plant metabolism

Bean plants. Bean plants at the two-leaf stage were cultivated in water containing [*thioureido*-¹⁴C]thiophanate-methyl or [*thioureido*-³⁵S]thiophanate-methyl for 1, 7 and 14 days. [¹⁴C]thiophanate-methyl was more easily absorbed through roots than [³⁵S]thiophanate-methyl. One day after application, about 20% of the ¹⁴C was detected in the roots in contrast to about 50% of the ³⁵S. However, about 40% of the applied [³⁵S]thiophanate-methyl remained in the roots, about 10% in the culture medium and a maximum of 5% in the leaves 14 days after application. About 20% of the ¹⁴C radioactivity was translocated from the roots to the leaves within 14 days of application. A qualitative determination of the nature of the ¹⁴C and ³⁵S radioactivity by TLC showed that thiophanate-methyl with both labels was present only in the roots and not in the leaves or stems. Carbendazim was found in all plant parts.

Other two-leaf bean plants were treated once with [*thioureido*-¹⁴C]thiophanate-methyl or [*thioureido*-³⁵S]thiophanate-methyl by leaf dotting and the radiolabel was measured 14 days after application. Sixty four to 72% of the radioactivity remained in the treated leaves, but 10 to 17% was detected in the surrounding air. Translocation from the treated leaves to the roots and leaves could also be detected (2 to 9%). Four ¹⁴C-labelled compounds were detected by TLC of which three were identified as thiophanate-methyl and the metabolites carbendazim and FH-432. Only two ³⁵S-labelled compounds could be detected, of which one was thiophanate-methyl and the other was not identified (Kosaka *et al.*, 1970; Noguchi *et al.*, 1971).

Five green snap bean plants with 3-4 cm pods were sprayed once with 50 mg/l of [*phenyl*-U-¹⁴C]thiophanate-methyl in aqueous acetone solution and kept for 14 days in a greenhouse. Pods, leaves and stems were analysed. The total residue calculated as thiophanate-methyl was 0.47 mg/kg in pods, 23.4 mg/kg in leaves and 0.96 mg/kg in stems. About 90% of the residual radioactivity was extracted with methanol. Carbendazim (45.3% to 56.9%) and DX-105 and FH-432 (together 6.7% to 9.2%) were found in all plant parts (Nippon Soda, 1977a).

Three pairs of soya bean plants with 3.5-4.5 cm pods were sprayed once with 700 mg/l of [*phenyl-U-¹⁴C*]thiophanate-methyl, one pair with a WP suspension in a greenhouse (group 1), one pair with an aqueous acetone solution outdoors (group 2), and the third pair with aqueous acetone solution in a greenhouse (group 3). The pods and leaves of all groups were analysed after 10 days. Table 8 shows the results. It is apparent that thiophanate-methyl was degraded more rapidly when sprayed as an acetone-water (1:1) solution (Nippon Soda, 1977b).

Table 8. Compounds found in soya beans 14 days after application of [*phenyl-U-¹⁴C*]thiophanate-methyl.

Compound	% of TRR					
	group 1		group 2		group 3	
	Pods	leaves	Pods	leaves	Pods	leaves
thiophanate-methyl	86.1	73.1	57.4	54.4	69.5	75.0
carbendazim	9.4	15.0	37.0	30.5	25.4	21.1
dimethyl 4,4'-(<i>o</i> -phenylene)bisallophanate (FH-432)	ND	3.9	5.6	8.7	3.4	3.1
1-(3-methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)-benzene (DX-105)	ND	1.0	ND	6.4	1.7	0.8

Apples. Potted young apple plants at a height of 70 cm were treated once with [*thioureido-¹⁴C*]thiophanate-methyl or [*thioureido-³⁵S*]thiophanate-methyl by petiole injection and the leaves were analysed for the radiolabel 14 days after application. The metabolic pattern in apple leaves was the same as in bean leaves (Kosaka *et al.*, 1970). Similar plants were also treated once with [*phenyl-U-¹⁴C*]thiophanate-methyl by leaf dotting and kept in a greenhouse. Leaves were sampled after 0, 7, 14, 28, 54 and 90 days. Most of the radioactivity present was recovered by washing the leaves with chloroform, indicating that only relatively little thiophanate-methyl had penetrated into them. The identified compounds were thiophanate-methyl and the metabolites carbendazim and FH-432 (Noguchi *et al.*, 1971).

Two apple trees with mature fruit in an orchard were sprayed three times with 3.9 kg ai/ha of [*phenyl-U-¹⁴C*]thiophanate-methyl at weekly intervals giving a total of 11.8 kg/ha (Alam *et al.*, 1994). Samples of apples taken after one and 7 days were rinsed and separated into peel and pulp. 93.8 and 89.7% of the TRR, (the sum of the radioactive residues in the peel, pulp and rinse) were identified in the 1-day and 7-day samples respectively. Table 9 shows the results.

Table 9. Main compounds found in apples 1 and 7 days after the last application of [*phenyl-U-¹⁴C*]thiophanate-methyl.

Compound	¹⁴ C, % of TRR and mg/kg as thiophanate-methyl			
	1 day PHI		7 day PHI	
	% of TRR	mg/kg	% of TRR	mg/kg
thiophanate-methyl	64.5	3.325	44.5	0.957
carbendazim	22.2	1.149	33.4	0.719
dimethyl 4,4'-(<i>o</i> -phenylene)bisallophanate (FH-432)	3.5	0.181	5.1	0.110
1-(3-methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)-benzene (DX-105)	1.3	0.068	2.1	0.046

TRR: total radioactive residue

Grapes. Potted young vines at a height of 70 cm were treated once with [*thioureido-¹⁴C*]thiophanate-methyl or [*thioureido-³⁵S*]thiophanate-methyl after 14 days (Kosaka *et al.*, 1970), or with [*phenyl-U-¹⁴C*]thiophanate-methyl (Noguchi *et al.*, 1971) by leaf dotting. The leaves were analysed after 14 days (Kosaka) or after 0, 7, 14, 28, 54 and 90 days in a greenhouse (Noguchi). Most of the radioactivity present was recovered by washing the leaves with chloroform, indicating that only relatively little [¹⁴C]thiophanate-methyl penetrated into them. The identified compounds were

thiophanate-methyl and the metabolites carbendazim and FH-432. FH-73 is a proposed intermediate but was not detected in the plants. Metabolism in grapes is similar to that in beans. Proposed metabolic pathways in plants are shown in Figure 4.

Figure 4. Proposed metabolic pathways of thiophanate-methyl in plants.

Environmental fate in soil

Degradation. [*Thioureido*-¹⁴C]-, [*methyl*-¹⁴C]- or [*thioureido*-³⁵S]-labelled thiophanate-methyl was applied to sandy loam or silty loam soils which were kept in the dark at 23°C and 33°C for 60 days. Thiophanate-methyl disappeared completely within 7 days in all cases and the main degradation product was carbendazim (Noguchi *et al.*, 1971).

[*Phenyl*-U-¹⁴C]thiophanate-methyl was applied to Japanese clay loam and light clay, which were kept in the dark at 15°C and 25°C for 28 days. The half-life in light clay was about one day at both temperatures and in clay loam about 4 days at 25°C and 7 days at 15°C. The main degradation product was carbendazim, which reached maximum levels of 32% and 66% of the TRR in light clay and clay loam respectively at 25°C after 28 days. The mineralization after 28 days reached 1% at 25°C and 0.2% at 15°C in light clay and 0.2% at 25°C and 0.2% at 15°C in clay loam (Nippon Soda, 1981).

Mineralization was investigated further in three Japanese soils. [*Phenyl*-U-¹⁴C]thiophanate-methyl was applied to sandy loam, clay loam and light clay soils which were incubated at 22°C in the dark for 64 days. After 64 days mineralization reached 6.5%, 26.3% and 20.3% in sandy loam, clay loam and light clay respectively. The main product was carbendazim (13%, 18% and 37% respectively). No volatiles except CO₂ were detected. Thiophanate-methyl did not accumulate in the soils (Nippon Soda, 1984a).

[*Phenyl-U-¹⁴C*]thiophanate-methyl was applied to sterilized Japanese sandy loam and exposed to sunlight in December (35°N latitude and 139° longitude) for 28 days. The initial half-life was calculated as 3.9 days after correcting for the dark control. The main photoproduct was carbendazim which reached 21% after 19 days exposure. Similar degradation patterns and rates were observed in both sunlight and darkness (Soeda and Shiotani, 1987a).

Solutions of thiophanate-methyl 70WP (0-5000 mg/l) were added to sandy loam or silty loam soils and kept at 30°C for 30 days. The counts of bacteria and actinomycetes were not affected. When solutions of thiophanate-methyl 50 WP (0-1000 mg/l) were percolated through sandy loam soil at 30°C for 10 days the counts of microflora were not affected. When 70 WP solutions (0-5000 mg/l) were incubated with silty loam soils at 30°C for 11 days the acceleration of respiration was proportionate to the dosage. When five strains of azotobacter were incubated at 30°C for 7 days in a medium containing thiophanate-methyl (0-500 mg/l) their growth was not affected (Kosaka *et al.*, 1972).

Adsorption

Adsorption/desorption isotherms were determined with thiophanate-methyl with the phenyl-¹⁴C label.

The Freundlich constants in three Japanese soils, sandy loam, clay loam and light clay were 4.30, 5.49 and 10.2 respectively (Nippon Soda, 1984b).

Adsorption/desorption experiments were carried out with Japanese sand, silt loam, sandy loam and clay loam and one river sediment. The sandy loam was also incubated with aged residues at 22°C for 2 days. The Freundlich constant K of the parent compound was 0.3, 0.6, 3.0 and 5.7 for sand, silt loam, sandy loam and clay loam respectively and 1.5 for the aquatic sediment. The constant of the aged residues for the sandy loam was 5.5. The adsorbed thiophanate-methyl was not desorbed easily (Soeda and Shiotani, 1987b).

The Freundlich constants of thiophanate-methyl and three metabolites in four US upland soils (sand, sandy loam, loamy sand and loam) and two US paddy field soils (loam and clay loam) are shown in Table 10. Again the adsorbed thiophanate-methyl was not desorbed easily.

Table 10. Freundlich constants K of thiophanate-methyl and related compounds in upland and paddy field soils (Shiotani, 1992).

Compound	Upland				Paddy field	
	sand	sandy loam	loamy sand	loam	loam	clay loam
thiophanate-methyl	0.27	0.66	1.46	0.97	1.47	14.14
carbendazim	0.45	3.77	5.71	4.74	4.47	88.24
dimethyl 4,4'-(<i>o</i> -phenylene)bisallophanate (FH-432)	0.28	0.68	1.31	0.75	1.06	10.11
1-(3-methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)-benzene (DX-105)	0.29	0.73	1.42	0.93	1.32	11.88

Mobility

The mobility of thiophanate-methyl was investigated with Japanese sandy loam, clay loam and light clay by TLC. A glass plate was coated with a water slurry of the soil at a thickness of 1 mm and [*phenyl-U-¹⁴C*]thiophanate-methyl was streaked onto the soil. The plate was developed with distilled water. Simetryne and linuron were used as standard compounds. Thiophanate-methyl showed

intermediate mobility (class 3) under these conditions while simetryne and linuron were in class 2 (Nippon Soda, 1984c).

Leaching

[*Phenyl-U-¹⁴C*]thiophanate-methyl was added to columns of Japanese sand, silt loam, sandy loam and clay loam. The leached radioactivity was 54.5%, 43.4%, 22.0% and 0.4% of that applied (Soeda and Shiotani, 1987c).

[*Phenyl-U-¹⁴C*]thiophanate-methyl was aged for 31 days at 20°C in standard soil Speyer 2.1 and the mixture added to a column of the same soil. The recovery of ¹⁴C was 1.1% in the leachate and 90% in the first 5 cm of the soil columns; 43% of the activity was from carbendazim (Bieber, 1992).

The leaching of 2-aminobenzimidazole (2-AB), a metabolite of thiophanate-methyl and carbendazim, was determined in columns of three German standard soils (two sand and one sandy loam). 2-AB was undetectable in the leachates from all three soils (Gorbach and Thier, 1989).

Environmental fate in water/sediment systems

Photodegradation in water

[*Phenyl-U-¹⁴C*]thiophanate-methyl was dissolved in sterile pH 5 buffer and exposed to sunlight in December (35°N latitude and 139° longitude). The half-life was 2.17 days and the main photoproduct was carbendazim which reached 50% after 5.5 days (Soeda and Shiotani, 1987d).

Aerobic aquatic degradation.

A small amount of filtrate from a ditch bed (containing 10 or 100 µg of biomass) and 100 or 1000 µg of [*phenyl-U-¹⁴C*]thiophanate-methyl was added to the oxygen-saturated water to prepare 0.1 and 1.0 mg/l test solutions at pH 7. The solutions were shaken at 20°C in the dark for 42 days and 52 days respectively. The half-life was about 15 days at 0.1 mg/l and 25 days at 1.0 mg/l. The main degradation product was carbendazim which reached 72.2% at 0.1 mg/l and 74.1% at 1.0 mg/l by the end of the experiment (Nippon Soda, 1982).

The degradation of [*phenyl-U-¹⁴C*]carbendazim in two aquatic model systems under laboratory conditions was investigated during 91 days incubation. The systems consisted of river and pond water with 2% of the corresponding sediments. The initial concentration of carbendazim was 2 mg/l and its half-life 31 and 22 days in the river water and pond water respectively. The extractable radioactivity in the water of both systems decreased rapidly and could not be detected after 91 days of incubation (Ritter, 1988).

METHODS OF RESIDUE ANALYSIS

Several analytical methods used in supervised residue trials were reported. The principle is that thiophanate-methyl and carbendazim are extracted and thiophanate-methyl is converted to carbendazim by refluxing under acidic or neutral conditions. The carbendazim is determined by UV spectrophotometry, HPLC with UV detection, derivative spectrophotometry or LC-MS-MS. The detection limits are 0.02 mg/kg for UV, 0.02 mg/kg for HPLC, 0.05 mg/kg for derivative spectrophotometry and 0.003 mg/kg for LC-MS-MS (Ono, 1973; Gomyo *et al.*, 1987, 1988a; Melkebeke, 1997). The limits of determination ranged from 0.02 to 0.2 mg/kg.

In a method provided by The Netherlands government, thiophanate-methyl is partly converted to carbendazim during the analysis, which involves extraction of the compounds with

acetone/dichloromethane/petroleum ether, clean-up on diol-bonded silica SPE, and HPLC with UV-fluorescence detection. The LOD, as carbendazim, was 0.05 mg/kg and recoveries were >97.6%. Another method using ethyl acetate extraction and TLC with a spray of fungal spores, had an LOD of 0.1 mg/kg and recovery >90%.

Two methods for animal products were reported. In one method for the determination of thiophanate-methyl, DX-15, 4-OH-TM, 4-OH-FH432 and FH-432, the analytes are extracted with acetonitrile, purified by solid-phase extraction on C-18 and NH₂ cartridges and analysed by HPLC with UV or fluorescence detection. The second method was developed for the determination of carbendazim, 5-HBC, 5-HBC-S and 2-AB and involves extraction with acid acetone to hydrolyse the sulfate conjugate, ethyl acetate partition, and clean-up with an NH₂ cartridge. In both methods the limit of determination is 0.2 mg/kg (Gomyo *et al.*, 1988b).

Stability of residues in stored analytical samples

The stability of thiophanate-methyl in crops at -30°C was determined after storage for 2 years. The residue remaining at the end of the study in relation to the initial level was 98, 90, 94, 83, 78 and 71% in pears, persimmons, cabbage, soya beans and rape seed respectively. In a study with applies at 4°C, residues of thiophanate-methyl and carbendazim after 82 days were 78.8 and 100% of the initial value respectively. In another study at -20°C for 6 months, 42.3 and 68.4% of the initial thiophanate-methyl and 50 and 128% of the initial carbendazim remained at the end. In potato, thiophanate-methyl residues after 176 days at -20°C were 58.4 and 67.1% of the initial value.

USE PATTERN

Table 11 shows the registered uses of thiophanate-methyl on the crops on which supervised trials were reported as of February 1998.

Table 11. Registered uses of thiophanate-methyl

Crop	Country	Formulation	Application				PHI, days
			Number	kg ai/ha	kg ai/hl	Mode	
Citrus	Greece	WP			0.05-0.1	foliar	60
Chinese citron	Japan	WP	7		0.023-0.035	foliar	14
Orange (Unshu)	Japan	WP	7		0.023-0.07	foliar	1
Pome fruits	Greece	WP			0.06-0.12	foliar	14
	Spain	WG/WP	2	0.42-0.84	0.035-0.07	foliar	21
Apple	Belgium	SC/WP	2		0.05	foliar	14
	Denmark	SC	4	1		foliar	14
	France	SC	3-4		0.0675	foliar	
	Italy	PA	2-3		0.03-0.06	foliar	
			WP			0.035-0.105	foliar
	Japan	WP			0.035-0.07	foliar	1
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	14
	Portugal	WP	5-6	0.7-1.05	0.07-0.105	foliar	7
	UK	SC	12	1.1	0.05-0.33	foliar	7
			SC	1		0.05	dipping
Pear	Belgium	SC/WP	1		0.05	foliar	14
	Denmark	SC	4	1		foliar	14
	Italy	PA	2-3		0.03-0.06	foliar	
		WP			0.035-0.105	foliar	

Crop	Country	Formulation	Application				PHI, days	
			Number	kg ai/ha	kg ai/hl	Mode		
	Japan	WP			0.035-0.07	foliar	1	
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	14	
	Portugal	WP	5-6	0.7	0.07	foliar	7	
	UK	SC	12	1.1	0.05-0.33	foliar	7	
Stone fruits	Greece	WP			0.25	foliar	14	
	Italy	WP			0.042-0.049	foliar		
	Germany	SC	3	0.035	0.007	foliar	10	
	Spain	WG/WP	2	0.42-0.84	0.035-0.07	foliar	21	
Apricot	France	SC	3		0.0675	foliar		
	Italy	PA			0.03-0.06	foliar		
	Japan	WP	3		0.047-0.07	foliar	21	
Cherry	Belgium	SC/WP	1		0.05	foliar	14	
	Denmark	SC	2-3	1		foliar	14	
	France	SC	3		0.0675	foliar		
	Japan	WP	3		0.047-0.07	foliar	14	
Peach	France	SC	3		0.0675	foliar		
	Italy	PA			0.03-0.06	foliar		
	Japan	WP			0.047-0.07	foliar	1	
Plum	Denmark	SC	2-3	1		foliar	14	
	France	SC	2		0.0675	foliar		
	Italy	PA			0.03-0.06	foliar		
Blackcurrant	Denmark	SC	3-4	1		foliar	14	
Gooseberry	Denmark	SC	3-4	1		foliar	14	
Raspberry	Denmark	SC	3-4	1		foliar	14	
Recurrent	Denmark	SC	3-4	1		foliar	14	
Grapes	France	SC	1	1.35		foliar		
	France	WP	1	0.35		foliar	3 months	
	Greece	WP			0.05	foliar	14	
	Italy	DP 3		0.9-1.2		foliar		
	Italy	PA/SC	2-4		0.035-0.042	foliar		
	Italy	WP			0.04-0.06	foliar		
	Japan	WP	3		0.035-1.4	foliar	petal fall	
	Portugal	WP	4	1.4	0.14	foliar	28	
	Spain	WG /WP	3	0.5-0.7	0.05-0.1	foliar	21	
	Strawberry	Belgium	SC/WP		1	0.05	foliar	14
Denmark		SC	3-4	1		foliar	14	
Greece		WP			0.07	foliar	14	
Japan		WP	3		0.14-0.233	root dipping	planting	
Spain		WG/WP	2	0.35-0.7		foliar	21	
Kiwifruit		Japan	WP 70	5		0.07	foliar	1
Persimmon		Japan	WP 70			0.047-0.07	foliar	1
Onion	Japan	WP			0.07-0.14	foliar	1	
	Spain	WG/WP	2	0.35-0.7		foliar	21	
Onion, Welsh	Japan	WP	1		0.35-3.5	root dipping	planting	
Brassica	Spain	WG/WP	2	0.35-0.7		foliar	21	
Cucurbits	Greece	WP			0.05-0.07	foliar	14	
Cucumber	Belgium	SC/WG/WP	1	1		foliar	3	
	Japan	WP			0.035-0.047	foliar	1	
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3	
	Spain	WG/WP	2	0.35-0.7		foliar	21	

Crop	Country	Formulation	Application				PHI, days
			Number	kg ai/ha	kg ai/hl	Mode	
	UK	SC	6		0.1	foliar	2
Gherkins	Belgium	SC/WG/WP	1	1		foliar	3
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3
Egg plant	Greece	WP	-		0.05-0.07	foliar	14
	Japan	WP			0.035-0.047	foliar	1
	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3
	Spain	WP	2	0.35-0.7		foliar	21
Melon	Belgium	SC/WG/WP	1	1		foliar	3
	France	SC	2	0.35		foliar	
	Japan	WP	-		0.035-0.047	foliar	1
	Spain	WG/WP	2	0.35-0.7	-	foliar	21
Pepper	Belgium	SC	1	1		foliar	3
	Belgium	WG/WP	1	0.98		foliar	3
	Spain	WG/WP	2	0.35-0.7		foliar	21
Pepper, green	Japan	WP			0.035-0.047	foliar	1
Pepper, sweet	Netherlands	SC/WP	2-3	0.56-0.7	0.07	foliar	3
Tomato	Greece	WP			0.07	foliar	14
	Japan	WP			0.035-0.047	foliar	1
	Netherlands	SC/WP	2-3	0.34-0.42	0.042	foliar	3
	Spain	WG/WP	2	0.35-0.7		foliar	21
Lettuce	Japan	WP 70	2		0.035-0.047	foliar	7
	Spain	WG/WP	2	0.35-0.7		foliar	21
Adzuki bean	Japan	WP	4		0.07-0.1	foliar	14
Bush bean	Belgium	SC/WG/WP	1-2	0.8		foliar	6
Dwarf green bean	UK	SC	1	1	0.16-0.33	foliar	
Field bean	UK	SC	2	0.25-0.5	0.125-0.375	foliar	flowering
		SC	2	0.45-0.5	1.0-1.6	aircraft	
French bean	France	SC	2	0.75		foliar	flowering
Kidney bean	Japan	WP	4		0.07-0.1	foliar	7
Soya bean	Japan	WP	4		0.07-0.1	foliar	14
String bean	Belgium	SC/WG/WP	1-2	0.8		foliar	6
Fodder Pea	Belgium	SC		0.8		foliar	7
		WP		0.8		foliar	14
Garden pea	Japan	WP	4		0.035-0.047	foliar	7
Pea	Belgium	SC		0.8		foliar	7
	Belgium	WP		0.8		foliar	14
	France	SC	2	0.75		foliar	
	UK	SC	2	0.5	0.08-0.25	foliar	21
Sugar beet	Belgium	SC/WG/WP		0.3		foliar	-
	Greece	WP			0.05-0.07	foliar	14
	Japan	WP	5		0.023-0.035	foliar	7
	Spain	WP	2	0.21-0.28	0.03-0.04	foliar	21
Celery	Belgium	SC/WP		0.5		foliar	14
	Japan	WP	2		0.047	foliar	7
	Spain	WG/WP	2	0.35-0.7		foliar	21
Cereals	Belgium	SC/WG/WP	-	0.3-0.4		foliar	28
	Denmark	SC	1	0.4-0.5		foliar	14
	Spain	WG/WP	1	0.35-0.7	0.07-0.14	foliar	21
Barley	France	SC	1	0.75		foliar	2 months

Crop	Country	Formulation	Application				PHI, days
			Number	kg ai/ha	kg ai/hl	Mode	
	Germany	SC	1	0.5	0.125	foliar	56
	Italy	WP		0.35-0.42	0.07-0.105	foliar	
	Japan	WP	3		0.028-0.07	foliar	14
	UK	SC	1	0.5	0.17-0.25	foliar	
Rice	Japan	WP	1		0.14-2.33		
Wheat	Denmark	WP	1-2	0.21-0.263		foliar	28
	France	SC	1	0.75		foliar	1 month
	Germany	SC	1	0.5	0.125	foliar	56
	Italy	PA		1.8-2.6	0.45-0.52	foliar	
		WP			0.32-0.4	dressing	
		WP		0.35-0.42	0.07-0.105	foliar	
	Japan	WP	3		0.028-0.07	foliar	14
Wheat, winter	UK	SC	1	0.5-0.7	0.17-0.35	foliar	
Cruciferous oily crops	France	SC 150	1	0.75		foliar	1.5 months
Rape	Denmark	SC	1	0.5		foliar	14
	Germany	SC	1	0.375	0.094	foliar	56
	UK	SC	2	1	0.33-0.5	foliar	21
Rape, winter	Germany	SC	1	0.5	0.083-0.167	foliar	56
Tea	Japan	WP	2		0.035-0.047	foliar	7

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of residue trials are shown in Tables 12 to 35. Trials with the same entry in the Tables were carried out at the same site. Some trial sites were divided into sub-plots separated from each other by a sufficient distance to avoid the possibility of contamination by spray drift. Residue data from sub-plots treated with exactly the same application regime are regarded as being from a single trial. Unless otherwise indicated, all trials were conducted outdoors with foliar sprays. Underlined or double underlined residues were from trials according to GAP or maximum GAP ($\pm 30\%$) respectively, and were used to estimate maximum residue levels and STMRs. Residues are the sum of thiophanate-methyl and carbendazim expressed as carbendazim.

Additional data were provided from trials carried out in the USA and Germany, but these were not evaluated because full study reports and/or labels were not supplied.

Citrus fruits. In two trials on Chinese citron in Japan at twice the GAP rate (7 x 0.023-0.035 kg ai/hl), residues 14 days PHI were 1.8 and 2.3 mg/kg in the peel and <0.02 mg/kg in the pulp. Residues in the peel decreased up to 75% from day 1 to 14, but did not change during the same period in the pulp (Table 12).

In two trials on oranges in Japan at the GAP rate (7 x 0.023-0.07.kg ai/ha), residues at 1 day PHI were 2.5 and 6.5 mg/kg in the peel, 0.06 and 0.09 mg/kg in the pulp and 0.09 and 0.14 mg/kg in the juice. The residues decreased approximately 90% in the peel after 14 or 28 days, but either increased or decreased during the same period in the pulp.

Table 12. Results from residue trials with thiophanate-methyl in Japan (1973) on oranges and Chinese citron with WP formulation

Application			PHI, days	Sample	Residues, mg/kg	Reference
kg ai/ha	kg ai/hl	No.				
Chinese citron						
4.2	0.07	8	1	peel	3.4	RD-9809
			1	pulp	<0.02	
			7	peel	2.33	
			7	pulp	<0.02	
			14	peel	1.8	
			14	pulp	<0.02	
4.2	0.07	8	1	peel	8.8	RD-9809
			1	pulp	<0.02	
			7	peel	7.8	
			7	pulp	<0.02	
			14	peel	2.3	
			14	pulp	<0.02	
Orange						
3.5	0.07	8	1	peel	2.5	RD-9809
			1	pulp	0.06	
			1	juice	0.09	
			7	peel	0.93	
			7	pulp	<u>0.11</u>	
			14	peel	0.19	
			14	pulp	0.03	
4.9	0.07	9	1	peel	6.5	RD-9809
			1	pulp	0.09	
			1	juice	0.14	
			7	peel	2.7	
			7	pulp	0.10	
			14	peel	0.89	
			14	pulp	<u>0.16</u>	
			28	peel	0.74	
28	pulp	0.12				

Apples. Thirty six trials were conducted in Europe and two in Japan. In France, two trials at the GAP rate (3-4 x 0.0675 kg ai/hl) gave residues of 0.57 and 0.31 mg/kg at a PHI of 1 day. Data from 16 dipping trials at 0.02-0.07 kg ai/hl gave residues from 0.25 to 1.3 mg/kg 78 or 135 days after treatment, but no post-harvest GAP was reported to evaluate them.

In one trial in Denmark and 16 in the UK above the GAP rate (1 or 1.1 kg ai/ha) or with excessive PHIs, residues after 8 to 16 applications up to 4.2 kg ai/ha ranged from <0.2 to 2.5 mg/kg after 2 to 78 days. In one trial in the UK at twice the recommended rate for post-harvest treatment (0.05 kg ai/hl) the residues decreased from 1.2 to 0.7 mg/kg between 74 and 137 days after the treatment (Table 13).

In two trials in Japan at the GAP rate (7 x 0.07 kg ai/hl), residues at the GAP PHI of 1 day were 0.25 and 1.0 mg/kg.

Table 13. Results from residue trials with thiophanate-methyl on apples.

Country, year	Form.	Application			Days after treatment	Residues, mg/kg	Reference	
		No.	kg ai/ha	kg ai/hl				
Denmark 1974	WP	10	1.75	0.35	2	0.62	EN/BBP-10.3.1975	
					4	0.36		
					8	0.55		
					16	0.42		
France	WP	3	0.49	0.07	1	<u>0.57</u>	C00146	
1971	WP	3	0.49	0.07	1	<u>0.31</u>		
1977	WP	1	90 sec. dip	0.02	78	0.25	15.12.1977	
	WP	1	90 sec. dip	0.035	78	0.42		
	WP	1	90 sec. dip	0.05	78	0.25		
	WP	1	90 sec. dip	0.07	78	0.54		
	SC	1	90 sec. dip	0.02	78	0.46		
	SC	1	90 sec. dip	0.035	78	0.38		
	SC	1	90 sec. dip	0.05	78	0.59		
	SC	1	90 sec. dip	0.07	78	0.75		
	1978	WP	1	90 sec. dip	0.02	135	0.37	13.02.1978
WP		1	90 sec. dip	0.035	135	0.58		
WP		1	90 sec. dip	0.05	135	0.73		
WP		1	90 sec. dip	0.07	135	0.84		
SC		1	90 sec. dip	0.02	135	0.47		
SC		1	90 sec. dip	0.035	135	0.73		
SC		1	90 sec. dip	0.05	135	0.78		
SC		1	90 sec. dip	0.07	135	1.3		
Japan 1973	WP	10	3.5	0.07	1 7 14	<u>0.25</u> 0.27 0.28	RD-9809	
	WP	10	1.8-4.2	0.07	1 7 14	<u>1.0</u> 0.82 0.29		
UK 1970	WP	8	2.2	-	3 14	2.1 1.5	RG/989 11	
	WP	8	2.2	-	3 14 42	2.5 1.3 1.0	11A	
	WP	8	2.2	-	3 14 56	2.2 0.8 0.3	13	
	WP	8	2.2	-	3 14 56	0.8 1.2 <0.2	17	
	WP	8	-	0.1	3	2.2	14	
	WP	8	-	0.1	3	1.7	18	
	1971	WP	12	1.1		78	0.1	RG/1341
		WP	12	1.5		78	0.1	
WP		16	0.56-1.1		24	0.5		
WP		15	0.77-1.5		24	1.1		
WP		12	0.84		70	0.1		
WP		12	1.1		70	<0.1		
WP		11	1.1		14	0.6		
WP		11	1.5		14	0.4		

Country, year	Form.	Application			Days after treatment	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
		1	dip ¹	0.1	74 54 84 115 119 123 137	1.2 1.5 0.9 1.5 1.0 1.1 0.7	RG/1392
1972	WP	8	1.1		85	0.1	RG/1581
	WP	8	1.1		88	0.1	

¹Results were corrected for recoveries

Pears. Two trials in Japan at the GAP rate (0.07 kg ai/hl) gave residues at 1 day of 0.54 and 0.94 mg/kg. In four trials in the UK at higher rates or longer or shorter PHIs than GAP (1.1 kg ai/ha, 7 days PHI) the residues after 3 to 60 days varied from 1.7 to <0.1 mg/kg. In two trials with post-harvest treatments at twice the recommended rate (0.05 kg ai/hl), residues were 1.2 mg/kg at day 0 and 0.9 and 1.3 mg/kg after 161 and 61 days respectively (Table 14).

Table 14. Results from residue trials with thiophanate-methyl on pears with WP formulation.

Country, year	Application			Days after treatment	Residues mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
Japan 1987	8	2.1	0.07	1	<u>0.54</u>	RD-9809
	8			3	0.76	
	8			7	0.37	
	8	3.5	0.07	1	<u>0.94</u>	RD-9809
	8			3	0.71	
	8			7	0.66	
UK ¹ 1970	7	2.2		3	1.7	RG/989
				14	0.7	
				56	0.4	
	7		0.1	3	1.7	RG/989
1971	7	1.1		60	<0.1	RG/1393
	7	1.5		60	<0.1	RG/1393
1972	1	dipping	0.1	0	1.2	RG/1639
				161	0.9	
		dipping	0.1	0	1.2	
				61	1.3	

¹Results were corrected for recoveries

Apricots. Eight trials were in Italy with 1 application of 0.76 to 2.16 kg ai/ha gave residues after 14 to 28 days of 0.07 to 0.39 mg/kg. The information on GAP was inadequate so the trials could not be evaluated (Table 15).

Table 15. Results from residue trials with thiophanate-methyl on apricots in Italy (1991-1992) with 1 application of SC formulation.

Application		PHI, days	Residue, mg/kg	Reference
kg ai/ha	kg ai/hl			
1.36	-	14	0.07	N.5 1993
1.45	-	21	0.09	
1.06	-	14	0.13	
0.76	-	14	0.08	
1.38	-	21	0.09	
0.99	-	21	0.11	
2.0	-	14	0.03	N.5 1994
		21	0.08	
		28	0.07	
2.16	-	14	0.39	
		21	0.35	
		28	0.19	

Cherries. Two decline trials in France below the recommended rate (3 x 0.0675 kg ai/hl) gave residues at day 0 of 2.1 and 3.6 mg/kg decreasing to 0.13 and 0.25 mg/kg after 20 days. One trial in the UK according to French GAP gave residues of 0.17 mg/kg at day 0 (Table 16).

Table 16. Results from residue trials with thiophanate-methyl on cherries.

Country year	Formulation	Application			PHI, days	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
France 1988	SC	1	0.45	0.045	0	2.1	F90A0288/1
					1	2.0	
					3	2.0	
					6	0.35	
					13	0.22	
					20	0.13	
	SC	1	0.90	0.090	0	3.6	F90A0588/2
					1	3.6	
					3	2.6	
					6	0.90	
					13	0.38	
					20	0.25	
UK 1973	WP	3		0.05	0	<u>0.17</u>	

Peaches. In France, 3 trials at the GAP rate (3 x 0.0675 kg ai/hl) gave residues from <0.05 to 0.13 mg/kg at 12 or 19 days. Two decline trials at lower rates showed that residues decreased by about 65 to 90% from day 0 to day 21 (Table 17).

Thirteen trials, two post-harvest, were conducted in Italy. One or 2 foliar applications of 0.51 to 1.68 kg ai/ha gave residues ranging from 0.03 to 0.48 mg/kg, but the spray concentration was not reported; GAP is 0.0675 kg ai/hl. Dipping in 0.25 kg ai/hl gave residues of 0.88 to 1.3 mg/kg after 0 to 14 days. No post-harvest GAP was reported.

In two trials in Japan at the GAP rate (0.47-1.4 kg ai/ha) residues at the GAP PHI of 1 day were 19 and 21 mg/kg in the peel and 0.33 and 0.17 mg/kg in the pulp.

Table 17. Results from residue trials with thiophanate-methyl on peaches.

Country year	Formulation	Application			Days after treatment	Sample	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl				
France	SC	3	0.675		12	fruit	0.13	F23B0188
1988	SC	3	0.675		19	fruit	0.08	
	SC	3	0.675		12	fruit	<0.05	
	SC	1	0.9	0.09	0 1 3 7 14 21	fruit	3.0 4.1 3.6 1.8 0.74 1.1	F90A0488/2
	SC	1	0.45	0.045	0 1 3 7 14 21	fruit	2.6 3.2 2.9 0.92 0.29 0.28	F90A0488/1
Italy	SC	1	1.68		15 22	fruit	0.06 0.09	N.5 1993
1991	WG	1	1.53		15 22	fruit	0.15 0.06	
	WG	1	1.09		15 22	fruit	0.13 0.12	
	SC	1	1.27		15	fruit	0.10	
	SC	1	0.85		21	fruit	0.03	
	WG	1	0.997		15	fruit	0.07	
	WG	1	0.66		21	fruit	0.35	
	WG	1	0.71		15	fruit	0.07	
	WG	1	0.51		21	fruit	0.03	
1992	SC	2	2.12		14 21 28	fruit	0.48 0.44 0.35	N.5 1994
	SC	2	2.40		14 21 28	fruit	0.44 0.28 0.47	
	SC	1	dip	0.25	0 7 14	fruit	1.2 0.88 1.1	
	SC	1	dip	0.25	0 14	fruit	1.2 1.3	
Japan	WG	7	3.5	0.07	1 1 3 3 7 7	peel pulp peel pulp peel pulp	21 0.33 36 0.40 24 <u>0.41</u>	RD-9809 trial-1
1989	WG	6	3.5	0.07	1 1 3 3 7 7	peel pulp peel pulp peel pulp	19 0.17 22 <u>0.22</u> 12 0.18	RD-9809 trial 2

Plums. In three trials in France according to GAP (3 x 0.0675 kg ai/hl), residues varied from 0.10 to 0.19 mg/kg after 2 to 19 days. Four decline trials with fewer applications showed residues from 0.66 to 0.95 mg/kg at day 0, which decreased to <0.05 mg/kg after 14 or 21 days (Table 18).

Five studies in Italy with 1 application of 1.09 to 1.71 kg ai/ha gave residues from <0.05 to 0.33 mg/kg after 15 to 28 days, but the spray concentration was not reported; GAP is 0.0675 kg ai/hl.

Table 18. Results from residue trials with thiophanate-methyl on plums with SC formulation.

Country, year	Application			PHI, days	Residues, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
France 1988	3	0.675		2	0.19	F23B0688
	3	0.675		19	0.10	F23B0588
	3	0.675		14	0.13	F23B0488
	1	0.459	0.09	0	0.95	F90A0688/2
				1	0.70	
				3	0.26	
				7	0.22	
				14	0.12	
	1	0.229	0.045	0	0.66	F90A0688/1
				1	0.75	
3				0.30		
7				0.10		
14				<0.05		
1	0.405	0.09	0	0.74	F90A0588/2	
			1	0.69		
			3	0.28		
			7	0.15		
			14	<0.05		
			21	<0.05		
1	0.220	0.045	0	0.66	F90A0588/1	
			1	0.55		
			3	0.35		
			7	0.08		
			13	<0.05		
			21	<0.05		
Italy 1991	1	1.68		15	<0.05	N.5 1993
				22	0.05	
	1	1.53		15	0.06	N.5 1993
			22	<0.05		
1992	1	1.09		15	<0.05	N.5 1993
				22	<0.05	
	1	1.20		14	0.33	N.5 1994
			21	0.25		
			28	0.18		
1992	1	1.71		14	0.10	N.5 1994
				21	0.05	
	1	1.20		14	0.33	N.5 1994
				21	0.25	
			28	0.18		
			28	0.03		

Berries. Twenty one trials in the UK on berries and currants with 3 to 8 applications of 1.12 to 8.4 kg ai/ha gave residues from <0.2 to 19 mg/kg 0 to 60 days after the last treatment. No GAP was reported with which to evaluate the trials (Table 19).

Table 19. Results from residue trials with thiophanate-methyl on berries and currants in the UK with WP formulation.

Crop year	Application			PHI, days	Residues, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
Blackberry 1973	3		0.05	0	4.6	RG/1786
Gooseberry 1972	4	1.12	0.05	0	1.5	RG/1430
				1	0.8	
				3	0.9	
	4	1.12	0.05	0	2.1	
	3	1.12	0.05	28	0.4	
3	1.12	0.05	0	1.2		
Raspberry 1972	8	1.12	0.05	1	7.1	RG/1439
				3	7.6	
Raspberry	7	1.12	0.05	0	3.3	RG/1439
				1	2.6	
				3	1.8	
Black currant 1971	6	3.78-6.72		1	4.4	RG/12883A
				4	6.5	
	6	3.78-6.72		7	4.1	RG/12883B
				14	2.9	
				1	5.6	
				4	6.2	
Black currant 1972	5	1.12	0.05	0	4.0	RG/1456
				4	1.3	
				4	1.3	
				5	2.1	
				4	0.9	
				5	1.3	
	4	6.42-8.40		60	0.9	RG/1614
				7	1.2	
	4	6.42-8.40		37	0.3	RG/1614
				7	0.5	

Grapes. In twenty trials in Italy with 2 applications of 0.5 to 2.6 kg ai/ha the residues after 14 to 28 days ranged from 0.13 to 2.1 mg/kg. The information on GAP in Italy was inadequate to evaluate the trials, but four trials complied with GAP in Spain (0.5-0.7 kg ai/ha, PHI 21 days) and one with GAP in Portugal (4 x 1.4 kg ai/ha, PHI 28 days). The residues in these at PHIs of 22 or 28 days ranged from 0.21 to 1.9 mg/kg (Table 20).

Two trials in Japan at the GAP rate (3 x 0.035-1.4 kg ai/hl) gave residues of 0.27 and 0.31 mg/kg after 74 and 62 days respectively. Four trials in Portugal at GAP application rates gave residues of 1.3 and 1.1 mg/kg at 28 days and from 1.1 to 3.2 at day 7.

Table 20. Results from residue trials with thiophanate-methyl on grapes.

Country year	Formulation	Application			PHI, days	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
Italy 1991	SC	2	2.60		15 22	0.23 0.13	N.4 1993
	WG	2	1.46		15 22	0.34 1.0	
	WG	2	1.46		15 22	0.58 1.2	
	SC	2	1.568		14 22	0.92 0.63	
	WG	2	1.02		14 22	0.96 0.80	
	WG	2	1.428		14 22	2.1 1.9	
	SC	2	1.68		15 22	0.27 0.30	
	WG	2	1.095		15 22	0.68 1.0	
	WG	2	1.53		15 22	0.94 1.5	
	SC	2	0.949- 0.988		15 22	0.905 0.57	
	WG	2	0.497- 0.553		15 22	0.62 <u>0.36</u>	
	WG	2	0.710- 0.800		15 22	1.3 <u>0.87</u>	
		SC	2	1.04		14 22	
WG		2	0.568		14 22	0.51 <u>0.21</u>	
WG		2	0.800		14 22	0.71 <u>0.56</u>	
SC		2	1.90- 2.44		15 22	0.84 1.1	
WG		2	1.292- 1.368		15 22	0.50 0.22	
WG		2	1.742- 1.912		15 22	1.5 0.91	
1992	SC	2	1.68		14 21 28	3.1 1.5 <u>1.9</u>	N.5 1994
	SC	2	2.50		14 21 28	0.38 0.87 0.24	
Japan 1991	WP	3	1.75	0.07	74	0.27	RD-9809
	WP	3	2.45	0.07	62	0.31	
Portugal 1996	WP	4	1.4	0.14	0 7 14 21 28	1.9 1.1 1.1 3.2 <u>1.3</u>	
	WP	4	1.4	0.14	0 7 14 21 28	0.75 2.2 0.91 1.4 <u>1.1</u>	

Country year	Formulation	Application			PHI, days	Residues, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
	WP	4	1.4	0.14	0	3.8	
					4	1.7	
					7	3.2	
	WP	4	1.4	0.14	0	4.8	
					4	2.1	
					7	2.9	

Strawberries. One trial in Denmark which exceeded the GAP rate (1.0 kg ai/ha) gave residues after 22 days of 0.96 mg/kg. Two trials in The Netherlands and 7 in the UK with 1 to 5 applications of 1.12 to 3.99 kg ai/ha gave residues after 3 to 31 days of <0.2 to 2.64 mg/kg (Table 21). The trials did not comply with reported GAP.

Table 21. Results from residue trials with thiophanate-methyl on strawberries with WP formulation.

Country, year	Application			PHI, days	Residues, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
Denmark 1974	3	1.5	0.075	22	0.96	EN/BBP-10.3.1975
				27	1.19	
				31	0.84	
Netherlands 1973	5	1.5	0.1	0	2.41	R 4023
				8	2.01	
				14	0.88	
	5	1.5	0.1	0	2.17	
				7	0.81	
				15	0.65	
UK 1970	1	1.68		0	8.14	RG/1287
				4	2.64	
				7	1.67	
1971	3	2.24		1	2.44	RG/1287 +RG/1319
				3	1.24	
	4	2.24-2.69		1	1.80	
				4	1.95	
	4	2.69-3.99		1	2.53	
				4	2.37	
1972	4	1.12		0	<0.2	RG/1440
	3	1.12		31	<0.2	
	3	1.12		31	<0.2	
	4	1.12		0	0.3	
	3	1.12		26	0.2	

Kiwifruit. Two trials in Japan at the GAP concentration rate of 0.07 kg ai/hl gave residues of 45 and 68 mg/kg in the peel and 0.10 and 0.61 mg/kg in the pulp at the GAP PHI of 1 day, but 0.36 and 0.20 mg/kg in the pulp at 3 days. Residues in the peel increased after 7 days (Table 22).

Table 22. Results from residue trials with thiophanate-methyl on kiwifruit in Japan (1988) with 5 applications of WP formulation

Application		PHI, days	Sample	Residue, mg/kg	Reference
kg ai/ha	kg ai/hl				
1.75	0.07	1	peel	68	RD-9809
		1	pulp	<u>0.61</u>	
		3	peel	62	
		3	pulp	0.36	
		7	peel	71	
		7	pulp	0.11	
2.8	0.07	1	peel	45	
		1	pulp	0.10	
		3	peel	44	
		3	pulp	<u>0.20</u>	
		8	peel	61	
		8	pulp	0.06	

Persimmons. One trial in Italy in 1992 with 1 application of 1.2 kg ai/ha of SC formulation gave residues of 0.08, 0.07 and 0.07 mg/kg after 14, 21 and 28 days. No relevant GAP was reported.

Onions. Two trials in Japan with 10 applications at the GAP concentration (0.14 kg ai/hl) gave residues of <0.02 and 0.04 mg/kg at the GAP PHI of 1 day.

One trial in The Netherlands and 7 in the UK with seed dressing and/or foliar treatments gave residues from <0.03 to 12.3 mg/kg after 0 to 268 days (Table 23). No relevant GAP was reported.

Table 23. Results from residue trials with thiophanate-methyl on bulb onions with WP formulation.

Country year	Application				PHI, days	Residue, mg/kg	Reference
	No.	Method	kg ai/ha	kg ai/hl			
Japan 1973	10	foliar	1.4	0.14	1	<u><0.02</u>	RD-9809
					7	<0.02	
					14	<0.02	
	10	foliar	2.6	0.14	1	<u>0.04</u>	
7					0.03		
14					<0.02		
Netherlands 1972	3	seed dress & foliar	0.02 kg ai/kg seed		28	<0.03	R4212
			0.75 (x2)		38	<0.03	
					41	<0.03	
UK 1973	1	foliar	1.12		0	3.2	RG2051
	2	foliar	1.12		0	3.5	
					78	<0.3	
					145	<0.3	
	1	foliar	1.12		4	1.8	
	2	foliar	1.12		2	12.3	
					54	<0.3	
					121	0.3	
	1	seed dress	0.25 kg ai /kg seed		248	1.1	
	1	seed dress	0.25 kg ai /kg seed		268	0.2	
	1	seed dress	0.25 kg ai /kg seed		268	0.3	
	2	seed dress & foliar	0.25 kg ai /kg seed		143	0.2	
	1	seed dress	0.25 kg ai /kg seed		249	0.2	

Brussels sprouts. Two trials in The Netherlands (1972) with 2 applications of 1.4 kg ai/ha (0.21 kg ai/hl) of WP formulation gave residues of 3.2 and 4.3 mg/kg after 21 days. No relevant GAP was reported for northern Europe.

Cucumbers and gherkins. One trial in Denmark and 3 trials in The Netherlands below or above the GAP concentration in The Netherlands (2-3 x 0.07 kg ai/hl) gave residues at PHIs of 1-3 days ranging from <0.1 to 0.51 mg/kg. Five trials in the UK (GAP 6 x 0.1 kg ai/hl) with foliar or drench treatments gave residues after 0 to 6 days from <0.2 to 0.3 mg/kg (Table 24). The UK trials could not be related to GAP.

Table 24. Results from residue trials with thiophanate-methyl on cucumbers with WP formulation.

Country, year	Application			PHI, days	Residues, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
Denmark 1974	1		0.07	0	0.20	EN/BBP
				1	0.26	
				4	0.19	
				7	0.07	
				10	0.04	
Japan 1973	6	0.7-1.2	0.047	1	0.27	RD-9809
				3	0.18	
				7	0.06	
	10	0.3-1.0	0.07	1	0.12	
				3	0.11	
				7	0.10	
Netherlands 1970	1		0.1	0	<0.1	R3581
	5		0.1	1	<0.1	
1972 (gherkins)	-		0.1	0	1.01	R4089
				3	0.51	
UK 1972	4	0.28 g ai /plant drench		0	<0.2	RG/1505
				3	<0.2	
				9	<0.2	
	4	1.12		0	0.3	
				3	<0.2	
	3	0.28 g ai /plant drench		0	<0.2	
				3	<0.2	
				7	<0.2	
	4	1.12		0	0.2	
				1	<0.2	
	3	0.28 g ai /plant drench		0	0.3	
				6	0.3	
				10	<0.2	

Mushrooms. Ten trials in The Netherlands with 1 application of 10.1 to 73.2 kg ai/ha gave residues of 0.21 to 1.3 mg/kg after 17 to 33 days. No relevant GAP was reported (Table 25)

Table 25. Results from residue trials with thiophanate-methyl on mushrooms in The Netherlands (1972/1973) with 1 application of WP formulation

kg ai/ha	PHI, days	Residues, mg/kg	Reference
14.0	22	0.21	R 4214
14.0	23	0.17	R 4214
48.8	28	0.7	RG/1575
73.2	22	0.4	RG/1575
10.7	33	0.5	RG/1792
16.2	33	0.3	RG/1792
12.2	24	0.4	RG/1792
20.1	17	1.1	RG/1792
10.1	17	0.3	RG/1792
26.5	19	0.6	RG/1792
26.5	17	1.3	RG/1792

Tomatoes. Two trials in Italy with 2 x 1.2 kg ai/ha gave residues of <0.02 to 0.11 mg/kg after 14 to 28 days. Eight trials in the UK with drench or foliar treatments gave residues of <0.2 to 0.6 mg/kg at day 0. No relevant GAP was reported.

In four trials in Japan at the GAP rate (0.035-0.047 kg ai/hl) or higher, residues at the GAP PHI of 1 day were 0.31 to 0.73 mg/kg (Table 26).

Table 26. Results from residue trials with thiophanate-methyl on tomatoes.

Country year	Formulation	Application			PHI, days	Residue, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
Italy 1992	SC	1	1.20		14 21 28	<0.02 <0.02 <0.02	N.7 1994
	SC	6	1.20		14 21 28	0.113 0.085 0.025	
Japan 1973	WP	10	1.05-4.2	0.07	1 7 14	0.69 0.56 0.31	RD-9809
	WP	10	1.05	0.07	1 7 14	0.31 0.19 0.12	
1989	WP	6	1.4	0.047	1 3 7	<u>0.73</u> 0.49 0.61	
	WP	6	1.4	0.047	1 3 7	<u>0.59</u> 0.49 0.46	
UK 1972	WP	4	2.24		0 1	2.3 2.0	RG/1513
	WP	4	2.24		0 0	1.5 1.8	
	WP	3	drench	0.05	0 1 4	0.6 0.7 0.2	
	WP	4	drench	0.05	0 14	0.3 <0.2	

Country year	Formulation	Application			PHI, days	Residue, mg/kg	Reference
		No.	kg ai/ha	kg ai/hl			
	WP	3	2.24		0	3.0	
					1	5.7	
	WP	3	drench	0.05	0	<0.2	
					9	<0.2	
	WP	5	2.24		0	2.2	
					1	2.3	
	WP	3	drench	0.05	0	0.2	
					5	0.2	
9					0.1		

Other fruiting vegetables. One trial on egg plant, one on melons and two on peppers in Italy with 1.2 kg ai/ha gave residues from <0.02 to 0.11 mg/kg after 9 to 23 days. No Italian GAP was reported but one trial on melons which complied with Spanish GAP (2 x 0.35-0.7 kg ai/ha) gave residues of 0.11 mg/kg at the GAP PHI of 21 days (Table 27)

Table 27. Results from residue trials with thiophanate-methyl on fruiting vegetables in Italy (1992) with 2 applications of SC formulation.

Crop	kg ai/ha	PHI, days	Residues, mg/kg	Reference
Egg plant	1.2	14	0.04	N.8 1994
		21	0.03	
		28	0.02	
Melon	0.8	14	0.06	
		21	<u>0.11</u>	
		28	0.15	
	1.2	14	<0.02	
		21	<0.02	
		28	<0.02	
Pepper	1.2	9	0.08	
		16	0.06	
		23	<0.02	
	1.2	14	0.02	
		21	<0.02	

Lettuce. Seven trials in the UK with 1-3 applications of 0.05 kg ai/hl or 1.2 kg ai/ha gave residues from 0.7 to 7.3 mg/kg after 0 or 1 days and <0.1 to 0.9 mg/kg after 8 to 60 days. In three trials in glasshouses at 0.05 kg ai/hl, residues after 14 to 49 days ranged from 1.1 to 6.7 mg/kg (Table 28). No relevant GAP was reported

Table 28. Results from residue trials with thiophanate-methyl on lettuce in the UK.

Formulation	Application			PHI, days	Residue, mg/kg	Reference
	No.	kg ai/ha	kg ai/hl			
WP	3	1.12		1 8 15	5.7 0.4 0.2	RG 1391
WP	3	1.12		1 3 8 15	0.7 0.4 0.4 0.3	
D	3	1.12		1 8 15	4.2 0.3 0.9	
D	3	1.12		1 3 8 15	6.1 0.7 0.2 0.5	
WP	2	1.12		0	7.3	RG 1507
WP	2	glasshouse	0.05	49	1.1	RG 1713
WP	2	glasshouse	0.05	20	6.7	
WP	2	glasshouse	0.05	14	1.2	
WP	2		0.05	14	<0.1	
WP	1		0.05	60	0.1	

Beans. Two trials in Japan on kidney beans according to GAP for azuki beans (4 x 0.07-0.1kg ai/hl, 14-day PHI) gave residues of 0.09 and 0.39 mg/kg at 14 days. In four other trials on kidney and azuki beans at higher rates residues varied from 0.07 to 0.19 mg/kg at 14 days (Table 29).

Sixteen trials were conducted in the UK with several varieties of bean. In one trial with dwarf beans and one with runner beans according to GAP (1 x 1.0 kg ai/ha) the residues were 1.3 and 1.0 mg/kg at 0 days respectively. Seven other trials with higher rates and/or excessive PHIs gave residues from <0.2 to 0.4 mg/kg in beans or pods.

In six trials on field beans according to GAP (2 x 0.25-0.5 kg ai/ha) the residues in the beans varied from <0.02 to <0.2 mg/kg after 6 to 32 days. In another trial at a double rate residues were <0.2 mg/kg after 80 days (Table 29).

Table 29. Results from residue trials with thiophanate-methyl on beans.

Country year	Bean	Formulation	Application			PHI, days	Sample	Residue, mg/kg	Reference
			kg ai/ha	kg ai/hl	No.				
Japan, 1975	Kidney	WP	1.4	0.14	3	14 21	bean	0.15 0.14	RD-9809
		WP	1.4	0.14	3	14 21	bean	0.17 0.19	
1993		WP	1.5	0.10	4	7 14 21	bean	0.32 <u>0.39</u> 0.27	
		WP	2.0	0.10	4	7 14 21	bean	0.11 <u>0.09</u> 0.05	
1993	Adzuki	WP	1.5	0.14	4	14 21 28	bean	0.07 0.07 <0.03	

Country year	Bean	Formulation	Application			PHI, days	Sample	Residue, mg/kg	Reference	
			kg ai/ha	kg ai/hl	No.					
		WP	1.5	0.14	4 4 4	14 21 28	bean	0.19 0.08 0.19		
UK, 1971	Dwarf	WP	2.24		1	32	bean	<0.2	RG/1340	
		WP	2.24		1	41	bean	<0.2		
		WP	2.24		1	40	bean	<0.2		
1972	Broad	WP	1.12		1	0	bean	1.3	RG/1530	
		WP	2.24		1	38	bean pod	<0.2 0.4	RG/1524	
	French	WP	1.12		1	30	bean	0.2	RG/1597	
		WP	1.68		1	30	bean	0.3		
	Runner	WP	1.12		1	0	bean	1.0	RG/1531	
	1973	Field	WP	1.12		1	80	bean	<0.2	RG/1888
	1986		SC	0.5		2	18	bean	<u>0.13</u>	D.Ag.313
SC			0.5		2	14	bean	<u><0.2</u>		
SC			0.5		2	14	bean	<u>0.21</u>		
SC			0.5		2	6	bean	<u><0.2</u>		
SC			0.5		2	14 19	bean	0.02 <u>0.06</u>	96-745	
SC	0.5			2	17 32	bean	<u>0.09</u> 0.06			

Peas. Two trials in Japan near the GAP rate (0.035-0.047 kg ai/hl) gave residues at 14 days of 0.03 mg/kg, but the GAP PHI is 7 days. Nine trials in France below the GAP rate (2 x 0.75 kg ai/ha) gave residues of <0.05 mg/kg in the peas and <0.12 or <0.13 mg/kg in the straw after 37 to 61 days. One trial gave a residue in straw of 1.6 mg/kg at 36 days. Eight trials in the UK according to GAP (2 x 0.5 kg ai/ha, 21 days PHI) gave residues at or below the LOD (0.01 mg/kg) after 14 to 35 days (Table 30).

Table 30. Results from residue trials with thiophanate-methyl on peas.

Country year	Formulation	Application			PHI, days	Sample	Residue, mg/kg	Reference
		kg ai/ha	kg ai/hl	No.				
Japan 1990	WP	1.4	0.025	4	14 21 28	peas	0.03 0.03 <0.03	RD-9809
	WP	1.4	0.025	4	14 21 28	peas	0.03 0.03 <0.03	
France	SC	0.45	0.025	2	37	peas straw	<0.05 <0.13	F11A0192
1992	SC	0.45	0.025	2	34	peas straw	<0.05 <0.12	F11A0392
	SC	0.45	0.025	2	50	peas straw	<0.05 <0.12	F11A0492
	SC	0.45	0.025	2	36	peas straw	<0.05 1.6	F11A0592
1993	WG	0.45	0.025	2	49	peas straw	<0.05 <0.12	F11A0193
	WG	0.45	0.025	2	61	peas straw	<0.05 <0.12	F11A0293

Country year	Formulation	Application			PHI, days	Sample	Residue, mg/kg	Reference
		kg ai/ha	kg ai/hl	No.				
	WG	0.45	0.025	2	49	peas straw	<0.05 <0.12	F11B0193
	WG	0.45	0.025	2	61	peas straw	<0.05 <0.12	F11B0293
	WG	0.45	0.025	2	48	peas straw	<0.05 <0.12	F11B0393
UK	SC	0.5		2	14	peas	<0.01	95-733
1995	SC	0.5		2	14	peas	<0.01	
	SC	0.5		2	19	peas	<u>0.01</u>	
	SC	0.5		2	20	peas	<u><0.01</u>	
1996	SC	0.5		2	27	peas	<u><0.01</u>	96-744
	SC	0.5		2	21	peas	<u>0.01</u>	
	SC	0.5		2	30	peas	<0.01	
	SC	0.5		2	35	peas	0.01	

Sugar beet. Two trials in Japan according to GAP (5 x 0.023-0.035 kg ai/hl) gave residues of 0.14 and 0.24 mg/kg in the tops and <0.04 mg/kg in the roots at the GAP PHI of 7 days (Table 31).

Table 31. Results from residue trials with thiophanate-methyl on sugar beet in Japan with WP formulation.

No.	Application		PHI, days	Sample	Residue, mg/kg	Reference
	kg ai/ha	kg ai/hl				
5	0.42	0.035	1	top	1.20	RD-9809
			1	root	<0.04	
			7	top	0.24	
			7	root	<u><0.04</u>	
			15	top	<0.15	
			15	root	<0.04	
5	0.35	0.035	1	top	0.53	RD-9809
			1	root	<0.04	
			7	top	0.14	
			7	root	<u><0.04</u>	
			14	top	<0.05	
			14	root	<0.04	

Celery. Two trials in The Netherlands (1972) with 0.7 kg ai/ha of WP formulation gave residues of 0.04 or 0.20 mg/kg in the roots and 0.05 or 1.1 mg/kg in the leaves after 22 or 11 days. The results were corrected for recovery. Neither the number of applications nor information on GAP were reported.

Barley. In fourteen trials in the UK with foliar applications at higher rates than GAP (1 x 0.5 kg ai/ha), residues were below the LOD (0.1 or 0.2 mg/kg) after 72 to 121 days. In another fourteen trials with seed dressing treatments at 0.54 kg ai/hl or 0.04-0.06 kg ai/kg seed residues after 135 to 164 days were similar. No GAP for seed dressing was reported (Table 32).

Table 32. Results from residue trials with thiophanate-methyl on barley in the UK (1973-1974).¹

Formulation	Application				PHI, days	Residue, mg/kg	Reference	
	Method	No	kg ai/ha	kg ai/hl				
P	Seed dressing	1		0.54	135	<0.2	RG/2011	
P	Seed dressing	1		0.54	135	<0.2		
P	Seed dressing	1		0.54	151	<0.2		
WP	Seed dressing	1		0.65	135	<0.2		
WP	Seed dressing	1		0.65	135	<0.2		
WP	Seed dressing	1		0.65	151	<0.2		
WP	foliar	1	1.25	0.7	84	<0.2		
WP	foliar	2	0.75		77	<0.1	RG/2184	
WP	foliar	1	0.75		77	<0.1		
WP	foliar	1	1.4		102	<0.1		
WP	foliar	2	1.4		79	<0.1		
WP	foliar	1	1.4		79	<0.1		
WP	foliar	1	1.4		119	<0.1		
WP	foliar	2	1.4		89	<0.1		
WP	foliar	1	1.4		89	<0.1		
WP	foliar	1	1.4		121	<0.1		
WP	foliar	2	1.4		91	<0.1		
WP	foliar	1	1.4		91	<0.1		
WP	foliar	2	0.75		72	<0.1		RG/2502
WP	foliar	1	0.75		72	<0.1		
WP	Seed dressing	1		0.04 kg ai/kg seed	164	<0.2		RG/2590
WP	Seed dressing	1		0.05 kg ai/kg seed	164	<0.2		
WP	Seed dressing	1		0.06 kg ai/kg seed	164	<0.2		
WP	Seed dressing	1		0.05 kg ai/kg seed	140	<0.2		
WP	Seed dressing	1		0.06 kg ai/kg seed	140	<0.2		
WP	Seed dressing	1		0.04 kg ai/kg seed	152	<0.2		
WP	Seed dressing	1		0.05 kg ai/kg seed	152	<0.2		
WP	Seed dressing	1		0.06 kg ai/kg seed	152	<0.2		

¹Results corrected for blanks and recoveries

Rice. Three trials in Japan with more applications (3) than the recommended GAP (1 x 0.14-2.33 kg ai/hl) gave residues in husked grain of 0.04 to 0.20 mg/kg after 15 or 30 days in dry straw and of 1.3 and 1.2 mg/kg after 15 and 30 days respectively (Table 33).

Table 33. Results from residue trials with thiophanate-methyl on rice in Japan (1988) with 3 applications of WP formulation.

Application		PHI, days	Sample	Residue, mg/kg	Reference
kg ai/ha	kg ai/hl				
1.5	0.1	15	grain (husked)	0.09	RD-9809
		30		0.04	
1.5	0.1	15	dry straw	1.26	
		30		1.16	
1.8	0.1	15	grain (husked)	0.20	
		30		0.05	

Wheat. In two trials in Japan at the GAP rate (3 x 0.07 kg ai/hl), residues in the grain after 14 to 30 days were <0.02 to 0.03 mg/kg. Twenty two trials in the UK at the GAP rate (1 x 0.5-0.7 kg ai/ha) or above gave residues after 46 to 111 days at or below the LOD (0.1 or 0.3 mg/kg).

In four trials in The Netherlands with 1 application of 2 to 3 kg ai/ha, residues after 34 to 73 days ranged from <0.02 to 0.05 mg/kg in the grain and from 0.07 to 0.10 mg/kg in the straw. No GAP was reported (Table 34).

Table 34. Results from residue trials with thiophanate-methyl on wheat with WP formulation.

Country year	Application			PHI, days	Sample	Residue, mg/kg	Reference
	No	kg ai/ha	kg ai/hl				
Japan 1988	3	0.98	0.07	14 21 30	grain	<0.02 <0.02 <0.02	RD-9809
	3	1.05	0.07	14 21 30	grain	0.03 0.03 <0.02	RD-9809
Netherlands	1	2		73	grain	<0.02	R4022
1973 ¹	1	2		64	grain	<0.02	
	1	3		34	straw grain	0.10 <0.05	R4572
	1	3		35	straw grain	0.07 <0.05	
UK ¹ 1973	1	0.56		46	grain	<u><0.1 (4)</u> ¹	RG/2011
1974	2	0.75		70	grain	<0.3	RG/2184
	1	0.75		70	grain	<u><0.3</u>	
	2	0.75		82	grain	<0.3	
	1	0.75		82	grain	<u><0.3</u>	
	2	0.75		83	grain	<0.3	
	1	0.75		83	grain	<u><0.3</u>	
	1	1.4		111	grain	<0.3	
	2	1.4		90	grain	<0.3	
	1	1.4		90	grain	<0.3	
	1	1.4		139	grain	<0.3	
	2	1.4		118	grain	<0.3	
	1	1.4		118	grain	<0.3	
	1	1.4		123	grain	<0.3	
	2	1.4		111	grain	<0.3	
	1	1.4		111	grain	<0.3	
	2	0.75		70	grain	0.1	RG/2502
	1	0.75		75	grain	<u>0.1</u>	
	2	0.75		83	grain	0.1	
	1	0.75		83	grain	<u><0.1</u>	
	2	0.75		82	grain	0.1	
1	0.75		82	grain	<u><0.1</u>		
1	0.75		82	grain	<u><0.1</u>		

¹Corrected for recoveries

Rape. In four trials in France with 1 or 2 applications of 0.45 kg ai/ha, residues after 65 to 87 days were < 0.05 mg/kg. No GAP was reported for France (Table 35).

Table 35. Results from residue trials with thiophanate-methyl on rape in France (1992) with SC formulation.

Application		PHI, days	Residue, mg/kg	Reference
No.	kg ai/ha			
2	0.45	79	<0.05	F04A0192
2	0.45	65	<0.05	F04A0292
2	0.45	87	<0.05	F04A0392
2	0.45	79	<0.05	F04A0492
1	0.45	78	<0.05	F04B0193
1	0.45	78	<0.05	F04B0293
1	0.45	81	<0.05	F04B0493
1	0.45	77	<0.05	F04B0693

Tea. Six residue trials on tea in Japan were with 1 application of 0.93 kg ai/ha (0.047 kg ai/hl) of WP formulation; GAP is 2 x 0.035-0.047 kg ai/hl. The residues were 1.8 and 1.6 mg/kg after 7 days, 1.3 and 1.4 mg/kg after 14 days, and 1.2 and 1.1 mg/kg after 21 days.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRL, mg/kg
Belgium	Potato	3
	Apple, Bush, bean Celery, Fodder Pea, Pea, Pear, Sour cherries, Strawberry, String bean	2
	Barley, Cucumber, Melon, Pepper, Gherkins	0.5
	Cereals, Leeks, Sugar beet	0.1
France	Apple Apricot Cherry Melon Plum	2
	Banana	1 for whole, 0.5 for pulp
	Peach	1
	Barley, Wheat	0.5
	Cruciferous oily crops, French bean	0.1
	Pea	0.05
Germany	Stone fruits	2
	Barley	0.5
	Rape, Rye, Wheat, Winter rape	0.1
Japan	Tea	20
	Fruits Vegetables	5
	Rice	2
	Beans and Peas, Cereals except rice, Root and Tubers, Sugar beet	1
Netherlands	Apple, Cucumber, Eggplant, Gherkins, Pear, Potato, Sweet pepper, Tomato	3
Spain	Grape, Onion, Strawberry	5
	Brassica, Celery, Cucumber, Eggplant, Green leguminosae, Lettuce, Pepper, Pome fruits, Stone fruits, Tomato	2
	Melon, Cereals, Watermelon	0.5
	Sugar beet	0.1
UK	Apple, Pear	2

Country	Commodity	MRL, mg/kg
Belgium	Potato	3
	Barley, Cucumber, Dwarf green bean, Field bean, Oilseed rape, Pea, Winter wheat	0.1
Poland	Citrus fruit	5
	Fruits, except Citrus; Mushrooms, Vegetables	1
	Cereal grains, Eggs, Meat and Meat Products, Milk, Milk Products, Potato, Tea	0.1

APPRAISAL

[See also BENOMYL (069)/CARBENDAZIM (072)]

Thiophanate-methyl was first evaluated in 1973 and the most recent evaluation of residue aspects was in 1994. The 1994 evaluation listed as desirable data from supervised trials according to currently registered uses on residues in fruits and vegetables arising from post-harvest treatments, as well as on lettuce, peppers, tomatoes and sugar beet, and on crops for which CXLs were listed. The CCPR in 1994 noted that the data on residues were not complete (ALINORM 95/24, para 194). The scheduled periodic re-evaluation by the 1998 JMPR was confirmed by the 1997 CCPR. Data on metabolism and supervised residue trials were provided by the manufacturer. Additional residue trials carried out in the USA and Germany were reported but have not been evaluated because full study reports and/or labels were not provided.

Metabolism studies were conducted in mice, rats, dogs, poultry, livestock and plants. The metabolic pathways of thiophanate-methyl in animals and plants includes hydroxylation, hydrolysis to carbendazim with subsequent metabolism, oxidation of the thiocarbonyl group, and formation of sulfate conjugates. In mice, labelled thiophanate-methyl was mainly excreted in the urine (66-78%) and faeces (17.5-27%) within 96 hours. In rats dosed daily with [¹⁴C]thiophanate-methyl, an average of 89.6% of the ¹⁴C was excreted every day (54.27% in the urine and 35.38% in the faeces). The main metabolites in the faeces and urine after exposure to labelled thiophanate-methyl at various doses and with various regimes were methyl 5-hydroxy-benzimidazol-2-ylcarbamate (5-HBC, 2.0-40.2%), unchanged parent compound (2.9-52.4%), 4-hydroxy-thiophanate-methyl (5.1-10.6%), dimethyl 4,4'-(4-hydroxy-1,2-phenylene)bisallophanate (0.1-6.2%) and carbendazim (2-5.3%). In one experiment the sulfate conjugate of 5-HBC accounted for 19-36% of the administered ¹⁴C.

In dogs dosed once, 74% of the total radiolabel was found in the urine and 14% in the faeces after 24 hours. In goats dosed for 5 days the cumulative percentages of ¹⁴C were 56% in the urine and 14% in the faeces. The residues in the edible tissues (liver, kidney, muscle and fat) constituted 2.1% of the administered dose. Milk contained 1.5% of the total dose and reached 1.59 mg/kg as thiophanate-methyl at day 4.

In poultry, thiophanate-methyl was mainly eliminated in the excreta (up to 94%), with only a small percentage of the total dose found in the tissues and eggs. In the tissues the highest residues were in the liver (1.7 mg/kg) and kidneys (1.2 mg/kg).

On average, 64% of the applied thiophanate-methyl was found unchanged in soya bean pods and apples 7 or 14 days after treatment. When bean plants were grown in water containing thiophanate-methyl labelled with ¹⁴C or ³⁵S the ¹⁴C label was translocated through the roots more readily than the ³⁵S. Approximately 20% of the ¹⁴C was translocated from the roots to the leaves within 14 days after application. The metabolites found in the pods and leaves of soya beans 14 days after the application of [*phenyl*-U-¹⁴C]thiophanate-methyl were the parent compound (54.4-86.1%), carbendazim (9.4-37%), dimethyl 4,4'-(*o*-phenylene)bisallophanate (FH-432, up to 8.7%) and 1-(3-

methoxycarbonylthioureido)-2-(3-methoxycarbonylureido)benzene (DX-105, up to 6.4%). Studies with young apple plants gave similar results.

Bean, apple and grape plants were treated by leaf dotting once with thiophanate-methyl labelled with ^{14}C or ^{35}S in the thioureido groups. After 14 days most of radioactivity remained in the treated leaves (64-72% in bean plants), and was recovered by washing in chloroform. The identified compounds were thiophanate-methyl, carbendazim and FH-432.

In studies of environmental fate [^{14}C]thioureido-, [^{14}C]methyl-, or [^{35}S]thioureido-labelled thiophanate-methyl was applied to sandy loam or silty loam soils which were kept in the dark at 23°C or 33°C for 60 days or exposed to sunlight for 28 days. Thiophanate-methyl disappeared completely within 7 days under dark conditions and had a half-life of 3.9 days in sunlight. In all cases the main degradation product was carbendazim.

When a series of thiophanate-methyl solutions (0-5000 mg/l) were incubated with sandy loam or silty loam soils at 30°C for 30 days the counts of microflora were not affected by the thiophanate-methyl.

Adsorption/desorption isotherms of labelled thiophanate-methyl and its metabolites were determined with four USA upland soils (sand, sandy loam, loamy sand and loam) and two USA paddy field soils (loam and clay loam). The Freundlich constants K ranged from 0.27 to 14.14 for thiophanate-methyl, 0.45 to 88.24 for carbendazim, 0.28 to 10.11 for FH-432 and 0.29 to 11.88 for DX-105. Sandy upland soils and clay loam paddy field soils had the lowest and highest values respectively. The adsorbed thiophanate-methyl was not easily desorbed.

In leaching studies with [*phenyl*-U- ^{14}C]thiophanate-methyl in soil columns 54.5%, 43.4%, 22.0% and 0.4% of the applied ^{14}C was recovered in the leachates from sand, silt loam, sandy loam and clay loam respectively.

[*Phenyl*-U- ^{14}C]thiophanate-methyl was degraded in sterile pH 5 aqueous buffer exposed to sunlight with a half-life of 2.17 days. Carbendazim was the main photoproduct and accounted for 50% of the initial ^{14}C at 5.5 days. Thiophanate-methyl in oxygen-saturated river water at pH 7, incubated under shaking and in the dark for 42 days at 0.1 mg/l and 52 days at 1.0 mg/l showed half-lives of about 15 and 25 days respectively. The major degradation product was carbendazim, which accounted for 72.2% of the initial ^{14}C at 42 days and 74.1% at 52 days.

In most residue analytical methods thiophanate-methyl and carbendazim are extracted and thiophanate-methyl is converted to carbendazim by refluxing in acidic or neutral conditions. The total carbendazim is determined by UV spectrophotometry, HPLC with UV detection, derivative spectrophotometry or LC-MS-MS. The detection limits are 0.02 mg/kg for UV, 0.02 mg/kg for HPLC, 0.05 mg/kg for derivative spectrophotometry and 0.003 mg/kg for LC-MS-MS. Limits of determination range from 0.02 to 0.2 mg/kg. In another method, thiophanate-methyl is partially converted to carbendazim during the analysis, which involves extraction of the compounds with acetone/dichloromethane/petroleum ether, clean-up by diol-bonded silica SPE and HPLC with UV-fluorescence detection. The LOD, as carbendazim, was 0.05 mg/kg and recoveries were >97.6%. In a method in which ethyl acetate extraction is followed by TLC with detection by a spray of fungal spores the reported LOD is 0.1 mg/kg with recovery >90%.

Two methods for animal products were reported. In one, which determines thiophanate-methyl, DX-15, 4-OH-TM, 4-OH-FH-432 and FH-432, the analytes are extracted with acetonitrile, cleaned up by solid-phase extraction (C-18 and NH_2) and determined by HPLC with UV or fluorescence detection. The second method was developed for the determination of carbendazim, 5-HBC, 5-HBC-S and 2-AB and involves acid extraction in acetone to hydrolyse the sulfate conjugate,

ethyl acetate partition, and clean-up on an NH₂ cartridge. In both methods the limit of determination is 0.2 mg/kg.

The stability of thiophanate-methyl and/or carbendazim in stored analytical samples was studied in many crops. Residues in pears, persimmons, cabbages, soya beans and rape seed were stable at –30°C for 2 years, with 71-98% of the initial residues remaining in the crop at the end of the study. In apples stored for 6 months at –20°C, 42.3-68.4% of the initial thiophanate-methyl and 50-128% of the carbendazim remained at the end of the study. In potatoes thiophanate-methyl residues were 58.4 and 67.1% of the initial residue after 176 days at –20°C.

The current definition of the residue is “carbendazim”. The Meeting noted however that about two-thirds of the residue in crops arising from the use of thiophanate-methyl was likely to be thiophanate-methyl (which would be determined as carbendazim), and concluded that the definition for compliance with MRLs should be *sum of thiophanate-methyl and carbendazim, expressed as carbendazim*. Since the ADI of thiophanate-methyl is nearly three times that of carbendazim, the same definition would avoid under-estimating the dietary risk and would therefore be appropriate for the estimation of STMRS.

Residues resulting from supervised trials

A number of residue trials were carried out on citrus fruit, apples, pears, apricots, cherries, peaches, plums, berries, grapes, strawberries, kiwifruit, persimmons, onions, Brussels sprouts, cucumbers and gherkins, mushrooms, tomatoes, egg plants, melons, peppers, lettuces, beans, peas, sugar beet, celery, barley, rice, wheat, rape and tea. As thiophanate-methyl residues are expressed as carbendazim, which can also occur from the use of benomyl or carbendazim, residue trials with thiophanate-methyl, benomyl and carbendazim were evaluated together and are described in Section 4.3.

RECOMMENDATIONS

The maximum residue levels estimated to arise from the use of thiophanate-methyl are covered by the MRLs recommended for carbendazim listed in the carbendazim monograph. The list also includes the STMRS estimated for benomyl, carbendazim and thiophanate-methyl.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: sum of thiophanate-methyl and carbendazim, expressed as carbendazim.

DIETARY RISK ASSESSMENT

The residues of benomyl, carbendazim and thiophanate-methyl are all expressed as carbendazim, which has the lowest ADI of the three compounds. A total of 34 STMRS were estimated for benomyl, 8 for carbendazim and 5 for thiophanate-methyl. If STMRS were estimated for more than one compound in a commodity, the highest STMR was used for the calculation. No MRLs were used.

International Estimated Daily Intakes of benomyl, carbendazim and thiophanate-methyl for the five GEMS/Food regional diets were in the range of 1 to 6% of the carbendazim ADI.

The Meeting concluded that the intake of residues of benomyl, carbendazim and/or thiophanate-methyl resulting from their uses that have been considered by the JMPR is unlikely to present a public health concern.

REFERENCES

- Alam, F. *et al.*, 1994. Nature of the Residues of ^{14}C -Thiophanate-methyl in Spray Treated Apples. Study No. Pan-Ag 93292, Pan-Agricultural Labs, Inc. Unpublished .
- Bieber, W. D. 1992. Leaching of Aged Thiophanate-methyl through Soil. Project No. NA 91 9820, NATEC Institut. Unpublished.
- Eldeib, M. *et al.*, 1993. Isolation, Characterization and Identification of Unknown Metabolites for Goats Liver Treated with ^{14}C -Thiophanate-methyl. Project No. 40875, ABC Laboratories. Unpublished .
- Fujino, A. *et al.*, 1973. The Balance and Metabolic Studies of Thiophanate-methyl in Animals. Study No. not assigned Nippon Soda Co. Unpublished.
- Gomyo, T. *et al.*, 1987. Analytical Method for Residues of Thiophanate-methyl in/on Crops and Soils by High Performance Liquid Chromatography Report No. RD-8243N Study No. EC-83, Nippon Soda Co. Unpublished.
- Gomyo T. *et al.*, 1988a. Analytical Method for Residues of Thiophanate-methyl and Its Degradation Product (MBC) in Crops by Derivative Spectrophotometry. Report No. RD-8819 Study No. EC-122, Nippon Soda Co. Unpublished.
- Gomyo, T. *et al.*, 1988b. Analytical Method for Thiophanate-methyl and Its Related Compounds in Animal Organs and Milk. Report No. RD-8847 Study No. EC-137, Nippon Soda Co. Unpublished.
- Gorbach S. and Thier W. 1989. Leaching of 2-Amino-benzimidazole, Possible Metabolite of Thiophanate-methyl. Hoechst Aktiengesellschaft. Unpublished .
- Hanlon, C.M. and Norris, K.J. 1992a. Metabolism of Fungicide ^{14}C -Thiophanate-methyl in Lactating Goats. Project No. 1210, Analytical Development Corporation and Colorado State University. Unpublished .
- Hanlon, C.M. and Norris, K.J. 1992b. Addendum 1 to Metabolism of Fungicide ^{14}C -Thiophanate-methyl in Lactating Goats. Project No. 1210, Analytical Development Corporation and Colorado State University. Unpublished .
- Iguchi, K. 1990. Thiophanate-methyl, Pure-Certification of Ingredient Limits. Report No. RD-9021, Study No. TR-896202, Nippon Soda Co. Ltd. Unpublished.
- Ishihara, K. 1990a. Thiophanate-methyl-Vapor Pressure. Report No. RD-9015, Study No. EC-224, Nippon Soda Co. Ltd. Unpublished.
- Ishihara, K. 1990b. Thiophanate-methyl-Dissociation Constant. Report No. RD-9016, Study No. EC-225, Nippon Soda Co. Ltd. Unpublished.
- Kosaka, S. *et al.*, 1970. Studies on the Biotransformation of Thiophanate-methyl in Animal and Plant (Part I). Nippon Soda Co. Unpublished.
- Kosaka S. *et al.*, 1972. Influences of Thiophanate-methyl to Soil Microorganisms and Fate of the Chemical in Soil. Nippon Soda Co. Unpublished.
- Kosaka, S. *et al.*, 1975. The Balance and Metabolic Study of Thiophanate-methyl on Rats. Nippon Soda Co. Unpublished.
- Martijn A. and Dobrat W, 1988. CIPAC Handbook volume D, p166-168.
- Melkebeke, T. 1997. Validation of an analytical method for residues of thiophanate-methyl in grapes. Project No. NOTOX 189045, NOTOX. Unpublished .
- Nakayama, K. 1990a. Thiophanate-methyl-Melting Point. Report No. RD-9026, Project No. TR-896305, Nippon Soda Co. Ltd. Unpublished.
- Nakayama, K. 1990b. Thiophanate-methyl-Stability. Report No. RD-9028, Project No. TR-896313, Nippon Soda Co. Ltd. Unpublished.
- Nakayama, K. 1992a. Thiophanate-methyl, Pure-Color. Report No. RD-9213, Project No. TR-2B9203, Nippon Soda Co. Ltd. Unpublished.
- Nakayama, K. 1992b. Thiophanate-methyl, Pure-Physical State. Report No. RD-9214, Project No. TR-2B9205, Nippon Soda Co. Ltd. Unpublished.
- Nakayama, K. 1992c. Thiophanate-methyl, Pure-Odor. Report No. RD-9215, Project No. TR-2B9204, Nippon Soda Co. Ltd. Unpublished.
- Nakayama, K. 1992d. Thiophanate-methyl, Pure-Melting Point. Report No. RD-9216, Project No. TR-2B9207, Nippon Soda Co. Ltd. Unpublished.
- Nakayama, K. 1992e. Thiophanate-methyl, Pure-Solubility. Report No. RD-9219, Project No. TR-2B9209, Nippon Soda Co. Ltd. Unpublished.
- Nakayama, K. 1992f. Thiophanate-methyl, Pure-Specific gravity. Report No. RD-9217, Project No. TR-2B9206, Nippon Soda Co. Ltd. Unpublished.

- Nakayama, K. 1993. Thiophanate-methyl-Storage Stability. Report No. RD-9332, Project No. 2G-9212R, Nippon Soda Co. Ltd. Unpublished.
- Nippon Soda. 1977a. Metabolism of ¹⁴C-Thiophanate-methyl in/on Green Bean Plants. Report No. RD-8969, Nippon Soda Co. Unpublished.
- Nippon Soda. 1977b. Metabolism of ¹⁴C-Thiophanate-methyl in/on Soybean Plants. Report No. RD-8970, Nippon Soda Co. Unpublished.
- Nippon Soda. 1981. Fate of Thiophanate-methyl in Soil. Report No. RD-8194N, Nippon Soda Co. Unpublished.
- Nippon Soda. 1982. Fate of Thiophanate-methyl in Water. Report No. RD-8205, Nippon Soda Co. Unpublished.
- Nippon Soda. 1984a. Biodegradation of Thiophanate-methyl in Soil. Report No. RD-8498N, Nippon Soda Co. Unpublished.
- Nippon Soda. 1984b. Adsorption and Desorption of Thiophanate-methyl in Three Different Soils. Report No. RD-8499, Nippon Soda Co. Unpublished.
- Nippon Soda. 1984c. Mobility of Thiophanate-methyl on the Soil (Soil TLC). Report No. RD-8497, Nippon Soda Co. Unpublished.
- Noguchi, T. *et al.*, 1971. Studies on the Biotransformation of Thiophanate-methyl in Animal, Plant and Soil (Parts II and III). Nippon Soda Co. Unpublished.
- Nomura, O. and Nakashima, N. 1987. Thiophanate-methyl-Water Solubility. • @Report No. **RD-8775**, Study No. EC-107, Nippon Soda Co. Ltd. Unpublished.
- Ono, S. 1973. Analytical Method for Residues of Thiophanate-methyl and 2-Methyl benzimidazole carbamate in Crops by UV Spectrometry. Nippon Soda Co. Unpublished.
- Ritter, A. 1988 Degradation of Carbendazim (HOE 017411) in Two Aerobic Aquatic Systems. Project No. 088132, RCC. Unpublished .
- Shiotani, H. 1992a. Thiophanate-methyl, Pure-Octanol/Water Partition Coefficient. Report No. RD-9212, Study No. EC-374, Nippon Soda Co. Ltd. Unpublished.
- Shiotani H. 1992b. Thiophanate-methyl-Batch Equilibrium (Adsorption/Desorption on Soils). Report No. RD-9204, Study No. EC-362, Nippon Soda Co. Unpublished.
- Soeda Y. and Shiotani H. 1987a. Thiophanate-methyl-Photodegradation on Soil. Report No. RD-8702, Study No. EC-75, Nippon Soda Co. Unpublished.
- Soeda Y. and Shiotani H. 1987b. Thiophanate-methyl-Batch Equilibrium (Adsorption/Desorption). Report No. RD-8730, Study No. EC-89, Nippon Soda Co. Unpublished.
- Soeda Y. and Shiotani H. 1987c. Thiophanate-methyl-Soil Column Leaching. Report No. RD-8731, Study No. EC-90, Nippon Soda Co. Unpublished.
- Soeda Y. and Shiotani H. 1987d. Thiophanate-methyl-Photodegradation in Water. Report No. RD-8701, Study No. EC-74, Nippon Soda Co. Unpublished.
- Soeda, Y. and Nomura, O. 1986 Thiophanate-methyl-Hydrolysis. Report No. RD-8679, Study No. EC-67, Nippon Soda Co. Ltd. Unpublished .
- Tanoue, T. 1992a. Thiophanate-methyl – Metabolism in Rats. Report No. RD-9131, Project No. EC-338, Nippon Soda Co. Unpublished .
- Tanoue, T. 1992b. Thiophanate-methyl – Metabolism in Rats Supplemental Report to NISSO EC-338 (MRID#42474802). Report No. RD-9131, Project No. EC-395, Nippon Soda Co. Unpublished.
- Watanabe, I. 1986. Thiophanate-methyl-Product Identity and Disclosure of Ingredients. report No. RD-8663, Study No. TL-6181, Nippon Soda Co. Ltd. Unpublished.
- Wright, M.C. 1992. ¹⁴C-Thiophanate-methyl Nature of the Residue in Laying Hens. Study No. BR-90-15, and XenoBiotec Laboratories. Unpublished.

