THIRAM (DITHIOCARBAMATES, 105)

EXPLANATION

Thiram was originally evaluated in 1965 (toxicology) and 1967 (toxicology and residues) and is included in the dithiocarbamate group of compounds.

Thiram is a protective fungicide used as a foliar treatment on fruits, vegetables and ornamentals to control *Botrytis* species, rust, scab and storage diseases, and as a seed treatment to control seedling blights and a number of fungi that cause "damping off" in seedlings. Thiram formulations are registered for use in many countries.

The compound was evaluated at the present Meeting within the CCPR periodic review programme.

IDENTITY

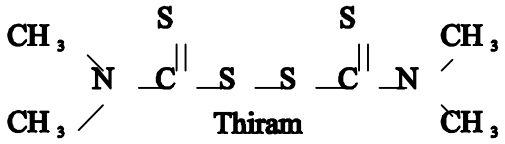
ISO common name: thiram

Chemical name

IUPAC: tetramethylthiuram disulfide
bis(dimethylthiocarbamoyl) disulfide

CA: tetramethylthioperoxydicarbonic diamide

CAS registry no: 137-26-8
CIPAC no: 24
EEC no: 205-286-2
Structural formula:



Molecular formula: $C_6H_{12}N_2S_4$

Molecular mass: 240.4

Physical and chemical properties

Pure active ingredient

Vapour pressure:	2.3 mPa at 25°C (by gas saturation method, Lemal 1985).
Melting point:	155-156°C.
Octanol/water partition coefficient:	54 ± 14. Log P_{OW} 1.73 (Lemal, 1983).
Solubility:	16.5 mg/l in water at 20° ± 1°C. 69.7 g/l in acetone at 25°C 205 g/l in chloroform at 25°C <10 g/l in ethanol at 25°C
Specific gravity:	1.36 g/cm^3 at 20°C.
Hydrolysis:	half-life <1 day at pH 9 half-life 6 days at pH 7 half-life 77 days at pH 5
Photolysis:	photodegradation half-life in water at pH 5 and 25°C is 8.8 hours

Lemal (1985) measured the vapour pressure of thiram by a gas saturation method. Nitrogen gas was passed through thiram coated on a support material with a very high surface area and maintained at 25°C, then through a cotton wool dust filter followed by traps containing methanol. The contents of the absorption traps were analysed by HPLC. The vapour pressure was calculated from the volume of nitrogen passed through the apparatus and the amount of thiram collected in the trap. In two runs the measured vapour pressure at 25°C was 2.4 and 2.2 mPa.

Lemal (1983) measured the octanol-water partition coefficient of thiram according to OECD Guideline 107 (OECD 1981). In a series of tests the values for log P_{OW} ranged from 1.568 to 1.851, with a median value of 1.782 and a mean of 1.734.

Technical material

Purity: 98.5%
Melting range: 135-146°C.

Formulations

80WG water dispersible granules containing 800 g/kg thiram.
80WP wettable powder containing 800 g/kg thiram.
75WG water dispersible granules containing 750 g/kg thiram.
65WP wettable powder containing 650 g/kg thiram.
50WG water dispersible granules containing 500 g/kg thiram.

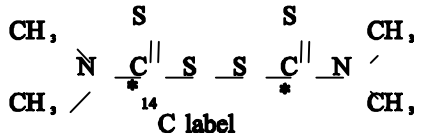
Combinations with other fungicides:
SILBOS DF water dispersible granules containing 640 g/kg thiram.
SILBOS T wettable powder containing 640 g/kg thiram.

DIRAC Express water dispersible granules containing 530 g/kg thiram.
RONILAN T wettable powder containing 530 g/kg thiram.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Information was made available to the Meeting on metabolism studies in rats, lactating goats and laying hens.



Gay *et al.* (1992) summarized the conclusions from a series of metabolism studies on rats with [*thiocarbonyl*-^{14}C]thiram. When rats were dosed orally with [^{14}C]thiram much of the ^{14}C (40-60%) was eliminated as volatiles in exhaled air, 25-35% was excreted in the urine and 2-5% in the faeces. After an interval of 96 hours 2-3% of the ^{14}C remained in the tissues. Polar metabolites and conjugates were identified in the urine.

Groups of rats (5 male + 5 female) were given single doses of [^{14}C]thiram at 125 mg/kg bw for the high-dose group and 1.9 mg/kg bw for the low-dose group (Gay, 1987). Excreta were collected for 7 days, when the animals were slaughtered for tissue collection. The total recovery of the administered ^{14}C was low, with 21 and 29% in the urine, 3.9 and 2.8% in the tissues and 4.1 and 2.4% in the tissues (recoveries in low-dose and high-dose groups respectively). The low total recovery suggested loss in exhaled air.

Exit gases were collected for 96 hours from metabolism cages containing groups of 3 rats given single oral doses of [^{14}C]thiram at 2.1-2.5 mg/kg bw (Norris, 1989). The majority of the volatile ^{14}C was produced in the first 24 hours, and its rate of production peaked between 2 and 4 hours after dosing. The total ^{14}C recovered in the expired air was 57-63% and in the urine 25-43% of the dose. The composition of the exhaled ^{14}C was not examined in this experiment, but the trapping system would have collected CO_2, CS_2 and COS.

Rats (6 male + 6 female) were dosed orally for 14 days with unlabelled thiram at 2 mg/kg bw then with [^{14}C]thiram at 2 mg/kg bw on day 15 (Nomeir and Markham, 1990). Expired air and excreta were collected for a further 96 hours and then the animals were slaughtered for tissue collection. Approximately 33-35% of the administered ^{14}C was eliminated in the urine, 2.6-5.3% in the faeces and 47-48% in the expired air. The nature of the volatile ^{14}C was not investigated in detail, but 75-85% of it was collected in a KOH trap suggesting CO_2 or COS, with the remainder collected in a reagent for CS_2.

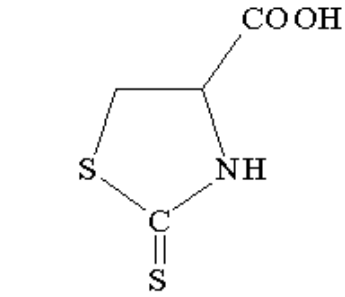
Norris (1991) identified by HPLC the metabolites in the urine of the rats from the single dose study of Gay (1987) and the multiple dose study of Nomeir and Markham (1990). There were no sex differences in the metabolism but the proportions of some of the metabolites depended on the dosage level and the time after dosing. Table 1 lists the proportions of the metabolites as percentages

of the ^{14}C in the urine samples.

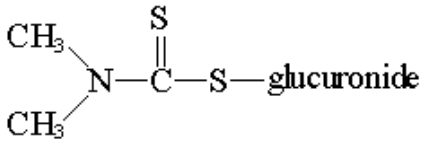
Table 1. Levels of metabolites (as % of total ^{14}C in the sample) in urine of rats given [^{14}C]thiram as single doses 125 mg/kg bw or multiple doses of 2 mg/kg bw/day for 15 days (Norris, 1991).

Metabolite	^{14}C, % of total in sample			
	Single dose		Multiple dose	
	Male, 0-24 hr sample	Female, 0-24 hr sample	Male, 4-8 hr sample	Female, 4-8 hr sample
U_1	13	7.8	1.4	1.7
Unidentified			0.3	0.4
U_2	5.6	8.7	12	11
Unidentified			5.1	4.0
U_3	37	42	40	36
U_4	3.4	2.4	1.6	0.6
U_5	34	36	36	42

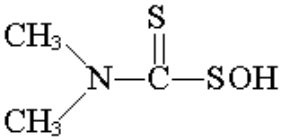
U_1 2-thioxo-4-thiazolidinecarboxylic acid



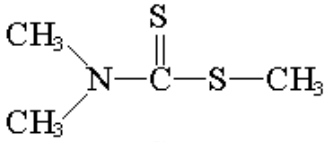
U_2 dimethyldithiocarbamoyl glucuronide



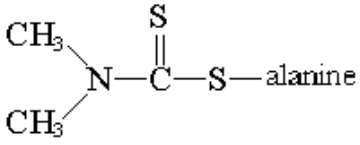
U_3 dimethyldithiocarbamoylsulfenic acid



U_4 methyl dimethyldithiocarbamate



U_5 dimethyldithiocarbamoylalanine



McManus (1991) fed rats with 50 ppm unlabelled thiram in the diet for 9 weeks and then gave them single oral doses of [^{14}C]thiram. The five urinary metabolites shown above were identified by HPLC and mass spectrometry.

Dalvi and Deoras (1986) showed that CS_2 was present in expired air from rats dosed with thiram by intraperitoneal injection.

Residues in the tissues, milk and excreta were measured in lactating goats (2 goats for the low dose (×1) and 1 for the high dose (×10), each animal weighing approx 40-50 kg) dosed orally twice daily for 4 consecutive days by capsule with [*thiocarbonyl*-^{14}C]thiram equivalent to 2.5 and 3.3 ppm (×1) and 23 ppm (×10) thiram in the feed (Norris, 1993b). The feed consumption was 2 kg /animal/day. The animals were milked twice daily; milk production was at least 800 ml per day. Respiration gases were collected from the low-dose animals for 10 hours after the final dose. Milk and excreta were collected throughout, and the goats were slaughtered 13 hours after the final dose for tissue collection. The ^{14}C was distributed as shown below.

Sample	^{14}C, % of (low) dose	
	Goat 1	Goat 2
Milk	1.3	1.0
Urine	9.2	9.6
Faeces	4.6	5.6
Tissues	7.2	7.5
Expired air	48	39
Total	70	63

A major part of the ^{14}C was eliminated in the respired gases, with smaller amounts in the urine and faeces. Approximately 60-70% of the dose was accounted for, but the value for the expired air is an estimate based on the 10-hour collection period. The value for the tissues includes the stomach and intestine contents, which accounted for almost half of the 7.2 and 7.5% reported.

The level of ^{14}C in the milk reached a plateau within 1.5 to 3 days of the first dose, and that in the urine by day 2 or 3, but the level in the faeces may still have been increasing at the completion of the study.

The ethanol+diethylamine traps (for CS_2 and COS) on the expired air collected 9.3 and 2.8% of the dose. Most of the ^{14}C in the expired air was present as CO_2.

The metabolism of thiram was quite extensive and much of the ^{14}C in the milk and tissues was present as very polar extractable material or bound residues. ^{14}C was present in glycogen, amino acids, proteins, lactose and saponifiable lipids. The only xenobiotic metabolites detected were CS_2 and COS. It is likely that thiram is rapidly converted to dimethyldithiocarbamate and then to dimethylamine and CS_2. CS_2 is converted to COS and carbonate. [^{14}C]carbonate then enters fat, protein and carbohydrates.

Table 2. Total ^{14}C (as thiram) in milk from goats dosed orally by capsule for 4 days with [^{14}C]thiram equivalent to 2.5 and 3.3 ppm (×1) and 23 ppm (×10) in the feed (Norris, 1993b).

Day	Total ^{14}C as thiram, mg/kg		
	x 1 dose		x 10 dose
0.5	0.024	0.027	0.27
1	0.036	0.040	0.33
1.5	0.051	0.054	0.47
2	0.044	0.047	0.36
2.5	0.056	0.064	0.40
3	0.048	0.060	0.45
3.5	0.045	0.070	0.48
4	0.050	0.074	0.48
% of dose in milk	*1.3*	*1.0*	*1.8*

Table 3. Distribution of radiolabel in tissues from goats dosed orally for 4 days by capsule with [^{14}C]thiram equivalent to 2.5 and 3.3 ppm (×1) and 23 ppm (×10) in the feed (Norris, 1993b).

Sample	Goats dosed at 2.5 and 3.3 ppm		Goat dosed at 23 ppm	
	^{14}C as % of total administered ^{14}C	^{14}C as thiram, mg/kg	^{14}C as % of total administered ^{14}C	^{14}C as thiram, mg/kg
Muscle	0.81 1.1	0.008 0.013	1.1	0.12
Kidneys	0.049 0.064	0.055 0.093	0.064	0.68
Liver	2.4 2.4	0.51 0.58	3.4	7.0
Blood	0.42 0.49	0.021 0.030	0.52	0.27
Fat	0.035 0.064	0.005 0.013	0.075	0.12

Residues in the tissues, eggs and excreta were measured in laying White Leghorn hens (groups of 4 for the low dose and 6 for the high dose, each bird weighing approx 1.5 kg) dosed orally by capsule once daily for 4 days with [*thiocarbonyl*-^{14}C]thiram equivalent to 0.6 and 6.0 ppm thiram in the feed (Norris, 1993a). The feed consumption was 80-110 g/bird/day. Eggs and excreta were collected throughout, and the birds were slaughtered 24 hours after the final dose for tissue collection.

Table 4 shows the distribution of the ^{14}C. The total recovery of the administered dose was only 61-68%. The likely reason is loss as volatiles. Liver was the tissue with the highest level of ^{14}C. A high percentage of the ^{14}C was extractable with chloroform or aqueous methanol, or was made soluble on enzymic or acid digestion.

The residues extracted by aqueous methanol from the liver were determined by reversed-phase HPLC and the resultant three peaks, comprising 4.7% of the total ^{14}C in the liver, were identified by mass spectrometry as dimethyldithiocarbamate ornithine, 2-thioxo-4-thiazolidinecarboxylic acid and dimethyldithiocarbamate glucuronide. Approximately 48% of the ^{14}C in the liver was identified as incorporated into natural products such as acids, amino acids, peptides and proteins. The ^{14}C residues in the other tissues were at quite low levels were characterized by ion-exchange chromatography also as natural products.

Thiram itself was identified in an aqueous methanolic extract of the excreta. Other

metabolites in the extract appeared to be conjugates of dimethyldithiocarbamate.

Table 4. Distribution of radiolabel in tissues, eggs and excreta from hens dosed orally for 4 days with [*thiocarbonyl*-^{14}C]thiram equivalent to 0.6 and 6.0 ppm thiram in the feed (Norris, 1993a).

Sample	Hens dosed at 0.6 ppm		Hens dosed at 6.0 ppm	
	^{14}C as % of total administered ^{14}C	^{14}C as thiram, mg/kg	^{14}C as % of total administered ^{14}C	^{14}C as thiram, mg/kg
Egg white, days 1-4	0.09	0.00-0.003	0.069	0.003-0.020
Egg yolk, days 1-4	0.075	0.00-0.006	0.058	0.001-0.044
Excreta, days 1-4	66	0.14-0.18	59	1.2-1.5
Muscle, breast	0.18	0.002	0.19	0.025
Muscle, thigh	0.17	0.003	0.21	0.036
Liver	1.2	0.11	1.0	0.89
Kidney	0.086	0.041	0.12	0.51
Fat	0.027	0.002	0.013	0.009
Heart	0.017	0.008	0.025	0.11
Blood	0.20	0.007	0.23	0.081
GI tract	0.49	0.007	0.44	0.053
Gizzard	0.035	0.004	0.040	0.041
Skin	0.049	0.003	0.052	0.029

The metabolic pathways are shown in Figure 1.

Plant metabolism

Information was made available to the Meeting on metabolism studies on apples and grapes when thiram was applied to the fruit and leaves, and on soya beans, cotton, wheat and sugar beet when it was used as a seed treatment.

Wyss-Benz (1994) applied [*thiocarbonyl*-^{14}C]thiram to the apples and leaves of two apple trees at a dose equivalent to 29.5 kg ai/ha (5 times the label rate) and harvested the fruit and leaves 0, 14, 28, 56 and 101 days after treatment. Surface radioactivity was removed for measurement by washing the fruit or leaves first with acetonitrile and then with acetonitrile/water (9+1). Apples, leaves, peel and pulp were subjected to an exhaustive extraction procedure with acetonitrile and water. Surface-washed apples from days 28 to 101 were homogenized and separated into juice and press cake for extraction and analysis.

The levels and distribution of ^{14}C on the surface and within the fruit and leaves are recorded in Table 5. Initially, as expected, most of the residue was on the fruit surface, but by day 14 only half of the remaining residue was on the surface. The ^{14}C incorporated into the fruit (not removed by acetonitrile washing) was quite persistent.

Figure 1. Metabolism of thiram by animals

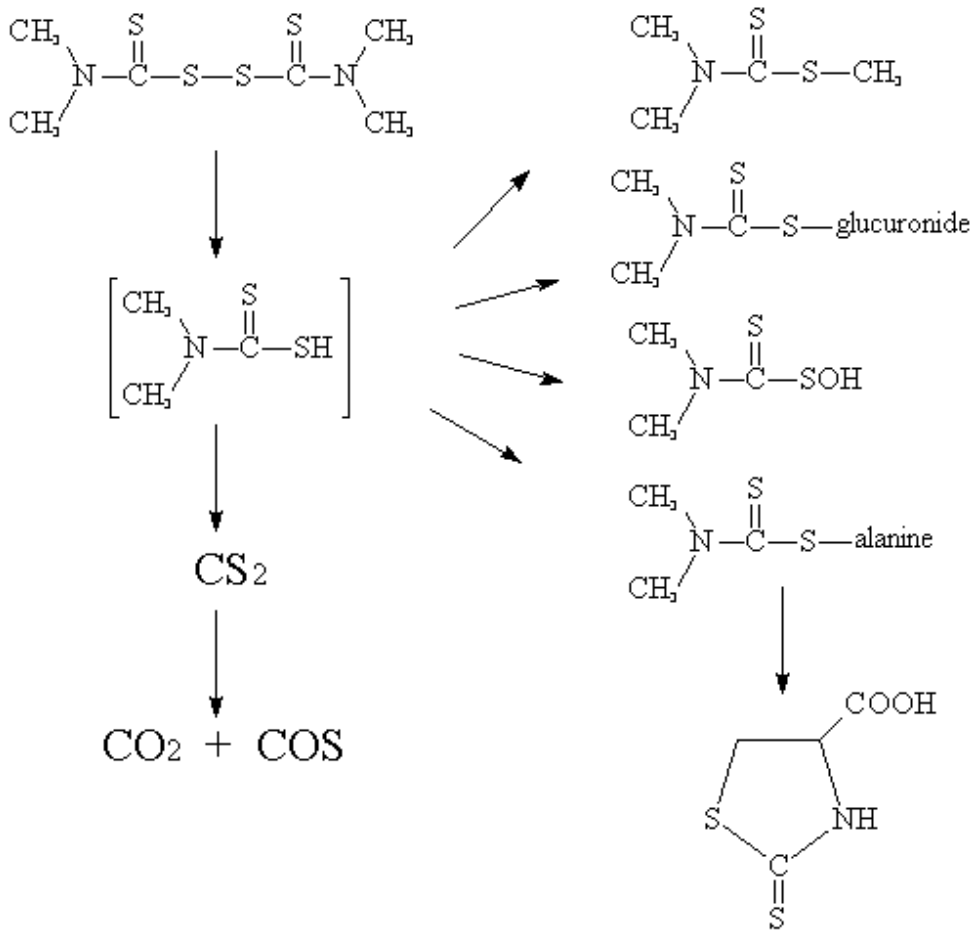


Table 5. Residues on the surface and within apples and leaves harvested after treating fruit and leaves of two apple trees with [^{14}C]thiram at a dose equivalent to 29.5 kg ai/ha (Wyss-Benz, 1994). Apple juice and press cake were prepared from acetonitrile-washed apples.

Sample	^{14}C in the apples or leaves expressed as mg thiram/kg and as % of total ^{14}C									
	0 days		14 days		28 days		56 days		101 days	
	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%
FRUIT										
MeCN washings of apples	173	94	10.9	51	0.92	13	0.58	8.0	0.038	0.9
Apple juice					2.1	29	3.2	44	1.98	47
Apple press cake					4.3	58	3.5	48	2.2	53
MeCN-washed apples	11.6	6.3	10.4	49						
Apples - TOTAL	185		21		7.3		7.3		4.2	
LEAVES										

Sample	^{14}C in the apples or leaves expressed as mg thiram/kg and as % of total ^{14}C									
	0 days		14 days		28 days		56 days		101 days	
	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%	^{14}C as thiram, mg/kg	%
MeCN washings of leaves	3094	82	380	57	125	30	23	8.5	4.9	3.7
MeCN-washed leaves	700	18	292	43	296	70	253	92	128	96
Leaves - TOTAL	3794		672		421		276		133	

The distribution of residues between peel and pulp in 5 apples harvested on day 101 was investigated further and is shown right. The major part of the ^{14}C residue was in the pulp.

Sample	^{14}C as thiram	of total residue
Washings	0.081 mg/kg of whole apples	2.7
Peel	5.2 mg/kg	38
Pulp	1.8 mg/kg	60

The residues in the extracts and acetonitrile washings were characterised by TLC and HPLC. A minor unidentified metabolite, more polar than thiram, was found in the surface washings (Table 6). Thiram was not found within the fruit except on day 0 by TLC at a level estimated to be less than 0.5 mg/kg. The main radioactive residue was very polar. The incorporated residue contained only a small percentage of the dimethyldithiocarbamoyl moiety (Table 7) as demonstrated by the release of small amounts of CS_2 under acid digestion. The ^{14}C was probably incorporated into natural plant products. The fruit and leaves showed different patterns of metabolites.

Table 6. Occurrence of thiram and unidentified metabolite RO in acetonitrile washings from fruit and leaves after treatment of apple trees with [^{14}C]thiram at a dose equivalent to 29.5 kg ai/ha (Wyss-Benz, 1994).

Fraction	^{14}C as thiram, mg/kg				
	0 days	14 days	28 days	56 days	101 days
FRUIT					
Thiram	164	9.5	0.78	<0.3	<0.3
Metabolite RO	7.1	*n*	*n*	*n*	*n*
Non-resolved ^{14}C	1.8	1.3	0.14	0.58	0.038
LEAVES					
Thiram	3008	367	103	*n*	*n*
Metabolite RO	86	13	21	*n*	*n*
Non-resolved ^{14}C	-	-	-	23	4.9

n: no detectable residues of ^{14}C (detection limit not stated)

Table 7. CS_2-liberating residues in acetonitrile-washed apples harvested at intervals from apple trees treated with [^{14}C]thiram at a dose equivalent to 29.5 kg ai/ha (Wyss-Benz, 1994).

Fraction	^{14}C as mg thiram equivalents per kg apple					
	0 days	14 days	28 days	56 days	101 days	101 days peel + pulp
Total residue, A	11.6	10.4	6.4	6.7	4.2	2.9
CS_2-liberating residue, B	0.104	0.214	0.23	0.22	0.12	0.058
B as % of total of A	0.9	2.1	3.5	3.3	2.8	2.0

Morgenroth and Wyss-Benz (1995) applied [*thiocarbonyl*-^{14}C]thiram four times to the grapes and leaves of two grape vines (variety Blauburgunder) at a dose equivalent to 3.2 kg ai/ha (maximum label rate). The growth stages for the 4 applications were 50% petal fall, closure of grapes, change of grape colour and 1 month before maturity. Fruit and leaves were harvested on days 0, 14 and 27 after the final treatment.

Surface radioactivity was removed for measurement by washing the fruit or leaves first with acetonitrile and then with acetonitrile/water (8+2). Surface-washed grapes were homogenized and separated into juice and press cake for extraction and analysis. Washed leaves and fruit components were subjected to an exhaustive extraction procedure with acetonitrile and water.

The total ^{14}C residues in the grapes and the acetonitrile surface washings are recorded in Table 8. The residues were quite persistent, with approximately one third of the total residues still on the fruit surface 27 days after the final application.

Two unidentified metabolites RO and R1, both more polar than thiram, were detected on the surface of the grapes by HPLC (Table 9), but the levels were substantially lower than those of thiram. Thiram itself constituted most of the surface residue on both fruit and leaves.

Approximately 5% of the residue incorporated within the fruit liberated CS_2 on acid digestion (Table 10), suggesting that it contained the dimethyldithiocarbamoyl moiety.

Most of the ^{14}C residue in the juice was shown by ultrafiltration to have a molecular weight below 500, and most could not be more positively identified. A glucose conjugate, 1-(*N*,*N*-dimethylthiocarbamoylthio)-1-deoxy-â-D-glucose hydrate, was identified at low levels in the juice from grapes harvested 27 days after the final application.

Much of the ^{14}C in the grapes was very polar or unextractable and had probably become incorporated into natural products.

Table 8. Residues on the surface and within grapes and leaves harvested after vines were treated 4 times with [^{14}C]thiram at a dose equivalent to 3.2 kg ai/ha (Morgenroth and Wyss-Benz, 1995). Grape juice and press cake were prepared from acetonitrile-washed grapes.

Sample	^{14}C in apples and leaves expressed as mg thiram/kg and as % of total ^{14}C or leaves.

	0 days		14 days		27 days	
	^{14}C as thiram mg/kg	%	^{14}C as thiram mg/kg	%	^{14}C as thiram mg/kg	%
FRUIT						
MeCN washings of grapes	8.6	61	3.5	38	3.4	35
Grape juice	3.1	22	3.6	39	4.2	44
Grape press cake	2.4	17	2.0	23	2.1	21
Grapes - TOTAL	14.1		9.1		9.7	
LEAVES						
MeCN washings of leaves	616	90	92	57	12	13
MeCN-washed leaves	69	10	69	43	81	87
Leaves - TOTAL	685		161		93	

Table 9. Thiram and unidentified metabolites RO and R1 in acetonitrile washings from fruit and leaves after treatment of grape vines with [^{14}C]thiram (Morgenroth and Wyss-Benz, 1995).

	^{14}C as thiram, mg/kg		
	0 days	14 days	27 days
FRUIT			
Thiram	8.5	3.2	3.2
Metabolite RO	0.20	0.24	<0.3
Metabolite R1	<0.3	0.082	<0.3
Non-resolved ^{14}C	-	-	0.21
LEAVES			
Thiram	608	85	9.8
Metabolite RO	8.1	6.9	<0.3
Non-resolved ^{14}C	-	-	2.1

Table 10. CS_2-liberating residues in acetonitrile-washed grapes harvested at intervals after vines were treated 4 times with [^{14}C]thiram at a dose equivalent to 3.2 kg ai/ha (Morgenroth and Wyss-Benz, 1995).

Fraction	^{14}C residues as mg thiram equivalents per kg grapes		
	0 days	14 days	27 days
Total residue	5.4	5.6	6.3
CS_2-liberating residue	0.24	0.33	0.35
CS_2 residue as % of total	4.5	5.8	5.6

Womer and Balba (1978, 1979) showed that wheat seedlings (5 weeks old) grown in a sandy loam soil from [*dimethylamine*-^{14}C]thiram-treated seed (334 mg thiram per kg seed) contained 0.25 mg/kg of ^{14}C expressed as thiram, of which 0.019 mg/kg was thiram. Some plants were grown to maturity; ^{14}C levels, as thiram, in the seed, chaff and straw were 0.05, 0.27 and 0.35 mg/kg respectively. The thiram level in the straw was <0.025 mg/kg.

After 4 weeks 62% of the recovered ^{14}C was in the soil (35% in plants) within 3 cm of the treated seeds, with a further 2.9% in the next zone 1.3 cm beyond the first. No ^{14}C was detectable beyond that zone. The pots (15 cm) had been watered with 50 ml water each day. The soil residues moved very little.

Harned and Tortora (1986) grew soya bean, cotton and wheat plants in a glasshouse and in the field from seed treated with [*thiocarbonyl*-^{14}C]thiram and measured the ^{14}C distribution in 30-day seedlings (Table 11) and mature plants (Table 12). The seed treatment rates (1×) were wheat 1.3 mg ai/g seed, cotton 1.4 mg ai/g seed, and soya beans 1.03 mg ai/kg seed. Some plants were also produced from seed treated at a fivefold rate. ^{14}C levels in the cotyledons and roots of the seedlings were higher than in the leaves and stems. In the mature plants the highest ^{14}C levels were in the roots and the lowest in the seeds. Autoradiography of the seedlings showed that the highest levels of ^{14}C were in the oldest parts of the plants.

Table 11. Distribution of ^{14}C in 30-day soya bean, cotton and wheat seedlings grown from [^{14}C]thiram-treated seed (Harned and Tortora, 1986).

Crop	Plant part	Total ^{14}C expressed as thiram, mg/kg	
		Indoor	Outdoor
Soya bean			
	leaf	0.50	0.29
	stem	1.5	0.085
	cotyledon	108	1.7
	root	8.5	2.7
Cotton			
	leaf	0.049	0.046
	stem	0.291	0.054
	cotyledon	2.6	2.5
	root	0.69	0.73
Wheat			
	leaf	1.1	0.47
	root	15	14

Table 12. Distribution of ^{14}C in mature soya bean, cotton and wheat plants grown from [^{14}C]thiram treated seed (Harned and Tortora, 1986).

Crop	Plant part	Total ^{14}C expressed as thiram, mg/kg dry weight of plant tissue			
		×1 rate		×5 rate	
		indoor	outdoor	indoor	outdoor
Soya bean					
	seed	0.019		0.15	
	pod	0.034		0.28	
	leaf	0.12		1.4	
	stem	0.29		3.2	
	root	0.87		8.0	
Cotton					
	seed	0.006		0.024	
	fibre	0.008		0.018	
	husk	0.11		0.14	
	leaf	0.035		0.094	
	stem	0.034		0.14	
	root	0.26		1.0	
Wheat					
	seed	0.078	0.005	0.51	0.036
	chaff	0.298	0.017	1.9	0.13
	leaf	0.822	0.025	4.1	0.14
	root		1.8		8.4

Nowakowski *et al.* (1986, 1987) used HPLC to separate and identify the thiram metabolites produced during the growing of soya bean, cotton and wheat seedlings in a glasshouse from seed treated at a fivefold rate as described by Harned and Tortora (1986). They showed that metabolites produced from [^{14}C]thiram in soya bean tissue cultures were similar to those obtained from plant extracts. Tissue culture was used to generate sufficient quantities for identification. They identified dimethyldithiocarbamoyl glycoside and dimethylthiocarbamoyl glycoside as the major metabolites in all the seedlings.

The two glycosides accounted for 70% of the ^{14}C in cotton seedlings and 50% in soya bean and wheat seedlings. A small amount of a cysteine conjugate was also identified. When aqueous wheat extract was treated with 50% sulphuric acid at 65°C only 3.4% of the ^{14}C was liberated as CS_2, suggesting that if any remaining metabolites contained the dithiocarbamoyl moiety they were largely unextractable.

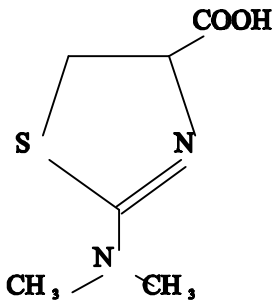
Liu and Robinson (1994a) applied [^{14}C]thiram at 0.062 g ai/ 100 g seed (the label rate) and 3.1 g ai/ 100 g seed (50×label rate) to soya bean seeds which were germinated and grown in a glasshouse. Forage, pod, seed and straw samples were taken for measurement of ^{14}C levels and identification of metabolites. The ^{14}C was relatively evenly distributed in the various plant parts (Table 13). There was some evidence that $^{14}CO_2$ had been evolved since ^{14}C was detected in control plants growing nearby.

Table 13. Distribution of ^{14}C in soya bean plants grown from [^{14}C]thiram-treated seed (Liu and

Robinson, 1994a).

Sample	^{14}C as thiram, mg/kg	
	Treatment: 1×label	Treatment: 50×label
Forage, 29 days after sowing	0.61	9.3
Forage, 69 days after sowing	0.13	4.2
Straw	0.33	9.4
Pods	0.22	6.9
Seeds	0.14	4.4

Extensive efforts were made to identify the ^{14}C compounds in the soya bean forage, straw and pods. Much of the ^{14}C had been incorporated into endogenous natural products such as sugars, fatty acids and citric acid, but the dimethyldithiocarbamoyl moiety of thiram had conjugated with amino acids and sugars. Thiram itself was not detected. The main metabolite identified was 2-dimethylamino-4-thiazolinecarboxylic acid which, in the case of the 50-fold treatment, constituted 22% of the ^{14}C in the 69-day forage sample, 18% of that in the straw, 41% in the pod and 11% in the seed.



2-(N,N-dimethylamino)-4-thiazoline carboxylic acid

Direct treatment of homogenized tissue with acidic stannous chloride released some $^{14}CS_2$, which showed that compounds or conjugates containing the dithiocarbamoyl moiety remained (Table 14).

Table 14. Nature of the volatile ^{14}C released by reacting acidic stannous chloride with homogenised tissue from soya bean plants grown in a glasshouse from seed treated with [^{14}C]thiram at 3.1 g ai/ 100 g seed (Liu and Robinson, 1994a).

Sample	Volatile ^{14}C as % of total ^{14}C in sample			
	CS_2	COS	CO_2	CO
Forage, 69 days	8.9	*n*	15.1	1.3
Straw	9.3	*n*	23.8	1.3
Pod	3.2	1.7	9.8	*n*
Seed	3.2	*n*	3.5	6.5

n: no detectable residue.

In a metabolism study [^{14}C]thiram at 0.1, 0.5 and 1.3 g ai/ 100 g seed (1, 5 and 13 times the label rate) was applied to wheat seed which was germinated and grown in a glasshouse (Johnson, 1994a; Liu and Robinson, 1994b). Forage, seed, chaff and straw samples were taken for measurement of ^{14}C levels and identification of metabolites. The ^{14}C was fairly evenly distributed among the various plant parts (Table 15). As in the soya bean study, ^{14}C was detected in control plants growing nearby suggesting that $^{14}CO_2$ had been produced.

Table 15. Distribution of ^{14}C in wheat plants grown from [^{14}C]thiram-treated seed (Liu and Robinson, 1994b).

Sample	^{14}C as thiram, mg/kg	
	Treatment: 1×label	Treatment: 13×label
Forage, 32 days after sowing	1.9	
Forage, 60 days after sowing	0.47	
Straw, 95 days	1.6	6.6 3.2[1]
Chaff, 95 days	0.32	4.9
Seed, 95 days	0.16	1.1

[1]Straw from a 5 x label rate treatment

The metabolism of thiram was similar in wheat and in soya beans. Again, much of the ^{14}C was incorporated into endogenous natural products such as sugars, fatty acids and citric acid, but there was some conjunction of the *N*,*N*-dimethyldithiocarbamoyl moiety with amino acids and sugars. Thiram itself was not detected. The main metabolite identified was 2-dimethylamino-4-thiazolinecarboxylic acid which, in the case of the 13-fold treatment, constituted 33% of the ^{14}C in the chaff, 29% in the straw, and 4% in the seed.

Direct treatment of homogenized tissue with acidic stannous chloride released some $^{14}CS_2$, which showed that compounds or conjugates containing the dithiocarbamoyl moiety remained (Table 16).

Table 16. Nature of the volatile ^{14}C released by reacting acidic stannous chloride with homogenized tissue from wheat plants grown in a glasshouse from seed treated with [^{14}C]thiram at 0.1 (×1), 0.5 (×5) or 1.3 (×13) g ai/100 g seed (Liu and Robinson, 1994b).

Sample	Total ^{14}C as thiram, mg/kg	Volatile ^{14}C as % of total ^{14}C in sample			
		CS_2	COS	CO_2	CO
Forage (X1), 60 days	0.47	*n*	*n*	*n*	*n*
Straw (×13)	6.6	2.3	*n*	21	*n*
Straw (×5)	3.2	6.8	*n*	8.4	4.7
Chaff (×13)	4.9	2.5	*n*	12	*n*
Wheat grain (×13)	1.1	8.9	*n*	8.7	*n*

n: no detectable residue.

In a metabolism study [^{14}C]thiram at 0.24 and 12 g ai/ 100 g seed (one and 50 times the label rate) was applied to sugar beet seed which was germinated and grown in a glasshouse (Johnson, 1994b; Liu and Robinson, 1994c). Samples of tops and roots were taken for measurement of ^{14}C levels and identification of metabolites. The ^{14}C levels were generally very low (Table 17). As in the soya bean and wheat studies, ^{14}C was detected in control plants growing nearby suggesting that $^{14}CO_2$ had been produced.

Table 17. Distribution of ^{14}C in sugar beet plants grown from [^{14}C]thiram-treated seed (Liu and Robinson, 1994c).

Sample	^{14}C as thiram, mg/kg	
	Treatment: 1×label	Treatment: 50×label
Immature tops, 100 days	0.006	0.15
Mature tops	0.012	0.096
Mature roots	0.008	0.32

Levels of metabolites were generally low. Incorporation of ^{14}C into sucrose, amino acids (such as glutamic acid) and acids of the citric acid cycle was established.

Direct treatment of homogenized tissue with acidic stannous chloride released some $^{14}CS_2$ from roots produced from seed treated at the 50-fold rate but levels of ^{14}C were generally too low for quantitative analysis (Table 18).

Table 18. Nature of the volatile ^{14}C released by reacting acidic stannous chloride with homogenized tissue from sugar beet plants grown in a glasshouse from seed treated with [^{14}C]thiram at 12 g ai/ 100 g seed (50-fold rate) Liu and Robinson (1994c).

Sample	Total ^{14}C as thiram, mg/kg	Volatile ^{14}C as % of total ^{14}C in sample			
		CS_2	COS	CO_2	CO
Roots	0.32	3.2	*n*	5.4	3.8
Immature tops	0.15	level too low for quantitative analysis			
Mature tops	0.096	level too low for quantitative analysis			

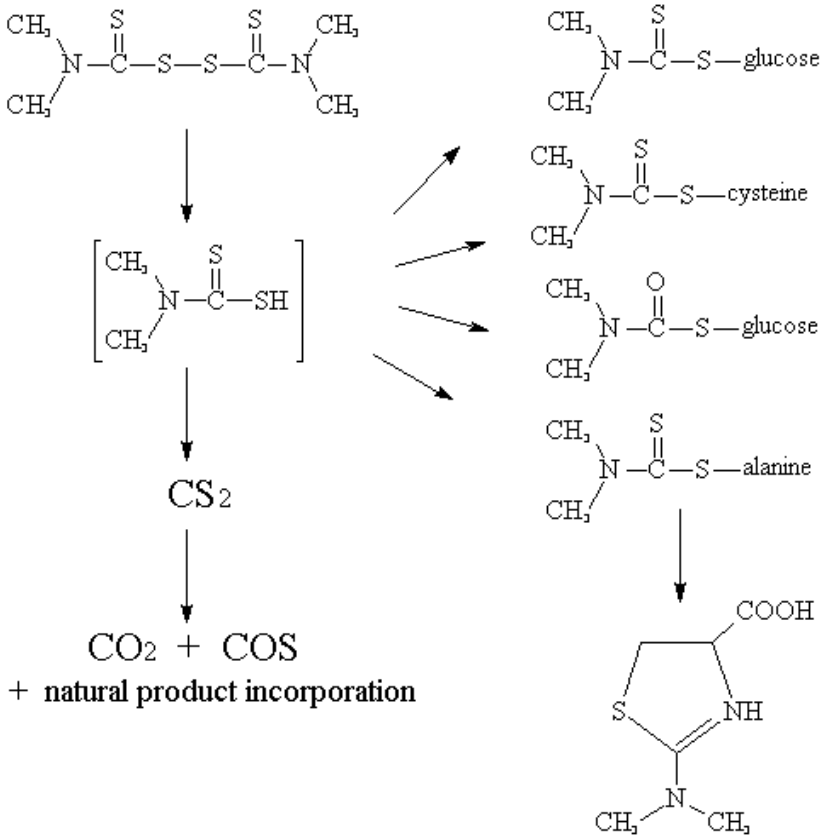
n: no detectable residue.

The metabolic pathways of thiram in plants are shown in Figure 2.

Environmental fate in soil

In a laboratory experiment [*thiocarbonyl*-^{14}C]thiram was incubated in a New York sandy loam soil in the dark at 20°C and 75% of field moisture capacity under aerobic conditions for 205 days (Morgenroth and Müller-Kallert, 1995). The initial thiram level in the soil was 20.3 mg ai/kg, chosen to represent a field application rate of 18 kg ai/ha. The system was continuously supplied with humidified air; evolved CO_2 was trapped. The characteristics of the soil were pH 6.7, organic carbon 2.4%, cation exchange capacity 14.4 meq/100g dry soil, clay 14.8%, silt 29.6%, sand 55.6%.

Figure 2. Metabolism of thiram by plants.



The levels of thiram and identified and unidentified degradation products in the soil at various sampling times are shown in Table 19. The disappearance of the parent compound was not first-order, but the half-life in the initial period was about 2 days, with 85% disappearance in 7 days and 97% in 14 days. The identity of the major product M6.5 was shown by GC-MS and HPLC-MS to be dimethyl carbamothioperoxoate. It reached its maximum level (1.8 mg/kg) at 4 days and exceeded the level of the parent compound after 42 days, but 99.8% of the parent had disappeared at this time.

Mineralisation of the residue was rapid with 9% of the applied ^{14}C evolved as $^{14}CO_2$ in 2 days and 50% within 21 days (Table 20). Bound or non-extractable residues reached a maximum of 48% of the applied dose at day 14 and thereafter declined slowly to 31% at day 205. The production of $^{14}CO_2$ was much slower when most of the residue was in the bound form. Fractionation of the soil organic matter showed that much of the unextractable ^{14}C was bound to the humin and humic acid fractions.

Table 19. Thiram and degradation products in a sandy loam soil during aerobic incubation in the dark for 205 days after an initial dosing with [^{14}C]thiram at 20.3 mg ai/kg (Morgenroth and Müller-Kallert, 1995).

Days	Thiram	Metabolite, mg/kg

		M6.1	M6.2	M6.3	M6.4	M6.5	M6.6	M6.7	M6.8	TMTU	TMU	TMTM
0	21	*n*	*n*	*n*	*n*	*n*	*n*	*n*	*n*	*n*	*n*	*n*
1	13.4	*n*	0.036	0.032	0.13	0.45	0.068	0.021	0.039	*n*	*n*	*n*
2	9.5	*n*	0.14	0.035	0.63	1.0	0.051	0.031	*n*	*n*	*n*	*n*
4	6.1	*n*	*n*	*n*	*n*	1.8	0.072	*n*	*n*	*n*	*n*	*n*
7	3.1	*n*	0.028	0.023	0.12	0.85	0.31	0.011	*n*	*n*	*n*	*n*
14	0.60	*n*	0.074	0.015	*n*	0.32	0.082	*n*	0.012	0.069	*n*	*n*
21	0.34	*n*	0.045	*n*	0.017	0.17	0.11	*n*	0.022	*n*	*n*	*n*
42	0.048	*n*	0.063	0.025	0.010	0.083	0.10	0.017	*n*	0.005	*n*	0.006
84	0.017	0.067	0.048	*n*	*n*	0.038	0.048	*n*	*n*	0.005	*n*	*n*
128	0.007	0.039	0.054	*n*	*n*	0.031	0.032	0.005	*n*	0.002	*n*	*n*
205	0.006	0.022	0.043	*n*	*n*	0.022	0.023	0.001	*n*	0.001	0.001	0.001

n: not detected
TMTM: tetramethylthiuram monosulphide
TMU: 1,1,3,3-tetramethylurea
TMTU: 1,1,3,3-tetramethylthiourea.

Table 20. Mineralisation of thiram in a sandy loam soil during aerobic incubation in the dark for 205 days after an initial dosing with [^{14}C]thiram at 20.3 mg ai/kg, as indicated by evolution of $^{14}CO_2$. (Morgenroth and Müller-Kallert, 1995).

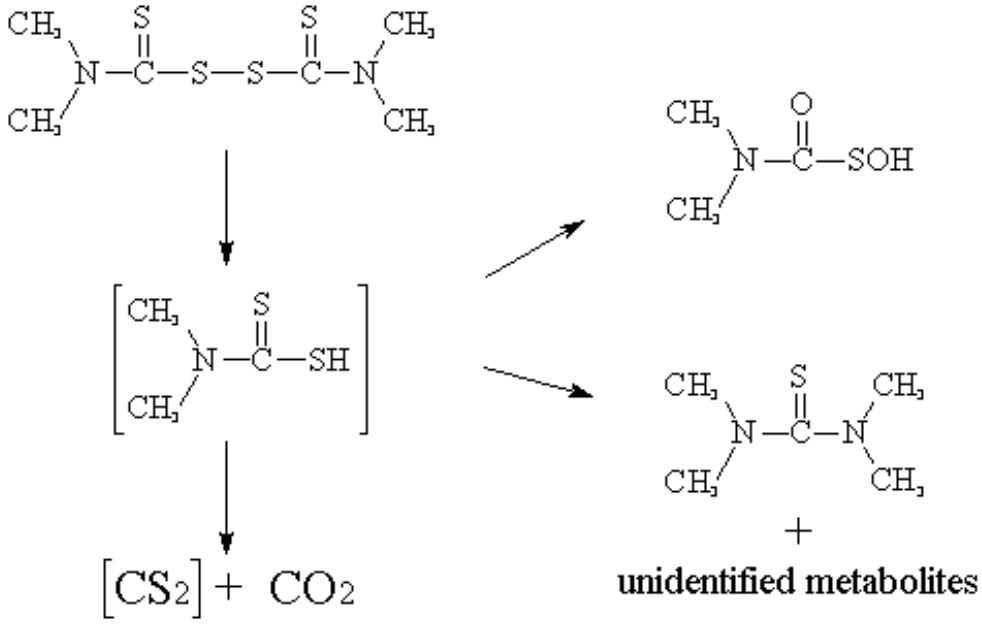
$^{14}CO_2$ as % of initial [^{14}C]thiram after days of incubation									
1	2	4	7	14	21	42	84	128	205
3.7	9.0	21.8	35.6	46.1	54.7	59.6	65.9	67.7	74.9

Burri (1995) applied [^{14}C]thiram to a thin layer of the same sandy loam soil at a rate equivalent to 18 kg ai/ha and exposed it to an artificial light source with a spectrum simulating sunlight for 21 days with a 12 hour light-dark cycle at 20°C. In both control and irradiated samples the percentage of extractable ^{14}C decreased with time, while the non-extractable ^{14}C reached 30% after 3 days and then remained reasonably constant.

The half-life for the disappearance of thiram from the control in the dark was 15.9 days and in the soil under artificial light 3.7 days. The total volatile ^{14}C produced by the soil under artificial light after 21 days amounted to 57% of the applied ^{14}C (37% as CO_2 and 20% probably as CS_2) while 11% was evolved by the control. The volatile ^{14}C compound captured in the trap matched CS_2 in an HPLC system, but was not further identified. No other products of photolysis were positively identified but they were generally minor or transient.

Morgenroth (1995) measured the adsorption and desorption properties of [^{14}C]thiram on four different soils, a sandy loam, loamy sand, silt loam and loam. Adsorption and desorption tests were carried out in 0.01M $CaCl_2$ at 20°C. Adsorption reached equilibrium after about 4 hours with high proportions of thiram adsorbed: it was not directly related to the organic carbon contents of the soils. Only small proportions of thiram could be desorbed from the soils. Thiram was judged to be slightly mobile to immobile in the soils tested.

Figure 3. Degradation of thiram in soil



Environmental fate in water/sediment systems

In a laboratory experiment [*thiocarbonyl*-^{14}C]thiram was incubated in aquatic systems of river water and sediment (Rhine) and pond water and sediment (Judenweiher) in the dark at 20°C under aerobic conditions for 101 days (Wyss-Benz, 1992). The system was continuously supplied with humidified air; evolved volatile compounds were trapped. The initial thiram levels in the water were 1.2 - 1.4 mg ai/l in the two experimental runs. The pH of the waters was 7.5-8.0. The organic carbon content of the river sediment, a loamy sand, was 0.62% and the pond sediment, a loam, 3.2%.

The decrease of thiram and the appearance of two identified products are shown in Table 21. The initial half-life of thiram was about 2 days with more than 90% disappearance within 7 days. Thiram itself was not detectable in solvent extracts of the sediments. Methyl dimethyldithiocarbamate (DMDTC-Me), CS_2 and CO_2 were identified as products. A number of other compounds were detected by HPLC, but were generally at low levels and could not be identified with any of the reference materials.

About half of the total ^{14}C disappeared from the water in 14 days. The ^{14}C in the sediments increased to a maximum of about 30% of that applied by days 14-30 and thereafter declined to 16-24% by day 101.

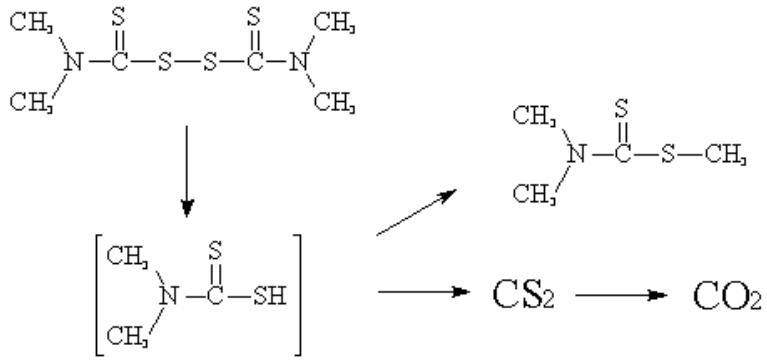
Table 21. Thiram and identified degradation products in the water phase of aquatic systems incubated with [^{14}C]thiram at 20°C in the dark under aerobic conditions (Wyss-Benz, 1992).

Days	^{14}C as thiram, mg/l					
	River			Pond		
	Thiram	DMDTC-Me	CS_2	Thiram	DMDTC-Me	CS_2
0	1.3	*n*	*n*	1.3	*n*	*n*
0.25	1.2	*n*	*n*	1.2	*n*	*n*
1	0.73	0.021	0.063	0.90	0.043	0.046
2	0.73	0.022	0.022	0.75	0.014	0.015
4	0.32	0.076	0.073	0.30	0.066	0.086
7	0.096	0.058	0.049	0.030	0.045	0.10
14	*n*	0.059	*n*	*n*	0.044	*n*
30	*n*	0.034	*n*	*n*	0.025	*n*
57	*n*	*n*	*n*	*n*	*n*	*n*
101	*n*	*n*	*n*	*n*	*n*	*n*

n: no detectable residue
DMDTC-Me: methyl dimethyldithiocarbamate

The degradation pathways of thiram in water/sedimant systems are shown in Figure 4.

Figure 4. Degradation of thiram in aerobic water/sediment systems.



METHODS OF RESIDUE ANALYSIS

Analytical methods

Thier (1979) described a regulatory analytical method for dithiocarbamate residues based on the generation of CS_2 by heating with stannous chloride and hydrochloric acid. The evolved CS_2 is collected in an ethanolic solution of cupric acetate and diethanolamine to form a colour which is measured with a spectrophotometer. Sample blank problems occur with some crops. With a 500 g sample the lower limit for reliable determination is generally around 0.1 mg/kg.

Dithiocarbamate residues can be measured by GLC head-space determination of the CS_2 evolved by treating the sample with stannous chloride and hydrochloric acid (Netherlands Ministry of Welfare, Health and Cultural Affairs, 1988). The method has been tested on many fruits and vegetables. In thiram trials on apples the limit of determination was 0.05-0.1 mg/kg (as CS_2) and recoveries were 85-121%.

Roland *et al.* (1992h) described an HPLC method for thiram residues in crops that measures thiram as the intact molecule and distinguishes it from other dithiocarbamate compounds. The residue is extracted from crop samples with dichloromethane or acetonitrile, and after clean-up on a C18 microcolumn with methanol/water and acetonitrile/water as eluting solvents, it is analysed on a C18 reversed-phase HPLC column with UV detection at 280 nm. Quantitative recoveries were achieved from strawberries and apples down to 0.2 mg/kg.

Weber (1993) validated the method on grapes and wine. Quantitative recoveries were achieved on grape samples fortified with thiram down to 0.1 mg/kg. To improve recoveries whole grapes were extracted in the frozen state and wine was ice-cooled before extraction. Low recoveries occurred in wine fortified at 0.1 mg/kg because thiram was being degraded. Weber (1994b) also validated the method for wet and dry grape pomace and must.

The results are summarized in Table 22. The LOD for the method with the substrates tested was 0.1 mg/kg.

Table 22. Analytical recoveries of thiram from fortified samples by the method of Roland *et al.* (Weber, 1993, 1994b).

Commodity	Fortification level, mg/kg	Recovery, %
Grapes	0.1 10	86-110, n=4 92-110, n=4
Wine	0.1 10	54-69, n=4 95-99, n=4
Wet pomace	0.1 0.2 0.5 1.0	110 95 108 120
Dry pomace	0.1 0.2 0.5 1.0	90 75 72 74
Must	0.1 0.2 0.5 1.0	80 90 88 100

Gatti (1992a) described a method very similar to that of Roland *et al.* (1992), and (1992b) a GLC head-space (CS_2 evolution) method which he tested on peaches, pears, apples, plums and cherries. Recoveries from spiked samples fell in the range 88-99% by HPLC and 93-105% by GLC, with each fruit tested once at 0.1 mg/kg and once at 4.0 mg/kg.

Stability of pesticide residues in stored analytical samples

Thiram residues were shown to be stable on frozen whole plums stored in closed plastic boxes at a freezer temperature below -20°C for 500 days (Roland, 1993). At each sampling the plums were analysed by a CS_2 evolution method and on three occasions by an HPLC method specific for thiram. The methods were in good agreement. The results are summarized in Table 23.

The method of sample preparation was shown to influence the analytical result. If plums were macerated in a blender thiram was decomposed by exposure to the macerate. Roland (1993) recommended that fruit for residue analysis should be stored whole, subjected to a minimum of cutting (into halves and quarters) while still frozen, and analysed immediately.

Table 23. Stability of thiram in whole plums in closed plastic boxes stored below -20°C (Roland, 1993).

Storage period, days	Thiram, mg/kg	
	By CS_2	By HPLC
0	7.9	7.1
35	8.3	7.9
90	8.8	-
183	7.6	-
363	6.9	-
500	8.1	7.8

The frozen storage stability of thiram was tested by fortifying apple juice and pomace at 1 mg/kg in extraction vials and storing them in a freezer at -20 ± 5°C (Leppert, 1995). Thiram was determined by a CS_2 evolution method. The residues were stable for the periods tested, up to 49 weeks (Table 24).

Table 24. Frozen storage stability of thiram residues in processed apple fractions fortified at 1 mg/kg and stored at -20 ± 5°C (Leppert, 1995).

Storage period	% thiram remaining after storage		
	Apple juice	Wet pomace	Dry pomace
0 day	90, 90	84, 89	95, 88
2 weeks	94, 90	84, 118	104, 83
35 weeks	94, 84		
49 weeks		80, 72	80, 82

Residue definition

The Meeting considered the definition of thiram residues in terms of the crop metabolism studies, the supervised trials where residues had been determined by both a CS_2 evolution method and an HPLC method, and the needs of enforcement agencies.

The metabolism studies suggest that thiram is the major part of the CS_2-evolving residue, particularly when the residue is reasonably fresh and at the higher levels. Analyses of samples in supervised trials by the HPLC and CS_2 methods are usually in good agreement, which also suggests that thiram itself is the main residue.

Thiram is different from the other dithiocarbamates because it can be determined by a specific method that measures the intact molecule and MRLs could be established for thiram separately. It would, however, be confusing for analysts and enforcement agencies interpreting analytical data for one compound to appear under two different residue definitions.

The 1995 JMPR (Report, Section 2.8.1), in explaining the current basis for the definition of residues in general, stated "Preferably no compound, metabolite or analyte should appear in more than one residue definition."

The Meeting agreed that thiram should be included in the definition of dithiocarbamate residues:

The MRLs refer to total dithiocarbamates, determined as CS_2 evolved during acid digestion and expressed as mg CS_2/kg.

For dietary intake estimations the supervised trials median residue (STMR) will be expressed as thiram because estimated intakes need to be in terms of thiram itself for comparison with its ADI. For acute intake estimations a residue, such as an MRL, expressed in terms of CS_2 must be multiplied by a molecular weight correction factor of 1.58 for comparison with its ADI.

USE PATTERN

Thiram is a protective fungicide and is used as a seed treatment to control a number of fungi that cause "damping off" in seedlings and to control seedling blights. It is also widely used as a foliar treatment on fruits, vegetables and ornamentals to control *Botrytis* species, rust, scab and storage diseases.

Thiram formulations are registered for use in many countries. The Meeting was provided with information on registered uses on fruits, vegetables and other crops (Table 25).

Table 25. Registered uses of thiram.

Crop	Country	Form	Application				PHI, days
			Method	Max rate per applic.	Spray conc. kg ai/hl	No.	
Alfalfa	Germany	DS	seed treat	0.26[1]		1	
Alfalfa	Netherlands	WG	seed treat	0.20		1	
Apple	Australia	WG WP	foliar spray		0.12		7
Apple	Canada	WP	foliar spray		0.075-0.17		1
Apple	Netherlands	WP WG	foliar	1.6-2.4	0.16		Note[2]
Apple	Netherlands	WP WG	foliar	2.0-3.0	0.20		Note[3]
Apple	Netherlands	WP WG	foliar	1.2-1.5	0.10	3 Note[4]	7
Apple	UK	WG	foliar	2.4	0.16		7
Artichoke	Italy	WG	spray		0.13-0.24	1-2	10
Asparagus	Belgium	WG	soaking		1.6	1	root
Asparagus	Italy	WG	spray		0.13-0.24	1-2	10
Asparagus	Netherlands	WP WG	foliar	1.6		5	
Asparagus	Netherlands	WG	spray	1.6	0.16	1	
Asparagus	Netherlands	WP WG	drench		0.16	1	Applied at planting
Barley	Poland	FS	seed treat	0.06-0.07			
Barley	Poland	WS	seed treat	0.075-0.11			
Barley	UK	SC	seed treat	0.06			
Bean	Denmark	SC	seed treat	0.21		1	
Bean	France	WG	spray			1-3	
Bean	Germany	DS FS	seed treat	0.20		1	
Bean	Netherlands	WG	seed treat	0.15		1	
Bean	Spain	WG WP	spray		0.08-0.19	1-3	15
Bean, broad	Poland	FS	seed treat	0.08		1	
Bean, bush	Poland	FS	seed treat	0.08		1	

[1] Rate refers to kg ai/ha for foliar treatments; kg ai/100 kg seed for seed treatments

[2] Applied during and just after blossom

[3] Applied before blossom

[4] Later applications

Crop	Country	Form	Application				PHI, days
			Method	Max rate per applic.	Spray conc. kg ai/hl	No.	
Bean, field	UK	SC	seed treat	0.06			
Beet	Denmark	SC	seed treat	0.53		1	
Beet	France	WG	seed treat	0.48		1	
Beet	Germany	WP	seed treat	0.39		1	
Beet, red	Poland	FS	seed treat	0.08		1	
Beetroot	Netherlands	WP	seed treat	0.40			
Beetroot	UK	SC	seed treat	0.30			
Bilberry	UK	WG	foliar		0.16		7
Blackberry	Belgium	WG	spray		0.2	1-2	14
Blackberry	Netherlands	WG	spray		0.20	1-2	14
Blackberry	Netherlands	WP WG	foliar	2.0, 2.4	0.20	10	28
Blackberry	UK	WG	foliar		0.16		7
Brassica veg	Netherlands	WP	seed treat	0.23			
Broccoli	UK	SC	seed treat	0.30			
Brussels sprouts	UK	SC	seed treat	0.30			
Cabbage	Germany	WP	seed treat	0.40		1	
Cabbage	Italy	WG	spray		0.13-0.24	1-2	10
Cabbage	UK	SC	seed treat	0.30			
Carrot	Italy	WG	spray		0.13-0.15	1-2	10
Carrot	Netherlands	WP	seed treat	0.24			
Carrot	UK	SC	seed treat	0.30			
Cauliflower	UK	SC	seed treat	0.30			
Celeriac	Netherlands	WP	seed treat	0.32			
Celeriac	UK	SC	seed treat	0.30			
Celery	Australia	WG WP	foliar spray		0.12		7
Celery	Canada	WP	foliar spray		0.11		7
Celery	Italy	WG	spray		0.13-0.24	1-2	10
Celery	Netherlands	WG	seed treat	0.40		1	
Celery	Netherlands	WP WG	seed treat	0.32			
Celery	Spain	WG WP	spray		0.08-0.19	1-3	15
Celery	UK	SC	seed treat	0.30			
Chard	Italy	WG	spray		0.13-0.24	1-2	10
Chard	Netherlands	WP	seed treat	0.20			
Cherries	Netherlands	WP WG	foliar	3.0	0.20	4	14
Chicory	Belgium	WG	spray		0.16	1-3	28
Chicory	Italy	WG	spray		0.13-0.24	1-2	10
Chicory	UK	SC	seed treat	0.30			
Clover	Germany	DS	seed treat	0.26		1	
Courgette	Italy	WG	spray		0.13-0.24	1-2	10
Courgette	UK	SC	seed treat	0.30			
Crab apple	UK	WG	foliar	2.4	0.16		7
Cranberry	UK	WG	foliar		0.16		7
Cucumber	Belgium	WG	spray		0.2	1-2	3
Cucumber	Germany	WP	seed treat	0.33		1	
Cucumber	Germany	DS	seed treat	0.33		1	
Cucumber	Italy	WG	spray		0.13-0.24	1-2	10
Cucumber	Netherlands	WG	soaking		16	1	3
Cucumber	Netherlands	WG	watering		0.32	1-2	
Cucumber	Netherlands	WP	seed treat	0.24			
Cucumber	Netherlands	WP WG	foliar G[5]	0.8 g ai/plant		2	3
Cucumber	Spain	WG WP	spray		0.08-0.19	1-3	15
Cucumber	UK	SC	seed treat	0.30			
Currants, black, red	Denmark	WP	spray	4.8		1-2	last applic. at flowering
Currants	Netherlands	WP WG	foliar	2.0, 2.4	0.20	10	28
Currants	Netherlands	WG	spray		0.20	1-2	14
Currants, black	UK	WG	spray		0.20-0.40	1-2	
Currants, black, red, white	UK	WG	foliar		0.16		7
Dewberry	UK	WG	foliar		0.16		7
Endive	Germany	WP	dusting G	0.98 g/m^2		1	42
Escarole	Belgium	WG	spray		0.16	1-3	28

[5] Glasshouse

Crop	Country	Form	Application				PHI, days
			Method	Max rate per applic.	Spray conc. kg ai/hl	No.	
Fennel	Italy	WG	spray		0.13-0.24	1-2	10
Flax	France	WG	seed treat	0.2		1	
Flax	Germany	WP	seed treat	0.26		1	
Flax	Germany	DS	seed treat	0.26		1	
Flax	Netherlands	WG	seed treat	0.20		1	
Fodder beet	Germany	DS	seed treat	0.39		1	
Garlic	France	WG	spray	2.0		1-2	
Garlic	Italy	WG	spray		0.13-0.15	1-2	10
Gherkin	Netherlands	WP	seed treat	0.24			
Gooseberries	Netherlands	WP WG	foliar	2.0, 2.4	0.20	10	28
Gooseberry	Belgium	WG	spray		0.2	1-2	28
Grapes	Australia	WG WP	foliar spray		0.12		7
Grapes	France	WG	spray	3.2		1-3	
Grapes	Greece	WP WG	spray		0.20-0.30	1-2	
Grapes	Italy	WG	spray		0.10-0.13		
Grapes	Spain	WG WP	spray		0.16-0.24	1-3	15
Grapes, wine	Germany	WG	foliar spray	0.96-2.6	0.16	3	stage[6]
Grass	Netherlands	WG	seed treat	0.15		1	
Horseradish	Italy	WG	spray		0.13-0.15	1-2	10
Kale	UK	SC	seed treat	0.30			
Kohlrabi	UK	SC	seed treat	0.30			
Lamb's lettuce	Netherlands	WP	seed treat	0.32			
Leek	Italy	WG	spray		0.13-0.24	1-2	10
Leek	Netherlands	WP	seed treat	0.40			
Leek	UK	SC	seed treat	0.30			
Legume veg	Netherlands	WP WG SC	seed treat	0.23			
Lentil	Italy	WG	spray		0.13-0.24	1-2	10
Lettuce	Australia	WG WP	foliar spray		0.12-0.16		7
Lettuce	Belgium	WG	spray		0.16	1-3	28
Lettuce	France	WG	spray			1-2	Applied at 17 leaves
Lettuce	Italy	WG	spray		0.13-0.24	1-2	10
Lettuce	Netherlands	WP	seed treat	0.30			
Lettuce	Netherlands	WG	spray G	0.20 kg ai/m^2		1-3	28
Lettuce	Netherlands	WG	seed treat	0.40		1	
Lettuce	Netherlands	WP WG	foliar G	8.0	0.8	1	Note[7]
Lettuce	Netherlands	WP WG	foliar	0.40-0.80	0.20	4	28
Lettuce	Netherlands	DP	dusting G	10		1	28
Lettuce	UK	DP	soil treat	9.6			21
Lettuce	UK	SC	seed treat	0.30			
Lettuce	UK	DP	foliar	4.0		2-3	21
Lettuce	UK	WG	foliar	g	0.32		21
Lettuce	UK	WG	foliar		0.32		14
Lettuce, head	Germany	WP	dusting	0.98 g/m^2		1	42
Lettuce, head	Germany	DP	dusting	9.8		1	42
Linseed	Netherlands	WP WG	seed treat	0.23			
Loganberry	UK	WG	foliar		0.16		7
Lupin	Germany	DS	seed treat	0.20		1	
Lupin	Netherlands	WG	seed treat	0.15		1	
Maize	Belgium	WP	seed treat	0.19-0.25		1	
Maize	France	WG	seed treat	0.16		1	
Maize	Germany	DS FS	seed treat	0.20		1	
Maize	Germany	WP SC	seed treat	0.20		1	
Maize	Netherlands	WG	seed treat	0.15		1	
Maize	Netherlands	WP WG	seed treat	0.23			
Maize	Poland	FS	seed treat	0.05-0.06			
Maize	UK	SC	seed treat	0.11			
Marrow	Italy	WG	spray		0.13-0.24	1-2	10
Melon	Italy	WG	spray		0.13-0.24	1-2	10
Melon	UK	SC	seed treat	0.30			

[6] Spraying up to growth stage 35
[7] Applied 1 week after planting

Crop	Country	Form	Application				PHI, days
			Method	Max rate per applic.	Spray conc. kg ai/hl	No.	
Mustard	UK	SC	seed treat	0.30			
Oats	Netherlands	WG	seed treat	0.15		1	
Oats	Poland	FS	seed treat	0.06-0.07			
Oats	Poland	WS	seed treat	0.075-0.11			
Oats	UK	SC	seed treat	0.06			
Oilseed rape	Germany	DS	seed treat	0.44		1	
Onion	Canada	GR	at sowing	1.7-6.2		1	
Onion	Canada	GR	at sowing	95 g /100 m row			
Onion	France	WG	seed treat	0.06		1	
Onion	France	WG	spray	2.0		1.2	
Onion	Germany	DS WP	seed treat	0.39		1	
Onion	Italy	WG	spray		0.13-0.15	1-2	10
Onion	Netherlands	WP WG	seed treat	0.40			
Onion	UK	SC	seed treat	0.30			
Parsley	Netherlands	WG	seed treat	0.40		1	
Parsley	Netherlands	WP WG	seed treat	0.32			
Parsley	UK	SC	seed treat	0.30			
Parsnip	UK	SC	seed treat	0.30			
Pea	Denmark	SC	seed treat	0.28		1	
Pea	France	WG	spray			1-3	
Pea	Germany	DS FS	seed treat	0.20		1	
Pea	Netherlands	WG	seed treat	0.15		1	
Pea	Poland	FS	seed treat	0.08		1	
Pea	UK	SC	seed treat	0.06			
Pea, field	Germany	WP SC	seed treat	0.20		1	
Peach	Canada	WP	foliar spray		0.11-0.17	4-7	7
Peach	Netherlands	WP WG	foliar	2.4 0.8-2.4 G	0.16	4	14
Pear	Australia	WG WP	foliar spray		0.12		7
Pear	Netherlands	WP WG	foliar	2.0-3.0	0.20	Note[8]	7
Pear	Netherlands	WP WG	foliar	1.6-3.0	0.16, 0.20	3	7
Pear	Netherlands	WP WG	foliar	1.2-1.5	0.10	Note[9]	7
Pear	Netherlands	WP WG	foliar	1.6-2.4	0.16	Note[10]	7
Pear	UK	WG	spray	4.5	0.16	1-6	7
Pear	UK	WG	foliar	2.4	0.16		7
Pepper, sweet	Italy	WG	spray		0.13-0.24	1-2	10
Pepper, sweet	Netherlands	WG	spray		0.20	1-3	3
Peppers, sweet	Netherlands	WP WG	foliar G	1.0-3.0	0.20	12	3
Peppers, sweet	Netherlands	DP	dusting G	2.0-3.0		2	3
Plum	Canada	WP	foliar spray	5.1		1	dormant
Plums	Netherlands	WP WG	foliar	3.0	0.20	4	14
Pome fruit	Belgium	WG	spray		0.1-0.2	1-6	28
Pome fruit	Denmark	SC	spray	1.4-5.3		1-2	Note**Errore. Il segnalibro non è definito.** 7
Pome fruit	Denmark	WP	spray	4.8		1-2	Note**Errore. Il segnalibro non è definito.** 7
Pome fruit	Denmark	SC	spray	1.9-6.4		1-2	Note[11]
Pome fruit	Denmark	WP	spray	6.4		1-2	Note[11]
Pome fruit	France	WG	spray		0.2	1-6	
Pome fruit	Germany	WP WG	foliar spray	1.5-2.4	0.1-0.16	12	10
Pome fruit	Greece	WP WG	spray		0.20-0.30	1-5	15
Pome fruit	Italy	WG	spray		0.15-0.20	1-6	10
Pome fruit	Netherlands	WG	spray	1.4-3.0	0.10-0.20	1-6	7
Pome fruit	Portugal	WG	spray		0.12-0.16	1-6	
Pome fruit	Spain	WG WP	spray		0.16-0.24	1-5	15
Poppy	Germany	WP	seed treat	0.39		1	
Poppy seed	Germany	DS	seed treat	0.39		1	

[8] Before blossom
[9] Later applications
[10] During and just after blossom
[11] Before flowering

Crop	Country	Form	Application				PHI, days
			Method	Max rate per applic.	Spray conc. kg ai/hl	No.	
Poppy seed	Netherlands	WP WG	seed treat	0.32			
Potato	Italy	WG	spray		0.13-0.15	1-2	10
Potato seed	Denmark	WP	seed treat	0.64		1	
Pulses	Netherlands	WP WG SC	seed treat	0.23			
Quince	UK	WG	foliar	2.4	0.16		7
Radish	Germany	WP	seed treat	0.20		1	
Radish	Netherlands	WG	spray G	0.80 g ai/m^2		1	
Radish	Netherlands	WP WG	foliar	8.0	0.8	1	
Radish	Netherlands	WP	seed treat	0.24			
Radish	UK	SC	seed treat	0.30			
Rape seed	France	WG	seed treat	0.15		1	
Rape seed	Germany	WP	seed treat	0.44		1	
Rape seed	Netherlands	WG	seed treat	0.30		1	
Rape seed	Netherlands	WP WG	seed treat	0.24			
Rape seed	UK	SC	seed treat	0.015			
Raspberry	Belgium	WG	spray		0.2	1-2	14
Raspberry	Netherlands	WG	spray		0.20	1-2	14
Raspberry	Netherlands	WP WG	foliar	2.0, 2.4	0.20	10	28
Raspberry	UK	WG	spray		0.16	1-2	7
Raspberry	UK	WG	foliar		0.16		7
Rye	Netherlands	WG	seed treat	0.20		1	
Rye	Netherlands	WP WG	seed treat	0.23			
Rye	Poland	WS	seed treat	0.075-0.11			
Rye	Poland	FS	seed treat	0.06-0.07			
Rye	UK	SC	seed treat	0.06			
Shallot	France	WG	spray	2.0		1-2	
Soya bean	Poland	FS	seed treat	0.08		1	
Spinach	Germany	WP	seed treat	0.20		1	
Spinach	Italy	WG	spray		0.13-0.24	1-2	10
Spinach	Netherlands	WP WG	seed treat	0.32			
Spinach	Netherlands	WG	seed treat	0.40		1	
Spinach	UK	SC	seed treat	0.30			
Stem kale	Germany	DS	seed treat	0.44		1	
Stone fruit	Australia	WG WP	foliar spray		0.12		7
Stone fruit	Belgium	WG	spray		0.2	1-3	14
Stone fruit	France	WG	spray		0.2	1-3	
Stone fruit	Greece	WP WG	spray		0.20-0.30	1-4	15
Stone fruit	Italy	WG	spray		0.13-0.15	1-5	10
Stone fruit	Netherlands	WG	spray		0.16-0.20	1-3	14
Stone fruit	Portugal	WG	spray		0.16-0.20	1-4	
Stone fruit	Spain	WG WP	spray		0.16-0.24	1-5	15
Strawberry	Australia	WG WP	foliar spray		0.12		7
Strawberry	Belgium	WG	spray G		0.2	1-4	14
Strawberry	Canada	WP	foliar spray		0.11-0.19		3
Strawberry	Denmark	SC WP	spray	5.3-6.0		1-2	7
Strawberry	Germany	WG	foliar spray	3.2	0.16	3	blossom
Strawberry	Greece	WP WG	spray		0.20-0.30	1-2	
Strawberry	Italy	WG	spray		0.13-0.15	1-3	
Strawberry	Netherlands	WG	spray	3.0	0.20	1-3	14
Strawberry	Netherlands	WP WG	foliar	1.0, 1.2	0.20	12	14
Strawberry	Netherlands	WP WG	foliar G	1.2-2.4	0.20	6	Note[12]
Strawberry	Portugal	WG	spray		0.12-0.16	1-4	
Strawberry	Spain	WG WP	spray		0.16-0.24	1-4	15
Strawberry	UK	WG	spray		0.20-0.40	1-3	7
Strawberry	UK	WG	foliar	1.6			7
Sugar beet	Belgium	WP	seed treat	0.75		1	
Sugar beet	Germany	DS	seed treat	0.39		1	
Swede	UK	SC	seed treat	0.30			
Swedish turnips	Germany	DS	seed treat	0.44		1	
Sweet corn	Netherlands	WP	seed treat	0.20			
Sweet corn	UK	SC	seed treat	0.11			

[12] Applied until beginning of flowering

Crop	Country	Form	Application				PHI, days
			Method	Max rate per applic.	Spray conc. kg ai/hl	No.	
Sweet potato	Canada	WP	dip roots		0.11	1	
Tomato	Belgium	WG	spray		0.2		3
Tomato	Italy	WG	spray		0.13-0.24	1-2	10
Tomato	Netherlands	WG	spray		0.20	1-3	3
Tomato	Netherlands	WP WG	foliar G	1.0-3.0	0.20	12	3
Tomato	Netherlands	DP	dusting G	2.0-3.0		2	3
Tomato	UK	WG	spray	4.5-7.2	0.32	1-3	7
Tree nuts	Greece	WP WG	spray		0.20-0.30	1-4	15
Tree nuts	Portugal	WG	spray	1.6-2.4	0.16-0.20	1-4	
Tree nuts	Spain	WG WP	spray		0.16-0.24	1-5	15
Triticale	Poland	FS	seed treat	0.06-0.07			
Triticale	Poland	WS	seed treat	0.075-0.11			
Triticale	UK	SC	seed treat	0.06			
Turnip	Germany	DS	seed treat	0.44		1	
Turnip	Germany	WP	seed treat	0.44		1	
Turnip	Italy	WG	spray		0.13-0.15	1-2	10
Turnip	UK	SC	seed treat	0.30			
Vetch	Netherlands	WG	seed treat	0.15		1	
Watermelon	Italy	WG	spray		0.13-0.24	1-2	10
Wheat	France	WG	seed treat	0.16		1	
Wheat	Poland	FS	seed treat	0.06-0.07			
Wheat	Poland	WS	seed treat	0.075-0.11			
Wheat	UK	SC	seed treat	0.06			
Witloof	Italy	WG	spray		0.13-0.24	1-2	10
Witloof	Netherlands	WG	spray G	0.20 kg ai/m^2		1-3	28
Witloof	Netherlands	WP	seed treat	0.30			

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data from supervised trials on fruit and vegetables are summarized in Tables 26-32.

Table 26	Apples. Belgium, France, Germany, Italy, Netherlands, Poland.
Table 27	Pear. Belgium, Germany, Italy, Spain.
Table 28	Peach. France, Italy, Spain.
Table 29	Plum. France, Italy. Cherries. Italy, Spain.
Table 30	Grapes. France, Germany.
Table 31	Strawberry. Belgium, France, Germany, Poland.
Table 32	Beans, dwarf French. Germany. Beans, French. France Cabbage, Savoy. Germany. Peas, green. France. Lettuce, head. Germany, Netherlands. Spinach. Germany, Netherlands. Tomato. France.

Thiram was determined by CS_2 evolution methods or by HPLC, and in some trials by both methods. Residues are reported in the Tables as thiram irrespective of the method of analysis. The molecular weight factor CS_2 x 1.58, was used to calculate the thiram residues if residues were quoted in the trial report as CS_2.

Where residues were not detected they are recorded in the Tables as below the limit of determination (LOD), e.g. <0.05 mg/kg. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure.

Residues in control samples are recorded only when they exceeded the LOD: this occurred in samples from 2 apple trials, 4 grape trials and 2 spinach trials analysed by the CS_2 evolution method, and in one apple and one grape sample analysed by the HPLC method.

Most of the trials were fully reported as well as being summarized. Some, especially older ones, were reported as detailed summaries rather than in full reports.

In some trials on apples, peaches, plums, cherries, strawberries and tomatoes other dithiocarbamates had been used on the crop during the growing season. Samples from such trials were considered valid for estimating thiram residue levels only if they had been analysed specifically for thiram by an HPLC method.

Thiram trials on apples were available from a number of European countries. Knapsacks were used for application in the Belgian trials of 1991-1993, where plot sizes were usually 8 or 16 trees, and in the French trial on plots of 6 trees. Thiram was applied by a tractor-mounted sprayer or axial fan blower in the German trials of 1989, and with a motorised knapsack and a wheelbarrow-mounted sprayer in the Italian trials where plot sizes were 6-12 trees.

Thiram was applied by knapsack sprayer in most of the trials on stone fruit and strawberries. Plot sizes for tree crops were 4-8 trees. Plot sizes in the strawberry trials ranged from 8 m of row to 100 m^2.

In a series of trials on grapes in France in 1992 thiram was applied with a back-pack air-blast sprayer. In each trial there were two plots whose ranged from 186-750 m^2. The plots were large enough to provide sufficient grapes for processing studies (Table 33). In a grape trial in France in 1991 thiram was applied with a knapsack atomizer to plots of 30 or 60 plants. Field samples were taken from each of 3 sub-plots.

Thiram residues in apples from 5 trials in The Netherlands in 1988 seem low by comparison with residues from other trials. Many of the residues were below the LOD (0.1 mg/kg). Details of sample storage conditions (temperature, duration, chopped or whole fruit) were not immediately available to confirm that residues had not disappeared during storage.

German trials on apples from 1971 to 1973 were reported on detailed summary sheets.

Table 26. Residues of thiram (expressed as thiram) in apples from foliar application of thiram in supervised trials in Belgium, France, Germany, Italy, The Netherlands and Poland. Underlined residues are from treatments according to GAP and are valid for estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
Belgium, 1991 (Golden Delicious)	WG	2.4	0.80	13	83	<0.05	<0.05	CRP/92/975 GD 7D
Belgium, 1991 (Jonagold)	WG	2.4	0.80	9 dt	7	1.6	1.8	CRP 92/974 BEVJG1
Belgium, 1991 (Jonagold)	WG	2.4	0.80	11 dt	90	<0.05	<0.05	CPR/92/972 JG 7 D
Belgium, 1991 (Jonagold)	WG	2.4	0.80	12 dt	14	1.9	2.3	CRP/92/973 91/BEVJG2
Belgium, 1992 (Golden Delicious)	WG	2.4	0.80	10 dt	0 7 14		7.7, 8.5 4.9, 5.2 2.5, 3.1 c 0.77	BEWGD B.A.7792C
Belgium, 1993 (Jonagold)	WG	1.8	0.16	5 6	9 0 7 14 21	<u>2.7</u> 4.3 3.5 1.6 1.4		304735 2097/93
Belgium, 1993 (Jonagold)	WG	1.8	0.16	5 6	9 0 7	<u>4.6</u> 5.8 4.3		304670 2097/93

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
					14 21	2.7 2.2		
France, 1993 (Starkrimson)	WG	1.6	0.16	5 6	7 0 14 21 28 35	1.9 2.8 2.4 1.9 1.7 0.4		304697 RA-2099/93
Germany, 1971 (Cox's Orange)	WP	2.9 +1.8 +1.8	0.11 +0.07 +0.07	3 dt	15	1.1		BBA 26/71 BBA 15/72 BBA 27/72
Germany, 1971 (Cox's Orange)	WP	1.8 +1.4 +2.9 +2.9	1 +0.8 +1.6 +1.6	4 dt	15	2.0		BBA 27/71 BBA 4/72 BBA 16/72
Germany, 1971 (Cox's Orange)	WP	1.8 +1.4 +2.9 +2.9	0.4 +0.32 +0.64 +0.64	4 dt	15	1.3		BBA 28/71 BBA 5/72 BBA 17/72
Germany, 1971 (Cox's Orange)	WP	2.9 +1.8 +1.8	0.64 +0.4 +0.4	3 dt	15	0.60		BBA 23/71 BBA 12/72 BBA 24/72
Germany, 1971 (Cox's Orange)	WP	2.9 +1.8 +1.8	0.32 +0.2 +0.2	3 dt	15	0.74		BBA 24/71 BBA 13/72 BBA 25/72
Germany, 1971 (Cox's Orange)	WP	2.9 +1.8 +1.8	0.16 +0.1 +0.1	3 dt	15	0.84		BBA 25/71 BBA 14/72 BBA 26/72
Germany, 1971 (Cox's Orange)	WP	1.8	0.4	3 dt	13	0.59		BBA 20/71 BBA 9/72 BBA 21/72
Germany, 1971 (Cox's Orange)	WP	1.8	0.1	3 dt	13	0.43		BBA 22/71 BBA 11/72 BBA 23/72
Germany, 1971 (Cox's Orange)	WP	1.8	0.2	3 dt	13	0.73		BBA 21/71 BBA 10/72 BBA 22/72
Germany, 1971 (Cox's Orange)	WP	1.8	1	3 dt	13	0.73		BBA 19/71 BBA 8/72 BBA 20/72
Germany, 1971 (Cox's Orange)	WP	1.8 +1.4 +2.9 +2.9	0.1 +0.08 +0.16 +0.16	4 dt	15	1.1		BBA 30/71 BBA 7/72 BBA 19/72
Germany, 1971 (Cox's Orange)	WP	1.8 +1.4 +2.9 +2.9	0.2 +0.16 +0.32 +0.32	4 dt	15	1.2		BBA 29/71 BBA 6/72 BBA 18/72
Germany, 1972 (Cox's Orange)	WP	1.4 +2.9 +2.9	0.08 +0.16 +0.16	3 dt	15	3.4		BBA 76/72 R/1800
Germany, 1972 (Cox's Orange)	WP	2.7	0.6	4 dt	12	1.2		BBA 77/72 U/450
Germany, 1972 (Cox's Orange)	WP	1.4 +2.9 +2.9	0.16 +0.32 +0.32	3 dt	15	4.7		BBA 75/72 R/900
Germany, 1972 (Cox's Orange)	WP	2.7	0.15	4 dt	12	1.1		BBA 79/72 U/1800
Germany, 1972 (Cox's Orange)	WP	2.7	0.3	4 dt	12	0.63		BBA 78/72 U/900
Germany, 1972 (Cox's Orange)	WP	2.7	0.1	4 dt	12	0.95		BBA 80/72 U/2700
Germany, 1972 (Golden	WP	1.8	1	1 dt	31	2.0		BBA 27/73

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
Delicious)		1.8 1.8 1.8	0.4 0.2 0.1	1 dt 1 dt 1 dt	31 31 31	1.1 0.90 0.82		BBA 28/73 BBA 29/73 BBA 30/73
Germany, 1972 (Cox's Orange)	WP	1.8 1.8 1.8 1.8	1 0.4 0.2 0.1	1 dt 1 dt 1 dt 1 dt	31 31 31 31	0.71 0.87 0.66 0.47		BBA 5/73 BBA 6/73 BBA 7/73 BBA 7/73
Germany, 1972 (Cox's Orange)	WP	1.8 1.8 1.8 1.8	1 0.4 0.2 0.1	1 dt 1 dt 1 dt 1 dt	31 31 31 31	0.87 0.81 0.85 0.57		BBA 1/73 BBA 2/73 BBA 3/73 BBA 4/73
Germany, 1972 (Cox's Orange)	WP	1.4 +2.9 +2.9	0.32 +0.64 +0.64	3 dt	15	4.7		BBA 74/72 R/450
Germany, 1972 (Cox's Orange)	WP	1.8	1	3 dt	15	2.5		BBA 69/72 D/180
Germany, 1972 (Golden Delicious)	WP	1.8 1.8 1.8 1.8	1 0.4 0.2 0.1	1 dt 1 dt 1 dt 1 dt	31 31 31 31	0.68 1.0 0.66 0.52		BBA 31/73 BBA 32/73 BBA 33/73 BBA 34/73
Germany, 1972 (Cox's Orange)	WP	1.8	0.1	3	15	0.81		BBA 72/72 D/1800
Germany, 1972 (Cox's Orange)	WP	1.8	0.4	3	15	1.0		BBA 70/72 D/450
Germany, 1972 (Cox's Orange)	WP	1.4 +2.9 +2.9	0.8 +1.6 +1.6	3 dt	15	3.5		BBA 73/72 R/180
Germany, 1972 (Cox's Orange)	WP	1.8	0.2	3	15	0.49		BBA 71/72 D/900
Germany, 1973 (Cox's Orange)	WP	0.45	0.1	2	18	0.35		BBA 85/73 U/IV
Germany, 1973 (Cox's Orange)	WP	0.45	0.1	2	14	0.81		BBA 84/73 D/IV
Germany, 1989 (Gloster)	WG	2.4	0.16	4	0 5 7 10 14 10 10	4.0 3.0 2.2 1.7 1.9 s 0.21 j 0.19		0318/89
Germany, 1989 (Golden Delicious)	WG	2.4	0.80	4 dt	0 5 7 10 14	2.8 1.3 1.7 1.7 1.0		0320/89
Italy, 1991 (Golden Delicious)	WG	2×2.6 +2×3.3 +1×3.5	0.15	5	0 7 10 15 20	4.9 1.5 2.5 1.6 1.1	5.2 - - - 1.0	58/F/91-6012
Italy, 1992 (Weime)	WG	2.6	0.15	5 dt	0 7 10 15 20	10.0 7.4 4.2 3.4 2.9	10.2 7.6 4.1 3.3 2.9	UCB 205
Italy, 1993 (Perleberg)	WG	2.3	0.15	4 5	7 0 10 21 28 35	6.0 6.5 0.7 1.1 1.1 0.7		304700 RA-2099/93
Netherlands, 1986 (Golden Delicious)	WP	2.4	1.6	6	7 7 14	11 9.8 17 21 c <0.2 0.2		KvW257 (1987)

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
					14	(3) 5.4 15 c 23 14		
Netherlands, 1986 (Golden Delicious)	WP	3.0	2.0	6	7 7 14 14	19 16 12 16 c <0.2 0.2 (3) 12 18 c 23 14		KvW257 (1987)
Netherlands, 1986 (Golden Delicious)	WP	4.5	2.0	6	7 14	6.8 6.0 6.3 8.9 5.7 7.3 3.8 6.8		KvW257 (1987)
Netherlands, 1986 (Golden Delicious)	WP	3.6	1.6	6	7 14	7.1 7.6 5.2 4.0 4.9 7.1 2.8 4.7		KvW257 (1987)
Netherlands, 1988 (Golden Delicious)	WP	3.0	0.20	5	7 14		0.46 0.12 0.40 0.33 <0.1 0.1 <0.1 0.22	RIVM 638201015
Netherlands, 1988 (Golden Delicious)	WP	2.2	0.16	5	7 14		<0.1 (4) 0.28 <0.1 (3)	RIVM 638201015
Netherlands, 1988 (Golden Delicious)	WP	2.4	1.6	5	7 14		0.47 1.8 0.56 0.27 0.33 0.14 0.76 0.34	RIVM 638201015
Netherlands, 1988 (Golden Delicious)	WP	3.1	2.0	5	7 14		1.6 6.3 4.0 0.4 1.2 0.88 0.41 0.25	RIVM 638201015
Netherlands, 1988 (Golden Delicious)	WP	2.3	0.16	5	7 14		<0.1 (4) <0.1 (4)	RIVM 638201015
Netherlands, 1988 (Golden Delicious)	WP	2.2	2.8	5	7 14		<0.1 (3) 0.25 <0.1 (4)	RIVM 638201015
Netherlands, 1988 (Golden Delicious)	WP	2.9	0.20	5	7 14		<0.1 (4) <0.1 (4)	RIVM 638201015
Netherlands, 1988 (Golden Delicious)	WP	1.8	1.6	5	7 14		<0.1 (4) <0.1 (4)	RIVM 638201015
Poland, 1994 (Starkrimson)	WG	2.4		4	7 14	7.0 3.8		
Poland, 1994 (Starkrimson)	WG	2.4		2	7 14	6.5 3.2		
Poland, 1994 (Starkrimson)	WG	3.6		4	7 14	8.5 8.1		
Poland, 1994 (Starkrimson)	WG	3.6		2	14	3.6		
Poland, 1994 (Spartan)	WG	3.6		2	7 14	2.9 1.5		
Poland, 1994 (Spartan)	WG	2.4		2	7 14	1.6 0.87		
Poland, 1994 (Spartan)	WG	2.4		4	7 14	3.2 1.7		
Poland, 1994 (Spartan)	WG	3.6		4	7 14	6.0 4.0		

dt: other dithiocarbamates also applied during the growing season.
c: control sample
s: sauce
j: juice

Table 27. Residues of thiram (expressed as thiram) in pears from foliar application of thiram in supervised trials in Belgium, Germany, Italy and Spain. Underlined residues are from treatments according to GAP and are valid for estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
Belgium, 1991 (Conference)	WG	2.4	0.80	12	14	0.69	0.68	CRP/92/977 Bevecon 2
Belgium, 1991 (Conference)	WG	2.4	0.80	12	6	0.77 1.1	0.73 1.1	CRB/92/978 Bevecon 1
Belgium, 1991 (Conference)	WG	2.4	0.80	13	56	<0.05	<0.05	91/CONF 10D CRP/92/976
Belgium, 1992 (Conference)	WG	2.4	0.80	14	1 3 6 13		4.6 1.4 1.4 1.6	BEWCON B.A.7792b
Germany, 1989 (Alexander Lucas)	WP	2.4	0.16	4	0 5 7 10 14	3.8 3.0 2.7 1.9 1.0		0319/89
Germany, 1989 (Alexander Lucas)	WP	2.4	0.80	4	0 5 7 10 14	1.5 1.1 1.1 0.90 0.90		0321/89
Italy, 1991 (Kaiser)	WG	2.3-2.9	0.15	12	0 7 10 15 20 30	1.9 0.56 0.54 0.45 0.23 0.17	2.0	57/F/91-6010
Italy, 1991 (Abate Fetel)	WG	2.6	0.15	12	0 7 10 15 20 30	5.7 4.0 6.1 3.2 3.3 3.1 2.8 2.6 4.3 1.6 0.70 2.6 0.37 0.51 0.39 0.33 0.24	5.7 4.3 6.5 - - - 0.53 0.55 0.39 0.33 0.36	UCB 912
Italy, 1992 (William)	WG	2.6	0.15	8	0 7 10 15 20 30	5.6 5.9 5.1 2.9 2.0 1.2	4.8 6.4 4.8 2.3 2.0 1.1	UCB 202[1]
Spain, 1994 (Ercolini)	WG	2.4	0.24	6	0 14 21		2.9 3.2 2.8 1.9 2.2 3.0 1.5 1.4 1.1	94020/01-FPBI

[1] No report for HPLC method but summary data supplied

Table 28. Residues of thiram (expressed as thiram) in peaches from foliar application of thiram in supervised trials in France, Italy and Spain. Underlined residues are from treatments according to GAP and are valid for estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
France, 1993 (Red Top)	WG	1.0-1.2	0.20	4 dt 5 dt	10 0 7 14 21	2.5 4.7 2.1 1.0 0.9		304654 RA-2083/93
Italy, 1991 (Dorata Tardiva Morettini)	WG	2.3	0.15	5	0 7 10 15	5.1 3.3 4.9 1.3 2.5 4.8 2.7 2.7 2.4 1.1 2.2 2.1	4.8 3.2 4.2 - - -	UCB 913

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
					20	1.2 2.5 1.6	0.93 2.5 1.5	
Italy, 1991 (Glohaven)	WG	1.8	0.15	5 dt	0 8 12 15 20	4.8 1.3 1.3 0.62 0.51	4.3	56-F-91/6009
Italy, 1992 (Red Haven)	WG	2.3	0.15	5	0 10 15 20 30	5.7 3.6 1.4 0.70 0.70	5.6 3.5 1.3 0.60 0.60	UCB 203
Spain, 1994 (Maria Serena)	WG	2.4	0.24	3	0 10 14		f 1.5 f 0.43 f 0.26	94020/01-FPPF
Spain, 1994 (Baby Gold)	WG	2.4	0.24	3	0 10 14		f 3.4 f 1.3 f 0.70	94020/01-FPPF

dt: other dithiocarbamates also applied during the growing season.
f: residues in fruit without stone

Table 29. Residues of thiram (expressed as thiram) in plums and cherries from foliar application of thiram in supervised trials in France, Italy and Spain. Underlined residues are from treatments according to GAP and are valid for estimation of maximum residue levels.

CROP Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
PLUMS								
France, 1994 (Ente 707)	WG	2.4	0.24	3	0 9 14		f 1.0 1.7 0.9 f 1.2 0.8 0.9 f 0.6 1.0 0.8	94020/02-FPPL
Italy, 1991 (San Alberto)	WG	2.6	0.15	3	0 7 10 15 20	4.5 2.4 2.8 0.78 0.52 0.45 0.83 0.69 0.75 0.33 0.24 0.28 0.18 0.31 0.25	4.3 2.3 2.4	UCB 911
Italy, 1992 (Stanley)	WG	2.6	0.15	3 dt	0 7 10 15 20	2.9 0.70 0.75 0.33 0.24	2.8 0.65 0.62 0.27 0.25	UCB 201
CHERRIES								
Italy, 1991 (Durone di Vignola)	WG	9.3-10.9	0.15	3 dt	0 7 14 18 23	2.1 1.4 2.8 1.5 1.9 4.2 0.16 0.26 0.12 0.34 0.39 0.32 0.40 0.069 0.074	1.7 1.5 2.7	59/F/91/6011
Italy, 1991 (Bigareau/Moreau)	WG	1.1-1.5	0.15	3	0 7 10 15 20	0.94 2.3 1.9 0.22 0.23 0.22 0.21 0.17 0.37 0.24 0.22 0.19 0.11 0.10 0.16	0.80 2.1 1.8	UCB 914
Italy, 1992 (Roma)	WG	1.5	0.15	3	0 7 10 15 20	6.6 1.6 0.41 0.90 0.70	6.8 1.5 0.40 1.1 0.76	UCB 204
Spain, 1994 (Sunburst)	WG	2.4	0.24	3	0 10 14		6.1 8.2 5.7 0.4 0.2 0.2 0.1 0.1 0.1	94020/01-FPKI

dt: other dithiocarbamates also applied during the growing season.

f: residues in fruit without stone

Table 30. Residues of thiram (expressed as thiram) in grapes from foliar application of thiram in supervised trials in France and Germany.

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
France, 1991 (Pinot Noir)	WG	3.2	0.8	1 dt 2 dt	70 44	0.26 0.33	<0.05 0.11	FR7/91, CRP/94/1295
France, 1992 (Merlot)	WG	3.2	1.6	3 4	32 21	9.3 11.7	2.6 5.6	28203 B001
France, 1992 (Pinot)	WG	3.2	1.2	3 4	33 21	2.4 2.5	1.1 2.2	28203 B004
France, 1992 (Pinot Noir)	WG	3.2	0.6-1.1	3 4	48 21	3.0 7.4	2.7 4.5	28203 B003
France, 1992 (Cot)	WG	3.2	1.4	3 4	32 21	0.8 4.3	0.7 2.3	28203 B002
France, 1994 (Cinsault)	WG	3.2	1.1	3	0 10 21 28 35		1.9 4.3 0.9 1.5 0.8 1.2 0.4 0.6 0.8 0.1 0.6 0.4 0.2 0.2 0.1	9402/01-FPWE loc 1
France, 1994 (Merlot)	WG	3.2	1.1	3	0 10 21 28 35		4.1 5.4 7.2 6.4 5.6 5.6 1.8 4.0 2.4 1.3 1.3 1.2 0.2 0.5 <0.2	9402/01-FPWE loc 2
Germany, 1992 (Riesling)	WG	2.4	0.24	3	0 21 28 35	1.7 c 5.1 3.0 3.3 3.0 c 1.7	c 1.9 1.1 0.8 0.7	DE/FR/03/92, DU3/30/92
Germany, 1992 (Portugieser)	WG	2.4	0.24	3	0 21 28 35	2.2 c 0.17 1.6 1.5 1.0 c 0.38	2.0 1.0 0.9 0.6	DE/FR/03/92, DU3/29/92
Germany, 1992 (Schwarzriesling)	WG	2.4	0.24	3	0 21 28 35	7.0 c 1.9 2.5 3.0 3.5 c 0.76	3.4 1.0 0.6 0.9	DE/FR/03/92, DU/60/92
Germany, 1992 (Muller Thurgau)	WG	2.4	0.24	3	0 20 28 34	3.8 c 0.76 1.9 2.9 2.7 c 0.51	2.5 1.2 0.5 1.2	DE/FR/03/92, DU/61/92

c: control sample.
dt: other dithiocarbamates also applied during the growing season.

Table 31. Residues of thiram (expressed as thiram) in strawberries from foliar application of thiram in supervised trials in Belgium, France, Germany and Poland. Underlined residues are from treatments according to GAP and are valid for estimation of maximum residue levels.

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
Belgium, 1991 (Elsanta, June bearing)	WP	1.6	0.23	8	0 7 14 21	3.0 <u>2.4</u> 0.44 0.05	3.3 <u>2.8</u> 0.45 0.06	CRP/92/863A
Belgium, 1991 (Selva Everbearing)	WP	1.6	0.23	3 4 5 6 7 8 9 10 11 12	11 7 6 7 8 7 8 6 8 7	0.32 0.85 1.0 1.0 1.2 <u>1.4</u> 1.1 1.0 1.8 1.2	0.32 0.72 0.97 0.93 1.3 1.3 1.1 0.99 0.92 1.5	CRP/92/865
Belgium, 1991 (Vicoda, June bearing)	WG	1.6	0.23	7	0 7 14 21	2.8 <u>1.2</u> 0.82 0.72	2.7 <u>1.4</u> 0.87 0.79	CRP/92/862A
Belgium, 1991 (Selva, Everbearing)	WG	1.6	0.23	3 4 5 6 7 8 9 10 12 12	11 7 6 7 8 7 8 6 1 7	0.85 0.97 0.85 1.9 0.91 1.4 0.89 1.6 1.2 1.3	1.0 1.1 1.0 <u>2.1</u> 0.84 1.2 0.92 2.0 1.1 1.6	CRP/92/864A
Belgium, 1992 (Selva, Everbearing)	WG	1.6 dt	0.23	5 6 7 8 9 10 11 12 13 14	7 7 7 6 7 7 7 6 7 7		2.3 <u>2.4</u> 0.64 2.2 1.4 1.3 1.2 1.5 4.5 5.8	BCSEL BA 7792a
Belgium, 1992 (Irvine, Everbearing)	WG	1.6	0.23	5 6 7 8 9 10 11 12 13 14	7 7 7 7 8 7 6 6 7 7		<u>3.1</u> 2.5 1.0 1.5 1.1 3.8 2.3 4.3 6.3 11	BCIRV BA 7792d
Belgium, 1993 (Elsanta)	WG	1.6	0.29-0.41	6	0 3 7 10 14		16 1.7 <u>2.1</u> 1.7 0.45	UCB B 93-3 B27-93 9301-RU-010-1
France, 1988 (Elvira)	WG	2.2	0.22	2	14	0.70		FR5 552/6
France, 1988 (Gorella)	WG	2.2	0.29	3 dt	13	0.92		FR8 850/6
France, 1988 (Gorella)	WG	3.2	0.42	3 dt	13	1.4		FR8 850/7
France, 1988 (Elvira)	WG	3.2	0.32	2	14	0.85		FR5 552/7
France, 1988 (Gorella)	WG	3.2	0.32	2	27	1.1		FR5 551/7
France, 1988 (Gorella)	WG	2.2	0.22	2	27	0.68		FR5 551/6
France, 1989 (Gorella)	WG	2.2	0.22	2	32	<0.2		F 869/89/547
France, 1989 (Gorella)	WG	2.2	0.22	2	21	0.8		F 869/89/548

Country, year (variety)	Application				PHI, days	Residues, as thiram, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
France, 1989 (Selva)	WG	2.2	0.22	2 dt	19	1.1		F 869/89/847
France, 1992 (Selva)	WG	3.2 PCT[13]	0.32	2	0 2 4 8 10 14	1.3 3.7 2.8 2.1 1.6 1.5 1.4		SPV 33 02
France, 1992 (Seascape)	WG	3.2 PCT	0.32	2	0 2 4 10 14	1.2 4.1 2.3 1.7 0.79 0.71		SPV 33 01
France, 1993 (Elsanta)	WG	2.4	0.35-0.54	4	0 3 7 10 14		7.7 4.1 2.3 1.0 0.54	UCB B93-10, 93101-RU-010-3, B93501
France, 1994 (Chandler)	WG	2.4	0.24	3	0 3 7 10 14		7.4 2.4 2.8 2.9 1.5	94020/01-FPEB loc 2
France, 1994 (Chandler)	WG	2.4	0.24	3	0 3 7 11 15		2.8 3.6 5.7 2.8 3.4 3.8 0.9 1.5 1.4 0.6 0.8 1.3 0.4 0.4 0.6	94020/01-FPEB loc 1
Germany, 1962 (Senga Sengana)	WP	0.96	0.16	1	0 3 7 14	0.2 <0.2 <0.2 <0.2		BBA
Germany, 1963 (Senga Sengana)	WP	2.4	0.4	1	3	<0.2		BBA
Germany, 1964 (Senga Sengana)	WP	0.49	0.025	3	10	0.79		BBA
Germany, 1964 (Senga Sengana)	WP	4 4 4 4	0.16 0.16 0.16 0.16	4 3 2 1	12 19 25 31	2.2 1.7 0.79 0.32		BBA
Germany, 1964 (Senga Sengana)	WP	2.4	0.4	3	10	1.7		BBA
Poland, 1994 (Senga Sengana)	WG	3.2		3	0 3 14	8.1 4.4 1.2		

dt: other dithiocarbamates also applied during the growing season

Table 32. Residues of thiram (expressed as thiram) in vegetables from seed treatment and foliar application of thiram in supervised trials in France, Germany and The Netherlands. Underlined residues are from treatments according to GAP and are valid for estimation of maximum residue levels.

VEGETABLES Country, year (variety)	Application	PHI, days	Residues, as thiram, mg/kg	Ref.

[13] Outdoor, plastic covered tunnel

	Form	kg ai/ha	kg ai/hl	No.		CS_2 method	HPLC method	
BEANS, DWARF FRENCH								
Germany, 1981 (Saxa)	DS	0.2 kg ai/100 kg seed			67	<0.1		BBA 3781
BEANS, FRENCH								
France, 1987 (Faria)	WG	2.2	0.45	1	20	0.32		42308 F/18/5
France, 1987 (Faria)	WG	2.2	0.45	2	7	0.22		42308 F/18/8
France, 1987 (Carlyn)	WG	2.2	0.45	1	28	0.25		FR2 52/5
France, 1987 (Carlyn)	WG	2.2	0.45	2	17	0.44		FR2 52/8
France, 1988 (Contender)	WG	2.2	0.45	2	16	0.32		F972/88/B4
France, 1988 (Contender)	WG	2.2	0.22	1	26	<0.2		F972/88/C4
CABBAGE, SAVOY								
Germany, 1981 (Marner Frühkopf)	DS	0.20 kg ai/ 100 kg seed			90	0.06		BBA 3681
LETTUCE, HEAD								
Germany, 1970 (Rapide)	DP	9.8	dust	g 1	59	<0.5		BBA 415/70
Germany, 1970 (Kordaat)	DP	9.8	dust	g 1	70	<0.5		BBA 1a/71
Germany, 1970 (Rapide)	WP	16	dust	g 2	45	<0.5		BBA 414/70
Germany, 1973 (Marty)	WP	0.96	0.16	g 1	21	4.0		BBA 26/73
Netherlands, 1975 (Zwart-duits)	WP	2.0	0.20	2	14 21 28	3.4 6.0 3.3 2.6 0.37 0.62 1.1 0.67 ≤0.2 (4)		KvW194 (1976)
Netherlands, 1975 (Zwart-duits)	WP	2.0	0.20	2	14 21	1.5 0.88 0.56 0.78 0.25 0.24 ≤0.2 (2)		KvW194 (1976)
Netherlands, 1980 (Desi minor)	WP	2.0	0.18	g 1	28 42	0.9 0.7 0.7 0.9 <0.3 (2) 0.3 0.4		KvW225 (1982)
Netherlands, 1980 (Desi minor)	WP	2.0	0.18	g 1	28 42	2.4 1.3 0.7 3.0 <0.3 (4)		KvW225 (1982)
PEAS, GREEN								
France, 1987 (Zorba)	WG	2.2	0.45	1 2	29 16	<0.2 0.22		42308 F87/INRA
SPINACH								
Germany, 1981 (Atlanta)	DS	0.20 kg ai/ 100 kg seed			40	leaves <0.03		BBA 3581
Netherlands, 1975 (Bergola)	WP	2.0	0.20	g 1	28 28 31 31	7.2 9.6 10 10 c <0.2 (2) 1.1 0.96 0.92 0.85 c 0.29 0.27		KvW189 (1975)
Netherlands, 1975 (Bergola)	WP	2.0		g 1	28	14 5.4 4.2 4.8 c <0.2 (2) 0.28 0.26 0.43 0.38 c 0.29 0.27		KvW189 (1975)
TOMATO								
France, 1988 (Rio Grande)	WG	2.2	0.45	4 dt	11	0.17 0.36		549/4 549/5
France, 1988 (Apla)	WG	1.3	0.67	4	19	<0.2 <0.2		C 16/4 C 16/5
France, 1989 (Trésor)	WG	2.2	0.22	4	8	<0.2		F885/89/4
France, 1989 (Trésor)	WG	3.2	0.32	4	8	<0.2		F885/89/5
France, 1989 (Donna)	WG	2.2	0.22	4	10	0.95		F885/89/50/4
France, 1989 (Donna)	WG	3.2	0.32	4	10	1.1		F885/89/50/5
France, 1989 (Donna)	WG	2.2	1.1	3	28	<0.2		F985/89/4
France, 1989 (Donna)	WG	3.2	1.6	3	28	<0.2		F985/89/5

g: glasshouse c: control sample dt: other dithiocarbamates also applied during the growing season.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information was available on the fate of thiram residues in commodities in commercial storage.

In processing

Information was provided on the fate of thiram during the processing of apples to juice and pomace and during the production of wine.

In an apple processing study in the USA thiram was applied 13 times at 11.6 kg ai/ha during the growing period in 1993 to Twenty-ounce apples on a farm in New York State (Armstrong, 1993; Leppert, 1995; Tufts, 1995). Apples (50 kg) were harvested 7 days after the final application and converted to juice and pomace according to a simulated commercial process. There was no washing step; the trial was designed to represent a "worst case" for residues. Thiram residues in apples, juice and pomace were measured by a CS_2 evolution GLC head-space method. The thiram residue level in the juice was about 30% of that in the apples, while the level in wet pomace was the same as in the apples. Wet pomace was heated at 77-88°C until the weight had decreased to 20-25% to produce dry pomace. The increase in the thiram level suggested that little of the residue had been lost during the drying process. The residues in the analysed commodities were as shown below.

	Thiram residue
apples	11.5 mg/kg
juice	3.3 mg/kg
wet pomace	11.8 mg/kg
dry pomace	42 mg/kg

In grape processing studies in France field-sprayed grapes were processed into juice, wine and raisins (Blaschke, 1995a,b) and only wine (Blaschke, 1995c,d). The thiram results are summarized in Table 33. Samples other than wine had been stored for about 18 months at ≤18°C before analysis. Wine was kept at 4-8°C.

Approximately 50 kg of grapes were crushed to produce wine, while 3 kg and 6 kg were used for juice and raisin production respectively. Crushing took place in September and the wine was bottled (for analysis) about 6 months later. The champagne in trial 28203B004 (Blaschke, 1995d) was matured in the bottles for an additional year. Wet pomace was dried in an oven for 5 to 8 days and lost 50-60% of its weight.

Grapes were stemmed manually and crushed to produce juice, which was heated to 85-88°C for 5 minutes and then refrigerated for up to 5 days. The supernatant clear juice was bottled and sterilized by heating at 100°C for 20 minutes.

In raisin production, the grape bunches were dried in an oven at 60°C for about 6 days and lost 84-91% of their weight. After drying, the stems were manually removed.

Although no other dithiocarbamate fungicides had been used on the crops (except in trial 28203B004 where mancozeb had been used at a very early stage approximately 17 weeks before harvest) the residue levels of thiram calculated from the CS_2 evolution method were substantially higher than thiram measured by HPLC. CS_2 residues were not detected in wine produced from untreated grapes and in only four grape samples from untreated plots (trial 28203B002, 0.08 and 0.07 mg/kg as CS_2, and trial 28203B002, 0.10 and 0.08 mg/kg as CS_2) which suggests the production of thiram metabolites containing the CS_2 group and with sufficient persistence and water-solubility to enter the wine. An unconfirmed possibility is that the liberated CS_2 was derived from rubber tubing or gloves.

Table 33. Residues of thiram (expressed as thiram) in grapes, juice, pomace, must, wine and raisins after foliar application of thiram to grapes in supervised trials in France. The application conditions in the trials are listed in Table 30 (supervised trials on grapes).

Commodity	Residues, as thiram, mg/kg							
	Blaschke, 1995b (France, 28203B001)		Blaschke, 1995a (France, 28203B002)		Blaschke, 1995c (France, 28203B003)		Blaschke, 1995d (France, 28203B004)	
HPLC method								
Grapes (PHI, days)	1.6 (33)	4.3 (22)	1.2 (33)	1.2 (22)	1.4 (49)	1.9 (22)	1.2 (34)	3.0 (22)
Juice	<0.1		<0.1	<0.1				
Must	<0.1	0.2	<0.1	<0.1	1.3	1.7	<0.1	0.3
Wet pomace	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dry pomace	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Wine	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Raisin	5.7	4.9	<0.1	<0.1				
CS_2 method								
Grapes (PHI, days)	9.3 (32)	12 (21)	1.3 (32)	4.3 (21)	3.0 (48)	7.4 (21)	2.4 (33)	2.5 (21)
Wine	0.9	0.9	0.22	0.25	0.98	0.74	0.12	0.19

Residues in the edible portion of food commodities

The thiram level in apple juice was about 30% of the level in the apples.

Thiram residues in grape juice and wine, by an HPLC method, were undetectable (<0.1 mg/kg).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Monitoring data for residues of dithiocarbamates (including thiram) in fruit and vegetable commodities in trade were available from The Netherlands, Belgium and Denmark (Tables 34-37).

Table 34. Residues of thiram (expressed as thiram) in domestic fruit and vegetable commodities in trade in The Netherlands, 1976.

Commodity	Number of samples				
	Analysed	No residues (≤0.05 mg/kg)	Residues >0.05 ≤1, mg/kg	Residues >1 ≤3, mg/kg	residues >3 mg/kg
Endive	100	98	0	1	1
Lettuce	590	582	6	1	1
Parsley	8	8	0	0	0
Celery	29	29	0	0	0
Spinach	52	52	0	0	0
Cauliflower	22	22	0	0	0
Brussels sprouts	48	48	0	0	0
Butter beans and French beans	16	15	1	0	0
Chicory	19	18	1	0	0
Leek	30	30	0	0	0
Strawberry	45	4	6	19	16[1]

[1] Residues of thiram exceeded the MRL in 12 strawberry samples. Levels were 4.2, 4.8, 5.0, 5.1, 5.5, 6.1, 7.8, 8.8, 8.9, 14, 14 and 15 mg/kg.

Table 35. Netherlands monitoring of food in commerce for dithiocarbamate residues for 1991-1994.

Commodity	Number of samples			
	Analysed	No residues (1991-93 LOD 0.2 mg/kg, 1994 LOD 0.05 mg/kg)	Residues detected, <MRL (NL)	Residues >MRL (NL)
Citrus fruit	64	59	4	0
Pome fruit	609	522	87	0
Stone fruit	404	362	42	0
Berries and small fruit	2478	2152	324	2[1]
Fruit, trop and sub-trop	180	164	16	0
Root and tuber veg.	332	310	19	3[2]
Bulb veg.	36	36	0	0
Fruiting veg.	731	656	75	0
Brassica veg.	167	126	41	0
Leaf and herb veg.	4356	3755	576	25[3]
Stem veg.	948	911	36	1[4]
Mushrooms	81	79	2	0
Pulses	89	83	6	0

[1] Fruits exceeding the MRL were grapes (1 of 549 samples) and "other small fruit" (1 of 39 samples)
[2] Residues in celeriac exceeded the MRL in 3 of 119 samples
[3] Vegetables with residues exceeding the MRLs were lamb's lettuce (8 of 267 samples), head lettuce (2 of 1517 samples), other lettuce (6 of 377 samples), endive (6 of 744 samples), spinach (2 of 204 samples) and parsley (1 of 359 samples)
[4] The MRL was exceeded in a sample of leeks (1 of 405 samples)

Dejonckheere *et al.* (1996) published a report on pesticide residues in fresh vegetables, fruits, and other selected food items in Belgium for 1991-1993. The survey included dithiocarbamate residues, which were measured by a CS_2 evolution colorimetric method (Table 36). The residues were detected more often and at higher levels in leafy vegetables.

Table 36. Dithiocarbamate residue monitoring data for Belgium for 1991-1993 (Dejonckheere *et al.*, 1996).

Commodity	Number of samples		LOD, mg/kg	Max detected residue, mg/kg
	Analysed	Residues detected		
Celery leaves	100	16	0.2	41
Endive	75	13	0.2	19
Grapes	108	0	0.2	<0.2
Lamb's lettuce	100	16	0.2	55
Leeks	108	2	0.2	2.8
Lettuce	112	16	0.2	33
Strawberries	73	1	0.2	5.2

Juhler *et al.* (1996) included dithiocarbamate residues in the 1994 survey of pesticide residues in Danish food by the National Food Agency of Denmark (Table 37). The samples were analysed by a colorimetric CS_2 evolution method. The LOD for each crop was not explicitly stated, but for this method would be expected to be close to 0.1 mg/kg. In many commodities dithiocarbamates were detected in 10-35% of the samples.

Table 37. Dithiocarbamate residue monitoring data for Denmark for 1994 (Juhler *et al.*, 1994).

Commodity	Domestic or import	Number of samples		Max detected residue, mg/kg (as CS_2)
		Analysed	Residues detected	
Apples	D	39	3	0.16
Apples	I	43	10	0.65
Apricots	I	2	1	0.12
Carambolas	I	6		
Celery	D	20		
Celery	I	20		
Cherries	D	13	4	0.14
Cherries	I	15	4	0.75
Cucumbers	I	16	5	0.35
Currants, black	D	10		
Currants red/white	D	10	1	0.4
Currants red/white	I	6	2	1.1
Gooseberries	D	7	3	0.37
Grapefruit	I	19	1	0.13
Grapes	I	63	10	0.75
Kiwifruit	I	37		
Lemons, limes	I	7		
Lettuce, iceberg/head	D	35	7	0.48
Lettuce, iceberg/ head	I	40	6	1.7
Mandarins/ clementines	I	23	2	0.33
Mangos	I	8	1	0.1
Nectarines	I	19	7	0.75
Oranges	I	27	2	0.18
Papayas	I	5	2	0.20
Passion fruit	I	2	1	1.6
Peaches	I	17	12	0.72
Pears	D	16	2	0.21
Pears	I	24	7	0.53
Peppers	I	27		
Plums	D	20	7	0.56
Plums	I	31	4	0.55
Potatoes	D	42		
Potatoes	I	25	2	0.19
Raspberries	D, I	12		
Strawberries	D	25	7	0.3
Strawberries	I	31	7	0.65
Tomatoes	I	26	5	0.29

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware of the following national MRLs (see explanatory notes on next page).

Country (residue definition)	Commodity and MRL
Argentina (CS)	apples 2; beans 0.5; carrots 0.1; celery 3; cherries 1; grapes 5; lettuce 3; melons 1; peaches 3; pears 2; plums 1; potatoes 0.1; tomatoes 3; turnips 0.1
Australia (CS)	fruits 7; vegetables 7
Austria (DT)	fruits 2; vegetables 2
Belgium (T)	apples 3; apricots 3; bananas 3; cherries 3; grapes 3.8; other fruits 3; peaches 3; pears 3; plums 3; potatoes 0.05; strawberries 3.8; vegetables 3
Brazil (T)	bananas 1; beans 7; peas 7
Canada (T)	apples 7; bananas 1; beans 7; celery 7; peaches 7; pears 7; strawberries 7; tomatoes 7
Chile (DT)	apples 3; carrots 0.5; cereals 0.2; cherries 1; grapes 5; lettuce 1; peaches 3; pears 3; plums 1; potatoes 0.1; tomatoes 3
Denmark (DT)	apples 2; apricots 2; bananas 2; bulb vegetables 0.5; carrots 0.5; cherries 2; foliar vegetables 2; grapes 2; other fruits 2; peaches 2; pears 2; plums 2; potatoes 0.1; strawberries 2; vegetables 1
EEC (T)	apples 3; apricots 3; bananas 3; cherries 3; grapes 3.8; other fruits 3; peaches 3; pears 3; plums 3; strawberries 3.8; vegetables 3
France (DT)	apples 1; apricots 1; bananas 2; beans 0.5; bulb vegetables 0.5; cherries 1; grapes 1; lettuce 4; other fruits 2; peaches 1; pears 1; plums 1; potatoes 0.05; tomatoes 1; vegetables 2
Germany (T)	apples 3; apricots 3; bananas 3; cherries 3; grapes 4; other fruits 3; peaches 3; pears 3; plums 3; potatoes 0.2; strawberries 4; tomatoes 1; vegetables 3
Greece (T)	apples 3; apricots 3; bananas 3; cherries 3; grapes 3.4; other fruits 3; peaches 3; pears 3; plums 3; strawberries 3.4; vegetables 3
Ireland (T)	apples 3; apricots 3; bananas 3; cherries 3; grapes 4; other fruits 3; peaches 3; pears 3; plums 3; strawberries 4; vegetables 3
Israel (DT)	apples 3; bananas 1; beans 0.2; carrots 0.2; celery 5; cherries 1; grapes 5; lettuce 0.5; melons 0.5; peaches 3; pears 3; plums 1; potatoes 0.1; strawberries 3; tomatoes 3
Italy (T)	apples 3; apricots 3; bananas 3; cherries 3; grapes 3.8; other fruits 3; peaches 3; pears 3; plums 3; potatoes 2; strawberries 3.8; vegetables 3
Japan (T)	apples 1; peaches 0.5; pears 0.5
Luxembourg (DT)	apples 2; apricots 2; beans 2; carrots 0.5; celery 0.2; cherries 1; garlic 0.5; grapes 2; lettuce 5; onions 0.5; peaches 2; pears 2; peas 2; plums 1; strawberries 2; tomatoes 2
Mexico (T)	apples 7; celery 7; peaches 7; strawberries 7; tomatoes 7
Netherlands (NL)	apricots 2; beetroot[14] 2; Brassica vegetables[14] 2; bulb vegetables 0.5; cane fruit (other than wild) 3; carrots[14] 2; celeriac[15] 2; celery[14] 2; cherries[16] 2; courgettes[14] 2; cucumbers[14] 1; currants (red black white) 3; gherkin 2; globe artichokes[14] 2; gooseberries 3; hops 25; leek[14] 2; legume vegetables (fresh)[14] 2; maize and rice[17] 0.5; melons[14] 1; nectarines 2; nuts[18] 2; oil seeds 0.1*; oranges 2; other cereals 0.5; other citrus fruit[14] 2; other cucurbits (inedible peel)[14] 2; other food commodities 0.05*; other Solanaceae 2; parsnips[14] 2; peaches 2; plums[16] 2; pome fruits[14] 2; radish[14] 2; salsify[14] 2; spinach and similar[17] 2; strawberries (other than wild)[19] 3; sweet corn[17] 2; table and wine grapes[19] 3; tea 0.1*; tomatoes[14] 2; water cress[14] 2; witloof[15] 2
New Zealand (DT)	fruits 7; vegetables 7
Poland (CS)	cereal grains 0.05; cucumber 1; eggs 0.05; fruits 2; leafy vegetables 5; meat and meat products (in fat) 0.05; milk and milk products 0.05; stalk and stem vegetables 5,; tomato 1; vegetables other 2
Singapore (T)	fruits 3; vegetables 3
South Africa (CS)	apples 3; apricots 3; grapes 3; peaches 3; pears 3; plums 3
Spain (DT)	apples 3; apricots 3; bananas 3; cherries 3; grapes 4; other fruits 3; peaches 3; pears 3; plums 3; potatoes 0.2; strawberries 4; vegetables 3
Sweden (DT)	carrots 0.5; fruits 1; potatoes 0.1; vegetables 1
Switzerland (DT)	foliar vegetables 2; fruits 2; potatoes 0.05; vegetables 2
UK (DT)	apples 3; apricots 3; bananas 1; beans 0.5; carrots 0.5; cherries 3; grapes 5; peaches 3; pears 3; plums 1; potatoes 0.1; strawberries 3; tomatoes 3
USA (T)	apples 7; banana 7; celery 7; cereals 0.5; onions 0.5; peaches 7; strawberries 7; tomatoes 7

* At or about the LOD

Residue definitions:
(T) thiram
(CS) mg CS_2/kg

[14] Residues from mancozeb, maneb, metiram, propineb and zineb, total with a maximum of 0.5 mg CS_2/kg.
[15] Residues from mancozeb, maneb, metiram, propineb and zineb, total with a maximum of 0.2 mg CS_2/kg.
[16] Residues from mancozeb, maneb, metiram, propineb and zineb, total with a maximum of 1 mg CS_2/kg.
[17] No residues from mancozeb, maneb, metiram, propineb and zineb (LOD 0.05 mg CS_2/kg).
[18] No residues from mancozeb, maneb, metiram, propineb and zineb (LOD 0.1 mg CS_2/kg).
[19] Residues from mancozeb, maneb, metiram, propineb and zineb, total with a maximum of 2 mg CS_2/kg.

(DT) sum of dithiocarbamates (mg CS_2/kg)
(NL) all compounds that give CS_2, sum of dithiocarbamates, expressed as CS_2 in mg/kg

APPRAISAL

Thiram was originally evaluated in 1965 (toxicology) and 1967 (toxicology and residues) and is included in the dithiocarbamate group of compounds. It was evaluated at the present Meeting within the CCPR periodic review programme.

Thiram is a protective dithiocarbamate fungicide used as a foliar treatment on fruits, vegetables and ornamentals to control *Botrytis* species, rust, scab and storage diseases, and as a seed treatment to control seedling blights and a number of fungi that cause "damping off" in seedlings. Thiram formulations are registered for use in many countries. The Meeting was provided with information on registered uses on fruits, vegetables and other crops.

The Meeting received extensive information on the metabolism of thiram in rats, farm animals, apples, grapes, soya beans, cotton, wheat and sugar beet, its environmental fate in soil and water/sediment systems, methods of residue analysis, the stability of residues in stored analytical samples, approved use patterns, supervised residue trials and the fate of residues during processing.

When rats were dosed orally with [*thiocarbonyl*-^{14}C]thiram much (40-60%) of the ^{14}C was eliminated as volatile compounds in exhaled air, 25-35% was excreted in the urine and 2-5% in the faeces. The volatiles were collected in traps suggesting the presence of CS_2, CO_2 and COS. Five polar metabolites and conjugates were identified in the urine: 2-thioxo-4-thiazolidinecarboxylic acid, dimethyldithiocarbamoyl glucuronide, dimethyldithiocarbamoylsulfenic acid, methyl dimethyldithiocarbamate, and dimethyldithiocarbamoylalanine.

A major part of the ^{14}C was eliminated in respiration gases from lactating goats dosed with [*thiocarbonyl*-^{14}C]thiram equivalent to 2.5, 3.3 and 23 ppm in the feed for 4 consecutive days. Most (90% or more) of the ^{14}C in the expired air was present in CO_2, with the remainder in CS_2 and COS. The levels of ^{14}C in the milk were quite low and reached their plateaux within 1.5 to 3 days of the first dose. The total ^{14}C in the milk constituted 1.0-1.8% of the administered dose. The levels of ^{14}C were much higher in the liver than in the other tissues.

The metabolism of thiram in goats was quite extensive and much of the ^{14}C in the milk and tissues was present as very polar extractable material or as bound residues. It is likely that thiram is rapidly converted to dimethyldithiocarbamic acid and then to dimethylamine and CS_2. CS_2 is converted to COS and carbonate. [^{14}C]carbonate then enters fat, protein and carbohydrates.

When laying hens were dosed with [*thiocarbonyl*-^{14}C]thiram equivalent to 0.6 and 6.0 ppm in the feed for 4 consecutive days approximately 1% of the dose was present in the liver, which had higher levels than the other tissues. Levels of ^{14}C in egg white and egg yolk were quite low throughout the 4 days, with approximately 0.15% of the administered ^{14}C appearing in the eggs.

About half of the ^{14}C in the liver was incorporated into natural products such as acids, amino acids, peptides and proteins. Three metabolites constituting only a small percentage of the ^{14}C were identified as dimethyldithiocarbamoylornithine, 2-thioxo-4-thiazolidinecarboxylic acid and dimethyldithiocarbamoyl glucuronide.

Apples and leaves on apple trees were treated with [*thiocarbonyl*-^{14}C]thiram and examined for ^{14}C periodically after treatment. Initially most of the ^{14}C was on the fruit and leaf surfaces, but by day 14 only half of the remaining residue was on the surface. By day 101 only 2.7% of the residue was on the surface with 38% in the peel and 60% in the pulp. Thiram itself was not detected within the fruit except on day 0. The residue incorporated in the fruit contained only a small percentage of the dimethyldithiocarbamoyl moiety as demonstrated by the release of small amounts of CS_2 by acid digestion, equivalent to 1-3.5% of the incorporated ^{14}C.

When grapes and vine leaves were treated with [*thiocarbonyl*-^{14}C]thiram the ^{14}C residues on and within the fruit were quite persistent. The residues on the leaf surfaces disappeared more quickly. In grapes harvested 27 days after the final thiram application 35% of the remaining ^{14}C was in surface washings, 44% in juice and 21% in press cake.

Most of the ^{14}C in the surface washings from grapes after 27 days was in thiram itself, but HPLC showed the presence of two metabolites both more polar than thiram. Approximately 5% of the ^{14}C residue within the grapes (harvested 0, 14 or 27 days after the final treatment) liberated CS_2 on acid digestion, which demonstrated that very little of it contained the dimethyldithiocarbamoyl moiety. Most of the ^{14}C residue in the juice was shown to have a molecular weight below 500, but could not be positively identified. Much of the ^{14}C in the grapes was very polar or unextractable and had probably become incorporated into natural products.

When soya bean, cotton and wheat plants were grown from [*thiocarbonyl*-^{14}C]thiram-treated seed, the ^{14}C levels in the cotyledons and roots of the seedlings were higher than in the leaves and stems. In mature plants the highest ^{14}C levels were in the roots and the lowest in the seeds.

The major metabolites in soya bean, cotton and wheat seedlings were identified as dimethyldithiocarbamoyl and dimethylthiocarbamoyl glycosides. When an aqueous wheat extract was treated with hot acid only 3.4% of the ^{14}C was liberated as CS_2, suggesting that if any remaining metabolites contained the dithiocarbamoyl moiety they were largely unextractable.

In further studies on soya beans and wheat produced from thiram-treated seed it was shown that much of the ^{14}C had been incorporated into endogenous natural products such as sugars, fatty acids and citric acid, but some of the dimethyldithiocarbamoyl moiety had conjugated with amino acids and sugars. Thiram itself was not detected.

The main metabolite identified was 2-dimethylamino-4-thiazolinecarboxylic acid, apparently produced from dimethyldithiocarbamoylalanine. When homogenized soya bean tissue (forage, straw, pod and seed) was digested with acid 3-9% of the ^{14}C in each tissue were released as CS_2 and 3-24% as CO_2. In straw, chaff and wheat grain the corresponding figures were 2-9% and 8-21%.

^{14}C levels in sugar beet tops and roots were generally very low in plants produced from [*thiocarbonyl*-^{14}C]thiram-treated seed. As in the soya bean and wheat studies ^{14}C was detected in control plants growing nearby, suggesting that $^{14}CO_2$ had been produced. Only 3.2% of the ^{14}C in the roots was released as CS_2 when the homogenized tissue was digested with acid, demonstrating that very little of the incorporated ^{14}C contained the dithiocarbamoyl moiety.

Thiram, [*thiocarbonyl*-^{14}C]-labelled, disappeared rapidly when incubated in a sandy loam soil under aerobic conditions at 20°C and 75% of field moisture capacity, with an initial half-life of about 2 days and 85% disappearance in 7 days. Mineralization was also rapid with 9% of the applied ^{14}C evolved as $^{14}CO_2$ in 2 days and 50% within 21 days. The major metabolite was identified as dimethylcarbamoperoxothioic acid, which reached its maximum concentration on day 4 of the incubation. There were a number of other minor metabolites, three of which were identified.

Labelled thiram disappeared with a half-life of 3.7 days when exposed on a thin layer of sandy loam soil to simulated sunlight. After 21 days the volatile ^{14}C amounted to 57%, 37% as CO_2 and 20% corresponding to CS_2 in an HPLC system, but not fully identified.

The adsorption and desorption properties of thiram were measured on four soils, a sandy loam, a loamy sand, a silt loam and a loam. Thiram was judged to be slightly mobile to immobile in the soils tested.

When [*thiocarbonyl*-^{14}C]thiram was incubated in aquatic systems of river or pond water and sediment in the dark at 20°C under aerobic conditions for 101 days the initial half-life of thiram was about 2 days with more than 90% disappearance within 7 days. CS_2, CO_2 and methyl dimethyldithiocarbamate were identified as metabolites. CS_2 and the ester reached their peak concentrations in the water on day 4.

The analytical methods for dithiocarbamates which rely on CS_2 evolution may be used for the determination of thiram residues. Such methods have been reviewed previously for mancozeb, maneb and propineb (1993 JMPR) and metiram (1995 JMPR). Methods where the generated CS_2 is measured by colorimetry or by head-space GLC have been shown to be suitable for thiram, as for the other dithiocarbamates. Limits of determination in various commodities are usually 0.05-0.1 mg/kg (as CS_2).

An HPLC method has been developed for thiram residues in crops that measures thiram as

the intact molecule and distinguishes it from other dithiocarbamates. The residue is extracted with solvent from crop samples and, after clean-up on a C18 microcolumn, determined on a C18 reversed-phase HPLC column with UV detection at 280 nm. Quantitative recoveries were achieved from fruit and processed fruit fractions down to 0.1-0.2 mg/kg. Low recoveries occurred in wine fortified at the 0.1 mg/kg level because thiram was being degraded.

Data were available on the frozen storage stability of thiram residues on plums and in apple juice and apple pomace.

Thiram residues were shown to be stable on frozen whole plums stored at a freezer temperature below -20°C for 500 days. At three of the samplings the plums were analysed by a CS_2 evolution method and by an HPLC method specific for thiram. The results were in good agreement. If plums were macerated in a blender thiram was decomposed by exposure to the macerate. It was recommended that fruit for residue analysis should be stored whole, subjected to a minimum of cutting (into halves and quarters) while still frozen, and analysed immediately.

Thiram residues in apple juice, wet pomace and dry pomace fortified at 1 mg/kg were stable at -20 ± 5°C for the intervals tested, 35 to 49 weeks.

The Meeting considered the definition of thiram residues in terms of the crop metabolism studies, the supervised trials where residues had been determined by both a CS_2 evolution method and an HPLC method, and the needs of enforcement agencies.

The metabolism studies suggest that thiram is the major part of the CS_2-evolving residue, particularly when the residue is reasonably fresh and at the higher levels. Analyses of samples in supervised trials by the HPLC and CS_2 methods are usually in good agreement, which also suggests that thiram itself is the main residue.

The 1995 JMPR (Report, Section 2.8.1), in explaining the current basis for the definition of residues, stated "Preferably no compound, metabolite or analyte should appear in more than one residue definition."

The Meeting agreed that thiram should be included in the definition of dithiocarbamate residues:

> *The MRLs refer to total dithiocarbamates, determined as CS_2 evolved during acid digestion and expressed as mg CS_2/kg.*

For dietary intake estimations the supervised trials median residue (STMR) will be expressed as thiram because intakes need to be in terms of thiram itself for comparison with its ADI. For estimates of acute intake a residue such as an MRL, which is expressed in terms of CS_2, must be multiplied by a factor of 1.58 for comparison with an acute reference dose expressed in terms of thiram.

The Meeting received data on thiram residues from supervised trials on apples (Belgium, France, Germany, Italy, The Netherlands, Poland), pears (Belgium, Germany, Italy, Spain), peaches (France, Italy, Spain), plums (France, Italy), cherries (Italy, Spain), grapes (France, Germany), strawberries (Belgium, France, Germany, Poland), dwarf French beans (Germany), French beans (France), Savoy cabbage (Germany), green peas (France), head lettuce (Germany, The Netherlands), spinach (Germany, The Netherlands), and tomatoes (France).

In the trials thiram was determined by CS_2 evolution methods or by HPLC, and in some trials by both methods. Residues are expressed as thiram in the following discussion.

In some trials other dithiocarbamates had been used on the crop during the growing season. Samples from such trials were considered valid for estimating thiram residue levels only if they had been analysed specifically for thiram by an HPLC method.

Thiram is registered for application up to 12 times on pome fruit in Germany at a spray concentration of 0.1-0.16 kg ai/hl or 1.5-2.4 kg ai/ha, with a 10-day PHI. Decline curves from pome fruit trials suggest that thiram residues decrease with a typical half-life of about 10 days and that data from 7-15 days, equivalent to a concentration range of ±30%, are within acceptable range of a 10

days PHI. The decline curves also suggest that applications more than 30-40 days before the final application will contribute less than 10% to the final residues, so they should not be increased by more than 4 or 5 applications.

Apples. Thiram residues in two Belgian trials (spray concentration 0.16 kg ai/hl, PHI 9 days) were 2.7 and 4.6 mg/kg, and from a French trial (spray concentration 0.16 kg ai/hl, PHI 14 days) 2.4 mg/kg. In two German trials, one at 0.2 kg ai/hl, 15 days PHI (which exceeds 14 days but the spray concentration is slightly higher than 0.16 kg ai/hl), and the other at 0.16 kg ai/hl with a 14-day PHI, thiram residues were 0.49 and 1.9 mg/kg. In three Italian trials according to the registered use pattern of 0.15-0.20 kg ai/hl with a PHI of 10 days thiram residues were 2.5, 4.1 and 1.1 mg/kg.

The pome fruit registration in The Netherlands permits thiram application rates of 1.4-3.0 kg ai/ha or spray concentrations of 0.10-0.20 kg ai/hl with a 7-day PHI. The registration is for a WG formulation, but the trials with WP formulations are considered comparable. The highest thiram residues in apples at rates of 2.4-3.1 kg ai/ha at a 7-day PHI in three trials in The Netherlands were 0.46, 1.8 and 6.3 mg/kg. In four other trials thiram residues were generally not detected (<0.1 mg/kg) at a PHI of 7 days, but the data could not be used because sample storage conditions before analysis were not available.

Four Polish trials in which apples were treated at 2.4 kg ai/ha and harvested 14 days later were evaluated according to the German use pattern on pome fruit (1.5-2.4 kg ai/ha and 10 days PHI). Thiram residues were 3.8, 3.2, 0.87 and 1.7 mg/kg.

In summary thiram residues in apples from trials according to GAP were Belgium 2.7, 4.6 mg/kg, France 2.4 mg/kg, Germany 0.49, 1.9 mg/kg, Italy 1.1, 2.5, 4.1 mg/kg, The Netherlands 0.46, 1.8, 6.3 mg/kg and Poland 1.7, 3.2, 3.8 mg/kg. The 15 residues in rank order (median underlined) were 0.46, 0.49, 0.87, 1.1, 1.7, 1.8, 1.9, 2.4, 2.5, 2.7, 3.2, 3.8, 4.1, 4.6 and 6.3 mg/kg.

Pears. Two trials in Belgium (2.4 kg ai/ha, 13 and 14 days PHI) and two in Germany (2.4 kg ai/ha, 10 days PHI) were evaluated against German GAP for pome fruit (2.4 kg ai/ha and 10 days PHI). The thiram residues were 0.69, 1.6, 1.9 and 0.90 mg/kg. Residue levels resulting from 12 and 14 applications (0.69 and 1.6 mg/kg) were similar to those from 4 applications (0.90 and 1.9 mg/kg).

Three trials in Italy (0.15 kg ai/hl, 10 days PHI) were according to Italian GAP for pome fruit (0.15-0.20 kg ai/hl, 10 days PHI). The thiram residues were 0.54, 4.3 and 5.1 mg/kg. A trial in Spain (0.24 kg ai/hl 14 days PHI) was according to Spanish GAP for pome fruit (0.16-0.24 kg ai/hl, 15 days PHI). The thiram residue was 3.0 mg/kg.

The thiram residues in pears from each of the eight trials in rank order (median underlined) were 0.54, 0.69, 0.90, 1.6, 1.9, 3.0, 4.3 and 5.1 mg/kg.

The Meeting noted that the registered use patterns were for pome fruits, that the use patterns in the apple and pear trials were similar and that the residue levels in the two fruits overlapped. The Meeting therefore agreed to evaluate the combined apple and pear data as applying to pome fruits. The thiram residues in apples and pears taken together in rank order (median underlined) were 0.46, 0.49, 0.54, 0.69, 0.87, 0.90, 1.1, 1.6, 1.7, 1.8, 1.9, 1.9, 2.4, 2.5, 2.7, 3.0, 3.2, 3.8, 4.1, 4.3, 4.6, 5.1 and 6.3 mg/kg. The highest residue, 6.3 mg/kg as thiram, is equivalent to 4.0 mg/kg dithiocarbamates as CS_2.

The Meeting estimated a maximum residue level of 5 mg/kg for dithiocarbamates in pome fruits arising from the use of thiram, and noted that this value was the same as the current recommendation for dithiocarbamates in pome fruits. The Meeting estimated an STMR of 1.9 mg/kg for thiram (as thiram) in pome fruit.

Stone fruits. The Italian registered use for thiram on stone fruit permits a spray concentration of 0.15 kg ai/hl and a PHI of 10 days. Thiram residues in peaches in 2 Italian trials matching these conditions were 2.7 and 3.6 mg/kg, and in two Spanish trials under conditions close to Spanish GAP for stone fruit (0.16-0.24 kg ai/hl, 15 days PHI, 14 days in the trials) they were 0.26 and 0.70 mg/kg.

In a French trial on plums which was also according to Spanish GAP the highest residue 14 days after the last of 3 applications was 1.0 mg/kg. In two Italian trials on plums according to Italian GAP for stone fruit the highest residues on day 10 were 0.83 and 0.62 mg/kg.

In two Italian trials on cherries according to Italian GAP the highest residues at the recommended PHI of 10 days were 0.37 and 0.41 mg/kg, but in the second trial a residue of 1.1 mg/kg occurred 15 days after the final treatment. Thiram residues of 0.1 mg/kg were found in cherries from a Spanish trial where the conditions were close to Spanish GAP.

The residue levels in peaches from 2 of the 4 relevant trials appeared to be outside the general population of the stone fruit residues, but 4 trials on peaches were in any case insufficient to support an MRL. The Meeting concluded that the residues in plums (0.62, 0.83 and 1.0 mg/kg) and cherries (0.1, 0.37 and 1.1 mg/kg) from the valid trials could be evaluated together. The residues in rank order (medians underlined) were 0.1, 0.37, 0.62,0.83, 1.0 and 1.1 mg/kg. The highest residue, 1.1 mg/kg as thiram, is equivalent to 0.69 mg/kg dithiocarbamates as CS_2.

The Meeting estimated a maximum residue level of 1 mg/kg for dithiocarbamates (as CS_2) in plums and cherries arising from the use of thiram, and an STMR of 0.72 mg/kg for thiram (as thiram) in plums and cherries.

Berries and other small fruits. Thiram trials on grapes in France and Germany could not be evaluated because corresponding GAP information was not available.

Thiram trials on strawberries in France could not be evaluated because corresponding information on GAP was not available. Full details of sample storage and handling were not available for the German trials.

The UK use pattern on strawberries allows thiram application of 1.6 kg ai/ha beginning at white bud burst, with repeats at 7-10 day intervals and a PHI of 7 days. In commercial practice there will be no more than 4 or 5 applications in a season. Seven strawberry trials with multiple applications in Belgium were evaluated against the UK use pattern. In four of the trials samples had been taken for analysis just before each application. Generally the number of applications did not seem to influence the level of the residues, although the highest residues were found in two of the trials after 13 and 14 applications. The highest thiram residues (median underlined) in each trial within the range of the UK use pattern resulting from up to 8 applications were 1.4, 1.4, 2.1, 2.1, 2.4, 2.8 and 3.1 mg/kg. The highest residue, 3.1 mg/kg as thiram, is equivalent to 2.0 mg/kg dithiocarbamates as CS_2.

The Meeting estimated a maximum residue level of 5 mg/kg for dithiocarbamates arising from the use of thiram, and an STMR of 2.1 mg/kg for thiram (as thiram), in strawberries.

Residue data on beans, Savoy cabbage, green peas, head lettuce and spinach could not be evaluated because there was no matching GAP or because the number of trials was too small.

The UK registration for thiram on tomatoes allows a spray concentration of 0.32 kg ai/hl and a PHI of 7 days. Four tomato trials in France at 0.22 and 0.32 kg ai/hl and 8 and 10 days PHI produced thiram residues of <0.2, <0.2, 0.95 and 1.1 mg/kg. The Meeting agreed that four trials in one year were inadequate to estimate a maximum residue level for tomatoes.

Information on the fate of thiram during the processing of apples and grapes was made available to the Meeting.

The levels of thiram in apple juice, wet pomace, and dry pomace were 0.29, 1.02 and 3.65 times the level in the apples, suggesting that little of the thiram was lost during the drying process.

In four studies in France field-sprayed grapes were processed to juice, wine and raisins. Thiram residues were not detected (<0.1 mg/kg) in wine by an HPLC method, but were found at 0.12-0.98 mg/kg (as thiram) by a CS_2 evolution method. The thiram residues measured in the grapes by the CS_2 method were also somewhat higher than by the HPLC method. The results obtained by the HPLC method were considered more reliable and were used for estimating processing factors. Since thiram residues were not detected (<0.1 mg/kg) in wine, juice, wet pomace or dry pomace by the HPLC method, the processing factors for grapes to wine for the 4 trials (2 sampling intervals) by the HPLC method were <0.023, <0.033, <0.053, <0.062, <0.071 (median) and <0.083 (3).

In two of the trials thiram residue levels were determined in raisins. In one they were 3.6 and

1.1 times those in the grapes and in the other they were not detected (<0.1 mg/kg). Because of the inconsistency the Meeting could not draw any conclusions about likely residues in raisins.

Monitoring data for dithiocarbamate residues on commodities in trade were provided from The Netherlands, Belgium and Denmark. In most commodities dithiocarbamates were detected in fewer than 15-20% of the samples.

RECOMMENDATIONS

On the basis of the data from supervised trials with thiram the Meeting concluded that the residue levels listed below are suitable for establishing MRLs. Consolidated recommendations for MRLs for dithiocarbamates are listed in the monograph on dithiocarbamates.

Thiram residues, as thiram, may be calculated from dithiocarbamate residues expressed as CS_2 from the relation thiram = $CS_2 \times 1.58$.

Definition of the residue

For compliance with MRLs: The MRLs refer to total dithiocarbamates, determined as CS_2 evolved during acid digestion and expressed as mg CS_2/kg.

For estimation of dietary intake: thiram.

Commodity		Recommended MRL[1], mg/kg		Based on PHI, days	STMR[2], mg/kg	STMR-P[2], mg/kg
CCN	Name	new	current			
FS 0013	Cherries	1		10-15	0.72	
FS 0014	Plums	1		10-14	0.72	
FP 0009	Pome fruits	5	5	7-15	1.9	
FB 0275	Strawberry	5		7	2.1	
	Apple juice					0.55
	Apple pomace, wet					1.9
	Apple pomace, dry					6.93

[1] Expressed as CS_2
[2] Expressed as thiram

FURTHER WORK OR INFORMATION

Desirable

The rates of hydrolysis of thiram at various pH values should be clarified. Full copies of the reports of the studies should be made available for review.

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