

METIRAM (186)

IDENTITY

Common name: metiram. No common name was accepted by ISO because the product appears to be a mixture rather than a complex (Tomlin, 1994).

Chemical name

IUPAC: zinc ammoniate ethylenebis(dithiocarbamate) - poly[ethylenebis(thiuram disulfide)]

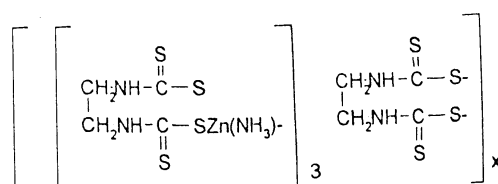
CA: metiram (composition not specified)

CAS No: [9006-42-2]

CIPAC No: 478

Synonyms: Polyram

Structural formula:



Molecular formula (monomer): $\text{C}_{16}\text{H}_{33}\text{N}_{11}\text{S}_{16}\text{Zn}_3$

Molecular weight: $(1088.6)_n$

Physical and chemical properties

Metiram pure active ingredient is inaccessible. In the manufacturing process ethylenediamine is reacted with carbon disulfide in ammonia solution to form an ammonium ethylenebis(dithiocarbamate). This intermediate is further reacted with zinc chloride and then with hydrogen peroxide to produce a polymeric precipitate. The gel-like filter cake (metiram TC, wet) consists of about 65% water, 30% metiram and 5% impurities which stabilize the structure of the polymer and optimise the fungicidal activity of the end product.

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The filter cake is suspended in an aqueous solution of the formulation components and spray-dried.

The Meeting was provided with information on the composition of metiram TC (Ohnsorge, 1992).

Physical properties

Density, Polyram DF:	1.742 g/cm ³ (Gückel, 1992)
Bulk density, Polyram DF:	loose 533 g/l. tapped 571 g/l (Gückel, 1992)
Vapour pressure, metiram premix:	<0.01 mPa at 26.2°C (Gückel, 1988)
Water solubility, metiram technical:	approx 2 mg/l at 20°C (Keller and Pawliczek, 1985)
Octanol-water partition coefficient:	0.46-94 at pH 5. 0.19-2.5 at pH 7-9. (Keller, 1985a). Difficult to interpret because metiram is polymeric and a mixture.

Metiram in DMSO/water solution was degraded by UV light of wavelength 300 nm (Sarafin, 1992).

Formulations

Polyram Combi, WP. 70% metiram (formerly declared as 80% metiram complex, dry).

Polyram DF, WG. 70% metiram (formerly declared as 80% metiram complex, dry).

METABOLISM AND ENVIRONMENTAL FATE

Abbreviations of metabolites mentioned in metabolism studies

EDA	ethylenediamine
EU	ethyleneurea
ETU	ethylenethiourea
EBIS	ethylenebisisothiocyanate sulfide
ETT	ethylenethiourea- <i>N</i> -thiocarboxamide
EDTC	ethylenediisothiocyanate
JB	Jaffe's base 1-(2-imidazolin-2-yl)-2-imidazolidinethione
IMD	2-imidazoline

Animal metabolism

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

Two lactating goats weighing 47 and 51 kg were dosed orally for 5 successive days by capsule with radiolabelled metiram, one with 1.49 g [*ethylenediamine*-¹⁴C]metiram and the other with 1.6 g [*thiocarbamoyl*-¹⁴C]metiram, equivalent to 1000 ppm metiram in the feed and 32 mg/kg bw (Holloway *et al.*, 1986). The feed intake was a concentrate ration at 2.4% bw per day and 400 g straw per day. Milk was collected throughout, and the animals were slaughtered 5 hours after the final dose for tissue and organ collection.

The distribution of ¹⁴C in the tissues, milk and excreta is shown in Table 1. The highest levels of metabolites were found in the thyroid, liver and kidneys.

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Table 1. Distribution of radiolabel in the tissues, milk and excreta from 2 goats dosed orally for 5 days with [ethylenediamine-¹⁴C]metiram or [thiocarbamoyl-¹⁴C]metiram equivalent to 1000 ppm in the feed (Holloway *et al.*, 1986).

Sample	thiocarbamoyl label		ethylenediamine label	
	¹⁴ C as % of total administered ¹⁴ C	¹⁴ C as metiram, mg/kg	¹⁴ C as % of total administered ¹⁴ C	¹⁴ C as metiram, mg/kg
Faeces	18		30	
Urine	11		22	
Milk, total	0.87	16	1.6	32
Muscle	0.97	20	1.3	29
Fat	0.04	3	0.06	4
Liver	0.93	83	1.3	118
Kidneys	0.14	84	0.17	97
Thyroid	0.01	128	0.02	346

Milk and tissues were examined for metabolites, but only EU and ETU could be positively identified. A major metabolite found in extracts of milk, kidneys, liver and muscle which could not be identified represented 40% and 66% of the ¹⁴C in day-4 milk, corresponding to 14 and 15 mg/kg. The estimated levels in the tissues were kidneys 48 and 39 mg/kg, liver 25 and 22 mg/kg, and muscle 7 and 4 mg/kg. The residues of ETU and EU are shown in Table 2.

Table 2. Identified metabolites in milk and tissues from 2 goats dosed orally for 5 days with [ethylenediamine-¹⁴C]metiram and [thiocarbamoyl-¹⁴C]metiram equivalent to 1000 ppm in the feed (Holloway *et al.*, 1986).

Sample	Metabolites, mg/kg as metiram			
	thiocarbamoyl label		ethylenediamine label	
	ETU	EU	ETU	EU
Milk, day 4	2	2	10	2
Kidneys	2	8	5	10
Liver	6	2	17	2
Muscle	10	10	17	4

Lactating goats (2 + 1 control, weighing 39, 44 and 41 kg) were dosed orally once daily for 5 days by gelatin capsule with 77 mg radiolabelled metiram ([¹⁴C]ethylenediamine) equivalent to 50 ppm in the feed (Wu, 1989). The feed intake was 1.5 kg/animal/day. Milk and excreta were collected throughout and animals were slaughtered 8 hours after the final dose for tissue collection.

Most of the ¹⁴C (75% of the dose) was excreted in the faeces. Excretion in the urine was also high; on the basis of the level of ¹⁴C in the day 5 evening sample it was estimated that 54% of the dose was excreted in the urine. The total ¹⁴C in the liver, kidneys, muscle and fat accounted for 1.5%, 0.17%, 0.03% and 0.02% of the administered dose respectively. The levels of ¹⁴C in the milk rapidly reached a plateau within 1-2 days, and the total ¹⁴C excreted in the milk (calculated from the level in the day 4 evening milk) accounted for approximately 0.77% of the dose.

Wu (1989) identified a number of the metabolites in the tissues and milk (Table 3). The total ¹⁴C levels expressed as metiram were milk 0.61, liver 6.3, kidneys 3.7, muscle 0.38 and fat 0.25 mg/kg.

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Jaffe's base was a major metabolite in the milk, kidneys and muscle, while ETU constituted 9.4% of the residue in the fat. A considerable percentage of the ^{14}C in each tissue and in milk had been incorporated into natural products such as lactose, amino acids and lipids. The proposed metabolic pathways are shown in Figure 1.

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Table 3. Distribution of metabolites and unknown compounds in milk and tissues from goats dosed orally once daily for 5 days by gelatin capsule with 77 mg radiolabelled metiram ($[^{14}\text{C}]$ ethylenediamine) equivalent to 50 ppm in the feed (Wu, 1989).

Metabolite	Metabolite distribution as % of total ^{14}C in sample (mean from 2 goats)				
	Milk	Liver	Kidneys	Muscle	Fat
EBIS/ETT	0.40	0.87	0.47	3.1	-
JB	29	3.2	40	11	2.2
ETU	1.8	1.3	0.52	2.1	9.4
EU	5.8	2.9	4.5	9.1	1.8
EDA	2.2	5.1	2.8	3.0	4.5
Allantoin	-	3.5	3.4	5.0	-
Creatine	-	1.6	-	3.2	-
<i>N</i> -acetyl-EDA	0.43	-	0.53	0.63	-
Hydantoin	-	0.63	-	3.7	-
Creatinine	-	2.7	-	1.9	-
Glycine	3.7	15	6.3	5.3	2.9
<i>N</i> -formyl glycine	-	4.1	2.9	-	1.4
Lactose	17	-	-	-	-
Lipids	4.8	3.0	1.4	1.6	44
Amino acids	21	44	26	29	22
Unknowns	14	12	12	20	5.3

A group of 30 laying hens weighing 1.3-1.8 kg were dosed orally for 7 days by capsule with radiolabelled 6 mg metiram ($[^{14}\text{C}]$ ethylenediamine), equivalent to 50 ppm metiram in the feed and 3.98 mg/kg bw (Merricks, 1988). The feed intake was 120 g/bird/day. Eggs were collected throughout, and birds were slaughtered 8 hours after the final dose for tissue and organ collection. Christman (1989) measured the levels of metiram and ETU in the tissues and eggs by chemical analysis. The results are shown in Table 4.

Table 4. Levels of metiram (as CS_2) and ETU in the tissues and eggs from hens dosed for 7 days with $[^{14}\text{C}]$ ethylenediamine-labelled metiram equivalent to 50 ppm in the feed (Merricks 1988; Christman 1989). Chemical analysis.

Sample	Metiram as CS_2 , mg/kg	ETU, mg/kg
Breast muscle	0.03 0.05	0.04 0.03
Thigh muscle	0.04 0.03	0.02 0.02
Fat	0.04 0.03	<0.01 <0.01
Liver	0.095 0.095	0.05 0.04
Egg white, day 6	0.02 0.02	0.05 0.07
Egg yolk, day 6	<0.02 <0.02	0.03 0.02

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Wu (1990) identified the metabolites in the tissues and eggs (Table 5). The total ¹⁴C levels expressed as metiram, mg/kg, were liver 3.7, kidneys 5.6, muscle 0.95, fat 0.24, skin 1.1, egg (day 5) 0.69, egg white (day 6) 0.61 and egg yolk (day 6) 1.0.

The major metabolite in all samples was EU. ETU was consistently present at 2-5% of the total ¹⁴C. Lipids and proteins contained ¹⁴C, showing that some of the metiram had been converted to natural products.

The metabolite pattern was reminiscent of those from mancozeb and maneb (1993 JMPR).

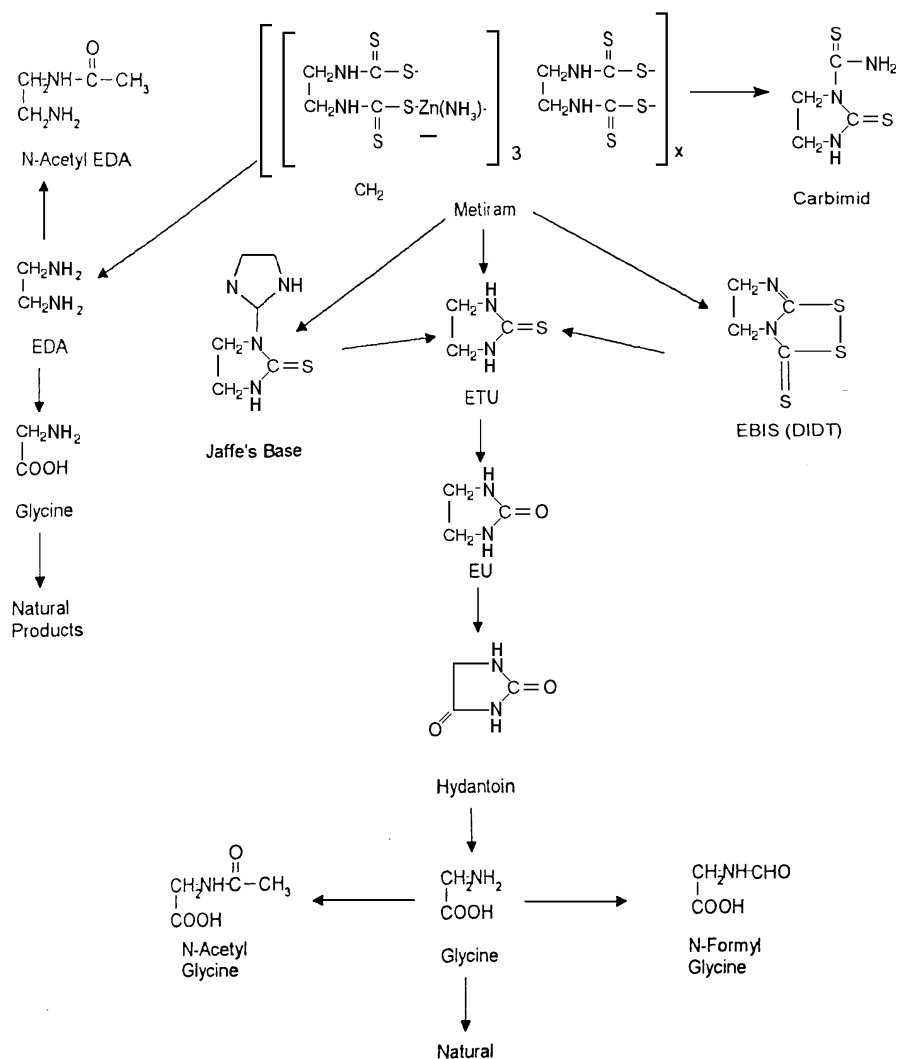
Table 5. Metabolites identified in the tissues and eggs from hens dosed for 7 days with [¹⁴C]ethylenediamine-labelled metiram equivalent to 50 ppm in the feed (Merricks 1988; Wu 1990).

Metabolite	Metabolite expressed as % of total ¹⁴ C in sample (mean from 2 goats)						
	Muscle	Fat	Liver	Kidneys	Skin	Egg white	Egg yolk
EBIS/ETT	3.4	8.3	3.2	1.7	1.7	3.6	9.2
JB	6.4	3.2	4.5	2.8	7.3	1.7	11
ETU	3.6	4.9	2.7	1.8	3.3	2.8	2.5
EU	33	14	9.4	8.4	17	49	14
EDA	2.6	1.9	4.5	3.1		1.2	2.9
Allantoin	0.44	1.0	1.1	4.8			
Creatine		5.5	8.0		0.93		
<i>N</i> -acetyl-EDA	1.4			0.16	1.2		
Hydantoin	8.1				2.7		
Creatinine			2.1	3.5	1.0		
Glycine			5.8	5.4	0.78		

Christman (1989) showed that ETU and JB do not produce CS₂ during the CS₂-generating step in the determination of metiram. EBIS does produce CS₂.

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Figure 1. Metabolic pathways of metiram in goats and laying hens.



Plant metabolism

Information was made available to the Meeting on metiram metabolism in apples and potatoes.

Apples, Cox's Orange variety, were treated 5 times with radiolabelled metiram ($[^{14}\text{C}]$ ethylenediamine) at 1.4 kg ai/ha, and harvested 82 days after the final treatment (Bieber and Kröhn, 1986a). Residues of ^{14}C expressed as metiram were 0.93, 1.08 and 4.8 mg/kg in the flesh, core and peel respectively. Methanol extracted 56-75% of the total ^{14}C in each fraction but only 27-37% of the ^{14}C residues in each fraction

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were soluble in acetone.

The acetone extracts from the flesh, core and peel were examined for the presence of ETU, EBIS, ETT, EDTC, EU and hydantoin, but they could not be detected. ETU levels would not have exceeded 0.005 mg/kg.

TLC analysis of the methanol extracts was not very successful, probably because of the content of sugar compounds. About 42% and 28% of the methanol-soluble ^{14}C from the peel corresponded on TLC to the metiram complex and oxalic acid respectively, and about 10% of that from the flesh to oxalic acid, but full identification was not possible. A further 10% corresponded to the metiram complex + glycine + *N*-acetylenediamine + *N*-formylglycine, but further identification was not possible.

Apples, Ana variety, were treated twice with radiolabelled metiram ($[^{14}\text{C}]$ thiocarbonyl) at 2.4 kg ai/ha, and harvested 4 days after the final treatment (Bieber and Kröhn, 1986b). Residues of ^{14}C expressed as metiram were 3.0, 0.57, 20 and 45 mg/kg in the whole apple, flesh, peel and leaves respectively.

Aqueous methanol and dichloromethane extracted 46% of the total ^{14}C in the apples. Extracts of the fruit, peel and leaves were examined by TLC for likely metabolites, but ETU, EDTC, EBIS, ETT, EDA, EU and hydantoin could not be positively identified. However, analytical interferences from natural compounds in some cases prevented detection at low levels. Of the ^{14}C extracted from the peel and whole apples about 44% corresponded on TLC to the metiram complex, but identification could not be confirmed.

Potato plants, Grata-Mittelfrühe variety, were treated 4 times with radiolabelled metiram ($[^{14}\text{C}]$ ethylenediamine) at 1.6 kg ai/ha, and tubers were harvested 28 days after the final treatment (Bieber and Kröhn, 1986c). Residues of ^{14}C expressed as metiram were 0.86 and 405 mg/kg in the tubers and tops respectively.

In the tubers 60% of the total ^{14}C was extractable with aqueous methanol. The extracts were examined for possible metabolites but ETU, EBIS, ETT and EDTC could not be detected. The level of ETU would not have exceeded 0.005 mg/kg. EU, hydantoin and EDA were possibly present at trace levels.

In the tops 34% of the ^{14}C was extractable into aqueous methanol: on TLC 60% of the extractable ^{14}C corresponded to the metiram complex and approximately 6% to ETU.

Potato plants, Holländer Erstlinge and Sieglind varieties, were treated twice with radiolabelled metiram ($[^{14}\text{C}]$ thiocarbonyl) at 1.6 kg ai/ha, and tubers were harvested 29 days after the final treatment (Bieber and Kröhn, 1986d). Residues of ^{14}C expressed as metiram were 0.12 and 1146 mg/kg in the tubers and dry tops respectively.

In the tubers 54% of the total ^{14}C was extractable with aqueous methanol. The extracts were examined by TLC for possible metabolites but EU, ETU, EBIS, ETT, EDTC and hydantoin could not be detected. The level of ETU would not have exceeded 0.001 mg/kg. EDA was possibly present at trace levels.

In the tops 28% of the ^{14}C could be extracted into aqueous methanol. TLC analysis suggested the presence of ETU at a maximum of 1.8 mg/kg but confirmation was not possible. Low levels of EU, EDTC, EBIS, oxalic acid, glycine, *N*-acetylenediamine and *N*-formylglycine could not be excluded. Of the ^{14}C extracted from the tops about 67% corresponded on TLC to the metiram complex or a compound only slightly modified, but identification could not be confirmed.

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Environmental fate in soil

Information was made available to the Meeting on the hydrolysis, photolysis, and degradation and mobility in soil of metiram, and on the hydrolysis and photolysis of ETU on soil.

Klein *et al.* (1985a) measured the aqueous hydrolysis rates of [ethylene-¹⁴C]metiram and identified the hydrolysis products. Hydrolysis is accelerated at acid and alkaline pH. The rate of dissolution may be the rate-determining step.

pH	Half-life (days) of suspended metiram
3	146
5	447
7	1075
9	174

The reaction products were examined after 40 days hydrolysis of the suspended material in buffer solutions at 25°C and after 30 days hydrolysis of metiram pre-dissolved in DMSO, also in buffer solutions at 25°C. ETU was the main hydrolysis product in all the samples except the suspended material at pH 3 (Table 6).

Table 6. Products of hydrolysis of metiram at 25°C (Klein *et al.*, 1985a).

Product	% of initial ¹⁴ C							
	Suspended				Pre-dissolved			
	pH 3	pH 5	pH 7	pH 9	pH 3	pH 5	pH 7	pH 9
EU	nd	nd	8.7	nd	nd	nd	4.3	13
ETU	25	95	87	67	69	95	91	87
Carbimid	nd	nd	nd	2.1	nd	nd	nd	nd
Hydantoin	3.8	5.4	nd	15	nd	nd	nd	nd
Unidentified polar	71	nd	4.2	13	28	4.8	5.2	nd

nd: not detected

Carbimid: 4,5-dihydro-1-thioformamido-1H-imidazole-2-thione

Klein *et al.* (1985b) showed that [ethylene-¹⁴C]metiram was degraded by UV photolysis. The identified products are listed in Table 7. ETU is a major photolysis product.

Table 7. Products of photolysis of [¹⁴C]metiram suspended in water or pre-dissolved in DMSO before being mixed with water (Klein *et al.*, 1985b).

Product	% of initial ¹⁴ C		
	Metiram suspended in water, UV 5 days at 25°C	Metiram pre-dissolved in DMSO, then in water, UV 5 days at 25°C	Metiram pre-dissolved in DMSO, then in water, UV (xenon) 5 days at 35°C
ETU	55		72
EU		37	12
Hydantoin	18	16	

Klein *et al.* (1986b) studied the photolysis of [ethylenediamine-¹⁴C]metiram applied at 8.5 mg/kg to a loamy sand (pH 5.7). The measured levels of the products of photolysis (or of metabolism by soil micro-organism) are shown in Table 8.

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Table 8. Products of photolysis (or metabolism by soil micro-organisms) in a loamy soil following UV irradiation of soil treated with [*ethylenediamine*-¹⁴C]metiram at 8.5 mg/kg (Klein *et al.*, 1986b).

Product	¹⁴ C expressed as metiram, mg/kg							
	Days of irradiation							Non-irrad
	0	1	2	4	8	12	30	30
EU	1.1	0.81	1.0	0.94	0.68	1.0	0.59	0.29
ETU	0.38	0.22	0.2	0.30	0.19	0.47	0.19	nd
Hydantoin	nd	0.55	0.53	0.69	0.67	0.58	0.37	nd
Carbimid	1.5	0.53	0.4	0.42	0.13	0.29	nd	0.24

nd: not detectable

Keller and Huber (1985) showed that [*ethylenediamine*-¹⁴C]metiram disappeared quickly from soil under aerobic conditions in laboratory incubation experiments. The dithiocarbamate remaining in the soil was measured by CS₂ evolution and spectrophotometry. The half-life was 25 hours in a loamy sand (pH 6.1) and 0.5 hours in a loam (pH 7.1). ETU and EBIS were identified and measured in methanol extracts of the soils. Conversion to these compounds occurred very rapidly and they, in turn, decreased within a few days (Table 9).

The mineralization rate of metiram was high with 42% of the ¹⁴C in loamy sand and 43% in loam volatilized during 1 year of aerobic incubation.

To study anaerobic mineralization samples were incubated for 30 days aerobically followed by 30 days under anaerobic conditions. The mineralisation rate was slightly less than in the same soils under aerobic conditions for 60 days.

Table 9. Formation and decline of ETU and EBIS during aerobic incubation of [*ethylenediamine*-¹⁴C]metiram for 60 days in a loamy sand and a loam (Keller and Huber, 1985).

Days	Loamy sand				Loam			
	ETU		EBIS		ETU		EBIS	
	mg/kg soil	% of initial ¹⁴ C	mg/kg soil	% of initial ¹⁴ C	mg/kg soil	% of initial ¹⁴ C	mg/kg soil	% of initial ¹⁴ C
0	0.22	2.2	4.3	43	0.30	3.0	5.6	57
1	0.23	2.3	1.7	17	0.31	3.3	2.7	28
2	0.05	0.5	0.80	8.3	0.46	4.9	1.1	12
4	0.05	0.5	0.50	5.4	1.2	13	0.52	5.5
7	-	-	0.45	5.1	1.0	11	0.28	3.0
14	-	-	0.23	2.9	-	-	0.19	2.0
21	-	-	0.14	1.9	0.12	1.4	0.06	0.7
30	-	-	0.17	2.4	0.06	0.7	0.22	2.7
60	0.03	0.5	0.03	0.5	-	-	0.09	1.3

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Klein *et al.* (1986a) identified the products formed from [*ethylenediamine*-¹⁴C]metiram incubated aerobically for 21 days in a loamy sand (pH 5.7) and their initial rates of disappearance.

Product	Initial half-life, days
ETU	1.6
EU	3.9
Carbimid	1.1
EBIS	1.7
Hydantoin	5.6

Rüdel (1990) studied the anaerobic degradation of [*ethylenediamine*-¹⁴C]metiram in a loamy sand, pH 5.8. Metiram was applied to the soil at 8.6 mg/kg and incubated aerobically for 23 hours, and then anaerobically at 20°C. The initial aerobic period was chosen because the aerobic half-life for metiram was estimated to be 22.7 hours. The half-life of the parent metiram under anaerobic conditions was 14.5 days, and 16% of the initial ¹⁴C was mineralised in 60 days. After 60 days the identified products were ethanolamine, glycine, ETU, carbimid, EBIS, hydantoin and EU.

Spare (1988a) investigated the leaching characteristics of [*ethylenediamine*-¹⁴C]metiram in four soil types: a sand (pH 6.5), a sandy loam (pH 6.5), a silt loam (pH 5.9) and a clay (pH 7.5). Samples of soils treated at 10 mg/kg with [¹⁴C]metiram were placed on top of soil columns (30 cm) and eluted slowly (3-12 days) with a volume of deionised water equivalent to a 51 cm length of the column. The distribution of ¹⁴C in the soil columns and leachates showed that leaching occurred most readily in the sand, and very little in the clay. Substantial amounts of the ¹⁴C still remained at the top of the column, with 15%, 35%, 80% and 70% remaining in the top 2.5 cm of the sand, sandy loam, clay and silt loam respectively. ETU was not detectable in methanol extracts of the soil columns.

	¹⁴ C as % of initial dose			
	sand	sandy loam	clay	silt loam
soil column	40%	62%	90%	88%
leachate	57%	28%	2%	13%

Sections of the soil columns, 0-2.5 cm, 2.5-5 cm, 5-7.5 cm and 7.5-10 cm, were analysed for dithiocarbamates by a CS₂ evolution method, but none were detected with an LOD, as CS₂, of 0.03 mg/kg (Larese, 1988e).

Spare (1988b) identified products of [¹⁴C]metiram in the leachates from the soil columns (Table 10). EU, hydantoin and IMD were the major compounds. ETU accounted for approximately 4% of the ¹⁴C in each of the leachates.

Table 10. Labelled compounds identified by TLC in leachates from soil columns to which [¹⁴C]metiram had been applied (Spare 1988b).

Compound	Compound as % of applied ¹⁴ C		
	sand	sandy loam	silt loam
ETU	2.4	1.3	0.5
IMD	14	4.0	4.1
EU	18	11	2.8
Hydantoin	12	9.1	2.2
Glycine	2.5	2.4	0.3
Oxalic acid	1.8	0.1	0.7

Carpenter (1987a) showed that the half-life of ETU on a silty loam exposed to a xenon arc UV lamp was 1.3 days, which was less than its half-life of 2.5 days on the same soil in the dark. TLC

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analysis of solvent extracts of the soil showed the presence of ETU, EU, 2-imidazoline and three unidentified compounds. The degradation products in the extracts of the exposed soil and the dark controls were the same. The conclusion was that photodegradation contributes little to the total degradation of ETU.

ETU was shown to be stable to hydrolysis at 25°C in the pH range 5 to 9 (Carpenter, 1987b). The degradation over 30 days in aqueous buffers at pH 5, 7 and 9 was so slight that no estimate of half-life was possible.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The analytical methods for metiram rely on acid hydrolysis to release CS₂, which is then measured colorimetrically or by gas chromatography. The methods are the same as those for the other ethylenebis(dithiocarbamates), mancozeb and maneb.

Metiram residues in the sample generate CS₂ when it is treated with stannous chloride and hydrochloric acid (BASF, 1978). The CS₂ is distilled into methanolic potassium hydroxide and forms a dithiocarbonate which is measured by UV spectrophotometry at 302 nm. Limits of determination are in the range 0.02-0.2 mg/kg depending on the type of sample. Alternatively, the dithiocarbonate is derivatized to produce methyl *N,N*-dipropyldithiocarbamate and determined by GLC. The limit of determination is about 0.02 mg/kg.

Tilting (1985b) used a similar method for the residue analysis of animal commodities, but collected the evolved CS₂ in pure methanol and determined it by GLC with a sulfur-selective FPD. Recoveries varied from 50 to 100%. Limits of determination were in the range 0.02-0.4 mg/kg (as CS₂). Tilting (1985a) also used the UV spectrophotometric method for the analysis of animal commodities but interferences were more prevalent than in plant samples.

The liberated CS₂ may also be measured colorimetrically (Thier and Zeumer, 1987b). A cupric acetate reagent forms yellow-coloured copper dithiocarbamate complexes which absorb light at 435 nm. Sample blanks occurred with a few crops: rape seed, rutabaga, cauliflower and Savoy cabbage.

In the method of the Dutch manual of analytical methods (Ministry of Welfare, Health and Cultural Affairs, 1988) metiram is converted to CS₂ by treatment with hydrochloric acid in the presence of stannous chloride. The CS₂ in the head-space is determined by GLC with either an ECD or an FPD in the sulfur mode.

Ethylenebisdithiocarbamates and propylenebisdithiocarbamates can be separated by gel permeation chromatography (Thier and Zeumer, 1987c). Because these residues are present only on the surface and not within harvested crops they are removed from the plant material with an aqueous solution of ethylenedinitrilotetra-acetic acid (tetrasodium salt). The disodium ethylenebisdithiocarbamates and propylenebisdithiocarbamates are separated on Sephadex LH-20 and determined by their UV absorbance at 285 nm. Routine limits of determination range from 0.05 to 0.5 mg/kg.

Methods for the residue analysis of ethylenethiourea were reviewed in the 1993 monograph on mancozeb. The GLC methods for ETU residues in plant and animal commodities which were used in the supervised trials were made available to the Meeting (BASF, 1980; Keller, 1985b). The method for ETU in plant materials has been published (Thier and Zeumer, 1987a).

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ETU was determined in grapes and wine by GLC after derivatization to *S*-benzyl-ETU (Chovancová *et al.*, 1985). Care was taken to minimise conversion of EBDCs to ETU during derivatization.

Zafiriou (1985) analysed apple and peach juices for ETU residues by a GLC method which measured ETU directly without derivatization. Good recoveries were achieved down to 0.02 mg/kg.

Stability of pesticide residues in stored analytical samples

Information was made available on the storage stability of metiram and ETU on apples, wet and dry apple pomace, apple juice, sauce, baby food, tomatoes, potatoes and sugar beets. Studies of the frozen storage stability of ETU in a number of commodities were included in the 1993 monograph on mancozeb.

Metiram was sprayed on apple orchards in New York and North Carolina and samples were collected 28 days after the final application (Bookbinder, 1988). Metiram was applied to each orchard 13 times (7×7.2 kg ai/ha + 6×5.4 kg ai/ha) using 3700 litres of spray per hectare. Apple samples were frozen after collection, shipped frozen to the analytical laboratory, and stored frozen (-20°C) until preparation and analysis. The results are shown in Table 11.

Metiram residues were stable in the frozen apples, with approximately 20% decline in 12 months. ETU residues were formed during storage and accumulated at the longer intervals demonstrating that ETU residues are stable in frozen whole apples at -20°C.

Table 11. Residues of metiram (as metiram) and ETU in field-treated apples from North Carolina and New York stored at -20°C (Bookbinder, 1988; Larese, 1989b). Apples were harvested 28 days after the last of 13 applications (7×7.2 kg ai/ha + 6×5.4 kg ai/ha).

Storage interval	Residues, mg/kg			
	NY apples		NC apples	
	Metiram	ETU	Metiram	ETU
0 day	3.8 3.7		5.8 6.0	
2 weeks	3.7 3.7		5.9 5.8	
1 month			5.8 5.7	0.11 0.13
3 months			5.2 5.1	0.26 0.24
6 months			5.05 4.95	0.16 0.16
12 months			4.79 4.69	0.24 0.32

Larese (1988a, 1989a) reported on the storage stability of metiram and ETU in spiked samples of diced apples frozen and stored at -20°C. The results are shown in Table 12. Metiram was stable for 12 months but ETU disappeared within weeks.

metiram

Table 12. Residues of metiram (as metiram) and ETU in spiked samples of apples stored at -20°C (Larese, 1988a,1989a).

Storage interval	Residues, mg/kg			
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg	
	Metiram	ETU	ETU, run 1	ETU, run 2
0 day	1.90 1.96	<0.01 <0.01	0.20 0.20	0.17 0.21
2 weeks	1.87 1.89	0.01 <0.01	0.01 0.01	0.17 0.18
1 month	1.91 1.90	0.01 <0.01	<0.01 <0.01	0.03 0.03
3 months	1.68 1.64	0.01 <0.01		0.02 0.03
6 months	1.65 1.67	<0.01 0.01		<0.01 <0.01
12 months	1.54 1.56	<0.01 0.01		<0.01 <0.01

Larese (1989c) fortified frozen apple commodities with metiram (2.0 mg/kg) or ETU (0.20 mg/kg) and measured the stability of the residues at -20°C during storage intervals up to 12 months. The results are shown in Table 13. Metiram was shown to be stable in the commodities studied: apple sauce, apple juice and apple baby food. There was little conversion of metiram to ETU. ETU itself in these substrates stable during storage.

Anomalous results for apple juice at the 1- and 3-months intervals were further investigated. A small change in the procedure had been inadvertently introduced which resulted in the presence of metiram during the derivatization of ETU, and some conversion of metiram to ETU was occurring. Later samples were analysed by the corrected procedure.

metiram

Table 13. Residues of metiram (as metiram) and ETU in spiked samples of frozen apple sauce, fresh apple juice, cooked apple juice and apple baby food stored at -20°C (Larese, 1989c).

Storage interval	Residues, mg/kg					
	Metiram added at 2.0 mg/kg				ETU added at 0.20 mg/kg	
	Metiram		ETU		ETU	
APPLE SAUCE						
0 day	1.96	1.93	<0.01	<0.01	0.17	0.17
2 weeks	1.83	1.86	<0.01	<0.01	0.14	0.16
1 month	1.89	1.91	<0.01	<0.01	0.16	0.12
3 months	1.83	1.90	<0.01	<0.01	0.14	0.17
6 months	1.88	1.84	0.01	<0.01	0.11	0.12
12 months	1.70	1.80	<0.01	<0.01	0.11	0.10
FRESH APPLE JUICE						
0 day	1.93	1.92	0.05	0.07	0.13	0.14
2 weeks	1.87	1.89	0.06	0.07	0.14	0.16
1 month	1.85	1.83	0.18	0.16	0.16	0.16
3 months	1.81	1.80	0.34	0.42	0.20	0.19
4.5 months			0.03	0.03		
6 months	1.82	1.76	0.03	0.02	0.15	0.12
12 months	1.57	1.65	0.03	0.03	0.13	0.14
COOKED APPLE JUICE						
0 day	1.84	1.85	0.03	0.03	0.15	0.15
2 weeks	1.83	1.80	0.05	0.06	0.12	0.13
1 month	1.82	1.79	0.13	0.14	0.13	0.13
3 months	1.85	1.87	0.32	0.32	0.20	0.20
4.5 months			0.04	0.05		
6 months	1.85	1.84	0.01	0.02	0.12	0.13
12 months	1.82	1.84	<0.01	<0.01	0.12	0.14
APPLE BABY FOOD						
0 day	1.91	1.92	0.03	0.04	0.22	0.23
2 weeks	1.92	1.89	0.04	0.04	0.16	0.18
1 month	1.95	1.96	0.03	0.04	0.22	0.20
3 months	1.95	1.93	0.07	0.06	0.21	0.19
6 months	1.90	1.84	0.06	0.06	0.22	0.19
12 months	1.88	1.81	0.03	0.03	0.18	0.18

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Data on the frozen storage stability of metiram and ETU in apple pomace are summarized in Table 14 (Larese, 1989d). The frozen commodities were fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 12 months at -20°C. Metiram was adequately stable under the conditions, and produced little ETU. ETU disappeared very quickly from wet pomace, but was stable in dry pomace.

Table 14. Residues of metiram (as metiram) and ETU in spiked samples of frozen wet and dry apple pomace stored at -20°C (Larese, 1989d).

Storage interval	Residues, mg/kg		
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg
	Metiram	ETU	ETU
WET POMACE			
0 day	1.86 1.87	<0.01 <0.01	0.18 0.16
2 weeks	1.89 1.89	<0.01 <0.01	<0.01 <0.01
1 month	1.81 1.86		
3 months	1.80 1.82	<0.01 <0.01	<0.01 <0.01
6 months	1.76 1.74	0.01 <0.01	<0.01 <0.01
12 months	1.60 1.58	<0.01 <0.01	<0.01 <0.01
DRY POMACE			
0 day	1.71 1.70	0.01 0.01	0.18 0.16
2 weeks	1.82 1.77	0.01 0.01	0.17 0.18
1 month	1.75 1.76	0.04 0.02	0.14 0.14
3 months	1.77 1.80	0.01 0.01	0.15 0.09
6 months	1.62 1.55	<0.02 <0.02	0.11 0.10
12 months	1.46 1.39	<0.02 <0.02	0.12 0.11

Data on the frozen storage stability of metiram and ETU in frozen diced tomatoes are shown in Table 15 (Larese 1988b, 1989e). The frozen tomatoes were fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 12 months at -20°C. Metiram was stable under the conditions, and produced very little ETU. ETU residues were reasonably stable for 12 months.

Table 15. Residues of metiram (as metiram) and ETU in spiked samples of frozen diced tomatoes stored at -20°C (Larese 1988b, 1989e).

Storage interval	Residues, mg/kg		
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg
	Metiram	ETU	ETU
0 day	1.89 1.87	<0.01 <0.01	0.20 0.20
2 weeks	1.94 1.95	0.01 0.03	0.17 0.17
1 month	1.91 1.90	0.01 0.01	0.15 0.12
3 months	1.80 1.83	0.01 0.01	0.14 0.15
6 months	1.76 1.72	0.01 0.01	0.16 0.16
12 months	1.73 1.67	0.02 0.02	0.12 0.12

The results of frozen storage stability studies on metiram and ETU in frozen diced potatoes are

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shown in Table 16 (Larese 1988c, 1989f). The frozen potatoes were fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 1 or 3 months at -20°C. Metiram was stable under the conditions, and very little ETU was produced. ETU disappeared very quickly with 70-80% loss in 2 weeks. Because of the early disappearance of ETU the first ETU run was abandoned after 1 month and the analyses repeated in run 2.

Table 16. Residues of metiram (as metiram) and ETU in spiked samples of frozen diced raw potatoes stored at -20°C (Larese, 1988c, 1989f)

Storage interval	Residues, mg/kg			
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg	
	Metiram	ETU (run 2)	ETU, run 1	ETU, run 2
0 day	1.92 1.96	0.01 0.01 (0.02 0.02)	0.19 0.20	0.18 0.18
2 weeks	1.92 1.89	0.02 0.02 (0.03 0.02)	0.06 0.02	0.07 0.05
1 month	1.89 1.91	0.02 0.09 (0.03 0.03)	0.03 0.02	0.07 0.06
3 months	1.77 1.75	(0.02 0.02)		0.05 0.05
6 months	1.67 1.69	(0.01 0.01)		0.01 <0.01
12 months	1.60 1.54	(0.02 0.01)		0.01 0.01

Data on the frozen storage stability of metiram and ETU in frozen diced sugar beet are shown in Table 17 (Larese 1988d, 1989g). The frozen beet was fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 1 or 3 months at -20°C. Metiram was stable under the conditions. ETU disappeared quickly with about 60% loss in one month. The first ETU run was therefore again abandoned after 1 month and the analyses repeated in run 2.

Table 17. Residues of metiram (as metiram) and ETU in spiked samples of frozen diced sugar beet stored at -20°C (Larese, 1988d, 1989g)

Storage interval	Residues, mg/kg			
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg	
	Metiram	ETU (run 2)	ETU, run 1	ETU, run 2
0 day	1.86 1.88	0.02 0.02 (0.02 0.02)	0.21 0.20	0.18 0.18
2 weeks	1.92 1.92	0.05 0.04 (<0.01 <0.01)	0.09 0.07	0.11 0.10
1 month	1.89 1.90	0.04 0.03 (0.02 0.01)	0.06 0.06	0.08 0.08
3 months	1.86 1.85	(0.01 0.03)		0.03 0.04
6 months	1.74 1.74	(0.02 0.01)		0.03 0.05
12 months	1.62 1.49	(<0.01 <0.01)		0.05 0.02

Residue definition

Metiram is a dithiocarbamate and will be included in the definition of dithiocarbamate residues. Supervised trials data have been generated using methods which measure the CS₂ evolved during acid digestion. In the regulatory analytical methods for dithiocarbamates metiram residues will behave in the same way as other dithiocarbamate residues.

An analyst using an enforcement method will measure the total evolved CS₂ produced by acid digestion of a sample, which will not indicate its source.

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The Meeting proposed a revised dithiocarbamate residue definition:

The MRLs refer to total dithiocarbamates, determined as CS₂ evolved during acid digestion and expressed as mg CS₂/kg.

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USE PATTERN

Metiram is a non-systemic fungicide with a very broad spectrum of activity. It is effective against downy mildews (*Peronospora sp.*), rust fungi (*Uromyces sp.*, *Puccinia sp.*) and a number of leaf spot fungi (*Septoria sp.*, *Venturia sp.*). Metiram is used on cereals, fruits, vegetables, tobacco and ornamentals.

Metiram inhibits the sporulation of fungi by specific binding to SH-containing enzyme systems within the fungi. Resistance to metiram is not expected to develop, because of this multi-site inhibition activity. Resistance has not developed in more than 30 years of use.

Metiram formulations are registered in many countries. The registered uses are shown in Table 18.

Table 18. Registered uses of metiram.

Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Apple	Argentina	WG	spray		0.12-0.16	4	20
Apple	Argentina	WP	spray			1-4	20
Apple	Australia	WP WG	spray		0.12-0.16		21
Apple	Belgium	WP	spray				10
Apple	Belgium	WP	mist	1.8			21
Apple	Bolivia	WG	spray		0.15-0.20	6-10	
Apple	Bulgaria	WP					14
Apple	Canada	WG	spray	4.8			45
Apple	Chile	WG	spray			7-10	14
Apple	Croatia	WP					28
Apple	Denmark	WP	mist	1.75			28
Apple	Greece	WP WG	spray				
Apple	Hungary	WG		1.8	0.58		30
Apple	Indonesia	WP					
Apple	Ireland	WG	spray	1.8	0.33		
Apple	Italy	WP WG	spray		0.10-0.14		28
Apple	Luxembourg	WP	spray	0.019	0.0019		14
Apple	Macedonia	WP					
Apple	Morocco	WP	spray				14
Apple	Mozambique	WP					
Apple	Netherlands	WG	mist				28
Apple	Netherlands	WP	mist			8	28
Apple	Netherlands	WP	spray	1.8	0.16	7-10	28
Apple	New Zealand	WP WG	spray		0.07-0.11	10	14
Apple	Paraguay	WP	spray				
Apple	Poland	WP					35
Apple	Portugal	WP WG	spray		0.14		7
Apple	Rumania	WP WG					
Apple	Sth Africa	WP	LV spray	4.6	0.40-0.52	9	21
Apple	Sth Africa	WP	spray	5.6	0.12-0.16	9	14
Apple	Switzerland	WP	spray	1.9			21
Apple	Turkey	WP	spray	1.5	0.15	2-3	28
Apple	Turkey	WG	spray	1.6	0.16	1-2	21
Apple	UK	WP	mist	0.038			14
Apple	USA	WP WG	spray	5.4	2.9	4	pre-flower
Apple	USA	WP WG	spray	2.7	1.5	7	77
Apple	Yugoslavia	WP					28
Apple	Zimbabwe	WP					14

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Apricot	Sth Africa	WP	spray		0.12-0.16		14
Asparagus	Australia	WP WG	spray	2.8	0.16-0.26		7
Asparagus	Belgium	WG	spray	2.5			28
Asparagus	Canada	WG	spray	2.6		4	after spears removal
Asparagus	Costa Rica	WP	spray	1.6			
Asparagus	Costa Rica	WG	spray	1.6	0.12-0.16		7
Asparagus	Dominican	WG	spray	1.4			7
Asparagus	Germany	WG	spray	0.84		1-4	
Asparagus	Germany	WP	spray	0.96		4	2
Asparagus	Greece	WP WG	spray	1.6			
Asparagus	Luxembourg	WG	spray	2.5			28
Asparagus	Paraguay	WP	spray			2	
Banana	Ecuador	WP	spray	0.72	0.36		14
Barley	Ireland	WG	spray	1.4	0.56	2	28
Barley	UK	WP	spray	1.4	0.56	1-2	28
Bean	Argentina	WG	spray		0.16	1-4	10
Bean	Argentina	WP	spray	1.6		3	10
Bean	Australia	WG	spray	2.8	0.26		7
Bean	Belgium	WG	spray		0.32		28
Bean	Bolivia	WG	spray	1.4	0.47	3-6	
Bean	Bulgaria	WP	seed treat				
Bean	Costa Rica	WG	spray	1.6			7
Bean	Costa Rica	WP	spray	1.4			
Bean	Dominican	WG	spray	1.4			7
Bean	Ecuador	WP	spray	1.6	0.16	3	7
Bean, Climbing	Germany	WP	dry dressing			1	2
Bean	Greece	WP WG	spray	1.4			
Bean	Luxembourg	WG	spray				28
Bean	Malaysia	WP WG					14
Bean	Paraguay	WP	spray			2	
Bean	Peru	WG		0.80			7
Bean	Spain	WP WG	spray		0.12-0.16		15
Bean	Sth Africa	WP	spray	1.6	0.16		3
Bean	Zimbabwe	WP					3
Bean, Broad	Peru	WP	spray			3-6	7
Bean, Dwarf	Germany	WP	dry dressing			1	2
Bean, Dwarf	Germany	WP	spray	0.96		2	7
Beet	Bulgaria	WP	seed treat				
Blueberry	Greece	WP WG	spray				
Blueberry	Paraguay	WP	spray				
Broccoli	Australia	WG	spray	2.8			7
Broccoli	Costa Rica	WG	spray	1.2	0.32-0.50		7
Broccoli	Mozambique	WP					
Brussels sprouts	Australia	WG	spray	2.8			7
Cabbage	Australia	WG	spray	2.8			7
Cabbage	Bolivia	WG	spray		0.20	5-15	
Cabbage	Costa Rica	WG	spray	1.2			7
Cabbage	Costa Rica	WP	spray	1.4			
Cabbage	Dominican	WG	spray	1.4			7
Cabbage	Germany	WP	dry dressing			1	2
Cabbage	Greece	WP WG	spray	1.4			
Cabbage	Ireland	WG	spray	1.4	0.64		
Cabbage	Malaysia	WP WG					14
Cabbage	Paraguay	WP	spray	0.005		2	
Cabbage	Poland	WP					
Cacao	Costa Rica	WP	spray				

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Cacao	Dominican	WG	spray				7
Cacao	Indonesia	WP	spray	0.64	0.16		
Carrot	Australia	WP WG	spray	1.8	0.16		7
Carrot	Bolivia	WG	spray	1.4	0.47	5-10	
Carrot	Canada	WG	spray	1.8			5
Carrot	Costa Rica	WP	spray	1.6			
Carrot	Dominican	WG	spray				7
Carrot	Greece	WP WG	spray	1.4			
Carrot	Mozambique	WP					
Carrot	Paraguay	WP	spray			2	
Cauliflower	Australia	WG	spray	2.8			7
Cauliflower	Mozambique	WP					
Celery	Argentina	WP					3
Celery	Australia	WP WG	spray	1.8	0.16		2
Celery	Belgium	WG	spray		0.16		28
Celery	Canada	WG	spray	2.6			14
Celery	Canada	DP	spray	3.5			14
Celery	Costa Rica	WP WG	spray	1.6			7
Celery	Dominican	WG	spray	1.4			7
Celery	Germany	WP	spray	1.4		4	28
Celery	Greece	WP WG	spray	1.4			
Celery	Luxembourg	WG	spray				28
Celery	Malaysia	WP WG					14
Celery	Paraguay	WP	spray			2	
Celery	Peru	WP	spray			3-6	7
Celery	Peru	WG		0.80		2-3	7
Celery	Poland	WP		1.6			
Celery	Spain	WP	spray		0.12-0.16		15
Cereals	Belgium	WG	spray	1.4			28
Cereals	Hungary	WG		1.4			52
Cereals	Italy	WP WG	spray	2.1			28
Cereals	Italy	WP	seed dressing				28
Cereals	Luxembourg	WG	spray	1.4			28
Cherry	Costa Rica	WP	spray				
Cherry	Greece	WP WG	spray				
Cherry	Paraguay	WP	spray			2-4	
Cherry	Switzerland	WP WG	spray				21
Citrus	Argentina	WG	spray		0.12-0.16		10
Citrus	Argentina	WP	spray			3	10
Citrus	Costa Rica	WG		1.6			7
Citrus	Cyprus	WP WG			0.15-0.20		7
Citrus	Dominican	WG	spray				7
Citrus	Greece	WP WG	spray				
Citrus	Jordan	WP	spray	1.2	0.2	1-3	
Citrus	Mozambique	WP					
Citrus	Paraguay	WP	spray				
Cotton	Costa Rica	WP	spray				
Cotton	Greece	WP WG	seed dressing				
Cotton	Paraguay	WP	spray				
Cotton	Peru	WG		0.80		1	7
Cotton	Peru	WP	spray			3-5	7
Cranberry	Costa Rica	WP	spray				
Cucumber	Australia	WG					2
Cucumber	Bolivia	WG	spray	1.4	0.23	3-15	
Cucumber	Costa Rica	WG		1.6	1.6		7
Cucumber	Costa Rica	WP	spray	1.4			
Cucumber	Dominican	WG	spray	1.4			7

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Cucumber	Israel	WG		2.0			5
Cucumber	Malaysia	WP WG					14
Cucumber	Mozambique	WP					
Cucumber	Paraguay	WP	spray			2	
Cucumber	Rumania	WP WG					
Cucumber	Spain	WP	spray		0.12-0.16		15
Cucumber	Zimbabwe	WP					14
Cucurbits	Mozambique	WP					
Cucurbits	Pakistan	WP					
Cucurbits	Spain	WP	spray		0.12-0.16		15
Currants Black, Red	Poland	WP					
Currant, Red	Costa Rica	WP	spray				
Currant, Red	Germany	WP	spray		0.12	4	35
Currant, Red	Greece	WP WG	spray				
Field crops	Saudi Arabia	WP	spray	0.80	0.20	1-3	
Fruit	Algeria	WP					
Fruit	Angola	WP	spray	0.50	0.20		
Fruit	Argentina	WP	spray				
Fruit	Peru	WP		2.2			
Fruit	Saudi Arabia	WP	spray	0.80	0.20	1-3	
Fruit	Tunisia	WP	spray			3-4	
Fruits, tropical	Costa Rica	WP	spray				
Garlic	Dominican	WG	spray	1.4			7
Garlic	Israel	WG		2.0			
Gooseberry	Costa Rica	WP	spray				
Gooseberry	Greece	WP WG	spray				
Gooseberry	Paraguay	WP	spray				
Gooseberry	Poland	WP					
Grape	Argentina	WG	spray	1.8	0.16	3	10
Grape	Argentina	WP	spray			3	10
Grape	Australia	WP WG	spray		0.12-0.16		14
Grape	Austria	WG	spray				14
Grape	Austria	WP	spray			6-8	14, 42
Grape	Bolivia	WG	spray		0.15-0.20	3-6	
Grape	Bulgaria	WP					14
Grape	Canada	WG	spray	1.6	0.16	1-3	45
Grape	Canada	DP	spray	4.7		1-3	45
Grape	Costa Rica	WP	spray				
Grape	Croatia	WP					
Grape	Czech	WP					21
Grape	France	WP	spray	2.5			
Grape	France	WG	spray	2.8			
Grape	Germany	WP	spray			1-8	56
Grape	Germany	WG	spray		0.16	1-6	56
Grape	Greece	WP WG	spray				
Grape	Hungary	WG		1.8	0.58		21
Grape	Italy	WP	spray	1.5	0.10-0.28	3	28
Grape	Italy	WG	spray				28
Grape	Jordan	WP	spray	1.2	0.2	1-3	
Grape	Macedonia	WP					
Grape	Mozambique	WP					
Grape	New Zealand	WG	spray		0.14	12	14
Grape	Paraguay	WP	spray			3	
Grape	Portugal	WP WG	spray		0.14-0.28		7
Grape	Rumania	WP WG					
Grape	Spain	WP WG	spray	2.4	0.12-0.16	1-6	15
Grape	Switzerland	WP WG	spray				21

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Grape	Tunisia	WP	spray	0.74	0.21	4	
Grape	Tunisia	WP	spray	2.8	0.28	3-4	
Grape	Turkey	WG	spray	0.64	0.16	2-3	56
Grape	Uruguay	WP	spray	2.4	0.16	4-6	25
Grape	Yugoslavia	WP					
Grape	Zimbabwe	WP				6-9	14
Grapes, table	Sth Africa	WP	spray	2.4	0.16		not after pea size
Grapes, wine	Sth Africa	WP	spray	2.4	0.16		14
Hops	Belgium	WG	mist		0.16-0.20		42
Hops	Czech	WP					
Hops	Germany	WP WG	spray		0.16	1-12	35
Hops	Hungary	WG		1.8	0.44		14
Hops	Ireland	WG	spray	1.4	0.14		
Hops	Luxembourg	WG	mist				42
Hops	Morocco	WP	spray				14
Hops	Poland	WP					
Hops	Switzerland	WG	spray			12	35
Hops	UK	WG	mist	1.6			
Hops	UK	WP	mist	1.4	0.56		
Hops	UK	WG	spray	1.6			
Leaf and stem vegetables	Australia	WP	spray	1.8	0.16		7
Legumes	Australia	WP	spray	2.8	0.26		7
Legumes	Cyprus	WP WG			0.15-0.20		7
Legumes	Panama	WP		1.6			
Lentil	Hungary	WG		1.1	0.19		21
Lettuce	Australia	WP WG	spray	1.8	0.16		7
Lettuce	Mozambique	WP					
Lettuce, cos	Paraguay	WP	spray	0.005		2	
Lettuce, head	France	WG		1.4			
Lettuce, head	Germany	WG	spray	0.84		1-2	21
Lettuce, head	Germany	WP	spray	0.96		1	21
Lettuce, head	Germany	WP	dry dressing			1	2
Lettuce, head	Greece	WP WG	spray	1.4			
Lettuce, head	Malaysia	WP WG					14
Maize	Bolivia	WG	spray	1.4	0.47	2-3	
Maize	Costa Rica	WP WG	spray		0.12-0.16		7
Maize	Dominican	WG	spray				7
Maize	Paraguay	WP	spray				
Maize	Peru	WP	spray			3-6	7
Maize	Peru	WG		0.80		2-3	7
Mango	Egypt	WG	spray	6.4	0.32	1-3	
Mango	Mozambique	WP					
Melon	Bolivia	WG	spray	1.4	0.23	3-15	
Melon	Costa Rica	WP WG	spray	1.6	1.6		7
Melon	Dominican	WG	spray	1.4			7
Melon	Israel	WG		2.0			5
Melon	Mozambique	WP					
Melon	Paraguay	WP	spray			2	
Melon	Zimbabwe	WP					14
Nectarine	Zimbabwe	WP					14
Onion	Bolivia	WG	spray	1.4	0.47	3-6	
Onion	Costa Rica	WP	spray	1.4			
Onion	Costa Rica	WP WG	spray	1.6	1.6		7
Onion	Dominican	WG	spray	1.4			7
Onion	Israel	WG		2.0			10

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Onion	Mozambique	WP					
Onion	Paraguay	WP	spray			2	
Onion	Peru	WG		0.80	0.13	1	7
Onion	Poland	WP		1.6			
Onion	Rumania	WP WG					
Pea	Argentina	WG	spray		0.16		10
Pea	Argentina	WP	spray				10
Peach	Bolivia	WG	spray		0.20	2-4	
Peach	Greece	WP WG	spray				
Peach	Mozambique	WP					
Peach	Paraguay	WP	spray			2-4	
Peach	Portugal	WP	spray				7
Peach	Sth Africa	WP	spray		0.16		14
Peach	Uruguay	WP	spray	3.6	0.24	3	25
Peach	Zimbabwe	WP					14
Peanut	Costa Rica	WP WG	spray		0.096-0.16		
Peanut	Dominican	WG	spray				
Peanut	Greece	WP WG	spray				
Peanut	Mozambique	WP					
Peanut	Panama	WP					
Peanut	Paraguay	WP	spray				
Pear	Argentina	WP	spray			1-4	20
Pear	Argentina	WG	spray		0.12-0.16	4	20
Pear	Australia	WP WG	spray		0.12-0.16		14
Pear	Belgium	WP	spray				10
Pear	Bolivia	WG	spray		0.15-0.20	6-10	
Pear	Chile	WG	spray			7-10	14
Pear	Denmark	WP	mist	1.75			28
Pear	Greece	WP WG	spray				
Pear	Italy	WP WG	spray		0.10-0.14		28
Pear	Morocco	WP	spray				14
Pear	Mozambique	WP					
Pear	Netherlands	WG	mist				28
Pear	Netherlands	WP	spray	1.8	0.16	7-10	28
Pear	Netherlands	WP	mist			5	28
Pear	New Zealand	WG	spray		0.07-0.11	10	14
Pear	Paraguay	WP	spray				
Pear	Poland	WP					35
Pear	Portugal	WP WG	spray		0.14		7
Pear	Rumania	WP WG					
Pepper, sweet	Argentina	WP					3
Peppers, sweet	Hungary	WG	greenhouse	1.4	0.23		7
Peppers, sweet	Spain	WP	spray		0.12-0.16		15
Pistachio	Argentina	WP	spray				
Plum	Germany	WG	spray		0.12	1-4	28
Plum	Germany	WP	spray		0.12	4	28
Plum	Greece	WP WG	spray				
Plum	Paraguay	WP	spray			2-4	
Plum	Sth Africa	WP	spray		0.16		14
Plum	Uruguay	WP	spray	3.6	0.24	3	25
Pome fruits	Belgium	WG	spray				14
Pome fruits	Cyprus	WP WG			0.15-0.20		7
Pome fruits	Czech	WP					21
Pome fruits	Germany	WG	spray		0.12	1-12	28
Pome fruits	Luxembourg	WG	mist				14
Pome fruits	Spain	WP WG	spray	2.4	0.12-0.16	1	15
Pome fruits	Switzerland	WP	spray				21

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Potato	Argentina	WG	spray		0.14-0.19		7
Potato	Argentina	WP	spray	1.4	0.34		7
Potato	Argentina	WP					3
Potato	Australia	WP WG	spray		0.12-0.16		7
Potato	Austria	WP	spray	1.7	0.29	3	14
Potato	Belgium	WG	spray	2.8			14
Potato	Bolivia	WG	spray	1.3	0.42	5-15	
Potato	Canada	WG	spray	1.8	3.3		1
Potato	Canada	DP	spray	2.3			1
Potato	Canada	DP	dry dressing			1-2	
Potato	Chile	WG	spray	1.8			
Potato	Costa Rica	WP WG	spray	2.0			7
Potato	Croatia	WP		1.6			14
Potato	Cyprus	WP WG			0.15-0.20		7
Potato	Czech	WP		1.6			7
Potato	Dominican	WG	spray	1.8			7
Potato	Ecuador	WP	spray	2.0	0.50	2-3	14
Potato	France	WP WG	spray	1.4	0.27-0.40		
Potato	Germany	WP	spray	1.4		4	14
Potato	Germany	WG	spray	1.3		1-5	14
Potato	Greece	WP WG	spray	1.4			
Potato	Guatemala	WG					
Potato	Hungary	WG		1.3	0.25		21
Potato	Indonesia	WP	spray	0.64	0.16		
Potato	Ireland	WG	spray	1.4	0.64		
Potato	Luxembourg	WG	spray	2.8			14
Potato	Macedonia	WP		1.6			14
Potato	Mozambique	WP					
Potato	Netherlands	WG	spray	1.7			
Potato	Netherlands	WP	spray	2.9			
Potato	Pakistan	WP					
Potato	Paraguay	WP	spray			2	
Potato	Peru	WP	spray	1.2		3-4	7
Potato	Peru	WP		0.55	0.092	2-4	7
Potato	Peru	WG		0.80		3-6	7
Potato	Poland	WP		1.4			14
Potato	Portugal	WP WG	spray		0.14		7
Potato	Rumania	WP WG		1.4			
Potato	Spain	WP	spray		0.12-0.16		15
Potato	Sth Africa	WP	spray	3.2	0.24		
Potato	Switzerland	WP	spray	3.2			21
Potato	Switzerland	WG	spray	2.4			
Potato	Tunisia	WP	spray			3-4	
Potato	UK	WP	spray	1.4	0.70		7
Potato	UK	WG	spray	1.6			7
Potato	Uruguay	WP	spray	1.4	0.36	8-15	25
Potato	USA	WP WG	spray	1.8	1.3	7	3, 14
Potato	Yugoslavia	WP		1.6			14
Potato	Zimbabwe	WP					3
Prunes	Sth Africa	WP	spray		0.16		14
Pumpkin	Bolivia	WG	spray	1.4	0.23	3-15	
Pumpkin	Costa Rica	WP	spray	1.4			
Rape	Argentina	WP	dry dressing				
Rape	Ireland	WG	spray	1.4	0.64		
Rape, winter	UK	WG	spray	1.6			GS ¹
Rape, winter	UK	WP	spray	1.4	5.6	1	GS ¹
Rice	Costa Rica	WG		1.6			7

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Rice	Dominican	WG	spray	1.4			7
Soya beans	Hungary	WG		1.1	0.28		21
Stone fruits	Argentina	WP	spray			1-4	14
Stone fruits	Argentina	WG	spray		0.16-0.32		10
Stone fruits	Australia	WP	spray		0.12	3-4	21
Stone fruits	Cyprus	WP WG			0.15-0.20		7
Stone fruits	Germany	WP	spray		0.12	4	21
Stone fruits	Spain	WP WG	spray	2.4	0.12-0.16	1	15
Strawberry	Belgium	WP	spray				14
Strawberry	Costa Rica	WP	spray				
Strawberry	Cyprus	WP WG			0.15-0.20		7
Strawberry	Greece	WP WG	spray				
Strawberry	Luxembourg	WP	spray	0.010	0.005		14
Strawberry	Paraguay	WP	spray				
Strawberry	Spain	WP	spray	2.4	0.12-0.16	1-6	15
Sugar beet	Bulgaria	WP	seed treat				
Sugar beet	Canada	WG	spray	1.8			21
Sunflower	Macedonia	WP		1.6			
Sunflower	Rumania	WG		1.1			
Sunflower	Yugoslavia	WP		1.6			
Sweet corn	Greece	WP WG	spray				
Tomato	Argentina	WG	spray		0.14-0.19		10
Tomato	Argentina	WP	spray				10
Tomato	Australia	WP WG	spray	1.8			2
Tomato	Belgium	WG	spray		0.16		14
Tomato	Belgium	WG	spray, greenhouse		0.16		3
Tomato	Canada	DP	spray	3.9			7
Tomato	Canada	WG	spray	2.6			7
Tomato	Chile	WG	spray	1.8			
Tomato	Costa Rica	WP WG	spray	2.4			7
Tomato	Croatia	WP		2.4			14
Tomato	Dominican	WG	spray	1.8			5
Tomato	Ecuador	WP	spray	2.4	0.16	1-4	5
Tomato	France	WG		1.4			
Tomato	Germany	WP	spray	2.9		1-4	5
Tomato	Germany	WP	dry dressing			1	2
Tomato	Greece	WP WG	spray	1.4			
Tomato	Hungary	WG	greenhouse	1.4	0.23		7
Tomato	Indonesia	WP	spray	0.64	0.16		
Tomato	Italy	WP WG	spray		0.10-0.14		28
Tomato	Luxembourg	WG	spray				14
Tomato	Luxembourg	WG	spray greenhouse				3
Tomato	Macedonia	WP		2.4			14
Tomato	Malaysia	WP WG					14
Tomato	Morocco	WG					30
Tomato	Mozambique	WP					
Tomato	Pakistan	WP					
Tomato	Paraguay	WP	spray	0.005		2	
Tomato	Peru	WG		0.80	0.13	3-6	7
Tomato	Poland	WP					5
Tomato	Portugal	WP WG	spray		0.14		7
Tomato	Rumania	WP WG					
Tomato	Spain	WP	spray		0.12-0.16		15
Tomato	Sth Africa	WP	spray	3.2	0.24		3
Tomato	Tunisia	WP	spray	1.2	0.20		

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Tomato	Turkey	WG	spray	0.56	0.14	2-3	5
Tomato	Uruguay	WP	spray	1.4	0.36	8-15	25
Tomato	Yugoslavia	WP		2.4			14
Tomato	Zimbabwe	WP					3
Vegetables	Angola	WP	spray	0.50	0.20		
Vegetables	Argentina	WP	spray				10
Vegetables	Cyprus	WP WG			0.15-0.20		7
Vegetables	Jordan	WP	spray	1.2	0.2	1-3	
Vegetables	Saudi Arabia	WP	spray	0.80	0.20	1-3	
Vegetables	Spain	WP WG	spray	2.4	0.12-0.16	1-6	15
Vegetables	Tunisia	WP	spray				
Watermelon	Bolivia	WG	spray	1.4	0.23	3-15	
Watermelon	Malaysia	WP WG					14
Wheat, winter	Ireland	WG	spray	1.4	0.64	1-2	42
Wheat, winter	UK	WP	spray	1.4	0.56	1-2	42

¹ GS: early growth stage, final application in December.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised trials on horticultural and agricultural crops are shown in Tables 19-41.

- Table 19. Apples. Germany.
- Table 20. Apples. Australia, Brazil, Canada, Hungary, Italy, the UK.
- Table 21. Pears. Germany.
- Table 22. Stone fruit. Australia, Germany.
- Table 23. Grapes. Austria, Germany, France, Hungary, Italy.
- Table 24. Strawberries. Germany, Switzerland, the UK.
- Table 25. Berry fruits. the UK.
- Table 26. Currants. Germany.
- Table 27. Bananas. Australia.
- Table 28. Cabbage. Germany.
- Table 29. Cauliflower. Germany.
- Table 30. Cucumber. Hungary, the UK.
- Table 31. Tomatoes. France, Germany, Hungary.
- Table 32. Lettuce. Australia, France, Germany.
- Table 33. Beans. Germany.
- Table 34. Peas. Germany.
- Table 35. Potatoes. Belgium, Germany.
- Table 36. Celery. Germany.
- Table 37. Wheat. Germany, Hungary.
- Table 38. Rape seed. the UK.
- Table 39. Hops. Germany.
- Table 40. Wheat forage. Germany.
- Table 41. Wheat fodder. Germany, Hungary.

Metiram-complex is the old name for technical material and contains 89% metiram. Old labels and use patterns quoting 80% ai are equivalent to modern labels quoting 70% ai. A different factor (2.09) is now used to calculate the metiram residue from the carbon disulfide content; formerly the factor was 2.35. Most of the application rates and spray concentrations in the trials are quoted on the old (metiram-complex) basis. The difference should be taken into account when comparing trials data with

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modern labels.

Where residues were not detected, they are recorded in the Tables as less than the limit of determination (LOD), eg <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. Only when residues were detected in control samples are they recorded in the Tables. This rarely happened.

Most of the trials were reported on detailed summary sheets. For many of them it was not clear whether the reported residues had or had not been adjusted for the analytical recovery. Recoveries were generally good, so there would be little difference between adjusted and unadjusted residues. ETU recoveries tended to be a little low, around 70%.

Dithiocarbamate residues are expressed as mg CS₂/kg throughout the tables and text. EBDC is used as an abbreviation for ethylenebisdithiocarbamates. ETU residues were determined in most of the trials.

Plot sizes in German apple trials ranged from 3 trees to 0.4 ha but were commonly 10-20 trees. The type of sprayer was not always recorded but the use of compressed air sprayers and atomizers is reported.

In the Canadian apple trials the trees were sprayed by hand gun and the plot size was 16 trees. Commercial sprayers or mistblowers were used in the UK apple trials where the plot size was 1 acre. The plot size in the Italian apple trials was 0.5 ha.

Plot sizes in the German trials on stone fruits and pears ranged from 4 trees to 160 m².

Compressed air sprayers and atomizers were used in the German grape trials where the plot size ranged from 15 to 400 m². Plot sizes in the French trials were 45 to 270 vines.

Mistblowers and HV sprayers were used in the UK strawberry trials where plot sizes ranged from 20 m² to 2 ha. In Germany strawberry trials were conducted on 20-25 m² plots. Plot sizes in German currant trials were 5-12 bushes, and in UK gooseberry trials 0.25-1 ha.

Plot sizes in the German vegetable trials were commonly 5-50 m². Compressed air sprayers were used for foliar application.

German supervised trials on hops were with plots of 1000 plants or 0.2-0.9 ha.

Table 19. Residues in apples from foliar applications of metiram in supervised trials in Germany. Underlined residues are from treatments according to GAP.

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
1971 (Cox's Orange)	WP		0.2	10	30	1.2		2221 F71/7E
1973 (James Griesves)	WP	3.2	0.32	3	0 3 5 7 10 14	0.7 0.6 - 0.2 <0.2 <0.2	<0.01	2221 F73/16A
1973 (Cox's Orange)	WP	3.2	0.32	3	0 3	0.3 <0.2		2221 F73/27A

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Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
					6 10 14	0.2 0.4 0.4	0.04	
1973 (James Grieves)	WP	3.2	0.32	3	0 3 5 7 10 14	0.6 0.6 0.3 0.3 <0.2 0.2	<0.01	2221 F73/15A
1973 (Golden Delicious)	WP	3.2	0.32	3	0 3 6 8 10 14	0.8 1.1 0.7 0.9 <0.2 1.7	0.01	2221 F73/26A
1973 (Golden Delicious)	WP	3.2	0.32	3	0 3 6 8 10 14	0.2 0.8 0.5 0.9 <0.2 0.2	0.02	2221 F73/25A
1973 (Jonathan)	WP	3.2	0.32	3	0 3 6 8 10 14	0.6 1.0 0.5 0.7 0.4 <0.2	0.03	2221 F73/29A
1973 (Cox's Orange)	WP	3.2	0.32	3	0 3 6 10 14	0.6 0.3 0.2 <0.2 0.3	0.05	2221 F73/28A
1975 (Cox's Orange)	WP	3 × 3.2+ 11 × 2.4	3 × 0.16+ 11 × × 0.12	14	0 4 7 10 14 21	1.1 0.31 0.42 0.29 <0.05 0.16	0.15 0.23 0.08 0.04 0.03 0.03	22201 F75/5A
1975 (James Grieve)	WP	3 × 3.2+ 11 × 2.4	3 × 0.2+ 11 × 0.15	14	0 4 7 10 14 21	2.6 0.73 0.93 0.69 1.00 <u>0.40</u>		22201 F75/6A
1975 (James Grieve)	WP	3 × 3.2+ 11 × 2.4	3 × 0.2+ 11 × 0.15	14	0 4 7 10 14 21	1.1 1.5 0.12 0.69 0.76 <u>0.60</u>		22201 F75/7A
1975 (Cox's Orange)	WP	3 × 3.2+ 11 × 2.4	3 × 0.2+ 11 × 0.15	14	0 4 7 10 14 21	3.0 2.3 0.59 0.32 0.54 <u>0.10</u>		22201 F75/8A
1976 (Cox's orange)	WP	2 × 1.6+ 11 ×	2 × 0.1+ 11 ×	13	7	2.5	0.04	2220 F76/20A

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Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
		2.4	0.15		14	2.2	0.04	
1976 (Jonathan)	WP	2 × 1.6+ 14 × 2.4	2 × 0.10+ 14 × 0.15	16	7 14		0.03 0.02	22201 F76/27A
1976 (Lody)	WP	2 × 1.6+ 5 × 2.4	2 × 0.1+ 5 × 0.15	7	35	<0.05	0.01	22201 F76/1E
1976 (Cox's Orange)	WP	2.4	0.15	12	7 14	1.8 1.9	0.03 <.01	22201 F76/26A
1976 (Jonathan)	WP	2.4	0.15	12	7 14	1.2 1.6	0.02 0.03	22201 F76/25A
1976 (James Grieve)	WP	2 × 1.6+ 8 × 2.4	2 × 0.1+ 8 × 0.15	10	15		0.02	22201 F76/2E
1976 (Golden Delicious)	WP	2.4	0.15	12	7 14	3.2 3.0	0.02 0.03	22201 F76/24A
1976 (Golden Delicious)	WP	3 × 2.4+ 12 × 1.8	3 × 0.12+ 12 × 0.09	15	0 7 14 19 28	8.7 0.49 0.16 <u>0.35</u> <u>0.26</u>	0.05 0.02 0.01 0.01 0.01	22201 F76/23A
1976 (Jonathan)	WP	3 × 3.2+ 12 × 2.4	3 × 0.20+ 12 × 0.15	15	0 7 14 21 28	2.5 2.6 3.1 <u>1.6</u> <u>2.0</u>	0.07 0.02 0.02 0.02 0.01	22201 F76/21A
1977 (Golden Delicious)	WP	1.2	0.06	19	0 7 14 21 28	0.80 0.50 0.70 <u>0.70</u> <u>0.60</u>	0.02 0.01 <0.01 <0.01 <0.01	28802 F77/1A
1977 (Golden Delicious)	WP	1.2	0.06	19	0 7 14 21 28	0.60 0.80 0.70 <u>0.40</u> <u>0.30</u>	0.02 0.01 <0.01 <0.01 <0.01	28802 F77/3A
1977 (Cox's Orange)	WP	1.2	0.06	19	0 7 14 21 28	1.0 0.50 0.80 <u>0.50</u> <u>0.80</u>	0.02 0.02 0.01 <0.01 0.01	28802 F77/2A
1977 (Jonathan)	WP	0.9	0.045	11	0 7 14 21 28	1.1 0.80 0.50 <u>0.30</u> <u>0.40</u>	0.03 0.01 <0.01 <0.01 <0.01	28802 F77/6A
1977 (Goldparmäne)	WP	0.9	0.045	11	0 7 14 21 28	1.0 1.3 0.50 <u>0.40</u> <u>0.70</u>	0.02 0.01 <0.01 0.01 <0.01	28802 F77/4A
1977 (Golden Delicious)	WP	0.9	0.045	11	0 7 14 21 28	1.0 0.50 0.50 <u>0.30</u> <u>0.40</u>	0.03 0.02 <0.01 <0.01 0.01	28802 F77/5A
1979 (Golden	WP	3 × 2.4+ 12 ×	3 × 0.16+ 12	15	21	<u>0.29</u>	0.01	22201 F79/4E

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Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
Delicious)		1.8	× 0.12					
1979 (Golden Delicious)	WP	3 × 2.4+ 12 × 1.8	3 × 0.16+ 12 × 0.12	15	21	<u>0.25</u>	<0.01	22201 F79/3E
1979 (Boskoop)	WP	4 × 2.4+ 11 × 1.8	4 × 0.16+ 11 × 0.12	15	21	<u>0.42</u>	<0.01	22201 F79/7E
1979 (Boskoop)	WP	4 × 2.4+ 11 × 1.8	4 × 0.16+ 11 × 0.12	15	21	<u>0.43</u>	<0.01	22201 F79/8E
1979 (Melrose)	WP	3 × 2.4+ 12 × 1.8	3 × 0.16+ 12 × 0.12	15	21	<u>0.37</u>	<0.01	22201 F79/6E
1979 (Melrose)	WP	3 × 2.4+ 12 × 1.8	3 × 0.16+ 12 × 0.12	15	21	<u>0.48</u>	0.01	22201 F79/5E
1980 (James Grieve)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0 7 14 21 28	2.1 1.8 0.64 <u>0.93</u> <u>0.63</u>	0.02 0.04 0.02 0.02 0.02	22201 F80/12A
1980 (Golden Delicious)	WP	2 × 2.4+ 12 × 1.8	2 × 0.16+ 12 × 0.12	14	0 7 14 21 28	1.3 1.2 0.58 <u>0.79</u> <u>0.58</u>	0.02 0.02 0.01 0.01 0.01	22201 F80/11A
1982 (James Grieve)	WP	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0 14 21 28 35	0.60 0.10 <u>0.10</u> <u>0.06</u> <u><0.02</u>	0.02 0.02 <0.01 <0.01 <0.01	22201 F82/5A
1982 (Jonathan)	WP	2.3	0.12	10	0 14 21 28 35	1.8 1.6 <u>0.89</u> <u>0.70</u> <u>0.78</u>	0.09 0.04 0.03 0.04 0.02	22201 F82/3A
1982 (Cox's Orange)	WP	1.8	0.12	10	0 14 21 28 35	1.6 1.0 <u>0.63</u> <u>0.60</u> <u>0.57</u>	0.02 0.01 0.01 0.01 0.01	22201 F82/6A
1982 (Gravensteiner)	WP	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0 14 21 28 35	0.10 0.07 <u>0.06</u> <u>0.02</u> <u>0.03</u>	<0.01 <0.01 <0.01 <0.01 <0.01	22201 F82/4A
1983 (Melrose)	WP	1.8	0.24	8	0 28 35 42 49	1.7 <u>0.45</u> <u>0.16</u> <u>0.28</u> <u>0.14</u>	0.02 0.01 <0.01 <0.01 <0.01	22201 F83/5A
1983 (James Grieve)	WP	1.8	0.12	8	0 28 35 42 49	1.6 <u>0.07</u> <u>0.10</u> <u>0.12</u> <u>0.04</u>	0.07 <0.01 <0.01 <0.01 <0.01	22201 F83/7A
1983 (Golden Delicious)	WP	1.8	0.12	8	0 28 35 42	1.8 <u>0.21</u> <u>0.10</u> <u>0.14</u>	0.06 0.01 <0.01 <0.01	22201 F83/4A

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Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
					49	<u>0.22</u>	<0.01	
1983	WP	2.3	0.12	8	0 28 35 42 49	2.7 <u>1.5</u> <u>0.32</u> <u>0.42</u> <u>0.20</u>	0.13 0.03 0.02 0.02 <0.01	22201 F83/6A
1988 (Gloster)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 35 42 49 56	2.4 <u>0.82</u> <u>0.69</u> <u>0.35</u> <u>0.77</u>	0.04 <0.02 <0.02 <0.02 <0.02	22226 F88/8A
1988 (Cox's Orange)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × × 0.12	14	0 35 42 49 56	0.12 <u>0.32</u> <u>0.10</u> <u>0.18</u> <u>0.37</u>	0.03 <0.02 <0.02 <0.02 <0.02	22226 F88/9A
1988 (Gloster)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 21 28 35 42	2.9 <u>0.57</u> <u>1.0</u> <u>0.38</u> <u>0.52</u>	0.04 <0.02 <0.02 <0.02 <0.02	22228 F88/3A
1988 (Jonagold)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × × 0.12	14	0 35 42 49 56	1.3 <u>0.38</u> <u>0.16</u> <u>0.23</u> <u>0.84</u>	0.03 <0.02 <0.02 <0.02 <0.02	22226 F88/10A
1988 (Cox's Orange)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × × 0.12	14	0 21 28 35 42	2.1 <u>0.32</u> <u>0.27</u> <u>0.62</u> <u>0.19</u>	<0.02 <0.02 <0.02 <0.02 <0.02	22226 F88/4A
1988 (Gloster)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 35 42 49 56	3.1 <u>0.54</u> <u>0.67</u> <u>0.20</u> <u>0.66</u>	0.03 <0.02 <0.02 <0.02 <0.02	22226 F88/8A
1988 (Jonagold)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × × 0.12	14	0 21 28 35 42	1.1 <u>0.24</u> <u>0.24</u> <u>2.0</u> <u>0.83</u>	<0.02 <0.02 <0.02 <0.02 <0.02	22226 F88/5A
1988 (Jonagold)		4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 21 28 35 42	2.1 <u>0.83</u> <u>0.71</u> <u>1.1</u> <u>0.16</u>	<0.02 0.03 0.03 <0.02 0.03	22226 F88/2A
1988 (Alkmene)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 21 28	4.2 <u>1.4</u> <u>0.76</u>	0.04 0.04 0.03	22226 F88/1A
1988 (Alkmene)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 35 42 49 56	3.2 <u>0.83</u> <u>0.28</u> <u>0.69</u> <u>0.44</u>	0.03 0.04 0.04 0.03 <0.02	22226 F88/6A
1988 (Jonagold)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 35	2.7 <u>0.36</u>	0.02 <0.02	22226 F88/7A

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Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
					42	<u>0.22</u>	<0.02	
					49	<u>0.36</u>	0.02	
					56	<u>0.22</u>	0.03	
1988 (Gloster)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0	2.5	0.09	22226 F88/3A
					21	<u>0.92</u>	0.02	
					28	<u>1.9</u>	<0.02	
					35	<u>0.50</u>	<0.02	
					42	<u>0.40</u>	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	2.4	<0.02	22228 F88/14A
					49	<u>0.21</u>	<0.02	
					56	<u>0.10</u>	<0.02	
					63	<u>0.06</u>	<0.02	
					70	<u>0.12</u>	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.8	0.03	22228 F88/10A
					35	<u>0.23</u>	<0.02	
					42	<u>0.19</u>	<0.02	
					49	<u>0.14</u>	<0.02	
					56	<u>0.41</u>	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.3	<0.02	22228 F88/5A
					21	<u>0.37</u>	<0.02	
					28	<u>0.26</u>	<0.02	
					35	<u>1.6</u>	<0.02	
					42	<u>0.39</u>	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.9	0.02	22228 F88/9A
					35	<u>0.14</u>	<0.02	
					42	<u>0.11</u>	<0.02	
					49	<u>0.16</u>	<0.02	
					56	-	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.7	<0.02	22228 F88/4A
					21	<u>0.12</u>	<0.02	
					28	<u>0.27</u>	<0.02	
					35	<u>0.16</u>	<0.02	
					42	<u>0.30</u>	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	1.3	0.03	22228 F88/15A
					49	<u>0.18</u>	<0.02	
					56	<u>0.11</u>	<0.02	
					63	<u>0.21</u>	<0.02	
					70	<u>0.12</u>	<0.02	
1988 (Cox's orange)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	0.91	<0.02	22228 F88/24A
					35	<u>0.18</u>	<0.02	
					42	<u>0.16</u>	<0.02	
					49	<u>0.10</u>	<0.02	
					56	<u>0.13</u>	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0	1.4	0.03	22228 F88/20A
					35	<u>0.22</u>	<0.02	
					42	<u>0.08</u>	<0.02	
					49	<u>0.08</u>	<0.02	
					56	<u>0.12</u>	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0	1.1	<0.02	22228 F88/19A
					35	<u>0.12</u>	<0.02	
					42	<u>0.11</u>	<0.02	
					49	<u>0.05</u>	<0.02	
					56	<u>0.18</u>	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	0.73	0.02	22228 F88/25A
					35	<u>0.20</u>	<0.02	
					42	<u>0.10</u>	<0.02	
					49	<u>0.11</u>	<0.02	

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Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
					56	<u>0.20</u>	<0.02	
1988 (Alkmene)	WG	4 × 2.4+ 8 × 1.8	4 × 0.32+ 8 × 0.24	12	0 35 42 49 56	4.7 <u>0.81</u> <u>0.54</u> <u>0.71</u> <u>0.18</u>	<0.02 <0.02 0.04 0.02 0.04	22228 F88/16A
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 35 42 49 56	2.0 <u>0.20</u> <u>0.24</u> <u>0.19</u> <u>0.11</u>	0.05 <0.02 <0.02 <0.02 <0.02	22228 F88/7A
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 21 28 35 42	2.0 <u>0.62</u> <u>0.67</u> <u>0.37</u> <u>0.59</u>	0.02 0.03 <0.02 <0.02 0.04	22228 F88/2A
1988 (Gloster)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0 35 42 49 56	1.6 <u>0.33</u> <u>0.19</u> <u>0.29</u> <u>0.13</u>	<0.02 <0.02 <0.02 <0.02 <0.02	22228 F88/23A
1988 (Gloster)	WG	4 × 2.4+ 8 × 1.8	4 × 0.32+ 8 × 0.24	12	0 35 42 49 56	2.0 <u>0.38</u> <u>0.22</u> <u>0.26</u> <u>0.24</u>	<0.02 <0.02 <0.02 <0.02 <0.02	22228 F88/18A
1988 (Gloster)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0 49 56 63 70	2.8 <u>0.19</u> <u>0.32</u> <u>0.21</u> <u>0.34</u>	0.04 <0.02 <0.02 <0.02 <0.02	22228 F88/13A
1988 (Alkmene)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0 49 56 63 70	5.7 <u>0.18</u> <u>0.27</u> <u>0.18</u> <u>0.21</u>	0.10 <0.02 <0.02 <0.02 <0.02	22228 F88/11A
1988 (Jonagold)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0 35 42 49 56	2.0 <u>0.39</u> <u>0.19</u> <u>0.10</u> <u>0.13</u>	0.18 <0.02 <0.02 <0.02 <0.02	22228 F88/22A
1988 (Alkmene)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 21 28 35 42	3.4 <u>1.3</u> <u>1.1</u> <u>0.77</u> <u>1.2</u>	0.08 0.02 0.05 0.03 0.03	22228 F88/1A
1988 (Alkmene)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0 35 42 49 56	3.7 <u>0.64</u> <u>0.67</u> <u>0.62</u> <u>0.51</u>	0.03 <0.02 0.03 <0.02 0.04	22228 F88/21A
1988 (Alkmene)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0 35 42 49 56	4.5 <u>0.78</u> <u>0.23</u> <u>0.33</u> <u>0.66</u>	0.05 0.02 0.02 0.02 <0.02	22228 F88/6A

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Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
1988 (Jonagold)	WG	4 × 2.4+ 8 × 1.8	4 × 0.32+ 8 × 0.24	12	0	0.64	0.06	22228 F88/17A
					35	<u>0.25</u>	<0.02	
					42	<u>0.16</u>	<0.02	
					49	<u>0.12</u>	<0.02	
					56	<u>0.19</u>	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × × 0.24	14	0	3.3	0.09	22228 F88/12A
					49	<u>0.17</u>	<0.02	
					56	<u>0.68</u>	<0.02	
					63	<u>0.12</u>	<0.02	
					70	<u>0.05</u>	<0.02	

Table 20. Residues in apples from foliar applications of metiram in supervised trials in Australia, Brazil, Canada, Hungary, Italy and the UK. Underlined residues are from treatments according to GAP

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
Australia (Vic), 1977 (Granny Smith)	WP	3.6	0.2	8	18	1.9	0.03	37900 F77/2A
					24	<u>2.1</u>	0.03	
					28	<u>1.6</u>	0.02	
					118	<u>0.20</u>	<0.01	
Australia (Vic), 1977 (Jonathan)	WP	3.6	0.2	8	10	2.6	0.03	37900 F77/1A
					15	2.0	0.03	
					21	<u>0.8</u>	<0.01	
					28	<u>1.0</u>	<0.01	
					71	<u>0.05</u>	<0.01	
Brazil, 1986 (Fuji)	WP	2.4	0.3	1	32	0.16	<0.01	22226 F86/2E
Brazil, 1986 (Fuji)	WP	1.2	0.15	1	32	<0.02	<0.01	22226 F86/1E
Canada, 1977 (Red Delicious)	WP	2.2	0.25	15	88	<u>0.2, 0.3, 0.4, 0.4</u>	<0.01 (4)	37900 F77/7E
Canada, 1977 (McIntosh)	WP	2.2	0.25	15	88	<u>0.5, <0.05 (2), 0.2</u>	<0.01 (4)	37900 F77/19E
Canada, 1977 (Golden Delicious)	WP	2.2	0.25	15	88	<u>0.5, 0.2, <0.05, 0.4</u>	<0.01, 0.02, <0.01, 0.01	37900 F77/11E
Canada, 1977 (Red Delicious)	WP	2.2	0.25	15	88	<u>0.2, 0.3, 0.4, 0.4</u>	<0.01 (4)	37900 F77/7E
Canada, 1977 (Spartan)	WP	2.2	0.25	15	88	<u>0.3, 0.3, 0.1, 0.1</u>	<0.01 (4)	37900 F77/15E
Hungary, 1990	DF	2.4	0.24	14 15	7	0.70, 0.17, 0.39		90/10604
					0	1.9, 1.7, 1.4		
					3	2.4, 0.87, 0.67		
					7	1.3, 0.59, 0.39		
					10	0.70, 0.78, 0.42		
					14	0.73, 0.47, 0.26		
					30	<u>0.12, 0.1, 0.18, 0.1, 0.20</u>		
					41	<u>0.18, 0.45, 0.27, 0.18, 0.17</u>		
					Italy, 1990 (Jonagold)	WP	1.2	
Italy, 1990 (Jonagold)	WP	1.2	0.16	5	29	<u>0.15</u>	<0.02	22201 F90/2E
Italy, 1990 (Cooper 7SB2)	WP	2.4	0.16	18	0	3.6	0.16	22201 F90/3A
					7	3.3	0.11	

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Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
					14 20 27 35 42	2.7 2.0 <u>2.1</u> <u>1.3</u> <u>2.6</u>	0.15 0.04 0.05 0.05 0.06	
Italy, 1990 (Golden Delicious)	WP	1.1	0.15	7	19	0.15	<0.02	22201 F90/3E
Italy, 1990 (Imperatore Dallago)	WP	2.9	0.16	17	0 7 14 21 28 35 42	1.6 0.82 0.62 0.62 <u>0.67</u> <u>0.62</u> <u>0.48</u>	0.02 0.02 <0.02 <0.02 <0.02 <0.02 <0.02	22201 F90/5A
Italy, 1990 (Golden Delicious)	WP	1.1	0.16	6	46	0.14	<0.02	22201 F90/4E
Italy, 1990 (Golden Delicious)	WP	1.9	0.16	15	0 7 14 21 28 35 42	2.2 0.95 0.69 0.88 <u>0.34</u> <u>0.24</u> <u>0.10</u>	0.02 0.03 <0.02 <0.02 <0.02 <0.02 <0.02	22201 F90/4A
UK, 1976 (Cox's Orange Pippin)	WP	3.2	0.57	7	47 55	0.57 0.34		37900 F76/5A1
	WP	3.2	0.57	8	18 29	0.27 0.30		37900 F76/9E1 F76/6A1
UK, 1976 (Golden Delicious)	WP	3.2	0.57	4	37 57	0.25 0.28		37900 F76/10E1 F76/7A1
UK, 1976 (Cox's Orange Pippin)	WP	3.2	0.57	9	42 61	0.52 0.13		37900 F76/11E1 F76/8A1
	WP	0.04	0.005	6	7 14	<0.05 <u><0.05</u>	<0.01 <0.01	37901 F79/1A
	WP	0.04	0.007	8	7 15	<0.05 <u><0.05</u>	<0.01 <0.01	37901 F79/2A
	WP	0.04	0.007	9	7 15	<0.05 <u><0.05</u>	<0.01 <0.01	37901 F79/3A
	WP	0.02	0.04	21	9 18	0.02 <u><0.02</u>	<0.01 <0.01	37901 F79/7A
	WP	0.04	0.007	8	7 14	<0.02 <u><0.02</u>	<0.01 <0.01	37901 F79/8A
	WP	0.04	0.012	8	19	<u>0.03</u>	0.01	37901 F79/1E
UK, 1980 (Cox's Orange Pippin)	WP	0.019	0.004	17	7	<0.02	<0.01	37901 F80/1E
	WP	0.019	0.003	19	6	<0.02	<0.01	37901 F80/3E
	WP	0.019	0.006	17	7	<0.02	<0.01	37901 F80/2E
UK, 1981 (Cox's Orange Pippin)	WP	0.02-0.04	0.011	10	7	0.04	<0.01	37901 F81/2E
	WP	0.004-0.01	0.016	19	7	0.05	<0.01	37901 F81/3E
UK, 1982 (Cox's Orange Pippin)	WP	0.038	0.014	10	14	<u><0.02</u>	<0.01	37901 F82/1E
	WP	0.035	0.010	6	14	<u>0.08</u>	<0.01	37901 F82/2E

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Table 21. Residues in pears from foliar applications of metiram WP in supervised trials in Germany. Underlined residues are from treatments according to GAP.

Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
1983 (Williams Christ)	1.8	0.12	8	0	1.3	0.05	22201 F83/8A
				28	<u>0.49</u>	0.03	
				35	<u>0.29</u>	<0.01	
				42	<u>0.21</u>	0.02	
				49	<u>0.21</u>	<0.01	
1983 (Conference)	1.8	0.24	8	0	3.9	0.10	22201 F83/9A
				28	<u>0.37</u>	0.03	
				35	<u>0.47</u>	<0.01	
				42	<u>0.33</u>	<0.01	
				49	<u>0.32</u>	<0.01	
1982 (Williams Christ)	1.8	0.12	10	0	0.93	0.02	37900 F82/1A
				14	0.37	0.01	
				21	0.49	<0.01	
				28	<u>0.24</u>	0.01	
				35	<u>0.22</u>	<0.01	
1983 (Williams Christ)	1.8	0.12	8	0	0.75	0.05	37900 F83/5A
				28	<u>0.36</u>	0.02	
				35	<u>0.11</u>	<0.01	
				42	<u>0.11</u>	<0.01	
				49	<u>0.12</u>	<0.01	
1983 (Conference)	1.8	0.24	8	0	2.0	0.05	37900 F83/6A
				28	<u>0.53</u>	0.02	
				35	<u>0.29</u>	0.02	
				42	<u>0.18</u>	<0.01	
				49	<u>0.11</u>	<0.01	

Table 22. Residues in apricots, cherries, peaches and plums from foliar applications of metiram WP in supervised trials in Australia and Germany. Underlined residues are from treatments according to GAP.

STONE FRUIT Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
APRICOTS							
Australia (SA), 1980	0.12	0.12		1	5.6		80/10200
				3	3.7		
				5	5.6		
				7	4.3		
Australia (SA), 1980	0.16	0.16		1	3.3		80/10200
				3	3.9		
				5	1.6		
				7	2.3		
CHERRIES							
Australia (SA), 1980	0.12	0.12		1	3.5		80/10200
				3	2.6		
				5	2.6		
				7	2.4		
Australia (SA), 1980	0.16	0.16		1	5.0		80/10200
				3	4.0		

metiram

STONE FRUIT Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
				5 7	5.2 2.7		
Germany, 1976 (Schattenmorelle)	3.2	0.16	4	0 7 14 21 28	1.9 1.6 0.50 <u>0.24</u> <u>0.50</u>	0.04 0.02 0.02 0.02 0.01	22201 F76/12A
Germany, 1973 (Schattenmorelle)	3.2	0.16	4	0 5 7 11 14 21	8.5 4.3 3.6 1.3 1.0 <u>1.0</u>	0.5	2221 F73/1A
Germany, 1973 (Schattenmorelle)	3.2	0.16	4	0 5 7 11 14 21	9.1 5.0 2.3 1.0 1.0 <u>0.7</u>	0.02	2221 F73/2A
Germany, 1976 (Schattenmorelle)	3.2	0.16	4	0 7 14 21 28	4.0 1.7 <0.05 <u>1.0</u> < <u>0.05</u>	0.07 0.03 0.03 0.03 <0.01	22201 F76/13A
PEACHES							
Australia (SA), 1980	0.12	0.12		1 3 5 7	7.2 2.2 2.3 1.2		80/10200
Australia (SA), 1980	0.16	0.16		1 3 5 7	9.1 8.4 5.7 4.3		80/10200
Australia (Qld), 1980	0.12	0.12		1 3 5 7	5.9 4.8 4.6 3.2		80/10200
Australia (Qld), 1980	0.24	0.24		1 3 5 7	6.6 9.7 5.9 5.9		80/10200
PLUMS							
Germany, 1973 (Tetzor)	3.2	0.16	4	0 5 7 10 14 21	0.63 0.16 0.15 <0.2 <0.2 <0.2		2221 F73/4A
Germany, 1979 (Hauszwetsche)	2.4	0.16	4	14	1.8 cooked 0.35	0.02 cooked 0.22	22201 F79/15E
Germany, 1976 (Auerbacher)	3.2	0.16	4	0 7 14 21 28	0.17 0.18 0.13 0.10 <u>0.08</u>	<0.01 <0.01 <0.01 <0.01 <0.01	22201 F76/14A

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STONE FRUIT Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
Germany, 1976 (Texar)	3.2	0.16	4	0	16	0.06	22201 F76/15A
				7	2.1	0.04	
				14	0.40	0.04	
				21	0.30	0.03	
				28	<u>0.40</u>	0.03	
Germany, 1979 (Auerbacher)	2.4	0.16	3	14	0.05 cooked 0.03	<0.01 cooked <0.01	22201 F79/13E
Germany, 1979 (Hauszwetche)	2.4	0.16	4	14	2.1 cooked 2.1	<0.01 cooked <0.02	22201 F79/14E

Table 23. Residues in grapes from foliar applications of metiram in supervised trials in Austria, Germany, France, Hungary and Italy. Underlined residues are from treatments according to GAP.

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS ₂	ETU	
Austria, 1982	WP	0.80	0.10	7	57	<u>0.61</u>	0.02	43000 F82/5E
Austria, 1982	WP	0.80	0.10	7	40	0.13	<0.01	43000 F82/3E
Austria, 1982	WP	0.80	0.10	7	40	0.20	<0.01	43000 F82/4E
France, 1980 (Ugni Blanc)	WP	0.32	0.16	11	15	0.14	0.02	43002 F80/2E
France, 1980 (Gamay Beaujolais)	WP	0.32	0.053	7	42	0.15	<0.01	43002 F80/3E
France, 1980 (Aramon)	WP	0.32	0.16	3	39	0.20	0.01	43002 F80/1E
France, 1980 (Pinot Noir)	WP	0.60	0.32	6	76	0.14	<0.01	43002 F80/5E
France, 1980 (Gros Lot)	WP	0.32	0.16	6	42	0.08	0.01	43002 F80/4E
France, 1981 (Grenache Blanc)	WP	1.6-3.2	0.32	13	36	0.14	<0.01	22201 F81/1E
Germany, 1973 (Scheurebe)	WP	3.2	0.16	6	0	2.7		2221 F73/20A
					5	1.0		
					7	1.8		
					10	1.7		
					14	1.6		
					21	1.1		
					28	1.1		
Germany, 1973 (Morio Muskat)	WP	3.2	0.16	6	0	1.7		2221 F73/22A
					5	6.1		
					7	3.1		
					11	1.0		
					14	0.7		
					21	0.7		
					28	<0.2		
Germany, 1973 (Müller Thurgau)	WP	3.2	0.16	9	66	<u><0.2</u>	0.01	2221 F73/1E
Germany, 1973 (Müller Thurgau)	WP	3.2	0.16	6	0	2.6		2221 F73/21A
					5	0.33		
					7	1.2		
					10	1.0		
					14	0.7		
					21	0.4		