METHIOCARB (132)

EXPLANATION

Methiocarb, or mercaptodimethur, an insecticide, acaricide, molluscicide, and bird repellent was identified by the 1995 CCPR as a candidate for periodic review (ALINORM 95/24A, Annex 1). It was scheduled for toxicological and residue reviews by the 1998 and 1999 JMPR respectively (ALINORM 97/24A, Appendix III). The most recent extensive reviews of methiocarb residue chemistry were in 1981 and 1983.

The manufacturer is Bayer AG.

IDENTITY

ISO common name: methiocarb
mercaptodimethur

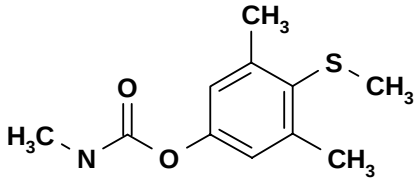
Chemical names:
IUPAC: 4-methylthio-3,5xylyl methylcarbamate
CA: 3,5-dimethyl-4-(methylthio)phenyl methylcarbamate

CAS Number: 2032-65-7

CIPAC Number: 165

Synonyms: BAY 37344
Mesurol

Structural formula:



Molecular formula: $C_{11}H_{15}NO_2S$

Molecular weight: 225.3

Physical and chemical properties

Pure active ingredient

Vapour pressure: 0.015 mPa at 20°C
0.036 mPa at 25°C

Melting point: 119°C

Octanol/water partition Coefficient:	log P_{ow} = 3.11 at 20°C and pH 4 log P_{ow} = 3.18 at 20°C and pH 7 degradation at pH 9 log P_{ow} = 3.08 at 20°C unbuffered (Krohn, 1995)
Solubility:	0.027 g/l at 20°C in water (Krohn, 1989) 1.3 g/l at 20°C in n-hexane 33 g/l at 20°C in toluene >200 g/l at 20°C in dichloromethane 53 g/l at 20°C in 2-propanol
Specific gravity:	1.236 g/cm^3 at 20°C
Hydrolysis:	half-lives of 763 days, 28 days, and 2.2 days at pH 5, 7, and 9 respectively (Saakvitne, 1981).
Photolysis:	the half-life in irradiated aqueous solution was 88 days and the half-life of dark controls was 238 days. The half-life of samples irradiated during the growing season was calculated to be 66 days. The major degradation product was the sulfoxide (Kesterson, 1988)
Dissociation constant:	methiocarb has neither basic nor acidic properties in aqueous systems (Placke, 1988)
Thermal stability:	Stable at room temperature.
Volatility:	Henry's Law constant, H = 1.216 x 10^{-4} Pa.m^3.mol^{-1} at 20°C (Krohn, 1993)

Technical material

Purity:	>97.0%
Melting range:	not specified
Stability:	stable for 24 months at ambient temperature.

Formulations

The following formulations were identified from the information supplied by the manufacturer and by national governments: GR (40 g/kg); GR (20 g/kg); WP (500 g/kg); RB (40 g/kg)); GB (40 g/kg); RB (20 g/kg); SC (500 g/l).

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Studies were submitted on the metabolism of radiolabelled methiocarb in the rat, cow (2 studies), and chicken (2 studies).

Rat. The metabolism of [1-*phenyl*-^{14}C]methiocarb was investigated in rats (Stanley and Johnson, 1976). The same study was considered by the 1998 WHO Core Assessment Group of the JMPR. [1-*phenyl*-^{14}C]methiocarb dissolved in ethanol was administered at dose levels of 20 mg/kg body weight to a group

of 3 female rats and 0.25 mg/kg bw to 3 male and 3 female rats. Most of the administered radioactivity was excreted with the urine, >90 % in the high dose group and >70 % in the low dose group.

Only small amounts of unconjugated metabolites were found in rat urine. The major metabolites identified in the organosoluble fraction were methiocarb phenol (M03) and methiocarb sulfoxide phenol (M04). After enzymatic hydrolysis about half of the radioactive material in the urine was rendered organosoluble. Identification of metabolites was by thin-layer chromatography only. The enzymatic hydrolysis released about 8% methiocarb phenol, 23% methiocarb sulfoxide phenol, and 1% methiocarb sulfone phenol from the high dose group and 20% methiocarb phenol, 43% methiocarb sulfoxide phenol, and 1% methiocarb sulfone phenol from the low dose group. The percentages refer to the administered dose.

Cow. Two studies were submitted on the metabolism of [1-*phenyl*-^{14}C]methiocarb in the dairy cow. In one study (Minor and Murphy, 1977a), a dairy cow (500 kg) was dosed orally once by gelatin capsule with the test substance (4.83 mCi/mmole) at a rate of 0.14 mg/kg bw. Urine samples were collected 4, 8, 24, 48, 72, 96, 120, and 144 hours after dosing. Faeces, milk, and blood samples were also collected at various intervals. The urine samples collected within 48 hours were extracted with chloroform, and the residual aqueous fractions were buffered with 0.07 M pH 5 phosphate and subjected to sequential sulfatase-glucuronidase and acid hydrolysis (2 N HCl under reflux for 2 h). The enzymatic and acid hydrolysates were extracted with chloroform. All chloroform extracts were radioassayed and analysed by TLC only.

Within 144 hours of dosing, 96% of the administered radioactivity was eliminated in the urine. Faecal matter contained 1% and milk <1% of the initial radioactivity.

About 1% of the radioactivity in the urine was organosoluble. Enzyme treatment released 50-70% of the initial radioactivity, and acid hydrolysis released 10-25%. The main metabolites identified were methiocarb phenol (25-29%), methiocarb sulfoxide phenol (26-32%), and methiocarb sulfone phenol (20-23%).

In a more detailed study (Minor and Murphy, 1977b), one dairy cow (about 500 kg) was given [1-*phenyl*-^{14}C]methiocarb, 0.14 mg/kg bw/day (72 mg/day), for 5 consecutive days. The cow had received a single dose one week before the study. The cow was slaughtered within three hours of the final dosing, and samples of brain, heart, kidney, muscle, omental fat, renal fat, and udder were frozen and pulverized. Milk was taken in the morning and evening of each day. All samples were radioassayed. The radioactive residues in milk peaked (0.062 mg/kg) on the third day. The total radioactive residues in various tissues and milk are shown in Table 1.

Table 1. Total radioactive residue (TRR) after oral administration of [^{14}C]methiocarb to a dairy cow (Minor and Murphy, 1977a).

Sample	TRR, µg/g as methiocarb
Kidney	0.108
Liver	0.073
Udder	0.014
Heart	0.011
Renal fat	0.011
Muscle	<0.01
Omental fat	<0.01
Milk (day 3, evening)	0.062

A liver sample (20 g, containing 0.073 mg/kg as methiocarb) was homogenized with methanol/water, and the extract was partitioned with chloroform. The residual aqueous fraction was

refluxed with 1N HCl for 2 hours, partitioned with chloroform, refluxed for 2 hours with 6 N HCl, and partitioned again with chloroform. A kidney fraction (30 g, 0.108 mg/kg) was treated similarly, but the 1N HCl reflux was omitted. The extracts and residues were radioassayed, and the extracts were analysed by TLC on silica gel plates with two-dimensional development.

A milk sample, not otherwise identified, was homogenized with acetone and the filtrate was partitioned with chloroform. The aqueous fraction was subjected to sequential enzymatic and acid hydrolysis. Extracts were radioassayed and analysed by TLC.

Unlabelled standards were used to identify the radioactive spots on the plates, but with no confirmatory analysis, e.g. HPLC. The distribution of the radioactivity is shown in Table 2.

Table 2. Identity and distribution of radioactive residues in extracts of milk, liver, and kidney (Minor and Murphy, 1977a).

Compound	% of TRR								
	Milk					Kidney		Liver	
	Organo soluble	Enzyme hydrol.	Acid hydrol.	Aqueous residue	Lost[1]	Organo soluble	Acid hydrol.	Organo soluble	Acid hydrol.
Methiocarb	0	0	<1			<1	0	12	2
Methiocarb sulfoxide (M01)	3	0	<1			0	0	4	3
Methiocarb sulfone (M02)	<1	0	0			<1	0	<1	1
Methiocarb phenol (M03)	0	0	<1			11	44	14	11
Methiocarb sulfoxide phenol (M04)	<1	25	2			7	0	7	2
Methiocarb sulfone phenol (M05)	<1	25	1			16	1	3	3
Unknown	15	0	<1	16	9	2	1	3	9
Total	103					84		74	

[1] Lost during initial precipitation of milk proteins with acetone.

Poultry. Two studies were conducted on the metabolism of [*phenyl*-^{14}C]methiocarb in poultry. In the first study (Stanley *et al.*, 1979a), eight White Leghorn laying hens were orally dosed once with 4.4 mg radiolabelled methiocarb/kg bw. All eggs collected during each time period (1, 2, 3, 4, 5, 6, 24, 48, 72, and 96 hours) were pooled, when available, and radioanalysed. All residues were $\leq$0.02 mg/kg.

Excreta were collected and pooled at the same times as the eggs. Radioactivity was determined in the lyophilized samples. About 85% of the dose was excreted within 96 hours, with 84% excreted within 24 hours. Lyophilized excreta samples were homogenized with methanol/water and filtered. The filtrates were concentrated to remove methanol and extracted with methylene chloride. The residual water fractions were heated at 100°C with 2 N HCl for 1 hour. The fractions were radioassayed and analysed by TLC.

In the first 24 hour period, a total of 33% of the dose in the excreta were unconjugated metabolites (organosoluble), 39% were conjugated (acid-released), 8% were water-soluble. The unconjugated metabolites were tentatively identified as methiocarb (<1%), methiocarb phenol (13%), methiocarb sulfoxide phenol (9%), methiocarb sulfone phenol (7%), and hydroxymethyl-methiocarb

sulfoxide (2%). The conjugated metabolites were tentatively identified as methiocarb phenol (21%), methiocarb sulfoxide phenol (1%), and methiocarb sulfone phenol (10%).

In a second study (Stanley *et al.*, 1979b), the eight hens that had been treated previously with a single dose of radiolabelled methiocarb were utilized after a 3-week withdrawal period. [1-*phenyl*-^{14}C]methiocarb, 6.74 mCi/mmole, was administered at 4.4 mg/kg bw each day for 5 consecutive days. Eggs, collected each day, all contained <0.1 mg/kg ^{14}C as methiocarb. The birds were killed after the fifth dose, and composite tissue samples were radioassayed. The results are shown in Table 3.

Table 3. Radioactive residues in tissues and eggs after the oral administration of phenyl-labelled methiocarb to chickens (Stanley *et al.*, 1979b).

Sample	Residue, mg/kg as methiocarb
Kidney	3.3
Liver	2.0
Heart	0.8
Skin	1.3
Fat	0.7
Gizzard	7.7
Muscle	0.45
Eggs	<0.1

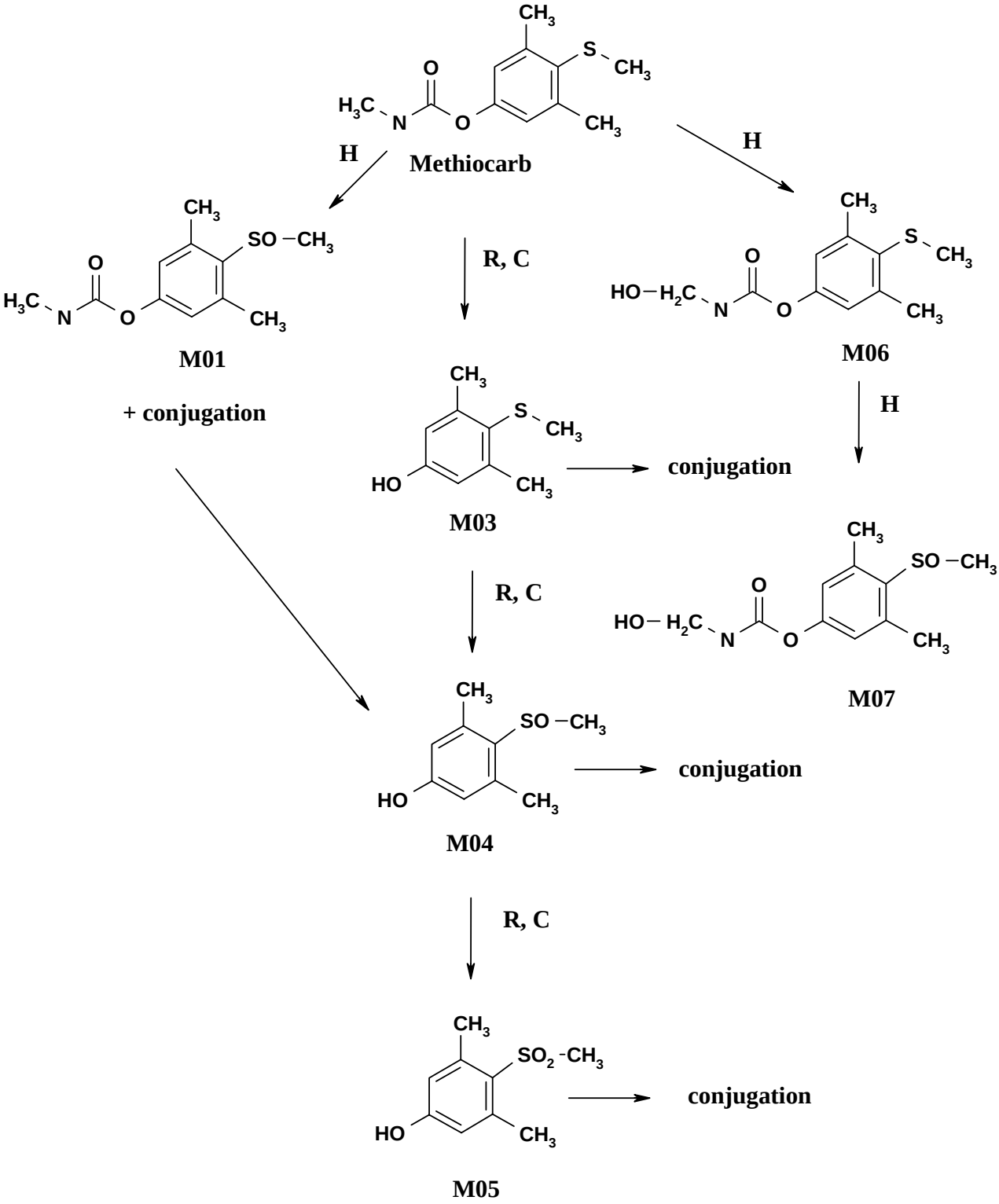
Tissue samples were extracted sequentially with organic solvents, and the residual water fractions were hydrolysed with 2 N HCl for 1 h at 100°C. This released 98% of the TRR from kidney, 92% from liver, 99% from fat and 98% from muscle. Extracts were analysed by two-dimensional TLC. There were no confirmatory analyses. Unlabelled standards were used to identify the radioactive spots. The findings are shown in Table 4.

Table 4. Identity and distribution of radioactive residues after oral administration of labelled methiocarb to chickens (Stanley *et al.*, 1979b).

Compound	% of TRR			
	Kidney	Liver	Fat	Muscle
Methiocarb	<1	<1	41	7
Methiocarb sulfoxide (M01)	<1	<1	1	5
Methiocarb phenol (M03)	2	7	14	8
M03 from acid hydrolysis	13	10	12	8
Methiocarb sulfoxide phenol (M04)	11	17	4	24
M04 from acid hydrolysis	18	7	5	4
Methiocarb sulfone phenol (M05)	4	9	2	2
M05 from acid hydrolysis	9	2	2	2
N-hydroxymethyl-methiocarb (M06)	<1	<1	7	5
N-hydroxymethyl-methiocarb sulfoxide (M07)	3	6	2	17
Total	60	58	90	82

The metabolic pathways proposed for methiocarb in animals are shown in Figure 1.

Figure 1. Proposed metabolic pathways of methiocarb in animals (C = chicken, H = hen, R-= ruminant).



Plant metabolism

Studies were provided on rice, tomato, lettuce, and apples. A rotational crop study was also submitted.

Àpples. A methiocarb WP formulation, 750 g/kg, containing [1-*phenyl*-^{14}C]methiocarb (10% of the total methiocarb) dissolved in water (101 g ai/100 l) was applied to run-off with a syringe to 24 apples on a dwarf Red Delicious apple tree in Kansas, USA (Morgan and Parton, 1974). The application was repeated 8 times at about 2-week intervals. The apples were harvested 14 days after the final treatment, or 77 days after the first application. Apples were also collected between applications.

In a separate experiment, a 50/50 mixture of radiolabelled and unlabelled methiocarb was dissolved in ethanol/water (266 g/100 l) and applied once at a rate of 750 µl/apple (2 mg methiocarb per apple) to each of 37 apples on another Red Delicious tree. The material was applied so as to avoid run-off. Apple samples were taken after 0, 4, 29, 36, and 43 days.

All apples were washed with benzene and separated into peel and pulp. Some peel fractions were extracted with acetonitrile/water (9:1), and others were hydrolysed with 0.1 N HCl for 30 min at 120°C. Three peeled apples were slurried with water and centrifuged, and the residual solid was extracted with acetone. The acetone and water extracts were combined and extracted with chloroform. A fraction of the water extract was also incubated with β-glucosidase and then hydrolysed with 0.1 N HCl as before.

Organic fractions were analysed by TLC only, using one solvent system (isopropyl ether/methanol, 8/1) and silica gel plates.

In the single application study, most of the radioactivity was in the benzene wash and decreased from 93% of the applied and 98% of the recovered activity on day 0 to 19% of the applied and 62% of the recovered radioactivity on day 43. The peel contained a maximum of 8.2% of the applied and 27% of the recovered radioactivity (on day 29). The organosoluble proportion of the peel residue decreased from 98% on day 0 to 36% on day 43, while the water-soluble proportion increased from 18% on day 4 to 54% on day 43. The insoluble residue was <10% at all times.

The residue in the pulp increased steadily from 0.04% of the applied ^{14}C to 4.8% of the applied and 16% of the recovered activity on day 29. The residue in the pulp slowly decreased or levelled off after day 29.

Without detailed substantiation, the “total residue” was characterized as methiocarb (65%), methiocarb sulfoxide (9%), and methiocarb sulfoxide phenol (18%).

In the multi-application study, the total radioactive residue in the apples was 8.04 mg/kg as methiocarb after 7 days and 4.52 mg/kg after 14 days. In the 14-day samples, 0.67 mg/kg (15% of the total radioactive residue) was in the pulp, and 82% of this was water-soluble.

Without detailed substantiation, it was stated that 95-97% of the benzene wash residue, 24% of the total radioactive residue, was methiocarb and 3-5% methiocarb sulfoxide. Methiocarb constituted 16% of the radioactive residue on the peel in the sample collected 14 days after the final application and methiocarb sulfoxide 1.4%. The peel contained 60% of the total radioactive residue. The residue on apples with the 14-day PHI was 4.52 mg/kg as methiocarb, consisting of 61% methiocarb, 6.5% methiocarb sulfoxide, 4.6% methiocarb phenol, 22% methiocarb sulfoxide phenol, and 1.1% methiocarb sulfone phenol.

Lettuce and tomatoes. A study on the uptake of radiolabelled methiocarb by lettuce and tomato plants was submitted (Strankowski and Murphy, 1976). Lettuce and tomato seedlings were treated with [1-*phenyl*-^{14}C]methiocarb, prepared as a 750 g/kg WP in water and applied at a rate of 1.12 kg ai/ha. The material

was applied to the ground (sand) and not to the aerial parts of the seedlings. Plants were harvested after 1, 3, 7, and 14 days, radioassayed and extracted. The extracts were analysed by TLC on silica gel plates.

The radioactivity was translocated rapidly in both lettuce and tomatoes, as indicated in Table 5. The major metabolites identified in the lettuce and tomato organic extracts were methiocarb (15–19 % on day 1, 1% on day 14), and methiocarb sulfoxide (34-52% on day 1, 2-3% on day 14). The enzymatic hydrolysis of aqueous fractions of lettuce seedlings at day 7 yielded methiocarb phenol and methiocarb sulfoxide phenol as 27% and 19% of the applied radioactivity respectively.

Table 5. Uptake of radiolabelled methiocarb by lettuce and tomato seedlings (Strankowski and Murphy, 1976).

Days after treatment	% of applied radioactivity[1]	
	Lettuce	Tomato
1	9	3
3	24	7
7	45	26
14	44	52

[1] Based on 50 µCi applied to each flat of seedlings.

Tomato. In separate experiments, tomato plants were grown in a greenhouse in nutrient solution and in soil. As the first fruits began to ripen, the radiolabelled methiocarb was applied at a rate of 1.12 kg ai/ha to the soil or nutrient solution. Tomatoes were harvested 1 and 7 days after addition of the methiocarb to the nutrient solution and 7, 14, 28, and 56 days after addition to the soil. Some leaves were also collected. The samples were radioassayed. The radioactivity in the tomato fruits grown in nutrient solution ranged from <0.007 to 0.013 mg/kg as methiocarb on day 1 and from 0.013 to 0.036 mg/kg on day 7. In the plants grown in soil the maximum residues in mature tomatoes were <0.007 mg/kg on day 7, 0.022 mg/kg on day 14, 0.066 mg/kg on day 28, and 0.025 mg/kg on day 56.

Rice. The metabolism of [1-*phenyl*-^{14}C]methiocarb in rice was reported (Strankowski, 1979). Rice was treated at planting with [1-*phenyl*-^{14}C]methiocarb formulated as a WP (750 g/kg) at a rate of 1.12 kg ai/ha. The aqueous mixture was applied as close to the exposed seeds as possible by pipette. Immature plants were harvested 14, 21, 28, and 35 days after treatment by cutting off the aerial portion at the ground.

In a separate plot, rice at the soft dough stage of grain maturity (132 days post-planting) was treated with radiolabelled methiocarb at a rate of 2.24 kg ai/ha. The mixture was formulated as a WP, 750 g/kg, and applied as a foliar spray. Plants were harvested 0, 1, 3, 6, 14, and 28 days after treatment. Nine days after the first application, some plants received a second treatment identical to the first and were harvested 0, 6, 14, 21, and 28 days after the second treatment. At each harvest the plants were separated into grain heads and stalks.

The same extraction procedure was used for all rice samples. The pulverized tissue was ultrasonicated with methanol/water and filtered. The filtrate was partitioned with chloroform, the aqueous fraction was incubated at 37°C for 20 hours with ß–glucosidase and then partitioned with chloroform. The aqueous layer was refluxed with 2 N HCl for 2 hours and again partitioned with chloroform. The solid residue from the initial extraction was also refluxed with 2 N HCl.

The extracts were analysed by one- and two-dimensional TLC on silica gel plates. Unlabelled standards were used for identifications, without confirmatory analyses. The distribution of the recovered radioactivity in the rice treated at planting is shown in Table 6, and that in the grain and stalks after foliar application is shown in Table 7.

Table 6. Distribution of ^{14}C in young rice plants after application of [^{14}C]methiocarb to seeds and soil at planting (Strankowski, 1979).

Days after treatment	% of recovered radioactivity[1]						
	Organo-soluble	Aqueous			Insoluble		
		Enzyme hydrol.	Acid hydrol.	Aqueous (not released)	Acid hydrol.	Aqueous (not released)	Not extracted
14	72	8	11	1	NA	NA	8
21	66	12	9	1	NA	0	12
28	61	NA	NA	24	9	3	2
35	61	6	12	1	14	4	2

NA = not analysed
[1]Extracts and extracted fractions were radioassayed, not initial samples. Thus, the reported values are percentages of the recovered radioactivity, not necessarily of the total radioactive residue in the plants.

Table 7. Distribution of ^{14}C in rice after foliar application (Strankowski, 1979).

Days after lst spraying	% of recovered radioactivity[1]						
	Organo-soluble	Aqueous			Insoluble		
		Enzyme hydrol.	Acid hydrol.	Aqueous (not released)	Acid hydrol.	Aqueous (not released)	Not extracted
Rice grain							
0	99	NA	NA	<1	NA	NA	1
14	75	NA	NA	10	12	2	1
28	63	NA	NA	9	20	5	3
Stalks							
0	98	NA	NA	1	NA	NA	1
14	85	NA	NA	7	NA	NA	8
28	72	2	7	2	13	3	2
Days after 2nd spraying							
Stalks							
0	95	NA	NA	2	NA	NA	3
14	83	NA	NA	7	NA	NA	10
28	68	NA	NA	9	17	3	3
Grain							
0	96	NA	NA	2	NA	NA	2
14	80	2	5	6	NA	NA	11
28	67	NA	NA	7	18	3	4

NA = not analysed
[1]Extracts and extracted fractions were radioassayed, not initial samples. Thus, the reported values are percentages of the recovered radioactivity, not necessarily of the total radioactive residue in the plants.

The compounds were identified by TLC only in both experiments. In the young rice plants harvested 14, 21, 28, and 35 days after soil/seed treatment methiocarb was a minor component, about 2% of the recovered radioactivity. The major metabolite at all intervals was methiocarb sulfoxide, 36-47%. Other significant metabolites were methiocarb phenol conjugate, 4-15%, methiocarb sulfoxide phenol 3-6%, methiocarb sulfoxide phenol conjugate 8-11%, and methiocarb sulfone phenol conjugate 3-5%.

The compounds identified in the rice and stalks after one or two foliar treatments are shown in Table 8.

Table 8. Identified compounds in rice after foliar application of radiolabelled methiocarb (Strankowski, 1979).

Compound	^{14}C, % of total recovered in extracts and fractions					
	Days after 1st spraying					
	0	1	3	6	14	28
GRAIN						
Methiocarb (M)	94	92	88	78	41	11
Methiocarb sulfoxide (M01)	2	4	5	12	25	32
Methiocarb sulfone (M02)	-	-	<1	1	1	3
Methiocarb sulfoxide phenol (M04)	<1	<1	<1	1	4	11
Methiocarb sulfone phenol (M05)	1	1	1	1	1	1
N-hydroxymethyl methiocarb sulfoxide (M07)	-	-	-	-	2	3
M03 conjugate	-	-	-	-	4	1
M04 conjugate	-	-	-	-	-	<1
M05 conjugate	-	-	-	-	1	2
	Days after 2nd spraying					
	0	1	6	14	28	NA
Methiocarb (M)	86	64	41	26	18	
Methiocarb sulfoxide (M01)	7	17	26	31	31	
Methiocarb sulfone (M02)	-	1	1	1	1	
Methiocarb sulfoxide phenol (M04)	1	2	5	9	9	
Methiocarb sulfone phenol (M05)	1	1	1	1	1	
N-hydroxymethyl methiocarb sulfoxide (M07)	<1	1	3	3	2	
M03 conjugate	-	-	2	9	10	
M04 conjugate	-	-	1	1	1	
M05 conjugate	-	-	1	2	2	
STALKS						
	Days after 1st spraying					
	0	1	3	6	14	28
Methiocarb (M)	90	88	81	70	42	20
Methiocarb sulfoxide (M01)	6	7	10	17	32	36
Methiocarb sulfone (M02)	-	-	-	<1	1	1
Methiocarb sulfoxide phenol (M04)	<1	1	2	3	4	10
Methiocarb sulfone phenol (M05)	1	1	1	1	1	2
N-hydroxymethyl methiocarb sulfoxide (M07)	-	-	<1	1	1	-
M03 conjugate	-	-	-	-	-	9
M04 conjugate	-	-	-	-	-	2
M05 conjugate	1	1	1	1	1	2
	Days after 2nd spraying					
	0	6	14	21	28	NA
Methiocarb (M)	80	54	34	27	15	
Methiocarb sulfoxide (M01)	10	22	35	35	35	
Methiocarb sulfone (M02)	0	1	1	1	1	
Methiocarb sulfoxide phenol (M04)	2	4	8	12	10	
Methiocarb sulfone phenol (M05)	2	1	1	2	1	
N-hydroxymethyl methiocarb sulfoxide (M07)	<1	1	-	-	2	
M03 conjugate	-	-	-	6	9	
M04 conjugate	-	-	-	2	1	
M05 conjugate	2	1	1	2	1	

NA = not analysed

A rotational crop study was conducted with [1-*phenyl*-^{14}C]methiocarb (Strankowski and Kottman, 1979). Radiolabelled methiocarb, formulated as WP 750 g/kg was incorporated into sandy loam soil (74% sand, 16% silt, 10% clay) at a rate of 5.6 kg ai/ha, and sweet corn was planted immediately as the primary crop. The sweet corn was harvested at normal maturity, and the land lay fallow until the next crop year. Rotational crops of wheat, sugar beet, and spinach were then planted. The crops were sampled at specific times through normal harvest, and the samples were radioassayed.

Mature samples of wheat heads, wheat stalks, wheat forage, sugar beet roots, and spinach were extracted with methanol/water and partitioned with chloroform. The extracts were analysed by one-dimensional TLC on silica gel plates. Unlabelled standards were used to identify the compounds. The results are shown in Table 9.

Table 9. Radioactive residues in one-year rotational crops grown in soil treated with [^{14}C]methiocarb at 5.6 kg ai/ha (Strankowski and Kottman, 1979).

Days after application	Methiocarb equivalents, mg/kg					
	Wheat			Sugar beet		Spinach
	Heads	Stalks	Forage	Tops	Roots	
399			0.150	0.108		
426			0.195	0.053	0.309	0.184
436			0.251	0.052	0.380	0.138
450				0.071	0.252	0.225
468				0.052	0.099	0.150
478						0.084
551	0.066	0.141	0.323			

The metabolites identified in the organosoluble extracts of wheat and spinach are shown in Table 10. No results for sugar beet were reported. Details of the identification procedures were not provided.

Table 10. Metabolites in rotational crops after treatment of soil with radiolabelled methiocarb (Strankowski and Kottman, 1979).

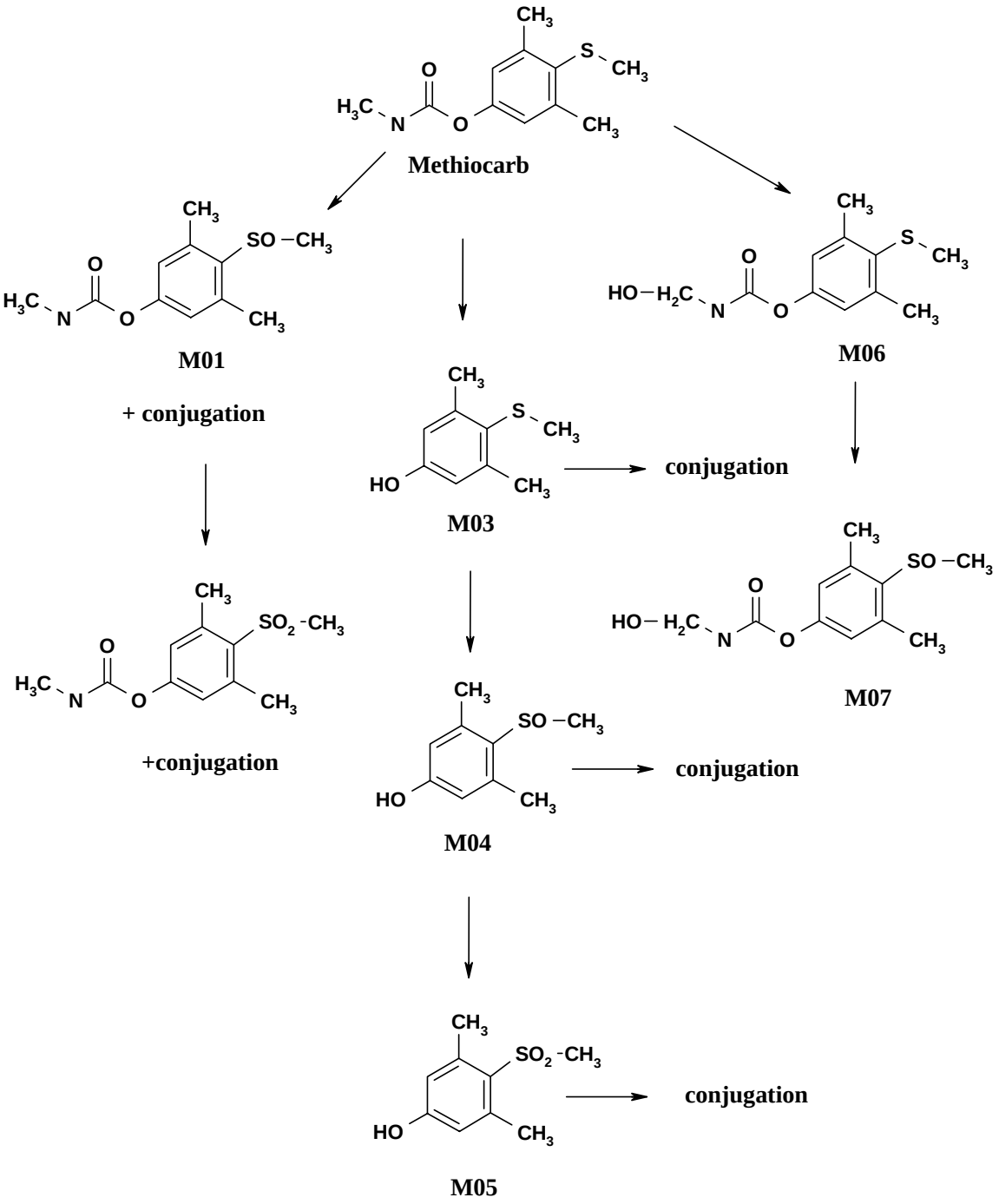
Compound	Sample							
	Wheat head (551 days)		Wheat stalk (551 days)		Wheat forage (551 days)		Spinach (450 days)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
N-hydroxymethyl-methiocarb	12	0.008	3	0.004	1	0.003	7	0.016
Methiocarb sulfoxide	6	0.004	4	0.006	12	0.039	0	0
Methiocarb sulfoxide phenol	14	0.009	7	0.010	6	0.019	26	0.058
N-hydroxymethyl-methiocarb sulfoxide	5	0.003	3	0.004	2	0.006	0	0
Methiocarb sulfone	11	0.007	8	0.011	10	0.032	0	0
Methiocarb sulfone phenol	0	0	0	0	0	0	2	0.005

A second rotational crop study was conducted with unlabelled methiocarb (Murphy and Morris, 1979). Methiocarb WP was applied to bare soil at rates of 1.4, 2.8, 5.6, and 11.2 kg ai/ha in Florida (sand) and Kansas (silty clay loam). Rotational crops were planted 30, 60, 90, 120, and 365 days after soil treatment. In Kansas sorghum, wheat, snap beans, peas, carrots and radishes were planted, and in Florida maize, black-eyed-peas and turnips. The crops were harvested at normal maturity and green forage samples of the cereals and green vines were taken during the growing season.

Samples were analysed for the combined residue of methiocarb, methiocarb sulfone and methiocarb sulfoxide. No residues (<0.02 mg/kg) were found in any edible portion of the vegetables or grain planted 30 or more days after any application of methiocarb to the soil, but some were found in green vines and green forage after application at 11.2 kg ai/ha. Maize forage from planting 30 days after treatment had a residue of 0.14 mg/kg; black-eyed pea vines had 0.15 mg/kg from the 30-day planting and 0.07 mg/kg from 90 days. Turnip tops from planting at 60 days had residues of 0.29 mg/kg.

The suggested metabolic pathways of methiocarb in plants are given in Figure 2.

Figure 2. Proposed metabolic pathways of methiocarb in plants.



Environmental fate in soil

Studies were provided on aerobic and anaerobic degradation, photolysis, adsorption of methiocarb, methiocarb phenol and methiocarb sulfoxide, and leaching of methiocarb.

The fate of methiocarb in sandy loam soil was studied by Stanley and Flint (1983). Soil was air-dried and milled. A 5.0 kg sub-sample, pH 7.3, was mixed with a benzene solution of [1-*phenyl*-^{14}C]methiocarb, [*methylthio*-^{3}H]methiocarb and unlabelled methiocarb at 7.5 mg/kg, equivalent to 11.5 kg ai/ha. The treated soil was placed in a plastic pan in a greenhouse and water was added weekly.

Five g soil samples were taken at 1, 2, 4, 8,12 and 16 weeks after treatment. The samples were extracted with methanol/water and the extracts partitioned with chloroform. The proportion of extractable radioactivity decreased from 76% at week 4 to 67% at week 16. The residual soils were heated under nitrogen in a steam bath with 1 N HCl for 2 hours, and the mixtures were centrifuged and decanted. The solids were washed with water and the combined acid extracts and water washes partitioned with chloroform. The acid treatment released 14-19% of the applied radioactivity.

The extracts were analysed by TLC, using three different solvent systems. $^{3}H:C^{14}$ ratios of individual components were use to confirm chromatographic identifications. The results are shown in Table 11.

Table 11. Distribution of radioactive residues in soil treated with methiocarb at a rate of 7.5 mg/kg (Stanley and Flint, 1983).

Compound	Radioactivity, % of applied, mg/kg as methiocarb			
	4 wks	8 wks	12 wks	16 wks
Methiocarb (organosoluble)	49/3.7	38/2.9	27/2.9	30/2.3
Methiocarb (acid released)	1.0/3.7	1.1/0.08	0.8/0.06	0.9/0.07
Methiocarb sulfoxide (organosoluble)	10/0.8	13/1.0	12/0.9	13/1.0
Methiocarb sulfoxide (acid released)	9.7/0.74	11/0.81	9.5/0.71	9.5/0.71
Methiocarb sulfoxide phenol (organosoluble)	5.3/0.4	10/0.8	11/0.9	15/1.1
Methiocarb sulfoxide phenol (acid released)	0.5/0.04	0.7/0.05	1.0/0.08	0.8/0.06
Methiocarb sulfone + methiocarb phenol + methiocarb sulfone phenol (organosoluble)	0.4/0.04	1.8/0.13	1.8/0.13	1.9/0.14
Methiocarb sulfone + methiocarb phenol + methiocarb sulfone phenol (acid released)	0.5/0.04	0.5/0.04	1.2/0.09	0.3/0.02

The degradation of [1-*phenyl*-^{14}C]methiocarb was further investigated under both aerobic and anaerobic conditions (Minor and Freeseman, 1989). The methiocarb was added as an ethanol solution to dry sandy loam soil at a concentration of 1.4 mg/kg dry soil. Replicate 100 g samples, pH 6.7, were prepared and stored in the dark at 24 $\pm$ 2˚C. Duplicate soil samples were extracted in a Soxhlet apparatus with chloroform/methanol after 0, 1, 3, 7, 14, 29, 64, 91 and 217 days, and analysed by HPLC. A 91-day sample was extracted with methanol and then refluxed for 2 hours with 2N HCl. The hydrolysate was partitioned with acetone/chloroform.

Extractable ^{14}C decreased from 100% of the applied radioactivity on day 0 to 27% on day 217 and bound residues increased from 0% on day 0 to 43% on day 217. Significant $^{14}CO_2$ appeared after 29 days and increased from 5% to 30% of the applied radioactivity by day 217. The recovery of ^{14}C approached 100% at all intervals.

The degradation was rapid, with methiocarb decreasing from 96% of the total radioactivity on day 0 to 3% on day 217, and biphasic. The first phase showed a half-life of 17.7 days and the second 111 days, assuming that the degradation followed first-order kinetics.

The compounds identified in the soil under aerobic conditions are shown in Table 12. The identity of methiocarb sulfone quinone was confirmed by GC-MS.

Table 12. Extractable radioactive compounds in sandy loam treated with [^{14}C]methiocarb (1.45 mg/kg) and incubated in the dark under aerobic conditions (Minor and Freeseman, 1989).

Time (days)	^{14}C, % of total applied							
	Extract-able	Methio-carb	Methio-carb phenol	Methio-carb sulfoxide	Methiocarb sulfoxide phenol	Methiocarb sulfone	Methiocarb sulfone phenol	Methiocarb sulfone quinone
0	100	96	2	2	0	0	0	0
1	98	91	0	7	<1	0	0	0
3	96	83	0	13	<1	0	0	0
7	94	70	0	21	3	0	0	0
14	84	48	0	28	8	0	0	0
29	75	24	0	30	16	1	3	0
64	50	8	0	13	18	1	7	2
91	44	6	0	8	15	1	9	3
217	27	3	0	2	7	0	7	8

To study anaerobic conditions, two 14-day aerobic samples were covered with water (pH 5) and purged continuously with nitrogen. At 0, 15, 29 and 64 days after the addition of water, samples were extracted in a Soxhlet apparatus with chloroform/methanol and the extracts analysed by HPLC and TLC. An aliquot of extracted 29-day soil was refluxed with methanol, and a separate aliquot was refluxed sequentially with 1 N HCl, 2 N HCl and 5N HCl.

Under anaerobic conditions there was little change in the proportion of extractable radioactivity, which decreased from 87% to 76% between day 0 and day 64. Volatiles never exceeded 4% of the applied radioactivity. The half-life of methiocarb was calculated to be 64 days (first-order kinetics). The identified compounds are shown in Table 13.

Table 13. Extractable radioactive compounds in sandy loam soil treated with [^{14}C]methiocarb and incubated in the dark under anaerobic conditions (Minor and Freeseman, 1989).

Time, days	^{14}C, % of total applied						
	Extract-able	Methio-carb	Methiocarb phenol	Methiocarb sulfoxide	Methiocarb sulfoxide phenol	Methiocarb sulfone	Methiocarb sulfone phenol
0	87	55	0	24	8	0	0
15	82	43	31	3	5	0	<1
29	80	37	37	2	3	0	<1
64	76	27	47	1	1	<1	<1

A similar anaerobic experiment was conducted with [1-*phenyl*-^{14}C]methiocarb sulfoxide, which was hydrolysed to methiocarb sulfoxide phenol within 3 days. After 49 days, methiocarb phenol was the major product.

On the basis of a study which was not available for submission the manufacturer provided detailed calculations of the half-lives of methiocarb and its degradation products under aerobic conditions in different soils (Schad, 1998). The results are shown in Table 14.

Table 14. Half-lives of methiocarb and its degradation products in various soils at 20°C under aerobic conditions (Schad, 1998).

Soil	Half-life, days				
	Methiocarb	Methiocarb sulfoxide	Methiocarb sulfoxide phenol	Methiocarb sulfone phenol	Compound 6 (structure unknown)
BBA2.2 (loamy sand)	1.6	6.3	2.2	20	54
Frankenforst	1.4	1.6	9.4	3.0	14
Höfchen (silt)	1.0	3.0	4.2	2.5	33

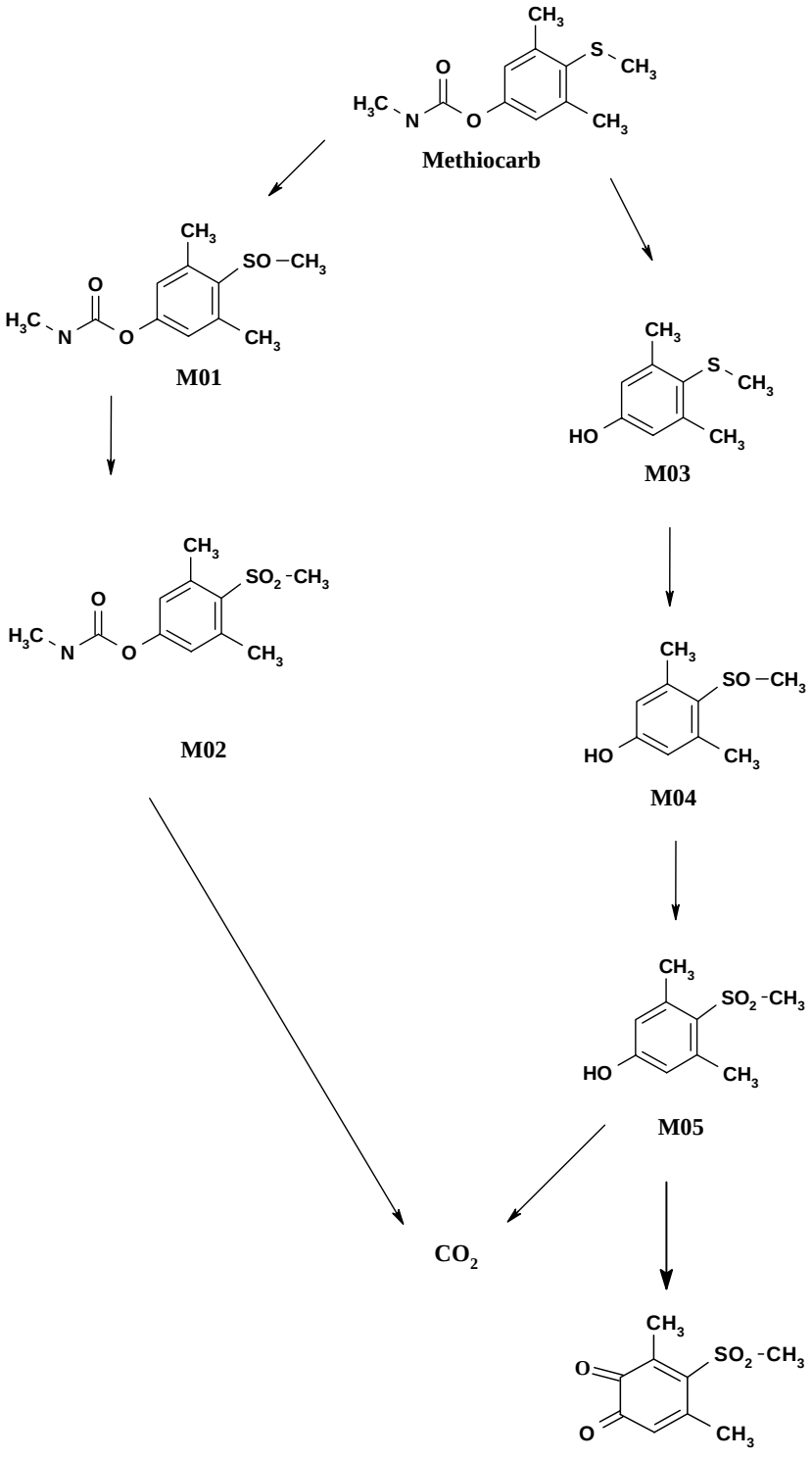
The photolysis of added methiocarb on a soil surface under natural sunlight was studied by Jackson *et al.* (1988) who added [1-*phenyl*-^{14}C]methiocarb to sandy loam soil (3.1 g) in 60 mm Petri dishes at a rate of 9.1 µg/g, or 28 µg/dish. The dishes were exposed to natural sunlight in Lexington, Kentucky, USA for 30 days. Dark control samples were also prepared. The mean temperature of the irradiated plates was 21.6 $\pm$ 1.4°C. The light intensity varied considerably over the 30 days, between 39 and 38909 µW/cm^2.

The soils were sampled on days 0, 5, 10, 15, 20 and 30. The soil samples were extracted with chloroform/methanol and the extracts and residual soils were radioassayed. The total recovery of radioactivity ranged from 80.5 (88.9% average of duplicates) to 104.4%, mean 98.2% $\pm$ 4.87%. Measured volatiles were insignificant. The extracts were analysed by HPLC, with confirmation by TLC.

Methiocarb was the major component of the residue at all times in both control and irradiated samples, accounting for 47% of the radiolabelled residue on irradiated soil and 75% on control soil after 30 days. The major degradation product was methiocarb sulfoxide, 23% of the residue on irradiated soil and 3.1% on control soil at 30 days. Methiocarb sulfoxide phenol was a minor component, 3.7% on irradiated soil at day 30 and not detected on the control soil. The residue not extracted by organic solvents was 10-15% of the total radiolabelled residue in irradiated soil <10% in control soil.

The results indicated that degradation was due to photolytic and other processes. The half-lives were 28 days for irradiated samples and 81 days for control samples.

Figure 3. Proposed degradation pathways of methiocarb in soil.



Ridlen and Pfankuche (1987a) studied the adsorption of [1-*phenyl*-^{14}C]methiocarb by soil. Duplicate portions of four soils (1.0 to 2.5 g) in individual silanized-glass culture tubes were mixed with 10 to 20 ml of treatment solutions containing 0.4, 0.8. 2.0 and 4.0 mg/l methiocarb, each 0.02 µCi/ml. The tubes were sealed and shaken gently in a horizontal position at 27 ± 2°C. The supernatants were sampled after 2, 6, 24 and 48 hours. After 48 hours the supernatants were removed and replaced by 0.01 M calcium chloride solution, and the linear shaking was resumed for an additional 5 days. The supernatants were extracted with chloroform and the extracts analysed by TLC on silica gel. The residual solids were radioassayed.

The methiocarb reached adsorption equilibrium in the water/soil systems within about 24 hours. Analyses of the water fractions revealed no significant degradation of the methiocarb. Freundlich adsorption and desorption constants were calculated (Table 15). The high K_d and K_{oc} values indicate adsorption of methiocarb to all the soils and low leaching potential.

Table 15. Soil adsorption and desorption coefficients of methiocarb (Ridlen and Pfankuche, 1987a).

Soil	Adsorption		Desorption	
	K_d	K_{oc}	K_d	K_{oc}
Sand (pH 4.3)	5.3	1000	8.2	1547
Sandy loam (pH 4.9)	4.3	632	6.7	985
Silt loam (pH 5.9)	9.0	600	16.2	1080
Clay loam (pH 6.3)	4.9	408	8.1	675

K_{oc}: >5000 immobile; 2000-5000 very low mobility; 500-2000 low mobility; 150-500 moderate mobility; <150, high mobility.

The adsorption of [1-*phenyl*-^{14}C]methiocarb sulfoxide was also studied by Ridlen and Pfankuche (1987b). The soils, pH 4.3-6.3, were treated with the radiolabelled methiocarb sulfoxide at a rate of 1.6 mg/kg, an approximation to a field application rate of 4.5 kg ai/ha, by mixing soil (2 g) in silanized-glass culture tubes with the radiolabelled methiocarb sulfoxide in 0.01 M aqueous calcium chloride solution (8 ml). The tubes were shaken continuously at 27 ± 2°C and the supernatants were sampled after 0.5, 2, 4 and 24 hours and extracted with chloroform. The supernatants were removed from the 24-hour samples and the residual soils were shaken with calcium chloride solution saturated with unlabelled methiocarb sulfoxide (to remove residual test solution) and extracted with chloroform. The experiment was repeated with a treatment solution containing 0.01 M potassium hydrogen phosphate adjusted to pH 4 with hydrochloric acid.

Liquid samples were radioassayed and the extracts were analysed by TLC. Only methiocarb sulfoxide phenol was found in the soil extracts after 24 hours. The amount of methiocarb sulfoxide adsorbed to the soil was below the level of detection of the analytical method, 0.05 µg/g. With the assumption that this was the concentration of methiocarb sulfoxide in the soils, the adsorption coefficients were calculated. They ranged from 0.2 mg/kg for sand and sandy loam to 0.5 mg/kg for silt loam, showing that methiocarb sulfoxide was poorly adsorbed to the soils. The aqueous phase of both the calcium chloride and the phosphate buffer systems contained methiocarb sulfoxide and methiocarb sulfoxide phenol, with the latter accounting for as much as 41% of the radioactivity (on silt loam) in the aqueous phase.

The adsorption of [1-*phenyl*-^{14}C]methiocarb sulfoxide phenol was investigated in calcium chloride solution at concentrations of 0.04, 0.21, 1.01 and 5.14 mg/l (Fent, 1996). Twelve g of each soil was mixed with 20 ml of test solution and shaken for 24 hours at 20 ± 1°C. The supernatants were removed and the residual soils shaken with 20 ml of 0.01 M calcium chloride solution. HPLC analyses of the supernatants after the 24-hour period indicated that >99% of the radioactivity could be assigned to unchanged methiocarb sulfoxide phenol. Freundlich adsorption and desorption constants are shown in Table 16.

Table 16. Adsorption and desorption coefficients for methiocarb sulfoxide phenol on four soils (Fent, 1996).

Soil	Adsorption		Desorption	
	K_d	K_{oc}	K_d	K_{oc}
Sand (pH 5.3)	0.1885	26.9	0.7384	105.5
Sandy loam (pH 6.3)	0.6611	26.7	1.5240	61.5
Silt loam (pH 7.3)	0.4342	48.2	1.3828	153.6
Silty clay (pH 7.4)	0.6466	101.0	1.6438	256.8

K_{oc}: 50-150, high mobility; 150-500, medium mobility, >500, low mobility

The leaching of [1-*phenyl*-^{14}C]methiocarb, specific activity 33.7 mCi/mmole, added as a water/acetonitrile solution to sandy loam soil that had been air-dried was reported (Ridlen, 1987). The concentration of methiocarb in the soil was 37 mg/kg. The moisture content of the soil was adjusted to 75% by the addition of water, and the soil mixture was aged for 30 days at 22-25°C under aerobic conditions. The moisture content was adjusted to 75% each week. No volatiles (<1% of total radioactivity) were detected during the ageing process. The aged soil (50 g) was extracted sequentially with chloroform and chloroform/methanol (Soxhlet). The combined extracts were concentrated and analysed by TLC. The residue in the aged soil consisted of 80% methiocarb, 7% methiocarb sulfoxide and 6% methiocarb sulfoxide phenol. About 6% of the total radioactivity remained in the soil after extraction.

Glass columns were packed with sea sand (100 g), air-dried test soil (30 cm) and the aged soil (20 g). The columns were saturated with 0.01 M aqueous calcium chloride and 1.1 l of 0.01 M aqueous calcium chloride solution was dripped continuously through the column over a 5-day period. The leachates were collected in 220 ml fractions and radioassayed, aliquots were extracted with chloroform, and the concentrated extracts were analysed by TLC. The used soil columns were frozen, segmented and radioassayed.

The distribution of the radioactivity in the soil columns and the leachates is shown in Table 17.

Table 17. Distribution of radioactivity in soil columns and leachates from soil treated with radiolabelled methiocarb and aged aerobically for 30 days (Ridlen, 1987).

Fraction	% of applied radioactivity[1]		
	Sand (pH 4.3)	Sandy loam (pH 5.0)	Silty loam (pH 5.9)
Applied aged soil	10	14	13
Column section			
0-5 cm	7	23	33
5-10 cm	11	21	17
10-15 cm	16	19	15
15-20 cm	13	7	9
20-25 cm	10	4	5
35-30 cm	4	4	1
Total soil	71	92	93
Leachate	23	7	3
Sand	<1	<1	<1
Used column wash	0	0	0
Total radioactivity accounted	94	99	96

[1] Average of 3 determinations on each of two soil columns.

In the leachate from the sand soil column 2% of the applied ^{14}C represented methiocarb, 12% methiocarb sulfoxide, 7% methiocarb sulfone and 1% methiocarb phenol. In the sandy loam leachate 2% represented methiocarb sulfoxide, 3% methiocarb sulfoxide phenol and 1% methiocarb phenol. In the silty loam leachate 1% of the applied ^{14}C was associated with methiocarb sulfoxide phenol.

Environmental fate in water

The fate of [1-*phenyl*-^{14}C]methiocarb in aerobic and anaerobic aquatic systems was investigated by Minor and Atwell (1979). The radiolabelled methiocarb was applied to pond water (100 ml) in glass jars at 2 mg/l for the aerobic study. For the anaerobic study, soil (100 g; 16% sand, 54% silt, 30% clay) was also added to each jar. The jars were wrapped in black plastic and maintained in a greenhouse environment. The temperature range was not reported. Jars were removed at intervals and the contents analysed. The aerobic and anaerobic pond water was radioassayed and extracted with ethyl acetate, and the extract was concentrated and analysed by TLC. The anaerobic samples were separated into soil and water fractions and the soils Soxhlet-extracted with chloroform/methanol. The soil residues were further extracted with 0.5 N NaOH. Extracts were analysed by one- and two-dimensional TLC.

At least 95% of the applied radioactivity in the aerobic samples and 84% in the anaerobic samples (29% of the radioactivity in the water fraction and 55% in the soil fraction) was organosoluble at day 21. By day 56, 42% of the radioactivity was bound to the soil and 22% was not recovered. The results are shown in Table 18. In the aerobic system the parent compound disappeared within 3 days. In the anaerobic environment 5% remained at day 3. The major products were methiocarb sulfoxide phenol and methiocarb phenol (63% and 34% respectively at day 14) in the aerobic system, and methiocarb phenol (51% in the soil, 21% in the water at day 28) in the anaerobic system.

Table 18. Radioactive residues in methiocarb-treated aquatic systems (Minor and Atwell, 1979).

Time, days	^{14}C, % of applied									
	Aerobic				Anaerobic					
	Water				Water			Soil		
	Methiocarb	Methiocarb phenol	Methiocarb sulfoxide phenol	Methiocarb sulfoxide	Methiocarb	Methiocarb phenol	Methiocarb sulfoxide	Methiocarb	Methiocarb phenol	Methiocarb sulfoxide phenol
0	97	1	0	1	97	1	1	-	-	-
3	0	80	20	0	18	45	0	10	14	<1
7	0	83	17	0	5	42	0	9	32	<1
14	0	34	63	0	2	35	0	6	34	
21	-	-	-	-	<1	28	0	5	48	1
28	-	-	-	-	<1	21	0	4	51	2
32	-	-	-	-	-	-	-	-	-	-
56	-	-	-	-	<1	2	0	3	26	1
112	-	-	-	-	0	0	0	1	3	<1

The fate of [1-*phenyl*-^{14}C]methiocarb was studied in buffered aqueous solutions maintained in the dark at 25°C (Saakvitne *et al.*, 1981). The solutions were quantified by radioanalysis and TLC. Half-lives were calculated for methiocarb assuming first-order kinetics (Table 19).

Table 19. Half-life values for the hydrolysis of [1-*phenyl*-^{14}C]methiocarb in sterile aqueous buffer solutions (Saakvitne *et al.*, 1981).

pH	Half-life, days, at 25˚C
5	763
7	28
9	2.2

At pH 5 the main product was methiocarb sulfoxide (<1-9%, days 0-51), and methiocarb accounted for 91-97% of the applied radioactivity. At pH 7 the major product was methiocarb phenol (46% at day 30) and at pH 9 methiocarb phenol (78% at day 7) and methiocarb sulfoxide phenol (10% at day 7). Minor products were about 1% *N*-hydroxymethyl-methiocarb sulfone (M08) and 2% *N*-hydroxymethyl-methiocarb (M06) at pH 9, and about 1% *N*-hydroxymethyl-methiocarb at pH 5 and pH 9.

The photochemical degradation of [1-*phenyl*-^{14}C]methiocarb was investigated in pH 5.0 aqueous solutions exposed to natural sunlight for 30 days in Kentucky, USA (Kesterson *et al.*, 1988). Replicate quartz tubes, both irradiated and dark controls, were maintained at 25°C and removed for analysis by radioassay and HPLC at 0, 0.25, 6, 12, 20 and 30 days. The HPLC identifications were confirmed by TLC. The mean total recovery of the radiocarbon from all samples was 102 $\pm$ 11.4%. Excluding one dark control, the recoveries ranged from 80% to 110%.

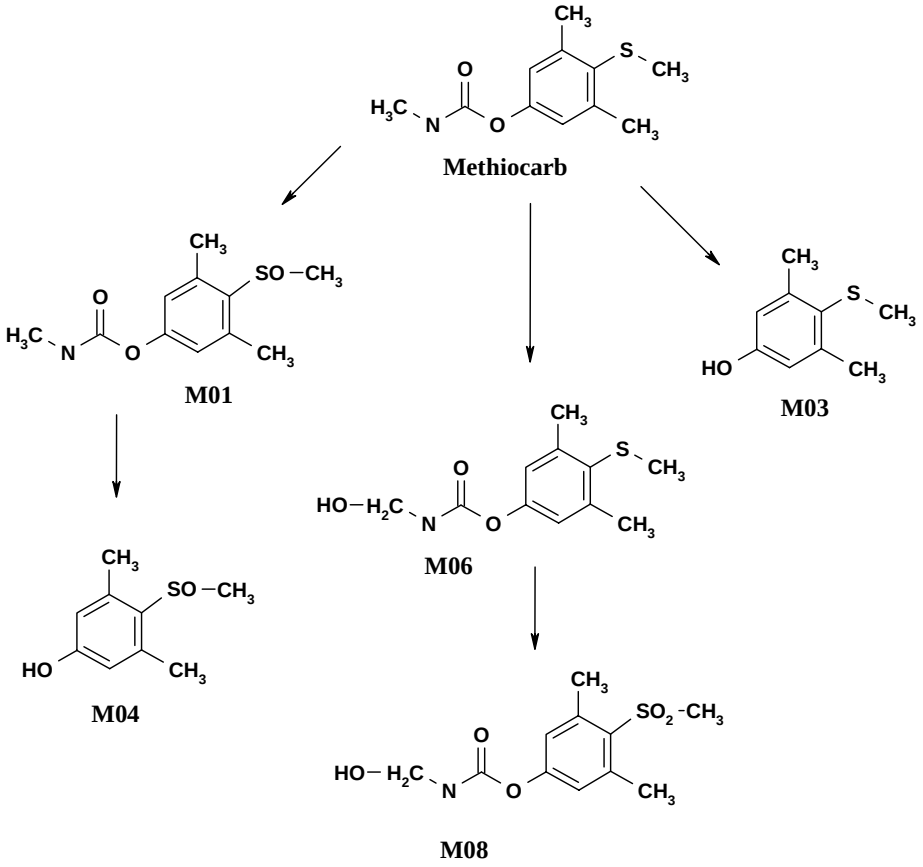
The only product found in both the irradiated and dark control tubes through day 20 was methiocarb sulfoxide, at a maximum of 1% in the control and 13% in the irradiated solutions. On day 30 a new product appeared, methiocarb sulfoxide phenol at a maximum of 3% in the irradiated and 0.8% in the control solutions.

The photolysis half-life was calculated to be 88 days, or 128 days when corrected for non-photolytic degradation.

The quantum yield for the direct photodegradation of methiocarb in water was calculated from the UV absorption data and the kinetic results of two photodegradation experiments in a merry-go-round irradiation apparatus to be 0.2825 (Hellpointner, 1989). This quantum yield was combined with UV absorption data to estimate the environmental half-life of methiocarb as a result of direct phtotodegradation in water. In spring and summer, the half-life was estimated to range from 4 to 19 days, depending on the latitude.

Proposed degradation pathways are shown in Figure 4.

Figure 4. Proposed degradation pathways of methiocarb in the aquatic environment.



METHODS OF RESIDUE ANALYSIS

Analytical methods

The government of The Netherlands supplied an official multi-residue method 1 (MMR1: Analytical Methods for Pesticide Residues in Foodstuffs, Ministry of Health, Welfare and Sport, 1996). Non-fatty samples such as fruits and vegetables are macerated with acetone and methylene chloride. There is no oxidation of methiocarb and its metabolites to a common compound. The concentrated extract is analysed by gas chromatography on a 30 m x 0.25 mm capillary column with a flame photometric or ion trap detector. The general recovery range is 80-100% and the limit of determination is <0.1 mg/kg.

In Bayer Method 171 (Thornton and Dräger, 1973) crop samples (100 g) are extracted with acetone and 0.05 N HCl. The filtrate is extracted with chloroform and the extract concentrated to dryness. The residue is dissolved in acetone (40 ml) and precipitated with an aqueous solution of ammonium chloride and phosphoric acid. The filtrate is extracted with chloroform (3 x 50 ml) and the extract concentrated to dryness, dissolved in acetone and oxidized with 0.1 M potassium permanganate (15 minutes at room temperature). The resulting sulfone is silylated. The derivative is injected into a gas chromatograph equipped with a 2 ft x 4 mm i.d. glass column packed with 5% DC 200 on Gas Chrom Q and operated isothermally at 170°C with a flame photometric detector in the sulfur mode. Calibration is by external oxidized and derivatized standards, 5 to 100 ng. A log-log calibration curve is used. A linear response can be obtained down to 0.03 mg/kg, in milk to 0.005 mg/kg. The absolute limit of detection is 0.01 mg/kg for all samples except milk.

Milk (200 ml) is blended with acetone (400 ml) and Hyflo Super-Cel (10 g). The filtrate is partitioned with chloroform. The chloroform extract is concentrated to dryness, and the residue dissolved in hexane and partitioned with acetonitrile. The acetonitrile extract is concentrated to dryness and oxidized as above. The residue from the oxidation step is dissolved in benzene and transferred to a Florisil column which is eluted sequentially with benzene and benzene/acetonitrile (95/5). The later eluate is concentrated to dryness and analysed as above.

Animal tissues (50 g) are chopped and blended with acetonitrile (200 ml). The mixture is filtered and the tissue is blended with hexane (200 ml). The combined extracts are shaken and the acetonitrile phase is washed with fresh hexane and analysed as above.

Recoveries from fortified samples are shown in Table 20. Each recovery is from one sample except where otherwise noted.

Table 20. Recoveries of methiocarb and metabolites from fortified commodities by Method 171 (Thornton and Dräger, 1973).

Sample	mg/kg added	Recovery, %		
		Methiocarb	Methiocarb sulfoxide	Methiocarb sulfone
Apple peel	0.5	88	90	120
	0.1	79	80	96
	0.05	118	86	68
Apple pulp	0.1	117	108	96
	0.05	78, 120	104, 98	82, 120
Maize kernels	0.1	120	70	70
	0.05	84, 88, 92	72, 91, 83	71, 73, 72
Maize forage	0.1	80	80	80
	0.05	100	-	-
Sugar beet tops	0.5	102, 99, 104	77, 75, 87	73, 65, 69
	0.05	92, 109, 85	87, 93, 86	97, 103, 91
Sugar beet roots	0.5	86, 92, 95	93, 107, 97	81, 82, 87
	0.05	100, 95, 115	95, 91, 86	117, 111, 107
Bovine fat	0.05	86	84	118
Bovine steak	0.05	102	88	112
Bovine milk	0.005	112	104	100
Lettuce	0.05	80	70	76
Cherry	0.05	94 (n = 2)	73 (n = 2)	91 $\pm$ 13 (n = 13)

Bayer Method 172 (Stanley and Strankowski, 1975) is a modification of Method 171. The oxidized product mixture is subjected to basic hydrolysis. The resulting sulfone phenols are transferred to acetone and derivatized with bis(trimethylsilyl)trifluoroacetamide (BSTFA). Extracts are analysed by GLC with a flame photometric detector in the sulfur mode. Recoveries are generally >80% and the limit of determination is 0.01 mg/kg (see method I340 below).

DFG analytical method 79-A-1 (Dräger, 1974) is a gas-chromatographic method applicable to apples, pears, soil, fat, meat, potatoes, maize, milk, beets, lettuce and white cabbage. It is very similar to method 171. Oily samples such as maize kernels are extracted with acetonitrile, as opposed to acetone/0.05 N HCl. For cabbage varieties, a thin-layer chromatographic separation of interfering constituents is required before silylation. Recoveries are stated to be generally above 87% at fortification levels of 0.05-0.5 mg/kg of each compound and at 0.005 mg/l for milk. Some specific recoveries are given in Table 21.

Table 21. Recoveries of methiocarb and metabolites from fortified samples by Method 79-A-1 (Dräger, 1974).

Sample	Fortification, mg/kg	Recovery, %		
		Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
Cauliflower, head	0.05	92	94	92
Cauliflower, stalks	0.05	99	96	96
Cauliflower, leaves	0.05	96	87	87
Apples	0.05	104	106	104
Pears	0.05	97	96	110
Strawberries	0.05	105	100	99
	0.5	104	96	100
Potatoes	0.05	78	73	76
Maize	0.05	88	72	82
Lettuce	0.05	108	105	109
Cabbage, white	0.1	97	109	100
Sugar beet, root	0.05	103	112	91
	0.5	91	83	99
Sugar beet, tops	0.05	95	97	89
	0.5	102	69	80

Bayer Method 00045, formerly I671 (Burger, 1988a,b) is used for the determination of methiocarb and degradation products in ground water. Benzanilide is added to the water sample (1 l) as an internal standard and the sample is passed through a solid phase extraction column (RP 18) at the rate of 1 ml/min. The column is dried with a nitrogen stream and eluted with acetonitrile/methanol (80/20). Numerous active ingredients, including methiocarb, are determined by TLC. Quantitative evaluation is by external standards, using peak heights measured by reflection densitometry. The reflectance curves of sample and standard peaks in each lane are plotted together in different colours at 6 measurement wavelengths. The recovery of methiocarb at 0.1 µg/l was 87.8 $\pm$ 4.0%, n = 5.

Bayer Method 00190 (Bachlechner, 1990) is an HPLC procedure for the determination of methiocarb, the sulfoxide and the sulfone individually in soil. A soil sample (50 g) is shaken with acetone/water (3/1, 300 ml) at pH 2.5 for 16 hours. The mixture is filtered and the filtrate is concentrated to an aqueous fraction of about 50 ml. The solution is cleaned up on solid phase extraction columns, using methylene chloride (200 ml) as eluant. The eluate is concentrated to dryness and dissolved in acetonitrile/water, pH 2.5. The extract is analysed by HPLC with a LiChrospher 60, RP-select B column, with post-column hydrolysis (0.05 N caustic soda, 90˚C) and derivatization (*o*-phthalaldehyde, 2-mercaptoethanol, borate buffer). The methylamine released from the hydrolysis of the carbamate reacts with the derivatizing agent to form 1-hydroxyethylthio)-2-methylisoindole, detected by fluorescence. Calibration is by external standards.

The practical limit of determination is 0.01 mg/kg per analyte and the limit of detection about 0.001 mg/kg per analyte. Recoveries were determined by fortifying three soils types separately with methiocarb, methiocarb sulfoxide and methiocarb sulfone at concentrations of about 0.01 to 0.15 mg/kg. The recoveries were 77-97%, n = 24, mean 87% $\pm$ 6% for methiocarb, 72-104%, n = 24, mean 90% $\pm$ 12% for methiocarb sulfone, and 80-114%, n = 24, mean 103% $\pm$ 11% for methiocarb sulfoxide.

Bayer Method 00014, formerly method I664 (Blass, 1988) is a variant of Method 00190 and is used for the determination of methiocarb, the sulfoxide and the sulfone in plant materials. Fatty substrates, such as nuts and artichokes (50 g) are extracted with acetonitrile and the extract is partitioned with hexane. The acetonitrile fraction is concentrated and the residue is partitioned between methylene chloride and water. The methylene chloride fraction is evaporated and the residue is cleaned up on Extrelut cartridges (fatty materials) or Florisil (artichokes). The analysis is completed as in Method 00190.

In modification M001 of Method 00014 (Blass, 1989d), fat-free plant materials such as cucumbers are macerated with dichloromethane and filtered. The filtrate is concentrated to dryness and cleaned up on an Extrelut cartridge as in Method 00014.

In a further modification, M002, of Method 00014 (Seym, 1991a) for residues of methiocarb and metabolites in the green foliage of cereals such as barley, samples (10 g) are macerated with dichloromethane (250 ml) and filtered. The filtrate is evaporated to dryness and the residue redissolved in hexane (5 ml). The extract is cleaned up on 1-g Bakerbond SPE silica gel cartridges that have been pre-washed with ethyl acetate and hexane. The analytes of interest are eluted with ethyl acetate. The analysis is completed as in Method 00014.

Modification M003 of Method 00014 (Seym, 1991b) is essentially M002 applied to wheat forage.

Modification M004 of Method 00014 (Seym, 1994a) is specific for strawberries, melons, tomatoes, leeks, lettuce and paprika. The method involves slight modifications to the extraction and clean-up. Plant material (50 g) is macerated with methylene chloride (200 ml). HCl (1 N, 5 ml) is also added for paprika, melon peel, lettuce and tomato. The mixtures are filtered and the filtrate is concentrated to an aqueous residue. Salt (15 g) is added (and for strawberry, leek and melon pulp only 1 N HCl, 3 ml), and the volume is adjusted with water to 50 ml. The solution is cleaned up on a Chem-Elut column. Extracts of leeks are further purified with a Florisil column. The analysis is completed as before.

Modification M006 of Method 00014 (Seym, 1998) was designed for leeks, red cabbage and white cabbage. The plant material (50 g) is blended with ethyl acetate (200 ml) and filtered. The filtrate is evaporated, mixed with 10% aqueous sodium chloride (18 ml) and 1.0 N HCl (2 ml) and cleaned up on a Chem-Elut CE 1020 column. The analytes are eluted with ethyl acetate/cyclohexane (85/15) and determined by HPLC. The limit of determination is 0.02 mg/kg and the limit of detection 0.006 mg/kg for each analyte.

Modification M007 of Method 00014 (Blass, 1998a) is specific for red and white cabbage. The cabbage (50 g) is macerated with acetonitrile (200 ml) and n-hexane (100 ml). The acetonitrile phase is evaporated to dryness and cleaned up on an Extrelut column or a Bakerbond SPE silica cartridge. The former is eluted with methylene chloride, the latter with acetonitrile.

Recoveries from fortified controls by Method 00014 and its modifications are shown in Table 22.

Table 22. Recoveries of methiocarb and its metabolites from fortified plant materials by HPLC Method 00014 and its modifications (Blass, 1988, 1989d, 1998a; Seym 1991a,b, 1994a, 1998).

Sample	Modification	Fortification, mg/kg	Recovery, %		
			Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
Artichoke		1.0	90	95	99
		0.04	82	89	96
Hazel nuts		1.0	96	97	96
		0.04	96	-	88
Tomato		1.0	88		-
		0.04	95	-	-
	M001	0.04	90	101	99
	M001	1.0	94	98	105
	M004	0.02	80	99	115
	M004	0.1	84	101	117
	M004	0.5	85		100
Strawberry		0.04	93	-	-
		1.0	98	-	-
	M001	0.04	82	90	94
	M001	1.0	91	94	95
	M004	0.05	80	90	114

Sample	Modification	Fortification, mg/kg	Recovery, %		
			Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
	M004	0.1	75 (68, 82)	95	124
	M004	0.5	74 (68, 79)	-	99
Strawberry jam	M001	0.04	92	87	96
	M001	1,0	94	88	95
Strawberry, canned	M001	0.04	79	81	93
	M001	1.0	90	85	90
Paprika		0.04	80	-	-
		1.0	92	-	-
	M001	0.04	91	120	94
	M001	1.0	87	113	97
	M004	0.02	76	97	106
	M004	0.1	74 (69, 79)	94	121
	M004	0.5	70 (61, 78)	89	113
Cucumber	M001	0.04	81	89	103
	M001	1.0	82	107	103
Wheat (summer), forage	M001	0.1	83	86	89
	M001	1.0	87	97	93
	M003	0.1	83	82	82
	M003	1.0	90	79	78
Wheat (summer), grain		0.04		103	
		1.0		101	
Wheat (summer), straw		0.04		102	
		1.0		122	
Barley (summer), grain		0.04	87	89	89
		1.0	93	93	99
Barley (summer), straw		0.1	79	83	87
		1.0	84	88	98
Barley (summer), forage	M002	0.1	87	93	78
	M002	1.0	82	84	80
Leek, stem	M004	0.02	90	109	106
		0.1	76	76	100
		0.5	76	-	97
	M006	0.02	82	105	100
		0.2	77	95	100
Melon, peel	M004	0.02	89	97	105
		0.1	75	97	125
		0.5	76	-	95
Melon, pulp	M004	0.02	88	96	101
		0.1	89	99	119
		0.5	93	89	108
Lettuce	M004	0.02	81	100	110
		0.1	80	101	130
		0.5	83	72	109
Cabbage, red	M006	0.02	83	99	99
		0.2	81	94	99
	M007	0.02	85	70	88
		0.10	100	79	91
		1.0	94	84	96
Cabbage, white	M006	0.02	75	87	85
		0.2	76	95	102
	M007	0.02	89	68 (63, 73)	84
		0.10	97	73	94

Sample	Modification	Fortification, mg/kg	Recovery, %		
			Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
		1.0	98	83	91

Method I340 is for the determination of methiocarb and five metabolites in poultry commodities (Delphia and Stanley, 1980). Ground tissue samples (50 g) are blended with acetonitrile (200 ml) and the extract partitioned with hexane (300 ml). Eggs are blended with acetone (200 ml) and the extract is partitioned with methylene chloride (300 ml) which is evaporated and the residue dissolved in acetonitrile and partitioned with hexane. The acetonitrile extract from tissues or eggs is evaporated to dryness and reconstituted in acetone, to which a precipitating solution of ammonium chloride is added. The mixture is filtered and the filtrate partitioned with methylene chloride. The solvent is changed to acetone and the analytes oxidized with permanganate. A methylene chloride extract of the oxidation mixture is changed to acetone and the mixture is hydrolysed with sodium hydroxide (2.5 N) at 60°C for 30 min. The product solution is acidified and extracted with methylene chloride. The analytes are derivatized with BSTFA (*N*,*O*-bis(trimethylsilyl)trifluoroacetamide) and determined by GLC on a 0.6 m x 2 mm i.d. column packed with 5% OV-225 with a flame photometric detector operated in the sulfur mode. Quantification is with external standards. The limit of determination is nominally 0.02 mg/kg. Some recoveries are shown in Table 23.

Table 23. Recoveries of methiocarb and metabolites from poultry fortified at 0.05 mg/kg, Method I340 (Delphia and Stanley, 1980).

Sample	Recovery, %					
	Methio-carb	Methiocarb sulfoxide	Methiocarb sulfone	*N*-hydroxymethyl-methiocarb	*N*-hydroxymethyl-methiocarb sulfoxide	*N*-hydroxymethyl-methiocarb sulfone
Muscle	88	78	76	84	78	116
Fat	92	96	76	100	120	92
Skin	88	76	82	80	96	96
Giblets	90	88	72	76	90	116
Eggs	98	120	94	76	78	102

Stability of pesticide residues in stored analytical samples

In a study of the stability of methiocarb and methiocarb sulfoxide in blueberries (Gronberg and Lemke, 1989) samples were fortified with radiolabelled methiocarb at 2.8 mg/kg or methiocarb sulfoxide at 3.3 mg/kg, stored in sealed jars at –23°C for 117-118 days, and analysed on day 0 and day 117 or 118. The samples were extracted with methanol and the extracts were radioanalysed, then analysed by HPLC with a radioactivity detector. A sample chromatogram was provided. About 1% loss of each compound occurred over the 117-118 days.

Summary information (giving fortification levels, storage periods and remaining percentages) was provided late in the JMPR evaluation process on the stability of methiocarb, methiocarb sulfoxide and methiocarb sulfone in beans and pods, bean vines, grapes, cabbage, rice grain, tomatoes, broccoli, Brussels sprouts and cauliflower (Anon., 1978). No details such as concurrent method recoveries (if any), sample chromatograms, exact temperatures of storage or procedures for fortification and analysis were provided. The information is shown in Table 24, but was insufficient to evaluate the results.

Table 24. Stability of methiocarb, methiocarb sulfoxide and methiocarb sulfone in plant commodities fortified separately with 1 mg/kg of each compound and stored at 0 to –10°C (Anon., 1978).

Commodity and analyte	Storage, days	Remaining, %
Methiocarb		
Beans with pods	0	100
	93	100
	216	100
	399	100
Grapes	0	100
	86	100
	209	88
	393	92
Bean vines	0	100
	88	84
	150	69
	369	83
Cabbage	0	100
	101	100
	182	100
	365	100
Cabbage	805	100
Rice grain	0	100
	95	67
	198	38
	360	58
Tomato	0	100
	90	100
	204	100
	389	100
Broccoli	804	79
Brussels sprouts	806	60
Cauliflower	805	100
Methiocarb sulfoxide		
Beans and pods	0	100
	93	94
	180	100
	403	88
Grapes	0	100
	86	100
	231	100
	397	93
Bean vines	0	100
	88	77
	150	82
	373	92
Cabbage	0	100
	101	88
	204	95
	370	95
Cabbage	805	54
Rice grain	0	100
	95	88
	190	80
	364	74
Tomato	0	100
	90	97
	204	09
	386	99
Broccoli	804	60
Brussels sprouts	806	52

Commodity and analyte	Storage, days	Remaining, %
Cauliflower	805	100
Methiocarb sulfone		
Beans with pods	0	100
	93	95
	180	90
	404	94
Grapes	0	100
	86	98
	231	93
	398	95
Bean vines	0	100
	88	92
	150	68
	374	74
Cabbage	0	100
	101	100
	204	100
	371	100
Cabbage	805	100
Rice grain	0	100
	95	83
	198	63
	365	62
Tomato	0	100
	90	100
	204	100
	386	100
Broccoli	804	34
Brussels sprouts	806	100
Cauliflower	805	100

Definition of the residue

The current residue definition for both plant and animal commodities is “sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb”. The Meeting concluded that it should be maintained.

USE PATTERN

Bayer AG provided labels or translated summaries of labels for uses of methiocarb in countries from which significant export of methiocarb-treated commodities is anticipated. Applications are generally foliar, as a seed treatment or granular to the soil. Additional information on uses was supplied by the governments of Australia, Germany, The Netherlands, Thailand and the UK. The registered uses are shown in Table 25.

Table 25. Registered uses of methiocarb.

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
All edible	UK	Pelleted bait. Draza 40 g/kg	0.22	+		1 or more	Broadcast; admixture at drilling	7	Slug and snail control. Admix with cereal, rye, clover, oilseed rape, brassica seeds
All edible	UK	Pelleted bait.	0.15			1 or more	Broadcast; admixture	7	Slug and snail control. Admix with

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		Draza 2 20 g/kg					at drilling		cereal, rye seed.
Almond	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Artichoke	Israel	WP, 500 g/kg	1.75			1	Foliar spray		
Asparagus	Italy	RB, 10 g/kg	0.1				Spreading	21	
Asparagus	Thailand	WP, 500 g/kg	0.75	750	0.05-0.1		Foliar	3	
Aubergine	Italy	WP, 500 g/kg			0.1		Foliar spray	21	Apply with normal volume pump
Aubergine	Italy	RB, 10 g/kg	0.1				Spreading	21	
Barley	Austria	RB 40 g/kg	0.12			2	Spreading	-	Slug and snail control
Barley	Belgium	RB, 40g/kg	0.12			2	Spreading		Slug and snail control
Barley	France	RB, 40 g/kg	0.12			1	Spreading		Slug and snail control
Barley	Germany	RB 20 g/kg	0.1			2	Post-sowing, up to stage 29. Even baiting		
Barley	Germany	GB, 40 g/kg	0.12			2	At drilling; post-sowing up to stage 29	7	
Barley	Ireland	RB, 40 g/kg	0.22			1	Spreading		Slug and snail control
Barley	Ireland	RB, 20 g/kg	0.15			1	Spreading		Slug and snail control
Barley	UK	RB, 40 g/kg	0.22				Admixture at planting. Spreading	7	Slug and snail control
Barley	UK	RB, 20 g/kg	0.15				Admixture at planting. Spreading		Slug and snail control
Bean	Italy	RB, 10 g/kg	0.1				Spreading	21	
Bean, green	Italy	RB, 10 g/kg	0.1				Spreading	21	
Bean	Spain	WP, 500g/kg			0.05-0.1		Foliar	7	
Beet	Belgium	FS, 500 g/l	10 ml/100, 000 seeds			1	Seed treatment		
Beet, red	Nether-lands	WP, 500 g/kg							
Berry	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast	7	
Cabbage	Austria	WP, 500 g/kg	0.25-0.50			1-2	Foliar spray	14	
Cabbage	Austria	RB, 40 g/kg	0.12			2	Spreading	14	Slug and snail control
Cabbage	Belgium	SC, 500 g/l	0.75			3	Foliar	14	
Cabbage	Belgium	RB, 40 g/kg	0.12			2	Spreading	14	Slug and snail control
Cabbage	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	Red, white, Savoy
Cabbage	Germany	GB, 40 g/kg	0.12			2	Baiting between plants	14	Red, white
Cabbage	Italy	WP, 500			0.1		Foliar	21	Apply with normal

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		g/kg							volume pump
Cabbage	Italy	RB, 10 g/kg	0.1				Spreading	21	
Cabbage	Nether-lands	WP, 500g/kg	1.5			1	Foliar	14	
Carrot	Italy	RB, 10 g/kg	0.1				Spreading	21	
Cauli-flower	Austria	RB, 40g/kg	0.12			2	Spreading	14	Slug and snail control
Cauli-flower	Belgium	RB, 40 g/kg	0.12			2	Spreading	14	Slug and snail control
Cauli-flower	Germany	RB, 20 g/kg; GB, 40 g/kg	0.1 0.12			2	Baiting between plants	14	
Cereals	Austria	RB, 40 g/kg	0.12			2	Spreading		
Cereals	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast	7	
Cereals	Sweden	RB, 40 g/kg							
Cereals	UK	RB, 20 g/kg RB, 40 g/kg	0.15 0.22				Admixture at seeding. Spreading. Aerial	7	
Chicory	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	Field and glasshouse
Clover	Italy	RB, 10 g/kg	0.1				Spreading	21	
Cotton	Spain	WP, 500 g/kg			0.05-0.1		Foliar	21	
Cotton	Thailand	WP, 500 g/kg	0.5	500	0.05-0.1		Foliar	21	
Cucumber	Belgium	SC, 500 g/l	0.6-0.8			1	Foliar	3	
Cucumber	Belgium	SC, 500 g/l	0. 4			1	Foliar	3	Glasshouse
Cucumber	Chile	WP, 500 g/kg	0.5				Foliar	15	
Cucumber	Greece	WP, 500 g/kg	0.8	500-800	0.1	2	Foliar	15	Field
Cucumber	Greece	WP, 500 g/kg	1.5	500-1500	0.1	2	Foliar	15	Glasshouse
Cucumber	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Cucumber	Nether-lands	SC, 500 g/l			0.05		Foliar	3	
Cucumber	Spain	WP, 500g/kg	0.5-1		0.05-0.1	2	Foliar	7	
Cucurbits	Italy	RB, 10 g/kg	0.1				Spreading	21	
Fruit	Austria	WP, 500 k/kg	1.5		0.5-1		Foliar	14	21-day grazing restriction
Gherkin	Belgium	SC, 500 g/l	0.0006-0.0008			1	Foliar	3	Glasshouse
Grapes	Australia	WP, 750 g/kg Mesurol 750			0.075-0.15	2	Cover spray	63	
Grapes	Chile	WP, 500 g/kg		1000-1500	0.05-0.075		Foliar		
Grapes	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Grapes	Italy	RB, 10 g/kg	0.1				Spreading	21	
Grapes	Spain	WP, 500 g/kg			0.05-0.1		Foliar, before		Table and wine

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
							flowering		
Grapes	Thailand	WP, 500 g/kg	2.5	2500	0.05-0.1		Foliar, 5-7 day interval	21	
Hazel nut	Spain	WP, 500 g/kg	5 g ai/tree trunk; -		-; 0.05-0.1		Tree trunk paint; Foliar	21	
Hazel nut	Turkey	WP, 500 g/kg	0.6		0.25-0.375	1	Foliar	90	
Hops	Spain	WP, 500 g/kg			0.05-0.1		Foliar	21	
Leek	Belgium	SC, 500 g/l	0.75			2-3	Foliar	21	
Leek	Nether-lands	SC, 500 g/l	0.5-0.75			3	Foliar	14	
Lettuce	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	Head, Cos, Leaf. Field and glasshouse
Lettuce, head	Germany	GB, 40 g/kg	0.12			2	Baiting between plants	14	Field and glasshouse
Maize	Austria	WP, 500 g/kg. FS, 500 g/l	0.50 kg ai/dt (1 kg formul-ation/100 kg seed)			1	Seed treatment	-	
Maize	Belgium	WP, 500 g/l	0.50 kg/dt			1	Seed treatment		
Maize	Germany	FS 500 g/l	1 L/100 kg seed			1	Seed treatment	-	
Maize	Italy	WP, 500 g/kg	0.5 kg ai/100 kg seed				Seed treatment		
Maize	Nether-lands	SC, 500 g/l	0.5 kg ai/100 kg seed			1	Seed dressing		
Melon	Italy	WP, 500 g.kg	0.8-1.0 (calcu-lated)		0.1	2	Foliar	7	
Melon	Nether-lands	SC, 500 g/l			0.05		Foliar	3	
Melon	Portugal	WP, 500 g/kg	0.8-1 (calcu-lated)		0.1	2	Foliar	7	Field and glasshouse
Nectarine	Chile	WP, 500 g/kg	0.5-1.12	1000-1500	0.05-0.075		Foliar		
Nectarine	Spain	WP, 500 g/kg			0.05-0.1		Foliar, before flowering		
Oats	Germany	RB 20 k/kg	0.1			2	Post sowing up to stage 29. Even baiting		
Oats	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Oilseed crops	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast to ground	7	
Oranges	Australia	WP, 750 g/kg Mesurol 750			0.075		Cover spray	42	
Orchards	Australia	GB, 20 g/kg	0.11; 0.22-				Broadcast to ground	7	

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		Mesurol	0.44						
Pastures	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast to ground	7	
Peach	Spain	WP, 500 g/kg			0.05-0.1		Foliar, before flowering		
Peas	Germany	FS, 500g/l	0.5 L/100 kg seed				Seed treatment		
Peas	Italy	RB, 10 g/kg	0.1				Spreading	21	
Peas	Nether-lands	FS, 500 g/l	0.25 kg/100 kg seed			1	Seed treatment		
Peas	Spain	WP, 500 g/kg			0.05-0.1		Foliar	7	
Pepper, bell	Chile	WP, 500 g/kg	0.6	600-800	0.05-0.075		Foliar	14	
Pepper	Italy	RB, 10g/kg	0.1				Spreading	21	
Pepper	Portugal	WP, 500 g/kg	0.8-1 (calcu-lated)		0.1	2	Foliar	14	Field and glasshouse
Pepper	Spain	WP, 500 g/kg	0.4-1		0.05-0.10	3	Foliar	7	
Pepper. Chili	Thai-land	WP, 500 g/kg	0.5	500	0.05-0.1		Foliar, 7-10 day interval	21	
Pome fruit	Italy	WP, 500 g/kg			0.1		foliar	21	Apply with normal volume pump
Pome fruit	Italy	RB, 10 g/kg	0.1				Spreading	21	
Potato	Ireland	RB, 40 g/kg	0.22			3	Spreading		Slug control
Potato	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Potato	Italy	RB, 10 g/kg	0.1				Spreading	21	
Potato	UK	RB, 40 g/kg	0.22			3	Spreading		
Radish	Italy	RB, 10 g/kg	0.1				Spreading	21	
Rape	Austria	RB 40g/kg	0.12			2	Spreading		
Rape	Belgium	RB, 40 g/kg	0.12			2	Spreading		
Rape	France	WP, 500 g/kg	2.5 kg ai/q seeds			1	Seed treatment		
Rape	France	WP, 500 g/kg			0.1		Foliar	15/	
Rape	France	RB, 40 g/kg	0.12			1	Spreading	15	
Rape	Germany	RB, 20 k/kg	0.1			2	Post-sowing up to stage 29-30. Even baiting	15	Slug and snail control
Rape	Nether-lands	WP, 500 g/kg	0.5			1	Foliar		
Rape	Sweden	RB, 40 g/kg							Last application at 4-5 leaves stage
Rape	UK	RB, 40 g/kg	0.22			2	Spreading		Slug and snail control
Rape	UK	RB, 20 g/kg	0.11			1	Spreading	7	Slug and snail control
Rye	Germany	RB, 20 g/kg; GB, 40	0.1 0.12			2	Post sowing up to stage 29.		

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		g/kg					Even baiting		
Rye	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Scarole	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	
Spinach	Germany	RB, 20 g/kg GB, 40 g/kg	0.1 0.12			2	Baiting between plants	14	Field and glasshouse. Field only for GB
Stone fruit	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Sugar beet	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Sugar beet	Italy	RB, 10 g/kg	0.1				Spreading	21	
Stone fruit	Italy	RB, 10g/kg	0.1				Spreading	21	
Sugar beet	Italy	WP, 500 g/kg	0.5 kg ai/100 kg seed				Seed treatment		
Sugar beet	Nether lands	WP, 500 g/kg							
Straw-berry	Austria	RB, 40 g/kg	0.12			2	Spreading		
Straw-berry	Belgium	RB, 40 g/kg	0.20			2	Spreading		Slug and snail control
Straw-berry	Finland	SC, 500 g/l	3		0.15		Foliar after harvest		
Straw-berry	Germany	RB, 20 g/kg GB, 40 g/kg	0.1 0.12			2	Baiting between plants	14	
Straw-berry	Ireland	RB, 40 g/kg	0.22			1	Spreading		Slug and snail control
Straw-berry	Ireland	RB, 20 g/kg	0.10			1	Spreading		Slug and snail control
Straw-berry	Italy	WP, 500 g/kg	0.7-1.2 (calcu-lated)		0.1	1	Foliar	21	
Straw-berry	Italy	RB, 40 g/kg	0.12-0.2			2	Spreading	14	Slug and snail control
Straw-berry	Italy	RB, 10 g/kg	0.1				Spreading	21	
Straw-berry	Portugal	WP, 500 g/kg	0.8		0.1	2	Foliar	7	Field and glasshouse
Straw-berry	Spain	WP, 500 g/kg	0.4-1		0.05-0.1	2	Foliar	15	Field and glasshouse
Straw-berry	Sweden	RB, 40g/kg	0.2			1	Spreading		Slug and snail control
Straw-berry	UK	RB, 40 g/kg	0.22			1	Spreading		Slug and snail control
Straw-berry	UK	RB, 20 g/kg	0.10			2	Spreading	7	Slug and snail control
Sun-flowers	Australia	GB, 20 g/kg Mesurol	0.05; 10 pellets/ m^2				Broadcast to ground	7	
Tomato	Chile	WP, 500 g/kg	0.6	600-800	0.05-0.075		Foliar	15	
Tomato	Italy	RB, 10 g/kg	0.1				Spreading	21	
Tomato	Portugal	WP, 500 g/kg	0.8-1 (calcu-lated)		0.1	2	Foliar	7	Field and glasshouse
Tomato	Spain	WP, 500	0.5-1		0.05-0.1	2	Foliar	7	Field and

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		g/kg							glasshouse
Triticale	Germany	RB, 20 g/kg	0.1				Post sowing up to stage 29. Even baiting		
Triticale	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Vegetables	Austria	WP, 500 g/kg	1.5	300-600	0.5-1		Foliar	14	21-day grazing restriction
Vegetables	Austria	RP, 40 g/kg	0.12			2	Spreading		
Vegetables	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast to ground	7	
Vegetables	Germany	RB, 20 g/kg	0.1			2	Spreading	14	
Vegeta-bles, leaf	Italy	RB, 10 g/kg	0.1				Spreading	21	
Water-melon	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Water-melon	Thailand	WP. 500 g/kg	0.5	500	0.05-0.1		Foliar, 5-7 day interval	10	
Wheat	Belgium	GB, 40 g/kg	0.12				Spreading	1-4	Slug and snail control
Wheat	France	RB, 40 g/kg	0.12			1	Spreading		Slug and snail control
Wheat	Germany	RB, 20 g/kg	0.1			2	Post sowing up to stage 29. Even baiting		
Wheat	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Wheat	Portugal	WP, 500 g/kg	3			1	Foliar, at milk growth stage	28	Bird repellent
Zucchini	Chile	WP, 500 g/kg	0.6	600-800	0.05-0.075		Foliar	15	

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of the residue trials are shown in Tables 26-41. The trials were reported in sufficient detail, with acceptable analytical information, unless otherwise noted. Double underlined residue values are from treatments according to GAP and are valid for use in the estimation of maximum residue levels and STMRs. The commodities covered by the Tables are as follows.

Table number	Commodity
26	Potato
27	Leek
28	Cabbage
29	Cabbage
30	Cauliflower
31	Peas
32	Pepper
33	Tomato

Table number	Commodity
34	Cucumber
35	Melon
36	Strawberry
37	Wheat
38	Barley
39	Maize
40	Hazelnuts
41	Rape

Information on supervised trials was supplied by Bayer AG.

Potatoes. Trials were reported from the UK (Seym and Walz-Tylla, 1993a). GAP in the UK and Ireland is up to three applications of a granular formulation at 0.22 kg ai/ha. No PHI is specified. Trials were conducted with Draza 4 RB in the UK in 1991. The details are shown in Table 26. Samples were stored frozen for 14 months before analysis.

Table 26. Residues of methiocarb and its metabolites in or on potatoes in the UK following application of methiocarb RB, 40 g/kg.

Location/ Year/ Ref. no.	Rate, kg ai/ha	No. of applications/ time of last application	PHI, days	Methiocarb/ sulfoxide/ sulfone, mg/kg	Method of analysis	Fortified control recoveries	
						Fort., mg/kg	Recovery, %
Thurston, Suffolk/ 1991/ 2038/91	0.22	3/ Starting of senescence, mature tubers	18	<0.02 <0.02 <0.02	00014/ M002/ E008	Methiocarb: 0.02 0.2 1.0 Sulfone: 0.02 0.1 1.0 Sulfoxide: 0.02 0.2 1.0	 72 74 66 88 68 74 66 88 97
Deal, Kent/ 1991/ 2038-91	0.22	3/ Starting of senescence, mature tubers	20	<0.02 <0.02 <0.02			

Leeks. A total of 11 field trials were reported from France and The Netherlands (Seym, 1994b, 1995a; Walz-Tylla and Deissler, 1998b). GAP for France was not reported. In The Netherlands up to 2 foliar applications of an SC formulation, 500 g/l, may be made at rates of 0.5-0.75 kg ai/ha, with a 14-day PHI. Similar GAP exists for Belgium, but the PHI is 21 days. GAP of The Netherlands was applied to the trials in France. The pertinent conditions and results are shown in Table 27. The residues were determined by HPLC Method 00014, modification M004. Recoveries in the 1993 trials from fortified controls (13 determinations, 0.02-0.5 mg/kg) were 75-93% for methiocarb, 52-112% for methiocarb sulfone (67-112% at or above 0.2 mg/kg) and 86-108% for methiocarb sulfoxide. In the 1994 trials recoveries of methiocarb were 57-87% (n = 6), of methiocarb sulfone 86-108% (n = 6) and of methiocarb sulfoxide 98-101% (n =6). Concurrent recoveries in the 1996 French field trials at fortification levels of 0.02-0.5 mg/kg (7 determinations) were 75-94% for methiocarb, 93-105% for methiocarb sulfone, and 94-112% for methiocarb sulfoxide. The limit of determination was 0.02 mg/kg per analyte. Control samples showed no residues (<0.02 mg/kg). Samples were stored frozen for 1-12 months before analysis.

Table 27. Residues of methiocarb and its metabolites in or on leeks from foliar application of methiocarb in France and The Netherlands (Seym, 1994b, 1995a; Walz-Tylla and Deissler, 1998b)

Location/ Year/ Variety	Form	Rate, kg ai/ha	Vol., l/ha	No./ interval, days	PHI, days	Methio-carb, mg/kg	Sulfone, mg/kg	Sulfoxide, mg/kg	Report no.
Bouafle, France/ 1993	Mesurol WP, 500 g/kg	0.75	280	3/14, 24	0 7 14 21	4.1 0.42 0.07 0.03	0.05 0.03 0.03 <0.02	0.94 0.32 0.15 0.06	2085/93
Ecquevilly, France/ 1993	Mesurol WP, 500 g/kg	0.75	280	3/14,24	0 7 14 21	4.2 0.37 0.10 0.04	0.06 0.05 0.03 <0.02	0.45 0.24 0.16 0.06	2085/93
Ecquevilly, France/1994/ Nepal	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 7 14 21	2.8 0.24 0.05 <0.02	0.05 0.06 0.02 <0.02	0.29 0.37 0.11 0.07	2070/94
Ecquevilly, France/ 1994/ Arkansas	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 21	2.4 0.04	0.04 <0.02	0.37 0.10	2070/94
Sorgues, France/1996	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 7 14 21 28	3.3 0.51 0.22 0.09 0.05	0.02 0.04 <0.02 <0.02 <0.02	0.47 0.34 0.17 0.09 0.06	2156/96
Lombez, France/ 1996 (2 replicates)	Mesurol WP, 500 g/kg	0.75	280	3/14,13-14	0 21	3.5; 2.7 0.13;0.16 (0.14)	0.04;0.05 <0.02;0.03 (0.03)	0.52;0.46 0.09;0.15 (0.12)	2156/96
Bonnetan, France/1996	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 7 14 21 28	5.0 0.51 0.13 0.07 0.02	0.07 0.08 0.05 0.03 <0.02	0.57 0.37 0.12 0.08 0.04	2156/96
PT Toll-ebeek, NL/ 1993	Mesurol SC, 500g/l	0.75	1000	3/11,9	0 7 14 21	2.0 0.12 0.03 <0.02	0.03 0.02 <0.02 <0.02	0.39 0.23 0.05 0.03	2085/93
PE Drot-erop-slagen, NL/1993	Mesurol SC, 500 g/l	0.75	1000	3/11,9	0 7 14 21	2.2 0.07 <0.02 <0.02	0.04 <0.02 <0.02 <0.02	0.38 0.10 0.02 <0.02	2085/93
AA Dongen, NL/1994	Mesurol SC, 500 g/l	0.75	1000	3/10,10	0 3 7 14 21	2.6 0.26 0.10 0.03 <0.02	<.02 0.04 <0.02 <0.02 <0.02	0.17 0.20 0.10 <0.02 <0.02	2070/94
RB Deurne, NL/1994	Mesurol SC, 500 g/l	0.75	1000	3/10,10	0 21	1.1 0.02	0.05 <0.02	0.61 <0.02	2070/94

Cabbages. Field trials were reported from Austria, Belgium, Germany and The Netherlands (Bayer AG, 1978, 1980c; Blass, 1998b; Walz-Tylla, 1998). GAP for Belgium is 3 foliar applications at 0.75 kg ai/ha of an SC formulation or 2 applications by spreading on the ground of an RB formulation at 0.12 kg ai/ha. The PHI is 14 days. GAP for Germany is 2 applications of RB formulations, baiting between plants, at 0.12 kg ai/ha, 14 day PHI. GAP for The Netherlands is one foliar application of a WP formulation at 1.5 kg ai/ha, 14 day PHI. GAP for Belgium for the SC formulation was applied to evaluate the trials in The

Netherlands and some of those in Germany. The trial conditions and results are shown in Tables 28 and 29. Samples were stored frozen for 1-10 months before analysis.

Table 28. Residues of methiocarb and its metabolites in or on cabbages from foliar application or ground application of baits (Bayer, 1978, 1980c).

Location/ Year/ species	Form.	Rate, kg ai/ha	Vol., l/ha	No./interval, days	PHI, days	Residue, mg/kg (methiocarb + sulfoxide + sulfone)	Report no.
Pfalz, Germany/ 1978/Savoy	4% RB	0.12	-	1	0 4 7 14 21	0.34 0.66 <0.05 <u>≤0.05</u> -	2103-78
Monheim, Germany/ 1978/Savoy	4% RB	0.12	-	1	<u>0</u> 4 7 14 21	<u>≤0.05</u> - - - -	2104-78
Bursheid, Germany/ 1978/Savoy	4% RB	0.12	-	1	<u>0</u>	<u>≤0.05</u>	2105-78
Pfalz, Germany/ 1980/White	4% RB	0.12	-	2/14	0 4 7 14 28	0.89 0.23 <0.05 <u>≤0.05</u> <0.05	2107-80
Bursheid, Germany/ 1980/White	4% RB	0.12	-	2/14	0 4 7 14 28	0.06 <0.05 <0.05 <u>≤0.05</u> <0.05	2108-80
Monheim, Germany/ 1980/White	4% RB	0.12	-	2/14	0 4 7 14 28	0.09 0.24 0.09 <u>≤0.05</u> <0.05	2109-80
Niederoster-reich, Austria/ 1981/White	WP 50%	1.5	600	1	0 14 21 28 35	0.52 0.09 0.05 <0.05 <0.05	

Table 29. Residues of methiocarb and its metabolites in or on cabbages (Walz-Tylla, 1998; Blass, 1998b).

Location /year /species	Application				PHI, days	Methio-carb, mg/kg	Methio-carb sulfone, mg/kg	Methio-carb sulf-oxide, mg/kg	Report no.
	Form.	kg ai/ha	Vol., l/ha	No. per interval, days					
Luttelgeest, NL/1996 /Round	Mesurol SC, 500 g/l	0.75	500	3/16,14	0 7 14 21	0.11 <0.02 <u>≤0.02</u> <0.02	<0.02 <0.02 <u>≤0.02</u> <0.02	0.10 0.08 <u>0.03</u> 0.03	2157/96
Luttelgeest, NL/1996 /Red	Mesurol SC, 500 g/l	0.75	500	3/16,14	0 7 14 21	0.09 <0.02 <u>≤0.02</u> <0.02	<0.02 <0.02 <u>≤0.02</u> <0.02	0.05 0.04 <u>0.03</u> 0.02	2157/96
Echteld, NL/1996 /Red	Mesurol SC, 500 g/l	0.75	500	3/14, 14	0 7 14 21	0.05 <0.02 <u>≤0.02</u> <0.02	<0.02 <0.02 <u>≤0.02</u> <0.02	0.06 0.03 <u>0.02</u> <0.02	2157/96

Location /year /species	Application				PHI, days	Methio-carb, mg/kg	Methio-carb sulfone, mg/kg	Methio-carb sulf-oxide, mg/kg	Report no.
	Form.	kg ai/ha	Vol., l/ha	No. per interval, days					
Brielle, NL/1996 /Round	Mesurol SC, 500 g/l	0.75	500	3/14,14	0 7 14 21	0.10 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.12 0.08 0.03 <0.02	2157/96
Laacherhof Germany/ 1997/ Round	Mesurol SC, 500 g/l	0.75	500	3/14,14	0 7 14 21	0.564 0.04 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.10 0.05 <0.02 <0.02	2004/97
Laacherhof Germany/ 1997/Red	Mesurol SC, 500 g/l	0.75	500	3/14,14	0 7 14 21	0.81 0.10 0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.15 0.10 0.03 <0.02	2004/97
Poederlee, Belgium/ 1997/ Round	Mesurol SC, 500 g/l	0.70-0.75	463-500	3/14,17	0 6 14 20	0.15 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.04 <0.02 <0.02 <0.02	2004/97
Poederlee, Belgium/ 1997/Red	Mesurol SC, 500 g/l	0.75	500	3/14,17	0 6 14 20	0.19 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.04 0.03 <0.02 <0.02	2004/97

NL = Netherlands
Recoveries in the NL trials (0.02-0.2 mg/kg, n=12) were 53-86% for methiocarb, 85-102% for methiocarb sulfone, and 85-134% for methiocarb sulfoxide. In the 1997 trials in Germany and Belgium (0.02-1.0 mg/kg, n=28), 78-118% for methiocarb, 73-126% for methiocarb sulfoxide, and 63-107% for methiocarb sulfone.

Cauliflower. Four trials in Germany were reported as summaries (Bayer AG, 1980d, 1981). GAP for Germany is 2 applications of an RB formulation to the ground at 0.12 kg ai/ha, with a 14-day PHI. Similar GAP exists in Austria and Belgium. The results of the trials are shown in Table 30. Analyses were by Method 171.

Table 30. Residues of methiocarb and its metabolites in cauliflowers in Germany (Bayer AG, 1980d, 1981).

Location/year	Application			PHI, days	Methiocarb + methiocarb sulfoxide + methiocarb sulfone, mg/kg	Report no.
	Form	kg ai/ha	No/interval, days			
Pfalz, 1980	4% GB	0.12		0 4 7 14	0.97 0.1 0.06 <0.05	2110-80 2111-80 2112-80
Burscheid, 1980	4% GB	0.12	2/14	14 (leaf) 28	<0.05 <0.05	
Laacherhof, 1980	4% GB	0.12	2/16	0 4 7 14 28	0.96 0.24 0.12 <0.05 <0.05	
Laacherhof, 1981	4% GB	0.12	2/11	0 4 7 14 28	<0.05 <0.05 <0.05 <0.05 <0.05	2105-81

Artichokes. Two trials were reported from Italy (Bayer AG, 1988). No GAP is reported for Italy, but GAP for Israel is one foliar application of a WP formulation at 1.75 kg ai/ha, with no specified PHI. The trials

were conducted at Brindisi in 1987 and 1988 (duplicate plots) with a 50% WP formulation applied twice at a rate of 1.0 kg ai/ha. Residues were <0.04 mg/kg on the flower heads at a PHI of 21 days. At 0 days the residues were 2.7 mg/kg in 1987 and 2.9 mg/kg and 1.2 mg/kg in 1988.

Peas. Eight trials were reported from Germany (Bayer AG, 1985, 1986). GAP for Germany is a seed treatment at 0.5 l per 100 kg of seed of a 500 g/l FS formulation. The formulation was applied in the field at planting. The results are shown in Table 31. The samples were stored from <1-12 months before analysis.

Table 31. Residues of methiocarb and its metabolites in trials on peas in Germany (Bayer AG, 1985, 1986).

Location/year	Application rate (kg ai/ha)	PHI, days	Sample	Residue,[1] mg/kg	Report no.
Klein-Niedesheim, 1985	0.90	65 84 65	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2103-85
Worms-Heppenheim, 1985	0.85	69 86 69	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2102-85
Laacherhof, 1985	1.1	63 99 63	Pea and pod Dry pea Vine	<0.05 <0.05 <0.05	2101-85
Versuchsgut Höfchen, 1985	1.1	97 132 97	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2100-85
Laacherhof, 1986	0.90	58 83	Vine Pea	<0.05 <0.05	2113-86
Versuchsgut Höfchen, 1986	0.90	62 91 62	Pea with pod Pea Vine	<0.05 <0.05 <0.05	2112-86
Worms-Heppenheim, 1986	0.85	63 75 63	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2111-86
Klein-Niedesheim, 1986	0.85	51 65 51 65 89	Pea and pod Pea Vine Straw Dry pea	0.07 0.08 0.04 0.08 0.06	2110-86

[1]Combined residues of methiocarb, methiocarb sulfone and methiocarb sulfoxide

Peppers. Five trials were reported from Spain (Bayer AG, 1989c, 1992f; Seym, 1997; Seym and Walz-Tylla, 1993b) and 2 glasshouse trials from Portugal (Seym, 1997). GAP is similar in both countries, 3 applications in Spain and 2 applications in Portugal at 1 kg ai/ha, with a 7-day PHI in Spain and a 14-day PHI in Portugal. Portugal's GAP includes field and glasshouse use. The formulation is 500 g/kg WP. Analyses were by HPLC Method 00014, E002, but in some cases only the total residue was reported. The results are shown in Table 32. Samples were stored for 1-6 months before analysis. The shorter PHI of Spain was applied to the trials in Portugal in determining which residue values were appropriate for estimating an STMR.

Table 32. Residues of methiocarb and its metabolites in peppers.

Location/ Year	Application			PHI, days	Methiocarb, mg/kg	Methiocarb sulfone mg/kg	Methiocarb sulfoxide mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval days					
Almeria, Spain/1988 Variety Ator	1.0	1000	3/14, 14	0 5 10 15	0.71 (total) 0.48 0.46 0.92			0720-88
Almeria, Spain/1988/ Variety Clovis	1.0	1000	3/14, 14	0 5 10 15	0.81 (total) 0.84 0.55 0.49			0719-88
Murcia, Spain/1990 Variety Gedeon (replicate plots)	1.0	1000	2/14	0 3 7 14	0.92; 0.60; 0.86 1.0; 0.49; 0.89 0.96; 0.78; 0.81 0.68; 0.49; 0.60	<0.04 <0.04 <0.04 <0.04	0.33;0.37;0.39 0.49;0.44;0.42 0.37;0.56;0.44 0.33;0.36;0.38	0194-90
Malgrat, Spain/1991 (see processing)	1.0 1.5	1000 1500	2/14	0 3 7 10	2.4 1.3 0.82 0.28	<0.04 <0.04 <0.04 <0.04	0.32 0.33 0.38 0.22	2103/91
Viladecans, Spain/1991 (see processing)	1.0	1000	2/14	0 3 7 10	2.2 1.2 1.1 0.15	<0.04 <0.04 <0.04 <0.04	0.20 0.25 0.43 0.14	2103/91
Figueiras, Portugal (glasshouse)/ 1993	1.0 1.2 1.0	1000 1155 1000	3/7, 9	0 3 7 14 28	0.57 0.33 0.36 0.22 0.17	<0.02 <0.02 <0.02 <0.02 <0.02	0.34 0.24 0.33 0.27 0.13	2087/93
Bordinheira, Portugal (glasshouse)/ 1994 (see processing)	1.2 1.3 1.3	1173 1306 1306	3/7, 9	0 3 5 7 14 28	0.18 0.08 0.09 0.13 0.03 0.03	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.05 0.06 0.08 0.10 0.03 0.24	2087/93

Method recoveries in Portugal (0.02-0.5 mg/kg, n = 11) were 61-81% for methiocarb, 85-99% for methiocarb sulfone, and 98-124% for methiocarb sulfoxide.

Tomatoes. Eight trials were reported from Southern Europe, 1 in Portugal and 7 in Spain (Bayer AG, 1989a,b, 1992a-c; Seym, 1997). GAP for Portugal and Spain is identical, 2 foliar applications of a WP 500 g/kg formulation at 0.1 kg ai/ha per application with a 7-day PHI. Both glasshouse and field applications are specified. The results are shown in Table 33. Samples were stored from 1 month to 16 months before analysis.

Table 33. Residues of methiocarb and its metabolites in tomatoes (Bayer, 1989a,b, 1992a-c; Seym, 1997).

Location/ Year Variety	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
Almeria, Spain/1988/ Caruso	1.0	1500	3/14, 14	0 5 10 15	0.18 (total) 0.13 0.12 0.17			0721-88
Almeria, Spain/1988/ Buffalo	1.0	1500	3/14,14	0 5 10 15	0.14 (total) 0.13 0.08 0.17			0722-88
Viladecans, Spain/ 1990	1.0	1000	2/15	0 3 7	0.23 0.18 0.06	<0.04 <0.04 <0.04	0.10 <0.04 0.05	0210-90

Location/ Year Variety	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
				15	<0.04	<0.04	<0.04	
Malgrat de Mar, Spain/1990	1.0	1000	2/15	0 3 7 15	0.42 <0.04 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.13 <0.04 <u>≤0.04</u> <0.04	0211-90
Matar, Spain/1990	1.0	1000	2/15	0 3 7 15	0.35 0.32 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.13 <0.04 <u>≤0.04</u> <0.04	0212-90
Santarem, Portugal/ 1993/ glasshouse	1.0 1.1	1000	2/15	0 3 5 7 14 21	0.99 0.97 0.72 <u>0.59</u> 0.34 0.26	<0.02 <0.02 <0.02 <u>≤0.02</u> <0.02 <0.02	0.23 0.28 0.25 <u>0.22</u> 0.26 0.08	2087/93 #0438-93
Viladecans, Spain/1993/ glasshouse	1.2 1.4 1.4	1209 1416 1416	3/13,13	0 3 5 7 14	0.48 0.30 0.13 0.13 0.08	<0.02 <0.02 <0.02 <0.02 <0.02	0.09 0.12 0.07 0.10 0.10	2087/93 #0431-93
Vicar, Spain/1993/ glasshouse	1.5 1.4 1.5	1500 1407 1500	3/12,14	0 7 14	0.70 0.45 0.42	<0.02 <0.02 <0.02	0.17 0.13 0.17	2087/93 #0440-93

Method recoveries in the 1993 greenhouse trials in Spain and Portugal (0.02-0.2 mg/kg, n=7) were 81-93% for methiocarb, 87-101% for methiocarb sulfone, and 99-112% for methiocarb sulfoxide

<u>Cucumbers</u>. Two trials were reported from Spain (Bayer AG, 1992e) and four glasshouse trials from France (Seym and Heinemann, 1995). An additional report on trials in The Netherlands was withdrawn by Bayer AG. No GAP was reported for France. In Spain, a WP formulation may be applied as a foliar spray at 1 kg ai/ha, two applications maximum, PHI 7 days. Italy has a similar application, but no maximum number of applications and a 21-day PHI. Samples were analysed by HPLC Method 00014, M001. The results are shown in Table 34. Samples were stored from 1-6 months before analysis.

Table 34. Residues of methiocarb and its metabolites in or on cucumbers.

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
Viladecans, Spain/ 1990	1.0	1000	2/15	0 3 7 15	0.11 0.08 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.10 0.08 <u><0.04</u> <0.04	0217-90
Matar, Spain/1990	1.0	1000	2/15	0 3 7 15	0.57 0.22 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.18 0.06 <u>≤0.04</u> <0.04	0215-90
Montfavet, France/1994 glasshouse	0.80	1066	1	0 3 7	0.23 0.13 <u>≤0.02</u>	<0.02 0.03 <u>≤0.02</u>	0.06 0.10 <u>0.05</u>	2036/94 #0144-94
Montfavet/, France/1994 glasshouse	0.79	1055	1	0 3 7	0.17 0.14 <u>0.03</u>	<0.02 0.02 <u>≤0.02</u>	0.05 0.10 <u>0.07</u>	2036/94 #0145-94
Bellegarde, France/1994 glasshouse	0.86	1153	1	0 3 7	0.17 0.09 <u>0.02</u>	<0.02 <0.02 <u>≤0.02</u>	0.04 0.10 <u>0.09</u>	2036/94 #0146-94

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
Bellegarde, France/1994 glasshouse	0.86	1145	1	0 3 7	0.15 0.04 <0.02	<0.02 <0.02 <0.02	0.04 0.07 0.07	2036/94 #0147-94

[1]In the French trials concurrent recoveries (0.02-0.2 mg/kg, n = 6) were 76-95% for methiocarb, 93-103% for methiocarb sulfone and 106-114% for methiocarb sulfoxide.

Melons. Seven trials on melons were reported from Southern Europe, 3 in France (Walz-Tylla and Deissler, 1998a), 2 glasshouse in Portugal and 2 in Spain (Seym, 1997). GAP was not reported for France or Spain. In Portugal and Italy a WP formulation may be applied twice at a maximum rate of 1 kg ai/ha with a 7-day PHI. The samples were analysed by HPLC Method 00014, M004. The results are shown in Table 35. The samples were stored frozen for 11-13 months before analysis. The residues in whole melons were calculated from the residues determined in the pulp and peel in those cases where whole melons were not analysed.

Table 35. Residues of methiocarb and its metabolites in or on melons (Walz-Tylla and Deissler, 1998; Seym, 1997).

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No. per interval, days					
Santeren, Portugal/ 1993	1.0	1000	2/18	0 pulp 3 7 14 28 0 peel 3 7 14 28 7 whole (2.08 kg whole, 1.47 kg pulp, 0.61 kg peel)	0.07 <0.02 <0.02 <0.02 <0.02 1.70 0.74 0.96 0.41 0.19 0.29	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.12 0.05 0.06 0.04 <0.02 1.20 0.64 0.55 0.32 0.16 0.20	2087/93 #0436-93
Alenquer, Portugal/ 1993	1.0	1000	2/14	0 pulp 3 5 7 14 28 0 peel 3 5 7 14 28 7 whole (4.14 kg whole, 3.46 kg pulp, 0.68 kg peel)	<0.02 0.07 <0.02 <0.02 <0.02 <0.02 0.39 1.70 0.68 0.63 0.33 0.15 0.11	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.03 0.08 <0.02 0.06 0.04 <0.02 0.46 0.74 0.33 0.59 0.25 0.17 0.15	2087/93 #0437-93
Santa Olive, Spain/ 1993	1.0	1000	2/14	0 pulp 3 5 7 0 peel	0.02 <0.02 <0.02 <0.02 1.20	<0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 0.40	2087/93 #0442-93

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No. per interval, days					
				3 5 7 7 whole (26.1 kg whole, 18.4 kg pulp, 7.74 kg peel)	0.26 0.38 0.29 0.09	<0.02 <0.02 <0.02 <0.02	0.15 0.21 0.22 0.08	
La Fortesa, Spain/ 1993	1.00	1000	2/14	0 pulp 7 0 peel 7 7 whole (22.4 kg whole, 15.3 kg pulp, 7.1 kg peel)	<0.02 <0.02 0.22 0.05 0.02	<0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 0.16 0.14 0.05	2087/93 #0443-93
Neuville su Oise, France/ 1996	0.75	1000	1	0 pulp 2 0 whole 2 3 5	<0.02 <0.02 0.42 0.25 0.18 0.08	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 0.44 0.27 0.22 0.11	2155/96
Ecque-villy, France/ 1996	0.75	1000	1	3 pulp 0 whole 3	<0.02 0.19 0.18	<0.02 <0.02 <0.02	<0.02 0.21 0.23	2155/96
Crique-beuf sur Seine, France/ 1996	0.75	1000	1	3 pulp 5 0 whole 2 3 5	<0.02 <0.02 0.21 0.09 0.15 0.08	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 0.23 0.10 0.17 0.10	2155/96

In the trials in Portugal, method recoveries (0.02-0.5 mg/kg, n = 10) from fortified control pulp were 73-93% for methiocarb, 88-102% for methiocarb sulfone, and 98-119% for methiocarb sulfoxide. Recoveries at 0.02 and 0.1 mg/kg (n = 5) from pulp were 95-99% for methiocarb, 92-100% for methiocarb sulfone, and 100-111% for methiocarb sulfoxide in Spain, and 77-95% for methiocarb, 88-104% for methiocarb sulfone, and 81-132% for methiocarb sulfoxide in France.

Strawberries. Fourteen residue trials on strawberries were reported from Europe (Bayer AG, 1974a,b, 1975, 1989d, 1992d; Seym, 1993b, 1995b; Seym and Walz-Tylla, 1993c; Heinemann and Walz-Tylla, 1997). GAP in Southern and Northern Europe is as follows.

Country	Formulation	Rate, kg ai/ha	No. of applications	PHI, days
Southern Europe				
Italy	WP	1.2	1	21
Italy	RB	0.2	2	14
Portugal	WP	0.8	2	7
Spain	WP	1	2	15
Northern Europe				
Austria	RB	0.12	2	
Belgium	RB	0.20	2	
Germany	RB	0.12	2	14
Ireland	RB	0.22	1	
Sweden	RB	0.2	1	
UK	RB	0.22	1	7

The results of the trials are shown in Table 36. Samples were analysed by HPLC Method 00014, M004, except in those trials conducted in the 1970s, in which the residues were oxidized to methiocarb

sulfone and determined by GLC with an FPD, as in methods such as 00040/E003 (Drüger, 1982). The shorter GAP PHI of Portugal was applied to evaluate the trials in Spain. Samples were stored from 0.5-14 months before analysis.

Table 36. Residues of methiocarb and its metabolites in strawberries.

Location/year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	Form	kg ai/ha/ l/ha	No., days					
Palafolls, Spain/1990	50 WP	1.0/ 1000		0 4 7 10 14	1.1 0.50 0.23 0.12 <0.04	<0.04 <0.04 <0.04 <0.04 <0.04	0.05 0.19 0.13 0.13 0.07	0340-90
San Pol de Mar, Spain/1990	50 WP	1.0/ 1000	2/15	0 4 7 10 14	4.7 0.97 0.46 0.36 0.16	<0.04 <0.04 <0.04 <0.04 <0.04	0.26 0.38 0.37 0.21 0.12	021490
Callela, Spain/1991[1] (see processing)	50 WP	1.0/ 1000	2/12	7 10 14	0.35 0.12 0.09	<0.04 <0.04 <0.04	0.19 0.14 0.12	020191 0201-91
Angeles, Spain/1993[2] glasshouse	50 WP	0.9/903 1.0/1000 1.0/1000	3/14, 14	0 7 14	0.24 0.28 0.10	<0.02 <0.02 <0.02	0.10 0.15 0.10	2086/93 04493
Alenquer, Portugal/1993[2]	50 WP	1.1/1066 1.2/1200	2/14	0 9 14	0.46 0.18 0.06	<0.02 <0.02 <0.02	<0.02 0.27 0.23	2086/93 0447-93
Salvaterra de Magos, Portugal/1993[2] glasshouse	50 WP	1.0/ 1000	2/14	0 7 10 14	0.53 0.30 0.27 0.40	<0.02 <0.02 <0.02 <0.02	0.14 0.17 0.21 0.31	2086/93 0446-93
La Cellera de Ter, Spain/1996[3]	50 WP	0.92/740 1.0/800 1.0/800	3/14, 14	0 7 14 21	1.3 0.08 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	1.4 0.21 0.07 0.03	2154/96 0581-96
St. Cebria de Vallalta, Spain/1996[3]	50 WP	1.0/800	3/12, 14	0 7 14 21	0.38 0.04 <0.02 <0.02	<0.02 <.02 <0.02 <0.02	0.45 0.13 0.05 <0.02	2154/96 0767-96
Thurston, Suffolk, UK/1991[4]	4 RB	0.22	1	7 14	<0.02 <0.02	<0.02 <0.02	<0.02 <0.02	2139/91
Upchurch, Kent, UK/1991[4]	4 RB	0.22	1	7 14	<0.02 <0.02	<0.02 <0.02	<0.02 <0.02	2139/91
Bergen op Zoom, NL/ 1974	4 GR	0.12	1	3 7 14	<0.05 <0.05 <0.05			2103-74
Laacherhof, Germany/1974 (triplicate plots)	4 GR	0.12	1	3 7 10 14 21	<0.05 <0.05 <0.05 <0.05 <0.05			2100-74
Gorsem, Belgium/1975 (duplicate plots)	4 GR	0.16	1	0 4 7 14	<0.05 <0.05 <0.05 <0.05			2103-75

Location/year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	Form	kg ai/ha/ l/ha	No., days					
Nyborg, Denmark/1988 (triplicate plots)	4 GR	0.12	1	1 3 8 	0.10 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04			0329-88; 0330-88; 0331-88

[1]Recoveries from fortified controls (0.04 mg/kg) were 86 and 88% for methiocarb, 88 and 110% for methiocarb sulfone, and 91 and 103% for methiocarb sulfoxide.
[2]Recoveries from fortified controls (0.02-0.2 mg/kg, n = 7) were 67-83% for methiocarb, 71-96% for methiocarb sulfone and 71-105% for methiocarb sulfoxide.
[3]Recoveries from fortified controls (0.02, 0.20 mg/kg, n = 4) were 69-89% for methiocarb, 94-105% for methiocarb sulfone and 88-100% for methiocarb sulfoxide.
[4]Recoveries from fortified controls (0.02-0.50 mg/kg, n = 8) were 71-84% for methiocarb, 65-95% for methiocarb sulfone and 86-107% for methiocarb sulfoxide.

Wheat. Numerous residue trials were reported for wheat, but the company requested the withdrawal of all except two reports of field trials with an RB formulation in the UK (Seym, 1993a). GAP for cereals in the UK specifies application of a 20 g/kg RB formulation at 0.15 kg ai/ha or a 40 g/kg RB formulation at 0.22 kg ai/ha, with a 7-day PHI. The number of applications is not specified. Admixture at seeding, spreading and aerial applications are permitted. In the two UK trials, one application was made at drilling together with the seed and the second was spread about the ground. Samples were analysed by HPLC Method 00014, E005. The results are shown in Table 37. Recoveries of methiocarb from forage (0.1 and 1.0 mg/kg) were 101, 94 and 95%, from grain (0.04 and 0.4 mg/kg) 100, 96 and 93%, and from straw 93, 94 and 75%. Recoveries of methiocarb sulfone from forage (0.1 and 1.0 mg/kg) were 123, 119 and 103%; from grain (0.04 and 0.4 mg/kg) 98, 97 and 97%, and from straw (0.1 and 1.0 mg/kg) 112, 114 and 79%. Recoveries for methiocarb sulfoxide from forage (0.1 and 1.0 mg/kg) were 72, 70 and 90%; from grain (0.04 and 0.4 mg/kg) 91, 90 and 98%, and from straw (0.1 and 1.0 mg/kg) 101, 99 and 90%. The samples were stored frozen for 20 months before analysis.

Table 37. Residues of methiocarb and its metabolites in wheat, UK, 1991 (Seym, 1993a).

Location	Appli-cation rate, kg ai/ha	No. of applications/ interval, days	PHI (days)	Sample	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
Thurston, Suffolk	0.22	2/48	0 94 94	Forage Grain Straw	≤0.1 ≤0.04 ≤0.1	≤0.1 ≤0.04 ≤0.1	≤0.1 ≤0.04 ≤0.1	2039/91
Pointon, Lincolnshire	0.22	2/62	0 98 98	Forage Grain Straw	≤0.1 ≤0.04 ≤0.1	≤0.1 ≤0.04 ≤0.1	≤0.2 ≤0.04 ≤0.1	2039/91

Barley. Field trials were reported from Germany (Bayer AG, 1980b). Additional trial data were withdrawn by Bayer. A 4% RB formulation was spread on the ground twice. Samples were analysed by GLC Method 00040 (171). The trial results are shown in Table 38. GAP for Germany is 2 applications at 0.1 kg ai/ha/application of a 4% RB formulation at drilling and/or up to growth stage 29. The PHI is 7 days. Samples were stored for 3-5 months before analysis.

Table 38. Residues of methiocarb and its metabolites in barley, Germany, 1980 (Bayer AG, 1980b).

Location/ year	Application rate, kg ai/ha	No. of applic./interval, days	PHI, days	Sample	Methiocarb + methiocarb sulfone + methiocarb sulfoxide), mg/kg	Report no.
Albig	0.12	2/14	0 14 92 92	Forage Forage Straw Grain	≤0.05 <0.05 ≤0.05 ≤0.05	2102-80
Bursheid	0.12	2/14	0 21 80 80	Forage Forage Straw Grain	≤0.05 <0.05 ≤0.05 ≤0.05	2101-80
Monheim	0.12	2/14	0 21 76 76	Forage Forage Straw Grain	≤0.05 <0.05 ≤0.05 ≤0.05	2100-80

Maize. Trials on maize after seed treatment or application during drilling were conducted in Germany with a 500 g/kg FS formulation (Bayer AG, 1982, 1983). No residues were detectable (<0.05 mg/kg each of methiocarb, methiocarb sulfone and methiocarb sulfoxide). GAP for Northern Europe (Austria, Belgium, Germany, The Netherlands) specifies a seed treatment at 0.5 kg ai per 100 kg seed. The results of the trials are shown in Table 39. Analyses were by GLC, Method 00040.

Table 39. Residues of methiocarb and its metabolites in maize, Germany (Bayer AG, 1982, 1983).

Location/year	Rate (kg ai/100 kg seed)	PHI, days	Sample	Residue, methiocarb + methiocarb sulfone + methiocarb sulfoxide, mg/kg	Report no.
Daubersbach, 1982	0.5 (0.15 kg ai/ha)	174	Kernel	≤0.05	2105-82
Rosenberg, 1982	0.5 (0.15 kg ai/ha)	178	Kernel	≤0.05	2104-82
Fadengreuth, 1982	0.5 (0.16 kg ai/ha)	169	Kernel	≤0.05	2103-82
Ascheberg, 1982	0.5 (0.12 kg ai/ha)	91 187	Forage Kernel	≤0.1 ≤0.05	2102-82
Klein-Niedesheim, 1982	0.5 (0.4 kg ai/ha; seed rate 80 kg/ha)	90	Forage	≤0.1	2101-82
Versuchsgut Laacherhof, 1982	0.5 (0.15 kg ai/ha; seed rate 30 kg/ha)	90 184	Forage Kernel	≤0.1 ≤0.05	2100-82
Rodingen, 1983	0.5 (0.15 kg ai/ha)	90 113	Forage Cob	≤0.1 ≤0.1	2103-83
Hartefeld, 1983	0.5 (0.15 kg ai/ha)	90 126	Forage Cob	≤0.1 ≤0.1	2102-83
Laacherhof, 1983	0.5 (0.15 kg ai/ha; seed rate 30 kg/ha)	90 156	Forage Cob	≤0.1 ≤0.1	2101-83
Höfchen, 1983	0.5 (0.15 kg ai/ha; seed rate 30 kg/ha)	90 152	Forage Cob	≤0.1 ≤0.1	2100-83

Hazelnuts. Five trials were reported from Turkey (Bayer AG, 1987). GAP for Turkey is one foliar application of a 500 g/kg WP formulation at 0.6 kg ai/ha, with a 90-day PHI. The samples (nut without shell) were analysed by HPLC Method 00014, with a stated limit of determination of 0.04 mg/kg per component. The results are shown in Table 40.

Table 40. Residues of methiocarb and its metabolites in hazelnuts (without the shell) (Bayer AG, 1987).

Location	Application rate, kg ai./ha	Vol., l/ha	PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
Ordu-Unye-Inkur Akpinarkoye	0.75	200	90	≤0.04	≤0.04	≤0.04	2104-87
Giresun, Merkex-Usgurkoyu	0.75	100	86	≤0.04	≤0.04	≤0.04	2102-87
Giresun, Merkez-Citilak Kale mah	2 DP formulation 0.70	-	86	≤0.04	≤0.04	≤0.04	2103-87
Giresun, Kesap, Cakirli	2 DP formulation 0.70	-	87	≤0.04	≤0.04	≤0.04	2200-87
Giresun, Desap, Karaderekoyu	2 DP formulation 0.70	-	87	≤0.04	≤0.04	≤0.04	2101-87

Rape seed. Field trials were reported from Germany, with both a WP formulation (foliar application) and an RB formulation (ground application) (Bayer AG, 1979a,b, 1980a). GAP for Germany specifies two applications of a 20 g/kg RB formulation at 0.1 kg ai/ha with a 15-day PHI. No GAP was reported for the use of the WP formulation in Germany, but in France the WP formulation may be applied at 0.1 kg ai/hl, 15-day PHI, and in The Netherlands at 0.5 kg ai/ha in 200-600 l of water per hectare, one application only, PHI not specified. The results are shown in Table 41. Samples were analysed by GLC Method 171, with a stated limit of determination of 0.05 mg/kg. Samples were stored for 1-15 months before analysis.

Table 41. Residues of methiocarb and its metabolites in rape seed, Germany (Bayer AG, 1979a,b, 1980a).

Location/ year	Form.	Application rate, kg ai/ha/ vol., l/ha)	No. of applications/ interval, days	PHI, days	Sample	Residue, mg/kg (methiocarb + methiocarb sulfoxide + methiocarb sulfone)	Ref. No.
Gau-Odernheim/ 1979	50 WP	0.75/ 600	1	30 60 291 291	Forage Forage Straw Seed	≤0.05 <0.05 ≤0.05 ≤0.05	2100-79
Monheim/ 1979	50 WP	0.75/ 600	1	30 60 60 83 83	Forage Forage Pod Straw Seed	≤0.05 <0.05 <0.05 ≤0.05 ≤0.05	2100-79
Burscheid/ 1979	50 WP	0.75 600	1	129 59 59 96 96	Forage Forage Pod Straw Seed	<0.05 ≤0.05 <0.05 ≤0.05 ≤0.05	2100-79
Gau-Odernheim/ 1980	4 GR	0.12	2/14	0 14 61	Forage Forage Forage	<0.05 <0.05 <0.05	2106-80
Bursheid/ 1980	4 GR	0.12	2/14	0 21 98 98	Forage Forage Straw Seed	0.54 <0.05 <0.05 <0.05	2105-80
Monheim/ 1980	4 GR	0.12	2/14	0 21 108 108	Forage Forage Straw Seed Forage on day of first application	<0.05 <0.05 <0.05 <0.05 2.6	2104-80

Location/ year	Form.	Application rate, kg ai/ha/ vol., l/ha)	No. of applications/ interval, days	PHI, days	Sample	Residue, mg/kg (methiocarb + methiocarb sulfoxide + methiocarb sulfone)	Ref. No.
Pfalz/1980	4 GR	0.12	2/14	0 20 97	Forage Forage Seed	4.5 <0.05 <0.05	2113-80

Animal feeding studies

A poultry feeding study was conducted with methiocarb and methiocarb sulfoxide (9:1) (Strankowski and Minor, 1976; Chemagro, 1976). Twenty laying hens, approximately 25 weeks old, were acclimatized for a 2-week period, then divided into groups of four birds each and placed on a diet containing 0, 20, 60, 120 or 360 mg methiocarb/methiocarb sulfoxide per kg feed. Fresh ration (Purina) was supplied daily for 28 days with water *ad lib*. Food consumption was measured daily for each group. The calculated average intakes (mg methiocarb/methiocarb sulfoxide per kg bw per day) were 0, 1.3, 3.6, 6.3 and 24. Body weights and feed consumptions were not reported. Eggs were collected on even days, combined by group (without the shell) and stored frozen. Egg production was constant within each group over the trial period.

The hens were weighed before the study and immediately before slaughter. The 120 and 360 ppm groups showed a weight loss of 2-13%. Giblets, muscle, fat and skin were collected by group. Tissues and eggs were extracted and analysed for methiocarb and methiocarb sulfoxide. Details were not reported. The results of the analyses are shown in Table 42.

Table 42. Residues of methiocarb and methiocarb sulfoxide in poultry tissues and eggs (Strankowski and Minor, 1976).

Feed concentration, mg methiocarb + methiocarb sulfoxide per kg feed	Methiocarb + methiocarb sulfoxide, mg/kg				
	Giblets (heart, gizzard, liver)	Muscle	Skin	Fat	Eggs (28 days)
0	<0.02	<0.02	<0.02	<0.02	<0.02
20	<0.02				<0.02
60	0.06		<0.02		<0.02
120	0.13	<0.02	<0.02	<0.02	0.03
360	0.13	<0.02	0.02	<0.02	0.06

In a cattle feeding study (Chemagro, 1970a) two cows and seven beef cattle, in groups of three, were dosed with 0.30, 0.90, or 3.0 mg methiocarb/kg bw/day for 29 days, equivalent to 10, 30, or 100 ppm in the diet assuming that the livestock would consume 3% of total body weight in dry feed daily. Both cows were in the 100 ppm group. The animals were slaughtered after the last dose and tissues analysed for total methiocarb.

In a separate feeding study (Chemagro, 1970b) three groups of three dairy cows were fed diets containing 10, 30, or 100 ppm methiocarb for 29 days. Residues were reported in the milk from day 29 only.

The results of the two studies are shown in Table 43.

Table 43. Residues of methiocarb in milk and tissues from dairy cows and beef cattle (Chemagro, 1970a,b).

Feeding level (ppm)	Sample	Methiocarb, mg/kg
10	Liver	<0.05
	Kidney	<0.05
	Muscle	<0.05
	Omental fat	<0.05
	Renal fat	<0.05
	Back fat	<0.05
	Milk (day 29)	0.007
30	Liver	0.08
	Kidney	<0.05
	Muscle	<0.05
	Omental fat	<0.05
	Renal fat	<0.05
	Back fat	<0.05
	Milk (day 29)	0.020
100	Liver	0.10
	Kidney	0.08
	Muscle	<0.05
	Omental fat	<0.05
	Renal fat	<0.05
	Back fat	<0.05
	Milk (day 29)	0.033

The calculated dietary burden for poultry and cattle is shown in Table 44.

Table 44. Estimate of residue intake of methiocarb by farm animals.

	Feedstuff in diet, %	Dry matter in feedstuff, %	Residue in crop, mg/kg	Dietary burden, ppm in feed
Dairy cattle				
Maize				
grain	40	80	0.1 *	0.05
stover	10	83	0.1*	0.01
Cereal (wheat)				
forage	60	25	0.1*	0.24
Total	100			0.30
Beef Cattle				
Maize				
grain	60	80	0.1*	0.14
stover	0	83	0.1*	0.00
Cereal (wheat)				
forage	25	25	0.1*	0.120
Total	100			0.24
Poultry				
Maize				
grain	80	88	0.1*	0.09
Cereal (wheat)				
grain	20	89	0.05*	0.011
Total	80			0.1

The 0.1 ppm in the diet for poultry is less than one thousandth of the concentration at which residues were detected in poultry products in the feeding study. The 0.3 ppm in the diet for cattle is one thirtieth of the concentration at which no residues (<0.05 mg/kg) were found in tissues and at which the residue in milk was 0.007 mg/kg.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were provided.

In processing

Processing studies were reported on potatoes, peppers and strawberries.

Potatoes. Potatoes without a methiocarb residue (<0.02 mg/kg) from the UK field trials (Table 26) were thinly peeled, washed gently and cooked under pressure in water (12 min at 110˚C). The experiment was designed to mimic household preparation. As no residues (<0.02 mg/kg) were found in the peel or cooked potatoes processing factors could not be determined (Seym and Walz-Tylla, 1993a).

Strawberries. Strawberries from field trials in Callela, Spain (Table 36) were processed into jam and preserved fruit, using a household procedure (Seym and Walz-Tylla, 1993c). The strawberries contained 0.17 mg/kg methiocarb and 0.16 mg/kg methiocarb sulfoxide at the 7-day PHI. Damaged fruits and the calyx and stalks were removed. The strawberries were washed in standing water with slow movement, then minced and mixed with a jelly sugar. The mixture was stirred and brought to the boil for 10 minutes. The resulting jam was placed in polystyrene boxes. For preserved fruit, washed strawberries were mixed with a sugar solution and pasteurized in an autoclave. All samples were stored at –20°C until analysed by an HPLC procedure, 00014, M001, E007. The mass balance of the residues was not reported.

Recoveries from control samples of jam and preserve fortified at 0.04 mg/kg of each analyte were 63 and 65% in preserve and 83 and 90% in jam for methiocarb, 103 and 104% in preserve and 71 and 72% in jam for methiocarb sulfone, and 91 and 95% in preserve and 92 and 105% in jam for methiocarb sulfoxide.

The results are shown in Table 45.

Table 45. Effect on residues of processing strawberries containing methiocarb and methiocarb sulfoxide[1] (Seym and Walz-Tylla, 1993c).

Sample	Methiocarb		Methiocarb sulfoxide	
	mg/kg	processing factor	mg/kg	processing factor
Strawberry	0.35	-	0.19	-
Washed strawberry	0.17	0.48	0.16	0.84
Strawberry jam	0.08	0.23	0.12	0.63
Strawberry preserve	0.09	0.26	0.09	0.47

[1]Methiocarb sulfone was absent from the fruit and processed fractions (<0.04 mg/kg).

Peppers. Processing studies (Seym, 1997; Seym and Walz-Tylla, 1993b) were conducted on peppers from field trials in Spain and Portugal (Table 32). The peppers from Spain (two trials) were washed and canned, and those from Portugal were washed. The results are shown in Table 46.

Table 46. Effect on residues of methiocarb and its sulfoxide[1] in peppers of washing and canning (Seym, 1997; Seym and Walz-Tylla, 1993b).

Location	Sample	PHI, days	Methiocarb		Methiocarb sulfoxide	
			mg/kg	processing factor	mg/kg	processing factor
Malgrat, Spain	Fruit	7	0.82	-	0.38	-
	Fruit washed	7	0.20	0.24	0.20	0.53
	Preserved	7	0.07	0.08	0.07	0.18
	Fruit	10	0.28	-	0.22	-
	Fruit washed	10	0.25	0.89	0.23	1.0
	Preserved	10	0.04	0.14	<0.04	0.18
Viladecans, Spain	Fruit	7	1.1	-	0.43	-
	Fruit washed	7	0.26	0.24	0.29	0.67
	Preserved	7	0.13	0.12	0.07	0.16
	Fruit	10	0.15	0.14	0.14	0.32
	Fruit washed	10	0.14	0.13	0.10	0.23
	Preserved	10	<0.04	0.04	<0.04	0.09
Bordinheira, Portugal	Fruit	7	0.13	-	0.10	-
	Fruit washed	7	0.06	0.46	0.09	0.90
	Fruit	14	0.03	0.23	0.03	0.30
	Fruit washed	14	<0.02	0.15	<0.02	0.20

[1]Methiocarb sulfone was absent from all samples.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Information was supplied by the governments of Australia and The Netherlands. Results of the analysis of fruit and vegetable samples purchased weekly from the Sydney wholesale markets are shown in Table 47.

Table 47. Monitoring of methiocarb residues in Australia (Sydney) from 1989 to 1995.

Commodity	No. of samples	No. with residues >0.01 mg/kg
Grapes	94	5 (< MRL of 0.1 mg/kg)
Strawberries	113	1 (< MRL of 0.1 mg/kg)
Citrus	1	0
Apples	1	0
Pears	2	0
Cherries	48	0
Nectarines	28	0
Peaches	139	0
Onion	1	0
Broccoli	2	0
Zucchini	1	0
Lettuce	1	0
Capsicum (pepper)	1	0
Mushroom	1	0
Tomato	1	0
Beans	2	0
Carrot	1	0
Potato	1	0
Celery	102	0

The Netherlands submitted monitoring data on residues of methiocarb in food in commerce for the period 1994-1996 and for 1997. The results are shown in Tables 48 and 49.

Table 48. Residues of methiocarb in food in commerce in The Netherlands, 1995-1996.

Commodity	No. of samples analysed	No. with residues ≥0.05 mg/kg (LOD)	Residues, mg/kg
Pome fruit	1496	0	
Apple			
Stone fruit	437	0	
Plums			
Berries and small fruit	667	1	0.24
Grapes, strawberries			
Miscellaneous fruit	191	1	0.07
Mangoes			
Root and tuber vegetables	1010	0	
Radish			
Bulb vegetables	97	0	
Onions			
Fruiting vegetables	1108	0	
Tomato	1525	4	0.05-0.34
Pepper (sweet)	951	0	
Cucumbers	206	0	
Courgettes			
Brassica vegetables	297	3	0.05-1.0
Chinese cabbage			
Leafy vegetables and fresh herbs			
Lamb's lettuce	268	0	
Lettuce	3306	0	
Iceberg lettuce	471	0	
Endive	1137	0	
Parsley	368	2	0.05
Stem vegetables	233	0	
Celery			
Other arable products	699	1	0.09
Processed products	23	0	

Table 49. Residues of methiocarb in food in commerce in The Netherlands, 1997.

Commodity	No. of samples analysed	No. with residues ≥0.05 mg/kg (LOD)	Residues, mg/kg
Berries and small fruits			
Grapes	196	1	0.22
Strawberries	779	4	0.05-1.3
Other fruits and fruit products	152	1	0.10
Root and tuber vegetables	164	1	1.4
Carrots			
Fruiting vegetables			
Peppers (sweet)	607	12	0.05-1.6
Cucumbers	249		
Brassica vegetables	116	1	1.1
Chinese cabbage			
Leaf vegetables and fresh herbs			
Lambs lettuce			
Lettuce	53		
Endive	828	1	1.1
Chervil	366	1	1.5
Parsley	8	1	0.09
Other leafy vegetables	85	1	0.08
	114	4	0.12-1.6
Stem vegetables	187	2	0.05-0.34
Celery			

NATIONAL MAXIMUM RESIDUE LIMITS

National MRLs were reported by Bayer AG and by the governments of Australia and The Netherlands.

Country, Residue definition Commodity	MRL, mg/kg	Notes
Argentina		
Sum of methiocarb, its sulfoxide and sulfone, expressed as methiocarb		
Apple	0.01	
Garlic	0.05	
Lettuce	0.2	
Onion	0.05	
Peach	0.1	
Pear	0.01	
Tomato	0.02 T	
Citrus fruit	0.1	
Grape	0.5	
Grape wine	0.1	
Other fruit	0.1 T	
Vegetables	0.1	
Wine	0.1	
Austria		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Fruit	0.2	
Lettuce	1	
Other plant commodities	0.05	
Belgium		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Cabbage	0.1	
Cucumber	0.3	
Leafy vegetables	1	
Leek	0.1	
Other plant commodities	0	<LOD 0.05 mg/kg
Croatia		
Hazel nut	0.05	
Maize/Corn	0.05	
Other vegetables	0.1	
Rape	0.05	
Root vegetables	0.2	
Sunflower	0.05	
Finland		
Plum	0.5	
France		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Berries	0.1	
Lettuce	0.2	
Other vegetables	0.1	
Rape	0.1	
Germany		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Lettuce and similar	1	
Other plant commodities	0.1	
Pome fruit	0.2	
Israel		
Sum of methiocarb, its sulfoxide and sulfone, expressed as methiocarb		
Forage crops	0.01	
Fruit	0.01	
Vegetables	0.01	
Italy		
Alfalfa	0.05	

Country, Residue definition Commodity	MRL, mg/kg	Notes
Almond	0.05	
Artichoke	0.05	
Asparagus	0.05	
Aubergine	0.05	
Bean	0.05	
Bean green	0.05	
Beet, sugar	0.05	
Cabbage	0.05	
Carrot	0.05	
Celery	0.05	
Clover	0.05	
Cucurbits	0.05	
Fennel, common	0.05	
Grape	0.05	
Herbs	0.05	
Leafy vegetables	0.05	
Lettuce and similar	0.05	
Other solanacea	0.05	
Pea, garden without pods	0.05	
Pepper, sweet	0.05	
Pome fruit	0.05	
Potato	0.05	
Radish	0.05	
Spinach and similar	0.05	
Stone fruit	0.05	
Strawberry	0.05	
Tobacco	0.05	
Tomato	0.05	
Luxembourg		
Lettuce	1	
Other plant commodities	0.05	
Pome fruit	0.2	
Malaysia		
Fruit	0.05	
Leafy vegetables	0.1	
Rice	0.5	
Root vegetables	0.1	
Vegetables excluding leafy vegetables	0.1	
Netherlands		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb sulfone		
Cucumber	0.5	
Flowering brassicas	0.1	
Head brassicas	0.1	
Leafy vegetables	1	
Lettuce and similar	1	
Melon	0.5	
Other vegetables	0.05	At or about the LOD
Leeks	1	
New Zealand		
Blueberry	25	
Cherry	7	
Paraguay		
Rice grain, hulled	0.05	
South Africa		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Apple	0.2	
Apple	0.05 E	
Apricot	0.05 E	
Citrus fruit	0.1	

Country, Residue definition Commodity	MRL, mg/kg	Notes
Grape	0.2	
Grape	0.05 E	
Nectarine	0.05 E	
Peach	0.05 E	
Pear	0.2	
Pear	0.05 E	
Plum	0.2	
Plum	0.05 E	
South Korea		
Barley	0.05	
Buckwheat, common	0.05	
Cabbage	0.2	
Cherry	5	
Grapefruit	0.05	
Lemon	0.05	
Oat	0.05	
Orange	0.05	
Other cereals	0.05	
Other citrus fruit	0.05	
Pe-tsai	0.2	
Peach	5	
Rice	0.05	
Rye	0.05	
Sorghum grain	0.05	
Wheat	0.05	
Spain		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Bean pods and/or immature seeds	0.2	
Beet, sugar	0.05	
Berry, wild	0.05	
Brassica vegetables	0.05	
Bulb vegetables	0.05	
Cacao	0.05	
Cereals	0.05	
Citrus fruit	0.05	
Coffee	0.05	
Cola	0.05	
Corn, sweet	0.05	
Cucumber	0.2	
Forage crops and straw	0.05	
Fruit and vegetables, dried	0.05	
Grape	0.05	
Herbs	0.05	
Hop	0.05	
Leafy vegetables	0.05	
Mushroom	0.05	
Nuts	0.05	
Oil plants seed	0.05	
Other berries and small fruits	0.05	
Other cucurbits with edible peel	0.05	
Other cucurbits with inedible peel	0.05	
Other legume vegetables	0.05	
Other solanacea	0.05	
Pea pods and/or immature seeds	0.2	
Pepper, sweet	1	
Pome fruit	0.05	
Potato	0.05	
Pulses	0.05	
Root and tuber vegetables	0.05	

Country, Residue definition Commodity	MRL, mg/kg	Notes
Rubus-Species (Cane fruit)	0.05	
Spices	0.05	
Stem vegetables	0.05	
Stone fruit	0.05	
Strawberry	0.2	
Sugar cane	0.05	
Tea	0.05	
Tobacco	0.05	
Tomato	0.2	
Tropical and subtropical fruit	0.05	
Switzerland		
Sum of methiocarb, its sulfoxide and sulfone, expressed as methiocarb		
All plant commodities	0.05	<LOD
Taiwan		
Sum of methiocarb, its sulfoxide and sulfone		
Melon	0.5	
Melon, Water-	0.5	
Uruguay		
Rice grain, hulled	0.05	
USA		
Methiocarb and cholinesterase-inhibiting metabolites		
Citrus fruit	0.02	
Corn, sweet (corn-on-the-cob)	0.03	
Maize/Corn fodder	0.03	
Maize/Corn forage	0.03	
Maize/Corn fresh	0.03	
Maize/Corn grain	0.03	
Peach	5	
Popcorn grain	0.03	

T = Temporary tolerance
E = Export tolerance
LOD = Limit of determination

APPRAISAL

Methiocarb was identified by the 1995 CCPR as a candidate for periodic review (ALINORM 95/24A, Annex 1). The periodic review of toxicology was in 1998 and the present evaluation is a periodic review of residue aspects. The most recent extensive residue reviews were in 1981 and 1983.

Animal metabolism

The metabolism of [*phenyl*-1-^{14}C]methiocarb was studied in rats, dairy cows and chickens.

[*Phenyl*-1-^{14}C]methiocarb was administered at dose levels of 20 and 0.25 mg/kg body weight to rats. Most of the administered radioactivity was excreted with the urine in 48 hours, >90% in the high-dose group and >70% in the low-dose group. The main metabolites in the organic extracts of the urine were methiocarb phenol and methiocarb sulfoxide phenol. The same study was evaluated in the 1998 review of the toxicology.

A dairy cow (500 kg) was dosed by capsule with radiolabelled methiocarb at 0.14 mg/kg bw/day for 5 consecutive days. The residue in the milk peaked at 0.062 mg/kg as methiocarb on day 3. The total residues in the meat and fat were not quantifiable, <0.01 mg/kg. The total residues in the kidneys and liver were 0.108 and 0.073 mg/kg respectively. The following metabolites were identified, by TLC only, in milk: methiocarb sulfoxide phenol and conjugates 27% of the TRR; methiocarb sulfone phenol and

conjugates 26% of the TRR; methiocarb sulfoxide 3% of the TRR; in kidney: methiocarb phenol and conjugate 55% of the TRR; methiocarb sulfoxide phenol 7% of the TRR; methiocarb sulfone phenol 17% of the TRR; in liver: methiocarb phenol and conjugate 25% of the TRR; methiocarb sulfoxide phenol and conjugate, 9% of the TRR; methiocarb sulfone phenol and conjugate 6% of the TRR; methiocarb and conjugate 14% of the TRR. Methiocarb was found only in the liver.

Eight hens were dosed with [^{14}C]methiocarb for 5 consecutive days at 4.4 mg/kg bw/day. All eggs contained <0.1 mg/kg methiocarb equivalents. The total residues were 0.45 mg/kg in the muscle, 0.7 mg/kg in fat, 2.0 mg/kg in liver and 3.3 mg/kg in kidney.

Tissue extracts were analysed by two-dimensional TLC only. The main residues in fat were methiocarb 41% of the TRR, methiocarb phenol and conjugate 26%, methiocarb sulfoxide phenol and conjugate 9% and *N*-hydroxymethyl-methiocarb 7% of the TRR. The main radioactive compounds in the muscle were methiocarb 7% of the TRR, methiocarb phenol and conjugate 16%, methiocarb sulfoxide phenol and conjugate 28% and *N*-hydroxymethyl-methiocarb sulfoxide 17%. The main residue in the liver were methiocarb phenol and conjugate 17% of the TRR, methiocarb sulfoxide phenol and conjugate 24%, methiocarb sulfone phenol and conjugate 11% and *N*-hydroxymethyl-methiocarb sulfoxide 6% of the TRR.

The Meeting concluded that the livestock metabolism studies were marginally acceptable and that the metabolism of methiocarb in ruminants and poultry was sufficiently understood. Critical data, such as feed consumption to determine the concentration of the administered pesticide on a feed basis, were not provided. Identifications were based only on TLC and should have been confirmed by other techniques. No detailed information was supplied on the periods of storage of the samples and extracts before analysis or of the stability of methiocarb and its metabolites under the storage conditions.

Methiocarb is extensively metabolized in ruminants and poultry by ester cleavage, followed by oxidation of the resulting phenol to the sulfoxide and sulfone. A competing pathway observed only in hens is hydroxylation of the carbamate methyl and oxidation of the sulfur to sulfoxide. The metabolites found in rat urine suggest a similar metabolism.

Plant metabolism

Studies were on rice, tomatoes, lettuce and apples.

In the apple study, [*phenyl*-1-^{14}C]methiocarb was applied directly to the surface of apples on a tree with a syringe, with both single and multiple applications. The total residue on the apples after the last of 8 treatments was 4.52 mg/kg as methiocarb, of which 0.67 mg/kg was in the pulp. Of the total radioactive residue, 24% was in the benzene wash of the whole apple, 60% in the peel and 15% in the pulp. The residue in the whole apple consisted of 61% methiocarb, 6.5% methiocarb sulfoxide, 4.6% methiocarb phenol, 22% methiocarb sulfoxide phenol and 1.1% methiocarb sulfone phenol.

In a study of the translocation of [*phenyl*-1-^{14}C]methiocarb from soil to lettuce and tomato seedlings the methiocarb was applied at 1.12 kg ai/ha to the sandy soil in which the plants were growing. Translocation was rapid. Seven days after the application, 45% of the applied radioactivity was in the lettuce plants and 26% was in the tomato plants.

Rice at the soft dough stage was sprayed with [*phenyl*-1-^{14}C]methiocarb at 2.24 kg ai/ha. Some plants were sprayed again at the same rate 9 days later. The plants were harvested 0, 6, 14, 21 or 28 days after the first or second application and separated into grain heads and stalks. In both rice grain and stalks, 95–98% of the recovered radioactivity was organosoluble on the day of application, but this decreased to 63–72% 28 days after both single and double applications. The organic extracts of grain and stalks were analysed only by TLC. The composition of the residue in the organic extracts on the day of the single application was 94% methiocarb, 2% methiocarb sulfoxide and about 1% each of methiocarb sulfone

phenol and methiocarb sulfoxide phenol in the stalks. *N*-hydroxymethyl-methiocarb sulfoxide was also detected in later samples. After 28 days the organic extract contained 11% methiocarb, 32% methiocarb sulfoxide, 11% methiocarb sulfoxide phenol and 3% each of *N*-hydroxymethyl-methiocarb sulfoxide and methiocarb sulfone in the grain and 20% methiocarb, 36% methiocarb sulfoxide, 10% methiocarb sulfoxide phenol and 2% methiocarb sulfone phenol in the stalks.

The Meeting concluded that the plant metabolism studies were marginally satisfactory and adequately defined the metabolism of methiocarb in plants. Only the studies on apples and rice determined the nature of the residues in the edible portions and the overall ^{14}C balance could not be determined from the information provided. Identifications were by TLC only: other techniques should have been used to confirm identities and to investigate unidentified compounds. No information was provided on the periods of storage of the samples and extracts or the stability of methiocarb and its metabolites under the storage conditions. The studies are not representative of such major uses as seed treatment and application to the soil as a bait or by incorporation.

Methiocarb is readily translocated. Metabolism is by ester cleavage and oxidation of the resulting phenols to sulfoxides and sulfones. The parent compound may also undergo conversion to the sulfoxide and sulfone and *N*-hydroxymethyl compounds. The metabolic products in livestock and plants are similar.

Environmental fate

Rotational crops. Two studies were conducted. In the first, radiolabelled methiocarb was incorporated into sandy loam soil at 5.6 kg ai/ha. Sweet corn was planted as the main crop and harvested at normal maturity. The land lay fallow until the following year when rotational crops of wheat, sugar beet and spinach were planted. At 399 days after application wheat forage contained 0.15 mg/kg methiocarb equivalents and sugar beet tops contained 0.108 mg/kg. At 450 days after application, sugar beet tops contained 0.071 mg/kg methiocarb equivalents, roots contained 0.252 mg/kg and spinach contained 0.225 mg/kg. Spinach taken 450 days after application and wheat heads (0.066 mg/kg), stalks (0.141 mg/kg) and forage (0.323 mg/kg) from 551 days after application were extracted and the extracts analysed by TLC. The main residue component in spinach was methiocarb sulfoxide phenol, 26% of the total radioactive residue (0.058 mg/kg). The main compounds in wheat forage were methiocarb sulfoxide at 12% (0.039 mg/kg) and methiocarb sulfone at 10%, in wheat stalks methiocarb sulfoxide phenol at 7% and methiocarb sulfone at 8% (0.011 mg/kg) and in the wheat heads *N*-hydroxymethyl-methiocarb 12% (0.008 mg/kg), methiocarb sulfoxide phenol at 14% and methiocarb sulfone at 11%.

In the second study, unlabelled methiocarb was applied to bare soils in the USA at rates of 1.4–11.2 kg ai/ha. Rotational crops (sorghum, wheat, snap beans, peas, carrots, radishes, maize, corn, black-eyed-peas, turnips) were planted at intervals of 30 days during 365 days after the application. Samples were analysed for combined residues of methiocarb, methiocarb sulfone and methiocarb sulfoxide. No residues were detected (<0.02 mg/kg total) in any edible portion of the vegetables or grain planted 30 or more days after application of the methiocarb at rates up to 11.2 kg ai/ha. Green vines and green forage contained total residues after treatment at 11.2 kg ai/ha of 0.14 mg/kg in corn forage (30-day plantback), 0.15 and 0.07 mg/kg in black-eyed pea vines at 30 and 90-day plantbacks respectively and 0.29 mg/kg in turnip tops (30-day plantback).

Degradation in soil

Soil was treated with 7 mg/kg [*phenyl*-1-^{14}C]methiocarb, equivalent to 11.5 kg ai/ha and watered weekly. Samples were taken at intervals up to 16 weeks, extracted and analysed by TLC. The proportion of organic- and water-extractable radioactivity decreased from 76% at week 4 to 67% at week 16. The distribution of radioactivity changed slightly during the period. Methiocarb accounted for 49% of the applied radioactivity at 4 weeks and 30% at 16 weeks. Methiocarb sulfoxide and its conjugate remained constant at 20–22% of the applied radioactivity. Methiocarb sulfoxide phenol increased from 5.3% to 15%.

A more detailed study under aerobic conditions with dry sandy loam soil at an application rate of 1.44 mg/kg showed that extractable residues decreased from 100% of the applied radioactivity on day 0 to 27% on day 217 and bound residues increased to 43% over the same period. Radioactive carbon dioxide appeared on day 29 and increased to 30% of the applied radioactivity on day 217. Methiocarb decreased from 96% of the residue on day 0 to 3% on day 217. On day 29 the main radioactive compounds as a percentage of the applied radioactivity were methiocarb 24%, methiocarb sulfoxide 30%, methiocarb sulfoxide phenol 16%, methiocarb sulfone 1% and methiocarb sulfone phenol 3%. The degradation followed biphasic first-order kinetics, with half lives of 17.7 days and 111 days.

A soil sample from the above experiment was taken after 14 days and the conditions made anaerobic by covering the sample with water (pH 5) and purging continuously with nitrogen. The system was sampled 0–64 days after conversion to the anaerobic environment. The extractable proportion decreased only slightly, from 87 to 76%. Methiocarb decreased from 55% to 27% and methiocarb phenol increased from 0 to 47%. Methiocarb sulfoxide was readily hydrolysed to methiocarb sulfoxide phenol. Volatile compounds accounted for <4% of applied radioactivity.

A more recent study with radiolabelled methiocarb applied to soil at a rate of 100 g ai/ha was not made available to the Meeting, but new half-lives based on first order kinetics were calculated in various types of soil. Under aerobic conditions, methiocarb had a half-life of 1–2 days and methiocarb sulfoxide a half-life of 2–6 days.

The photolysis of [*phenyl*-1-^{14}C]methiocarb on the surface of sandy loam soil exposed to natural sunlight was compared with controls maintained in the dark. After 30 days methiocarb accounted for 47% of the radiolabelled residue on irradiated soil and 75% on control soil. The main product was methiocarb sulfoxide, 23% of the radiolabelled residue on irradiated soil at 30 days and 3.1% on the control soil. Both photolytic and non-photolytic degradation was occurring. Calculated half-lives were 28 days for irradiated samples and 81 days for dark controls.

Adsorption and desorption constants for various soils were determined for [*phenyl*-1-^{14}C]methiocarb, [*phenyl*-1-^{14}C]methiocarb phenol, [1-*phenyl*-^{14}C]methiocarb sulfoxide and [*phenyl*-1-^{14}C]methiocarb sulfoxide phenol. Methiocarb sulfoxide was rapidly degraded and was not adsorbed by soil; within 24 hours of application the soil contained only methiocarb sulfoxide phenol. Methiocarb showed moderately high K_d values, suggesting significant adsorption to all types of soil. The K_d for adsorption ranged from 4.3 ml/g in sandy loam to 9.0 ml/g in silt loam and for desorption from 6.7 in sandy loam to 16.2 in silt loam. The K_d for adsorption of methiocarb sulfoxide phenol ranged from 0.19 in sand to 0.66 in sandy loam and for desorption from 0.74 in sand to 1.6 in silty clay. Methiocarb sulfoxide phenol showed low adsorption to all the soils.

In a leaching experiment [*phenyl*-1-^{14}C]methiocarb was added to sandy loam soil at 37 mg/kg. The soil was aged aerobically for 30 days and an aliquot was extracted and analysed. The residues in the aged soil consisted of 80% methiocarb, 7% methiocarb sulfoxide, 6% methiocarb sulfoxide phenol and 6% insoluble. The leaching rate with 0.01 N aqueous calcium chloride solution through sand, sandy loam and silty loam was compared. Over a 5-day period 1.1 l of the aqueous solution was passed through columns of soil topped with the treated soil (20 g). The leachate from sand, sandy loam and silty loam contained 23%, 7% and 3% of the applied radioactivity respectively. Sand retained 71% of the applied radioactivity, sandy loam 92% and silty loam 93%. The sand leachate contained 2% methiocarb and 12% methiocarb sulfoxide and the sandy loam and silty loam contained more methiocarb sulfoxide than methiocarb, although the concentrations were very low. The results indicate that methiocarb sulfoxide is more readily leached than methiocarb.

Fate in water/sediment systems. The degradation of [*phenyl*-1-^{14}C]methiocarb in aerobic and anaerobic aquatic systems was investigated. The radiolabelled material was added to pond water at 2 mg/l in glass jars. For the anaerobic study, preconditioned soil was also added. The jars were wrapped in black plastic

and maintained in a greenhouse. Jars were removed at intervals of 0–112 days and the contents radio-analysed, extracted and the extracts analysed by TLC. In the aerobic system methiocarb disappeared in 3 days and in the anaerobic system 5% remained after 7 days. By day 56 42% of the radioactivity was bound to the soil in the anaerobic system. The main products in the aerobic system (water phase) were methiocarb phenol and methiocarb sulfoxide phenol. The main product in the anaerobic system was methiocarb phenol.

The half-lives of [*phenyl*-1-^{14}C]methiocarb in buffered aqueous solutions were determined in the dark at 25°C. On the basis of first-order kinetics, the half-lives were 320, 21 and 0.21 days at pH 5, 7 and 9 respectively. Methiocarb is unstable under alkaline conditions. At pH 5 the main product was methiocarb sulfoxide (1-9%) and at pH 7 methiocarb phenol, 46% at day 30. At pH 9 after 7 days, the main compounds were methiocarb phenol 78% and methiocarb sulfoxide phenol 10%. At pH 5 and 7 about 1% of *N*-hydroxymethyl-methiocarb was found and at pH 9 about 1% of *N*-hydroxymethyl-methiocarb sulfone.

The photochemical degradation of [*phenyl*-1-^{14}C]methiocarb in pH 5.0 aqueous solution at 25°C exposed in quartz tubes to natural sunlight for 30 days. Controls were maintained in the dark. The only product identified was methiocarb sulfoxide, 13% of the applied radioactivity when irradiated and 1% in the dark. The photolysis half-life was calculated as 88 days and 128 days corrected for non-photolytic degradation.

The Meeting concluded that the environmental fate of methiocarb is adequately known. In both soil and aqueous environments, methiocarb is degraded to the sulfoxide or loses the carbamate group, yielding methiocarb phenol. The half-life of methiocarb in soil has been variously determined as 1–2 days and 18 days, with the former more reflective of typical concentrations of methiocarb in soil. Methiocarb is relatively stable to sunlight, both on soil and in water. It is adsorbed by soils of various types and is not readily leached, whereas methiocarb sulfoxide is leached. Methiocarb sulfoxide phenol is formed by the rapid degradation of methiocarb sulfoxide in soil and is not adsorbed by a range of soils. Methiocarb is unstable in alkaline aqueous solutions with a half-life of 0.21 days.

The degradation products found in soil and water do not differ from those found in plant metabolism studies, except methiocarb sulfone quinone, which accounted for 8% of the extractable radioactivity in sandy loam soil incubated under aerobic conditions in the dark for 217 days.

Analytical methods

Numerous analytical methods are available both for data collection and for enforcement. Generally, the GLC methods determine the sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone as methiocarb sulfone after a potassium permanganate oxidation step. The HPLC methods determine methiocarb, methiocarb sulfone and methiocarb sulfoxide as individual compounds.

In the GLC methods, such as Bayer Method 171 and DFG Method 79-A-1, plant samples are extracted with acetone and 0.5 N HCl. The filtrate is extracted with chloroform and the chloroform solvent changed to acetone. The acetone solution is precipitated with ammonium chloride and phosphoric acid, the filtrate extracted with chloroform and the chloroform again changed to acetone. This solution is oxidized with 0.1 M potassium permanganate for 15 minutes at room temperature. The residues are silylated and determined by GLC with a flame photometric detector. Variations of the sample preparation are available for milk and animal tissues. Calibration is with external standards, using a log-log calibration curve. The validated limit of determination is 0.05 mg/kg except for milk, for which it is 0.005 mg/kg.

In Bayer Method 172 basic hydrolysis follows the permanganate oxidation. The resulting sulfones and sulfone phenols are cleaned up, derivatized and determined as before. The limit of determination is 0.01 mg/kg. Recoveries are generally >80%.

Method I340 is a modification of Bayer Method 172 for poultry commodities. The ground tissue sample is extracted with acetonitrile and partitioned with hexane. Eggs are blended with acetone and partitioned with methylene chloride. The solvent is changed to acetonitrile and the solution is partitioned with hexane. The acetonitrile extracts of tissues and eggs are evaporated, redissolved in acetone and precipitated with ammonium chloride solution. The mixture is filtered and oxidized as in Method 171. The methylene chloride extract of the oxidation mixture is hydrolysed with sodium hydroxide, 2.5 N at 60°C for 30 min. The hydrolysis products are derivatized with BSTFA and determined as in Method 171. A capillary column is specified. The limit of determination is 0.02 mg/kg.

HPLC methods, such as Bayer Method 00014 and its many modifications, employ specific extraction procedures for green foliage of grain, fatty substrates (nuts) and fat-free materials (cucumber). Modification M004 is specifically designed for strawberries, melons, tomatoes, leek, lettuce and bell peppers. Plant material is macerated with methylene chloride and the extract is concentrated to an aqueous residue, to which is added salt, HCl (for strawberries, leeks and melons only) and water. The solution is cleaned up on a solid-phase extraction column and the methylene chloride eluate is analysed by HPLC.

HPLC includes post-column hydrolysis (0.05 N caustic soda, 90°C) and derivatization with *o*-phthalaldehyde and mercaptoethanol in borate buffer. The methylamine released by the basic hydrolysis of the carbamate reacts with the derivatizing agent to form 1-hydroxyethylthio)-2-methylisoindole, detected by fluorescence. Fortified recoveries indicate limits of determination of 0.04 or 0.02 mg/kg for each analyte, with limits of detection of about 0.006 mg/kg.

The Meeting concluded that adequate analytical methods exist for enforcement and data collection for methiocarb, methiocarb sulfoxide and methiocarb sulfone.

Stability of residues in stored analytical samples

Methiocarb and methiocarb sulfoxide were stable in blueberries stored frozen for 118 days at–23^{o}C. The study was performed with samples fortified at 2.8 mg/kg and 3.3 mg/kg with radiolabelled methiocarb and methiocarb sulfoxide respectively. The percentage remaining was approximately 99% after the storage interval.

Summary information only was supplied on the stability (at 0 to –10^{o}C) of methiocarb, methiocarb sulfoxide and methiocarb sulfone in beans, grapes, cabbage, rice, tomatoes, broccoli, Brussels sprouts and cauliflower. Except for Brussels sprouts and broccoli, the data indicated that methiocarb and the metabolites are stable for up to 380 days. Details were not provided and concurrent method recoveries were not performed at each storage interval.

Samples from field trials were stored frozen for 1 month to 2 years before analysis.

The Meeting concluded that the information on storage stability is inadequate, except for berries, and that the residues reported from field trials might be understated if methiocarb and its sulfone and sulfoxide metabolites are unstable under the storage conditions used for the samples. Understated residues will give rise to the estimation of erroneous maximum residue levels and STMRs. The Meeting therefore concluded that the validity of the trials (except on berries) could not be assured and recommended the withdrawal of all existing MRLs. The Meeting could not recommend MRLs except for strawberries, pending the review of adequate data on storage stability. Maximum residue levels were provisionally estimated however.

Definition of the residue

Plant and animal metabolism studies indicate that methiocarb is extensively metabolized to phenolic derivatives by cleavage of the carbamate and by oxidation of methiocarb and the phenolic derivatives to

sulfoxides and sulfones. A minor metabolic path involves hydroxylation of the carbamate methyl group and oxidation to the corresponding sulfoxide. The analytical methods determine methiocarb, methiocarb sulfoxide and methiocarb sulfone, either as methiocarb sulfone or individually. The current definition of the residue is "sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb".

The 1998 toxicology review established both a chronic ADI and an acute reference dose for methiocarb. It was noted that methiocarb sulfoxide, as well as methiocarb, is of acute dietary concern.

The Meeting concluded that the residue should be defined both for enforcement of MRLs and for the estimations of dietary intake as "the sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb".

Residues resulting from supervised trials

Residues reported as below the LOD (limit of determination) for the individual components of the residue were assigned the value of the LOD. For example if methiocarb, methiocarb sulfoxide and methiocarb sulfone were each <0.02 mg/kg on cabbage, the value used for deriving the MRL and the STMR would be 0.02 mg/kg. If the method determined the three compounds as one derivative and the result was reported as below the LOD, the value of the LOD was again used, for example <0.05 mg/kg total residue would be taken as 0.05 mg/kg. For residues with individual component(s) exceeding the LOD, the residue was taken as being the sum of the residues exceeding the LOD. For example if the residue on cabbage was reported as 0.15 mg/kg methiocarb, <0.02 mg/kg methiocarb sulfoxide and 0.06 mg/kg methiocarb sulfone, the residue would be taken to be 0.21 mg/kg. This procedure is appropriate, as the residue in many cases is predominantly (60%) one compound.

Potatoes. Two trials were reported from the UK. GAP is 3 ground applications of an RB formulation at 0.22 kg ai/ha with no specified PHI. The UK trials complied with GAP with PHIs of 18 and 20 days. The residues were not quantifiable (<0.02 mg/kg).

The Meeting could not estimate a maximum residue level or STMR because two trials were an inadequate number.

Leeks. Eleven field trials were reported from France and The Netherlands. GAP for France was not reported. In The Netherlands, up to 2 foliar applications of an SC formulation, 500 g/l, may be made at rates of 0.5-0.75 kg ai/ha, with a 14-day PHI. GAP is similar for Belgium, but the PHI is 21 days. The trials in France were evaluated against Belgian GAP. One trial in The Netherlands did not comply with GAP, because the PHI was 21 days.

The residues in rank order were 0.02, 0.03, 0.08, 0.14, 0.18, 0.25, 0.29 (2), 0.30 and 0.39 mg/kg. The Meeting estimated a provisional STMR of 0.22 mg/kg and a maximum residue level of 0.5 mg/kg.

Cabbages. Fifteen field trials were reported from Austria, Belgium, Germany and The Netherlands. GAP for Austria specifies 2 foliar applications of a WP formulation at 0.5 kg ai/ha with a 14-day PHI or a spreading application of an RB formulation at 0.12 kg ai/ha with a 14-day PHI. GAP for Belgium allows 3 foliar applications of an SC formulation at 0.75 kg ai/ha with a 14-day PHI or 2 spreading applications of an RB formulation at 0.12 kg ai/ha with a 14-day PHI. In Germany GAP requires 2 applications of an RB formulation at 0.12 kg ai/ha with a 14-day PHI and in The Netherlands one foliar application of a WP formulation at 1.5 kg ai/ha with a 14-day PHI.

Six trials in Germany complied with maximum GAP for the RB formulation and eight in Germany, Belgium and The Netherlands with Belgian GAP for the SC formulation.

The residues in rank order were 0.02 (4), 0.03 (4) and 0.05 (6) mg/kg. The Meeting estimated a provisional STMR of 0.03 mg/kg and a maximum residue level of 0.1 mg/kg.

Cauliflowers. Four trials were reported from Germany, where GAP is two baiting applications of an RB or GB formulation at 0.12 kg ai/ha with a 14-day PHI. Four trials were conducted under maximum GAP conditions, but the incorrect commodity was analysed in one trial. The three relevant residues were all <0.05 mg/kg.

The Meeting agreed that four trials were inadequate for the estimation of a maximum residue level and STMR, but concluded that the data on cabbages could be extrapolated to cauliflowers since GAP is identical and the application is ground, not foliar where differences in plant habit might lead to different residue levels. The Meeting estimated a provisional maximum residue level and STMR for cauliflower of 0.1 mg/kg and 0.03 mg/kg respectively.

Artichokes. Two trials were reported from Italy. The only reported GAP is for Israel: one foliar application of a WP formulation at 1.75 kg ai/ha, no PHI specified. The Italian trials did not comply with this GAP.

No maximum residue level or STMR could be estimated.

Peas. Eight trials were reported from Germany. GAP is a seed treatment at 0.5 l of a 500 g/l FS formulation per 100 kg of seed. The eight trials were under maximum GAP conditions and quantifiable residues were found in only one trial.

The residues in the peas were 0.05 (7) and 0.08 mg/kg. The residues in the pea vines were 0.05 (7) and 0.04 mg/kg. The Meeting estimated a provisional STMR for peas and vines of 0.05 mg/kg each and maximum residue levels of 0.1 mg/kg and 0.05 mg/kg respectively.

Pepper. Five trials were reported from Spain and 2 glasshouse trials from Portugal. GAP for Spain is 3 foliar applications of a WP formulation, each 1.0 kg ai/ha, with a 7-day PHI. GAP for Portugal is the same, but with a 14-day PHI. The more demanding PHI of Spain was applied to the trials in Portugal. Six trials were at maximum GAP and one was at an application rate more than 30% above the maximum.

The residues in the six trials in rank order were 0.27, 0.49, 0.84, 0.92, 1.33 and 1.53 mg/kg. The Meeting estimated an STMR of 0.88 mg/kg and a maximum residue level of 2 mg/kg.

Tomatoes. Eight trials were reported: 1 from Portugal and 7 from Spain. GAP for both Spain and Portugal specifies 2 foliar applications of a WP formulation at 1.0 kg ai/ha, with a 7-day PHI, for both field and glasshouse applications. Two glasshouse trials in Spain were at more than 30% above GAP rate, with residues at 7 days of 0.22 and 0.59 mg/kg. The remaining six trials were under maximum GAP conditions.

The residues in rank order were 0.04 (2), 0.11, 0.17 (2) and 0.81 mg/kg, the last from a glasshouse trial. The Meeting estimated a provisional STMR of 0.14 mg/kg and a maximum residue level of 1 mg/kg.

Cucumbers. Six trials were reported: 4 from France and 2 from Spain. The French trials were in glasshouses. GAP for France was not reported. GAP for Spain, against which the trials in France were evaluated, is 2 foliar applications of a WP formulation at 1.0 kg ai/ha, with a 7-day PHI. The six trials were at or within 30% of maximum GAP.

The residues in rank order were 0.04 (2), 0.07, 0.09, 0.11 and 0.12 mg/kg. The Meeting estimated a provisional STMR of 0.08 mg/kg and a maximum residue level of 0.2 mg/kg.

Melons. Seven trials were reported: 3 from France, 2 glasshouse from Portugal and 2 from Spain. No GAP was reported for France and Spain, but the trials can be covered by GAP in Portugal and Italy (two foliar applications of a WP formulation at 1.0 kg ai/ha, with a 7-day PHI). Six trials were at or within 30% of maximum GAP, but the analyses in Spain and Portugal were of the pulp and peel, not whole melons. The residue in the whole melons was calculated from the reported weights of peel and pulp. In 1 trial in France the PHI was more than 30% below GAP.

The residues in the whole melons in rank order were 0.07, 0.17, 0.18, 0.19, 0.26 and 0.49 mg/kg and in the pulp 0.02 (4) and 0.06 (2) mg/kg. The Meeting estimated a provisional STMR of 0.02 mg/kg and a maximum residue level of 1 mg/kg.

Strawberries. Fourteen trials were reported: 6 from Spain, 2 from Portugal, 1 from Germany, 1 from Denmark, 1 from Belgium, 1 from The Netherlands and 2 from the UK. GAP in Portugal and Spain calls for 2 foliar applications of a WP formulation at 0.8 and 1.0 kg ai/ha respectively, with 7- and 15-day PHIs respectively. The shorter PHI of Portugal was applied to evaluate the trials in Spain. GAP in northern Europe requires the ground application of an RB formulation: in Belgium 2 applications, each 0.20 kg ai/ha, no PHI; in Germany 2 applications, each 0.12 kg ai/ha, 14-day PHI; in the UK 1 application, 0.22 kg ai/ha, 7-day PHI and in Sweden 1 application, 0.2 kg ai/ha, no PHI. GAP in Denmark and The Netherlands was not reported. German GAP was applied to evaluate the trials in The Netherlands and Denmark. All trials were at or within 30% of maximum GAP.

The residues from the application of a granular formulation to the ground in rank order were 0.02 (2), 0.04 and 0.05 (3) mg/kg; and from foliar applications of a WP formulation 0.17, 0.29, 0.36, 0.43, 0.45, 0.54, 0.71 and 0.83 mg/kg. The latter is the critical GAP. The Meeting estimated an STMR of 0.44 mg/kg and a maximum residue level of 1 mg/kg.

Cereal grains. Two trials on wheat were reported from the UK, where GAP for cereal grains requires application of an RB formulation at 0.15 kg ai/ha–0.20 kg ai/ha, with a 7-day PHI. The number of applications is not specified. In the field trials two applications were made, one at drilling and one on the ground 94 and 98 days before harvest of grain and straw and 0 days before the harvest of forage. Three barley trials were reported from Germany. GAP for barley, oats, rye, wheat and triticale specifies up to 2 applications of an RB formulation at 0.1 kg ai/ha. The PHI is not specified, although the practical PHI is governed by the growth stage, up to growth stage 29. The trials were at or within 30% of maximum GAP. No quantifiable residues were found in the grain, straw and fodder of wheat or barley. The residues in the grain, straw and fodder in rank order were <0.04 (2), <0.05 (3) mg/kg, <0.05 (3), <0.1 (2) mg/kg, <0.05 (3) and <0.1 (2) mg/kg respectively.

The Meeting concluded that the use of a bait formulation applied to the surface of the ground and not incorporated into the soil is unlikely to leave methiocarb residues in the grain commodities. The Meeting therefore judged five trials to be adequate for this GAP and estimated provisional maximum residue levels of 0.05*, 0.1* and 0.1* mg/kg for the grain, straw and fodder respectively of barley, oats, rye, wheat and triticale. The Meeting also estimated STMRs of 0 mg/kg for the grain, straw and fodder of these cereals.

Ten trials on maize in Germany were according to GAP: seed treatment or application at drilling with an FS formulation at 0.5 kg ai/100 kg seed.

The residues in maize grain (kernel and cob) in rank order were <0.05 (5) and <0.1 (4) mg/kg. The residues in the forage were all <0.1 mg/kg (6 samples).

The Meeting estimated provisional STMRs of 0 mg/kg and maximum residue levels of 0.1* mg/kg for maize grain and forage.

Rape seed. Seven trials were reported from Germany, where GAP specifies two applications of an RB formulation at 0.1 kg ai/ha with no specified PHI. The practical PHI is at growth stage 29–30. Three trials were with foliar application of a WP formulation for which no GAP in Germany was reported, but the trials were evaluated against GAP in The Netherlands (one foliar application of the WP formulation at 0.5 kg ai/ha with no specified PHI). These three trials were within 30% of the maximum GAP conditions. The remaining four trials were with a GR formulation, not RB. Residues from the granular formulation were found in rape forage on the day of application in two of the four trials at 0.54 and 2.6 mg/kg.

The Meeting regarded three trials with a foliar application as too few for the estimation of a maximum residue level or an STMR and recommended withdrawal of the existing MRL.

Hazelnuts. Five trials were conducted in Turkey where GAP is one foliar application of a WP formulation at 0.6 kg ai/ha, with a 90-day PHI. Nuts without shells were analysed. All the trials were at maximum GAP and all 5 residues were below the LOD of 0.05 mg/kg.

The Meeting estimated a provisional STMR of 0.05 mg/kg and a maximum residue level of 0.05* mg/kg.

No residue trials were reported for artichokes, broccoli, Brussels sprouts, citrus, lettuce, sugar beet or sweet corn. The Meeting recommended the withdrawal of the existing MRLs.

Animal feeding studies

In a poultry feeding study hens were fed a diet containing methiocarb and methiocarb sulfoxide (9:1) for 28 days, at rates ranging from 0 to 360 ppm in the feed. At 120 ppm residues were below the limit of determination (<0.02 mg/kg) in muscle, skin and fat, 0.03 mg/kg in eggs and 0.13 mg/kg in giblets (liver, etc.). At 360 ppm residues were <0.02 mg/kg in the muscle and fat, 0.02 mg/kg in skin, 0.06 mg/kg in eggs and 0.13 mg/kg in giblets.

A dairy cow feeding study was reported in which the animals were dosed daily for 29 days with the equivalent of 0, 10, 30 and 100 ppm methiocarb in the feed. Maximum total methiocarb residues in milk on day 29 were 0.007 mg/kg at the 10 ppm feeding level, 0.020 mg/kg at the 30 ppm level and 0.033 mg/kg at the 100 ppm level. No residues (<0.05 mg/kg total methiocarb) were found in any tissue at any feeding level, except 0.08-0.1 mg/kg total methiocarb in liver at 30 and in kidney at 100 ppm.

The livestock feed items for which provisional maximum residue levels were estimated were maize grain, maize forage (ruminant feed only), pea vines (ruminant only), cereal grains and cereal forages (ruminant only). The residues in all these except pea vines were below the limits of determination. From the estimated maximum residue levels, 0.1* mg/kg for maize grain and forage, 0.05* mg/kg for cereal grains, 0.1* mg/kg for cereal forages and 0.05 mg/kg for pea vines, the diets were calculated to contain methiocarb residues of 0.1 ppm for poultry, 0.24 ppm for beef cattle and 0.30 ppm for dairy cattle.

The 0.1 ppm diet for poultry is at least a factor of 1000 below the concentration at which residues were detected in poultry products in the feeding study. The Meeting concluded that poultry maximum residue levels could be estimated at the practical limit of determination of the analytical methods, 0.05* mg/kg, and STMRs at 0 mg/kg for poultry meat and eggs.

The estimated low concentrations of methiocarb and metabolites in the ruminant diet, about 0.3 ppm, might be expected to yield residues below the enforcement limits of determination (0.005 mg/kg for milk, 0.05 mg/kg for tissues). Assuming a 600 kg animal and a dietary intake of 20 kg/day, the intake can be estimated at 0.000010 g methiocarb/kg bw/day. This is an order of magnitude below the dosing level in the metabolism study (0.00014 g/kg bw/day). In that study, the total fat and muscle residues were each <0.01 mg/kg and the total milk residue was 0.06 mg/kg. In the ruminant feeding study, no residues (<0.05

mg/kg) were found in any commodity after 29 days at a 10 ppm feeding level (30 times the maximum theoretical intake), except in milk at 0.007 mg/kg. The metabolism and feeding studies both indicate that total methiocarb residues in ruminant commodities will be below the limits of determination of the analytical methods (<0.02–0.05 mg/kg, 0.005 mg/kg for milk). The Meeting estimated provisional maximum residue levels for ruminant commodities at the practical limit of determination, 0.05* mg/kg for tissues and 0.01 mg/kg for milk, and STMRs for milk and ruminant tissues at 0 mg/kg.

Fate of residues in storage and processing

No relevant studies were reported. Processing studies for the preparation of strawberry jam and preserves and for the canning of peppers were reported to the Meeting. A potato processing study was reported, but the residue on the potatoes was below the limit of determination.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting recommended withdrawal of the existing CXLs but recommended an MRL and estimated an STMR for strawberry as shown below.

Definition of the residue for compliance with MRLs and estimation of dietary intake: sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb.

CCN	Commodity	MRLs , mg/kg		STMR
		New	Previous	mg/kg
VS 0620	Artichoke, Globe	W	0.05 *	
VB0400	Broccoli	W	0.2	
VB0402	Brussels sprouts	W	0.2	
VB0041	Cabbages, Head	W	0.2	
VB0404	Cauliflower	W	0.2	
GC0080	Cereal grains	W	0.05 *	
FC 0001	Citrus fruits	W	0.05 *	
PE 0112	Eggs	W	0.05 *	
TN 0666	Hazelnuts	W	0.05 *	
VL 0482	Lettuce, Head	W	0.2	
VL 0483	Lettuce, Leaf	W	0.2	
MM0095	Meat (from mammals other than marine mammals)	W	0.05 *	
ML0106	Milks	W	0.05 *	
PM 0110	Poultry meat	W	0.05 *	
SO 0495	Rape seed	W	0.05 *	
FB 0275	Strawberry	1		0.44
VR 0596	Sugar beet	W	0.05 *	
VO 0447	Sweet corn (corn-on-the-cob)	W	0.05 *	

FURTHER WORK OR INFORMATION

Desirable

1. A study of the stability of residues in stored analytical samples covering the crops and storage conditions of the trials reported in support of MRLs. The residue trials data reviewed above may be used after adequate storage stability has been demonstrated.

2. Metabolism studies, plant and livestock, including a demonstration of the stability of methiocarb and its metabolites in the samples and extracts.

DIETARY RISK ASSESSMENT

Chronic intake

The Meeting recommended withdrawal of the existing CXLs, but recommended an MRL and estimated an STMR for strawberry. The International Estimated Daily Intakes (IEDIs) for the 5 GEMS/Food regional diets, based on the single STMR, were 0% of the ADI. The Meeting concluded that the intake of residues of methiocarb resulting from the one use that has been considered by the JMPR is unlikely to present a public health concern. The Meeting agreed that a new assessment of chronic dietary risk should be carried out if new MRLs are recommended.

Acute intake

The International Estimate of Short Term Intake (IESTI) was 23% of the acute RfD for the general population and 38% for children for strawberries, the one food commodity considered. The Meeting concluded that the intake of residues of methiocarb resulting from the use that has been considered by the JMPR is unlikely to present a public health concern.

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