PART C

RESIDUES

1 Metabolism

The company provided several plant and animal metabolism studies. The metabolism of methiocarb has been reviewed by the JMPR in 1999, as part of the periodic review programme. All of the metabolism studies reviewed by the JMPR were made available to the NRA as part of this review. The JMPR evaluation of the metabolism data is reproduced below. Additional studies available to the NRA that were not reviewed by the JMPR are also considered.

Reference: JMPR (1999) FAO Plant Production and Protection Paper, 157. Evaluations. Part 1-Residues. Volume 1. 20-29 September 1999, Rome, 2000.

The following is reproduced from the JMPR (1999) periodic review of methiocarb.

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 gelatine 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 ≤0.02 mg equiv/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).

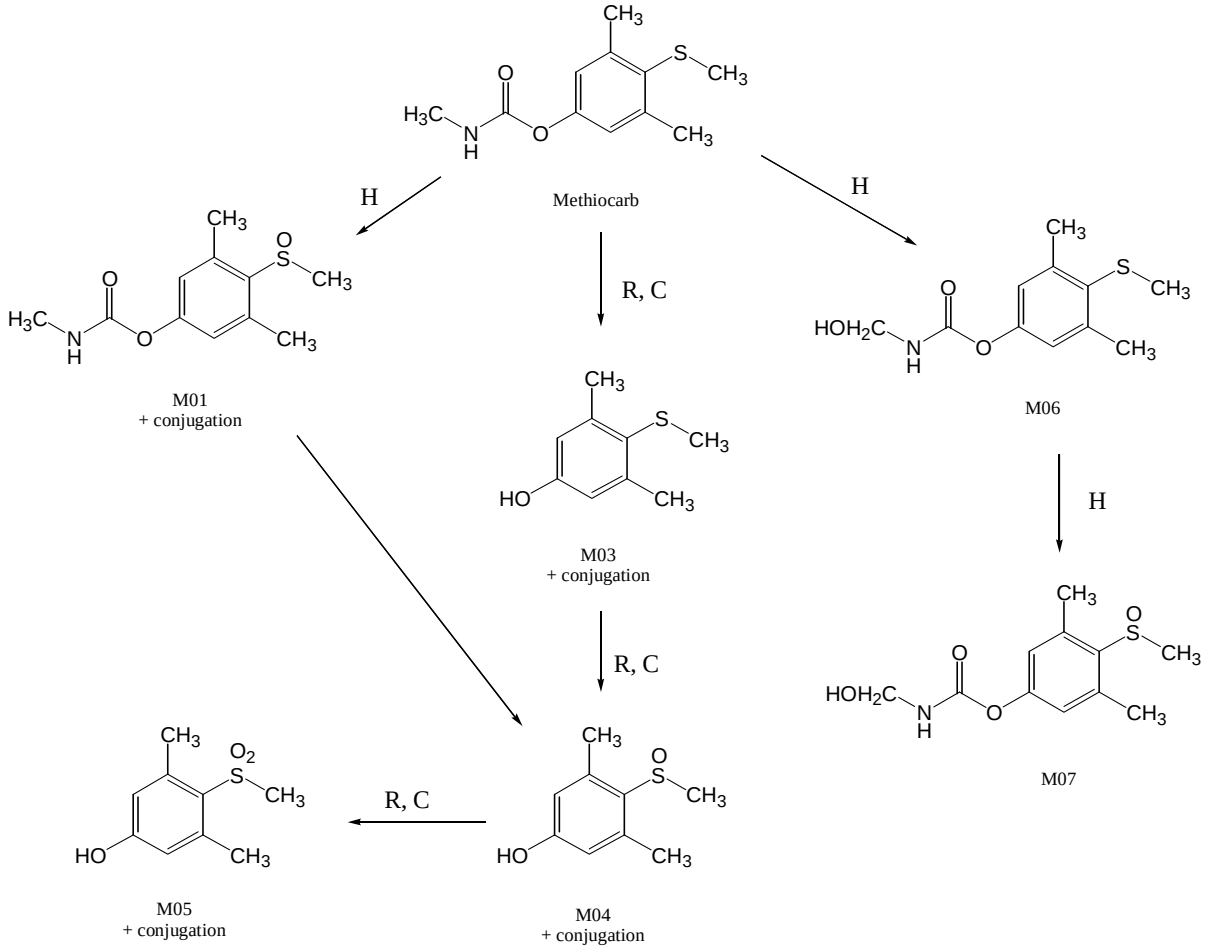
Sample	Residue, mg/kg as methiocarb
Kidney	3.3
Liver	2.0
Heart	0.8
Skin	1.3
Fat	0.7
Gizzard	7.7
Muscle	0.45
Eggs	<0.1

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.

Apples. 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 and methiocarb sulfoxide constituted 16% and 1.4%, respectively, of the radioactive residue on the peel in the sample collected 14 days after the final application. 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 equivalents, 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	

Compound	^{14}C, % of total recovered in extracts and fractions					
	Days after 1st spraying					
	0	1	3	6	14	28
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

Days after application	Methiocarb equivalents, mg/kg					
	Wheat			Sugar beet		Spinach
	Heads	Stalks	Forage	Tops	Roots	
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).

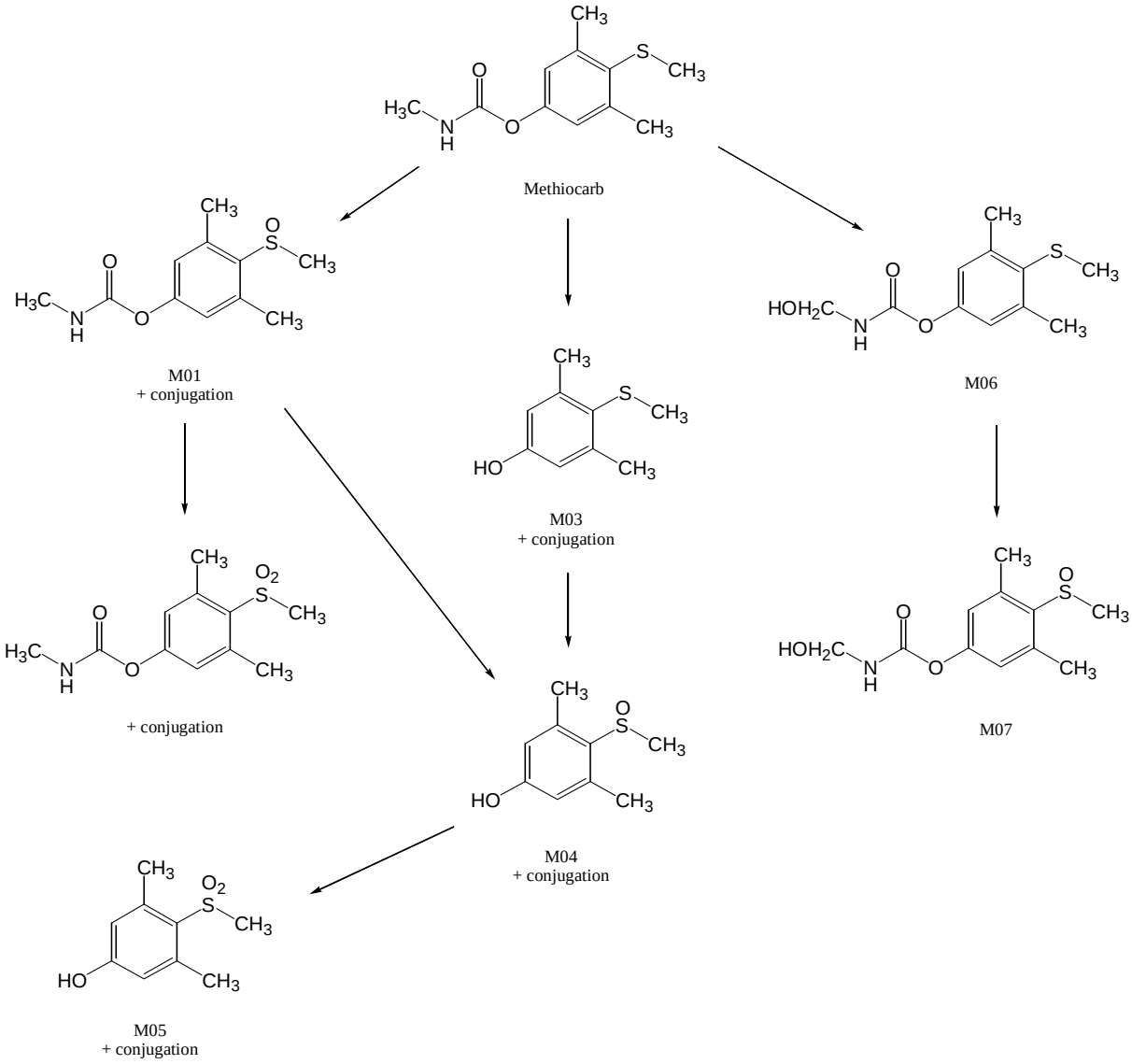
Compound	Sample							
	Wheat head (551 days)		Wheat stalk (551 days)		Wheat forage (551 days)		Spinach (450 days)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
N-hydroxymethyl-methiocarb	12	0.008	3	0.004	1	0.003	7	0.016
Methiocarb sulfoxide	6	0.004	4	0.006	12	0.039	0	0
Methiocarb sulfoxide 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.



Additional studies provided to the NRA that were not reviewed by the JMPR are evaluated below.

Reference: Church, D. D. (15 June 1969) Metabolism of 4-(methylthio)-3,5-xylyl methylcarbamate (BAY 37344) on Apples and Beans, Report number 25,160, Chemagro Corporation

Golden Delicious apples and surrounding leaves were sprayed with a 50% WP formulation containing [carbonyl-^{14}C]methiocarb at a rate equivalent to 0.5 lb ai/100 gal (0.05 kg ai/100 L). Representative samples of apples were collected at 0, 3, 6, 10 and 17 days after application. Surface residues were first removed from the apples by dipping in benzene, then apples were peeled. Residues were extracted from frozen blended peel and flesh (separately) with acetone, then further extracted with chloroform.

Bean plants were injected with 25 μL solution of a mixture of ^{3}H and ^{14}C-labelled methiocarb in ethanol/water (1:1) in the stem at ground level 15 days after germination. Each injection contained 1.2×10^{7} dpm ^{3}H-methylthio and 7.88×10^{5} dpm ^{14}C-carbonyl labelled methiocarb. At 0, 1, 2, 3 and 4 days after injection, bean plants were clipped at ground level then residues extracted in the same manner as for apples, described above. The dose rate was not specified.

The level of radioactivity in organosoluble, water-soluble and unextractable material was determined by LSC. Extracts were analysed by TLC with comparison against authentic samples of methiocarb, and its sulfoxide and sulfone. Water-soluble material and unextractables were subjected to enzyme treatment.

Results

Recovery of radioactivity from apples treated with ^{14}C-methiocarb (%)

DAT	0	3	6	10	14	17
% in peel	100.0	47.0	41.3	21.1	21.8	18.3
% in pulp	NA	1.2	1.5	2.5	2.2	2.5
% lost	NA	51.8	57.2	76.4	76.0	79.2

More than 50% of radioactivity in apples was lost prior to the first sampling point (3 DAT). This was attributed to rain that fell prior to sampling.

Relative distribution of ^{14}C-methiocarb in apple peel (%)

DAT	0	3	6	10	14	17
Methiocarb				16.1		8.0
Methiocarb Sulfoxide				68.7		70.5
Total organosoluble	100.0	90.0	80.0	61.8	66.5	54.9
Water solubles		5.1	10.0	21.7	20.0	25.6
Unextractables		4.9	9.2	16.5	13.5	19.5

Approximately 80% of radioactivity in peel was identified as methiocarb and the sulfoxide. The majority of radioactive residues were organosoluble.

Relative distribution of ^{14}C-methiocarb in beans (%)

DAT	0	1	2	3	4
^{14}C-Methiocarb	98.6	65.3	53.3	48.1	50.3
^{14}C-Methiocarb Sulfoxide		10.7	16.9	16.7	16.6
^{14}C-Methiocarb sulfone		<1.0	<1.0	<1.0	<1.0
^{14}C-Total organosoluble	100.0	90.0	80.0	61.8	66.5
^{14}C-Water solubles		5.1	10.0	21.7	20.0
^{14}C-Unextractables		4.9	9.2	16.5	13.5
^{3}H-Total organosoluble	105.4	77.1	81.8	78.8	75.4
^{3}H-Water solubles		2.2	8.3	15.1	17.1
^{3}H-Unextractables		1.2	2.8	6.0	5.5

The majority of radioactivity was organo-soluble. Approximately 70% or more of radioactivity was identified as methiocarb, its sulfoxide and sulfone.

Reference: Strankowski, K. J. and Parker, G. D. (10 February 1981). [^{14}C] ®Mesurol Rotational Crop Study, Mobay Chemical Corporation Agricultural Chemicals Division, Report number 69270

Greenhouse grown rice (var. Oryza sativa) was sprayed with ring-^{14}C-methiocarb 4 months after planting at a rate equivalent to 5.61 kg ai/ha (5 lb ai/acre). Thirty days after application half of the rice was harvested. At 30, 120, 365 and 601 days post spraying, rotational crops of wheat, red beets and kale were planted in harvested areas. At 39 days post-treatment the remaining half of rice was harvested and rotational crops were planted at 120, 365 and 601 days post-treatment. Crop and soil samples were taken at ¼, ½, ¾ and full maturity of the rotational crops and analysed for total radioactive residues and for metabolite residues.

The distribution of radioactive residues in crop parts (rotational crops) at various planting intervals after application to the preceding rice crop are shown below. Residues are expressed in mg methiocarb equivalents/kg.

Residues in mature wheat (mg methiocarb equiv/kg)

Planting interval	Matrix	Methiocarb	Methiocarb sulfoxide	Methiocarb sulfone	N-hydroxymethyl methiocarb	N-hydroxymethyl methiocarb sulfoxide	Total
30 days	Heads	0	0.945	0.052	0	0.107	1.104
	Stalks	0	0.279	0.026	0.026	0.041	0.372
	Forage	0	1.315	0.129	0.187	0.316	1.947
120 days	Heads	0	0.440	0.043	0	0.068	0.551
	Stalks	0	0.122	0.018	0	0.018	0.158
	Forage	0	0.920	0.329	0.054	0.216	1.519
365 days	Forage	0	0.016	0	0	0	0.016
601 days	Heads	0	0.026	<0.006	0	<0.006	0.036
	Stalks	0	0.017	0	0	0	0.017
	Forage	0	0.128	0	0	0	0.128

Residues in soil and mature beet and kale (mg methiocarb equiv/kg)

Planting interval	Matrix	Methiocarb	Methiocarb sulfoxide	Methiocarb sulfone	N-hydroxymethyl methiocarb	N-hydroxymethyl methiocarb sulfoxide	Total
30 days	Beet tops	0	0.057	<0.006	0	<0.006	0.062
	Beet bulbs	0	0.025	<0.006	0	<0.006	0.027
	Kale	0	0.191	0.027	0	0.024	0.242
	Soil	0.519	0.305	<0.006	0	0	0.828
120 days	Beet tops	0	0.029	<0.006	0	0	0.032
	Beet bulbs	<0.006	0.010	<0.006	0	<0.006	0.012
	Kale	0	0.114	0.020	0	0.008	0.142
	Soil	0.227	0.564	0.015	0	0	0.806

365 days	Beet tops	0	<0.006	0	0	0	<0.006
	Beet bulbs	0	<0.006	0	0	0	<0.006
	Kale	0	<0.006	<0.006	0	0	<0.006
	Soil	0.018	0.275	0.029	0	0	0.322
601 days	Soil	<0.006	0.099	0.017	0	0	0.121

The major residue in all samples was methiocarb sulfoxide. Significant residues were found in crops planted up to 120 days after application at 5.6 kg ai/ha. The application rate used for rice was more than 12× the maximum application rate approved for crop use of methiocarb pellets in Australia.

Reference: Gronberg, R.R, Everett, L.J, The metabolic fate of 4-(methylthio)-3,5-xylyl methylcarbamate (BAY 37344), 4-(methylsulfinyl)-3,5-xylyl methylcarbamate (BAY 37344 sulfoxide), and 4-(methylsulfonyl)-3,5-xylyl methylcarbamate (BAY 37344 sulfone) in white rats, Report number 26819, 21 October 1969

Rats orally administered radiolabelled methiocarb, methiocarb sulfoxide and methiocarb sulfone exhibited the same metabolic pattern, excreting 85-90% of the carbonyl-^{14}C-label within 48 hours of treatment. Rats treated with ^{14}C-carbonyl labelled material released up to 68% as CO_2, 20-30% radioactivity in urine and 2-4% in faeces, within 48 hours. Rats treated with methylthio-^{3}H labelled material excreted 85% of radioactivity in urine and 8% in faeces within 48 hours of dosing. Overall recovery of radioactivity in these experiments was >90%. Highest tissue concentrations of radioactivity were found in liver and kidney. The major metabolites in urine were conjugates of methiocarb, its sulfoxide and sulfone. The major route of metabolism of methiocarb, sulfoxide and sulfone was hydrolysis of the carbamate linkage followed by conjugation.

Reference: Stanley, CW, Johnson, GA, Metabolism of ® MESUROL Phenol by Rats, Report number 88899, 23 January 1985

Three male rats were orally administered ring-^{14}C-labelled methiocarb phenol as a solution in ethanol/water (1:1) by oral intubation injection directly into the stomach, at a rate of 0.19 mg/kg bw (equivalent to 0.25 mg/kg bw of methiocarb). Greater than 77% of radioactivity was eliminated in urine within 48 hours of dosing. About 4% of the radioactivity in urine was extractable in chloroform and found to be methiocarb phenol. Upon hydrolysis, radioactivity in the aqueous phase was identified mainly as methiocarb phenol indicating that the radioactivity was present mostly as conjugated methiocarb phenol. Approximately 81% of radioactivity was recovered in the experiment.

Reference: Ackerman, ME, Wilkes, LC, Total residues in tissues, organs, blood, eggs and faeces following oral administration of carbon-14 labelled Mesurol to poultry, Report number 44324, 9 May 1975

Carbon-14-labelled methiocarb was orally administered to sixteen chickens via a tube as a single dose of 4.414 mg ai/kg bw. Faecal material was collected at 3, 6, 12, 24, 48, 72 and 96 hours post-treatment. Eggs were collected at 24-hour intervals. Blood was sampled prior to sacrifice 6, 24, 48 and 96 hours after treatment. Tissues were collected at sacrifice and total radioactivity was determined by combustion. Radioactivity was not characterised in the study.

Radioactive residues in eggs peaked between 48 and 96 hours post dose, at approximately 0.05 mg equiv/kg. Highest levels of radioactivity in faeces were detected in samples collected at 3 and 6 hours post-dose. Radioactive residues in tissues, skin, blood and plasma are shown below. Highest residues were detected in samples collected 6 hours post-dose. Total recovery of radioactivity in faeces was approximately 90% in the animals sacrificed 96 hours after dosing.

	Radioactive residues (mg equiv/kg) / sampling time			
Sample	6 hours	24 hours	48 hours	96 hours
Whole blood	1.59	0.094	0.016	<0.006
Plasma	2.35	0.152	0.019	<0.006
Breast muscle	0.136	0.030	<0.006	<0.006
Thigh muscle	0.222	0.038	<0.008	<0.006
Heart muscle	0.522	0.038	<0.007	<0.006
Skin	0.929	0.488	0.309	0.058
Fat	0.314	<0.014	<0.006	<0.006
Liver	0.479	0.066	0.012	<0.006
Kidney	1.36	0.081	<0.012	<0.007

1.1 Summary of metabolism studies

The metabolism of methiocarb in plants occurs by carbamate ester cleavage and oxidation to sulfoxides and sulfones. The predominant residue components in plants treated with methiocarb were methiocarb and methiocarb sulfoxide, with lesser amounts of methiocarb sulfone and methiocarb sulfoxide phenol. In animals, methiocarb is metabolised extensively by carbamate ester cleavage followed by oxidation of the resulting phenol to the sulfoxide and sulfone. Predominant residues in animal tissues and excreta were methiocarb phenol, methiocarb sulfoxide phenol and methiocarb sulfone phenol.

2 Analytical methodology

Several analytical methods used for the determination of methiocarb residues in a range of food commodities were submitted to the NRA. A number of additional methods were evaluated by the JMPR in 1999, however these studies were not provided to the NRA for this review.

2.1 Individual methods

In the method of Strankowski and Stanley (1975 and 1981) crop samples are extracted using acetonitrile. The filtrate is extracted with hexane and evaporated to dryness. Animal tissues (poultry and fish) are extracted with acetonitrile then filtered, and the filter cake is further extracted with hexane. The acetonitrile and hexane filtrates are combined and the hexane layer is removed and concentrated under reduced pressure. For fat and skin samples the order of hexane and acetonitrile extractions is reversed (i.e. hexane extraction was performed prior to the acetonitrile extraction). The filtrates are combined then the hexane layer is removed and concentrated. Eggs are extracted with acetone, filtered, then the filter cake is washed with chloroform. The acetone filtrate is further extracted with hexane then the hexane and chloroform filtrates are combined and concentrated.

Waxes and pigments are removed from the extracts by the addition of ammonium chloride solution followed by silica gel column cleanup (some crops only). Methiocarb and methiocarb sulfoxide are oxidised to the sulfone using 0.1 M potassium permanganate ($KMnO_4$) solution and the resultant solution is extracted with chloroform. The non-oxidised material is cleaned up by passing through an alumina-florisil column, hydrolysed in basic media then silylated with bis(trimethylsilyl)-trifluoroacetamide. Analysis is by GC with flame photometric detection and comparison against standard curves of each compound.

The method may be used to determine methiocarb, its sulfoxide and sulfone either individually (no oxidation step) or as total methiocarb residues (oxidation step included). The oxidation step assists in the removal of plant and animal co-extractives, as well as methiocarb-derived phenols. Procedural recoveries of methiocarb, it sulfoxide and sulfone are shown below. The limit of quantitation of the method is determined to be 0.05 mg/kg for each compound.

Sample	mg/kg added	Methiocarb	Methiocarb sulfoxide	Methiocarb sulfone
Artichoke, bean (dry), bean and pod (mixed), bean vine, broccoli, Brussels sprouts, cabbage, cauliflower, cherries, lettuce, orange peel, orange pulp, peaches, tomato	0.1 0.05	62-106 (mean 89) 64-104 (92) (n=15)	73-112 (93) 65-102 (91) (n=15)	80-107 (97) 66-103 (93) (n=15)
Fish (edible offal)	1.0 (n=2)	80 (mean 80)	90 (90)	77-80 (79)
Poultry (muscle, giblet, skin, fat, egg)	0.1 0.05 0.02 (eggs only)	74-101 (86)(n=5) 79-103 (93) 88	79-105 (92) 80-106 (92) 88	73-115 (92) 78-101 (92) 115

The method has a limit of quantitation of 0.05 mg/kg for plant and animal commodities, with the exception of eggs, which has an LOQ of 0.02 mg/kg.

The method of Thornton (1969) is a GC method used for determination of methiocarb, its sulfoxide and sulfone, in apples and pears. The method involves initial extraction with acetone, precipitation of pigments and waxes (NH_4Cl) and oxidation of methiocarb and its sulfoxide to the sulfone using $KMnO_4$. The mixture is silylated using bis-trimethylsilyl trifluoroacetamide then analysed by GC with flame photometric detection with quantification by comparison against a standard curve. Recoveries for the method are given below. The method has a limit of quantitation of 0.05 mg/kg for apples and pears and 0.5 mg/kg for apple pomace and dry corn kernels.

		Recoveries (%)		
Sample	mg/kg added	Methiocarb	Methiocarb sulfoxide	Methiocarb sulfone
Apple peel	0.5	87	92	115
	0.1	80	81	97
	0.05	58	88	66
Apple pulp	0.1	117	113	100
	0.05	104	103	101
Pear peel	0.5	98	103	101
Pear pulp	0.1	86	96	116
	0.05	103	107	111
Moist apple pomace	0.5	83	88	83
Dry apple pomace	0.5	96	86	82
Dry corn kernel	0.5	70	74	73

The method of Bakowski *et al* (1994) involves determination of methiocarb parent residues in liver by GC/MS following derivatisation of the carbamate with heptafluorobutyric anhydride. Full details of the extraction procedure were not reported. Recoveries ranged from 97-110% with fortification at 0.01 mg/kg.

The method of Howard *et al*. involves determination of methiocarb parent residues from apples by LC with UV detection, and using supercritical fluid extraction. Recoveries were 67% and 74% with fortification at 83 and 2 ppm, respectively.

Liu et al. published a multiresidue method using HPLC to determine a variety of thermally labile and non-volatile pesticides in fruits and vegetables. Samples were initially extracted with maceration using acetone then filtered, and the filtrate was further extracted with methylene chloride and petroleum ether. After drying over anhydrous sodium sulphate the extracts were concentrated and analysed by HPLC. Methiocarb was determined with detection using mass spectrometry in the positive ion mode. Recovery of methiocarb from apples, beans, lettuce, peppers, potatoes and tomatoes fortified at 0.5 mg/kg was 87.7-110.4%. The limit of detection was reported as 0.25 mg/kg for methiocarb (only).

The method of Page and French (1992) is a multiresidue method for determination of 8 carbamate pesticides, including methiocarb, in vegetables, fruits and feeds. Residues are extracted from samples using acetone with blending, then partitioned with 5% dichloromethane and hexane. Further cleanup is achieved by passing the extracts through an aminopropyl-SPE cartridge. Analysis is by reverse phase (C8) HPLC with post-column fluorometric detection. Recoveries of methiocarb were high. Mean recovery from various commodities was 97% and 87% with fortification at 0.05 and 5.0 mg/kg, respectively. Detection limits of less than 0.01 mg/kg were reported.

Ely et al (1993) reported a method used in a residue trial on blueberries. Fruit was blended with acetone and residues were extracted with chloroform. Following oxidation with potassium permanganate and cleanup on a silica gel column residues were determined by reverse phase (C18) HPLC with UV detection. The limit of detection was 0.2 mg/kg.

3 Residue definition

The available plant and animal metabolism studies indicate that methiocarb is extensively metabolised to phenolic derivatives by cleavage of the carbamate, and by oxidation of methiocarb and the phenolic derivatives to sulfoxides and sulfones. In plants the major residues include methiocarb, methiocarb sulfoxide and methiocarb sulfone, and their conjugates. In animals, the majority of residues are present as phenolic derivatives of methiocarb, such as methiocarb phenol and methiocarb sulfoxide phenol, and their conjugates.

The analytical methods determine methiocarb, methiocarb sulfoxide and methiocarb sulfone, either as methiocarb sulfone or individually. The current residue definition (sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb) is appropriate for plant and animal commodities.

4 Residue trials

Several residue trials were available for review, however most were only summaries of the full studies and full details of field and analytical phases of the trials were not provided. Few of the trials addressed GAP in Australia.

Methiocarb was extensively reviewed by the JMPR in 1999, however none of the residue trials addressed GAP in Australia.

4.1 Grapes

Reference: F. K. Miller, U. Kiigemagi, P. A. Thomson, D. A. Heatherbell, M. L. Deinzer, Methiocarb Residues in Grapes and Wine and their Fate during Vinification, *J. Agric. Food. Chem.*, **1985**, 33, 538 – 545. Study number IM1473

The trial described in this reference did not address the current Australian use pattern for the registered 750 g/kg WP formulation, however processing data were generated for grape juice, pomace, must and wine of Pinot Noir and Riesling grapes.

Pinot Noir and white Riesling grapes were treated with methiocarb (75% WP formulation) as three or four applications at weekly intervals by handgun, concentrate sprayer or aircraft at either 2.2 or 4.5 kg ai/ha. Grapes were picked 1 and 7 days after the last application then processed into must and wine. Methiocarb residues were determined in the whole grapes, juice, must, pomace and wine.

Vinification of grapes was carried out using the following procedure. Yeast starter culture was prepared using a 2% inoculum of rehydrated dry wine yeast in 1:1 grape juice/water at 41°C, then incubated at room temperature for 3 hours. Grapes were crushed then untreated juice was fortified with methiocarb (75% WP). Potassium pyrosulfite solution (1%) was added to Riesling grape juice to adjust the SO_2 level to 50 ppm. Juices were allowed to settle overnight then racked and sealed with fermentation locks, and wines were fermented to dryness at 15°C (Riesling) or 20°C (Pinot), then held at 3.5°C, then bottled. Riesling was adjusted to 30 ppm free SO_2 prior to bottling.

Residues (mg/kg) and processing factors for grapes and fermentation products

		1 DALA samples				7 DALA samples			
Sample	App'n. rate (kg ai/ha)	M	Processing factor	MSO_2	Processing factor	M	Processing factor	MSO_2	Processing factor
Pinot noir grapes	4.5	22	-	22	-	16	-	36	-
Pinot noir must	4.5	10	0.45	9.9	0.45	7.1	0.44	5.7	0.16
Pinot noir pomace	4.5	28	1.27			16	1.0		
Pinot noir wine	4.5	7.4	0.34	9.7	0.44	7.9	0.49	4.6	0.13
Pinot noir grapes	2.2					12	-		
Pinot noir must	2.2					4.9	0.41		
Pinot noir pomace	2.2					26	2.17		
Pinot noir wine	2.2					3.6	0.30		
White Riesling grapes	4.5	38	-	25	-	25	-	19	-
White Riesling juice	4.5	15	0.39	12	0.48	5.1	0.20	8.8	0.46
White Riesling pomace	4.5	40	1.05						
White Riesling wine	4.5	4.8	0.13	8.0	0.32	3.3	0.13	4.9	0.26

M = methiocarb; MSO_2 = methiocarb sulfone

Average processing factors for grapes, juice, must, pomace and wine

	Pinot Noir		White Riesling	
Grape variety	Methiocarb	Methiocarb sulfone	Methiocarb	Methiocarb sulfone
Grapes	1.0	1.0	1.0	1.0
Juice	-	-	0.30	0.47
Must	0.43	0.31	-	-
Pomace	1.47	-	1.05	-
Wine	0.38	0.29	0.13	0.29

Methiocarb residues concentrate slightly in pomace compared to whole grapes but are reduced in juice, must and wine.

Reference: South African Bureau of Standards, Residue trials with Mesurol in grapes in South Africa, (from Bayer Australia Limited Submission 110, 22/12/78), Report numbers 311/8918/A488 and 311/8904/C356

The following residue trials did not address GAP in Australia because methiocarb was applied as a foliar spray when fruit was present. Only a non-English summary of the residue trial was available. Results are summarised below.

Trial/report no.	Location	Grape variety	Appn rate	PHI (days)	Methiocarb Residues (mg/kg)
311/8918/A488 (16.6.65)	Keurfontain Estates, Sth Afr.	Barlinka	0.12 kg ai/100 L	0 7	1.0 0.4

				14	<0.2
311/8904/C365 (27/12/76)	Keurfontain, Sth Afr.	Morio-Muscat	0.24 kg ai/100 L	0 14 22 29 36	10.52 10.0 9.24 4.31 4.48
		Muller-Thurgau	0.24 kg ai/100 L	0 14 22 29 36	5.87 4.97 4.14 5.66 2.09

Reference: New Zealand Department of Scientific and Industrial Research, H. H. York and Co. Limited, Residue trials with Mesurol in grapes in New Zealand, (from Bayer Australia Limited Submission 110, 22/12/78), Report number 65/454/1, JLL AY 424. Trial location: Te Kauwhata, New Zealand.

The following residue trials did not address GAP in Australia because methiocarb was applied as a foliar spray when fruit was present. Mesurol 75% WP was applied to grapes (var. Gewartz Traminer and Pinot Meunier) as a spray solution containing 100 g product/100 L (equivalent to 75 g ai/100 L or 1.33 kg ai/ha, with a spray volume of 1778 L/ha).

PHI (days)	Residues (mg/kg)	
	Gewürtz Traminer	Pinot
0	4.3	
3	1.9	2.9
6	1.3	2.8
8	3.4	1.6
12	1.1	0.8
14	0.45	0.65
17	0.45	0.75
27	0.5	0.3
31	-	0.55
35	-	0.2

Only a summary of the trial was available. The analytical method used involved extraction of residues, hydrolysis and derivative formation then analysis by GC. The metabolite 4-methylthio-3,5-xylenol is included in the total methiocarb residue. No further details of the method were provided. It is not clear whether the results reported include methiocarb sulfoxide and sulfone.

Reference: Bayer Australia Limited, Residue trials with Mesurol in grapes in Australia, (from Bayer Australia Limited Submission 110, 22/12/78), Report numbers 14/77, 15/77, 16/77.

The following residue trials did not address GAP in Australia because methiocarb was applied as a foliar spray when fruit was present. Grapes were sprayed once with Mesurol 75% WP at either 1.9 kg ai/ha just prior to harvest, or at 5.5 kg ai/ha 29 days before harvest. No spray volumes were reported.

Trial/report no.	Location	Grape variety	Appn rate	PHI (days)	Methiocarb Residues (mg/kg)[1]
Bayer, 14/77 (17.8.77)	Lexton, SA	Gordo	1.9 kg ai/ha	2 9 16 28	25.3 18.4 14.7 1.3
Bayer, 15/77 (30.8.77)	Renmark, SA	Shiraz	1.9 kg ai/ha	1 7 15 25	28.4 20.1 13.7 6.0
Bayer, 16/77 (30.8.77)	Lexton, SA	Gordo	5.55 kg ai/ha	29	2.4

[1] Residues determined as methiocarb sulfone.

Only a summary of the residue trials was provided.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Grapes in Australia, Study numbers 32/86, 33/86.

The following residue trials did not address GAP in Australia because methiocarb was applied as a foliar spray when fruit was present. Grapes were treated with Mesurol 75% WP as a foliar spray at 150 g ai/100 L (3.15 kg ai/ha) when grapes were 4-5 weeks from maturity. Sultanas were treated with potassium carbonate solution prior to drying for 16 days. Residues were extracted with acetonitrile then oxidised to methiocarb sulfone with potassium permanganate solution then methiocarb, its sulfoxide and sulfone, were determined by GC with FID detection. Recoveries were 95% for grapes at 10 ppm and 88% for sultanas at 0.1 ppm. The limit of detection was stated as 0.01 mg/kg. Results were corrected for recovery.

Trial reference, date	Location	No. applications (interval)	Rate	PHI	Methiocarb residues (mg/kg)
Bayer, 32/86	Monash, SA	1	150 g ai/100 L (2100 L/ha)	0 7 14 21 37*	3.5 4.7 5.5 7.7 2.3*
Bayer, 33/86	Monash, SA	2 (7 days)	150 g ai/100 L (2100 L/ha)	0 7 14 21 37*	18.5 22.0 8.0 4.9 4.4*

* sultanas dried for 16 days following treatment with potassium carbonate solution.

Reference: JMPR (1981) FAO Plant Production and Protection Paper, 42. Evaluations. 23 November – 2 December 1981, Rome, 1982 (page 336).

Three residue trials on grapes in the USA were reported in the 1981 JMPR review of methiocarb and are reproduced below. The trials did not address Australian GAP as methiocarb was sprayed on vines when fruit was present. Spray volumes were not reported.

	Application				Methiocarb residues (mg/kg)[1]		
Trial location, year	No.	Rate (kg ai/ha)	Formulation	PHI (days)	Grapes	Juice	Wine
USA, 1977	3-4	2.2	75 WP	0 3 7-8	2 – 9 (4.2) 1.8 – 6.1 (2.7) 1.4 – 4.0 (2.7)	-	-
USA, 1973	3	2.2	75 WP	0 10	1.9 2.9	1.7 2.6	0.9 2.2
USA, 1977	6	2.2	75 WP	0 10	2.6 2	1.7 1.6	1.1 1.0

[1] Mean residues are shown in parentheses where a range was given.

Processing factors are calculated at 0.50, 0.42, 0.76 and 0.47× for grapes to juice and 0.89, 0.90, 0.80 and 0.65× for grapes to wine. The average processing factors for juice and wine are 0.54× and 0.81×, respectively.

Reference: Nüßlein, F. Determination of residues of methiocarb, methiocarb sulfone and methiocarb sulfoxide in/on grape following spray application of Mesurol 50 WP in the field in Italy, Portugal, Spain, Greece and Southern France. Report no. RA-2048/01, Bayer AG, 12 December 2002. Includes study numbers R 2001 0122/8, 0123/6, 0329/8, 0330/1 and 0332/8. NRA study no. 6310.

Methiocarb formulated as a 50% wettable powder was applied as a spray three times to grape vines at a rate of 2 kg product/ha using 1000 L water/ha. The concentration of methiocarb in the spray mixture was 0.1%. In the French trial a spray volume of 100 L/ha was used giving a spray concentration of 1% methiocarb. The first application was made at growth stage 61 (beginning of flowering) then 7 days later, with the final application 35 days before harvest (growth stages: between 77-berries beginning to touch and 84-softening berries). The interval between the 2nd and 3rd applications were 52-69 days except the French trial were the interval was 7 days.

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg in fruit, giving a total LOQ of 0.03 mg/kg. The maximum storage interval between sampling and analysis was approximately 12 months.

Recoveries were as follows:

Chemical	Sample	Fortification level (mg/kg)	Average recovery (%)
Methiocarb	Bunches	0.01	95
		0.1	91
	Berry	0.01	94
		0.1	91
Methiocarb sulfone	Bunches	0.01	106
		0.1	97
	Berry	0.01	101
		0.1	94
Methiocarb sulfoxide	Bunches	0.01	106
		0.1	100
	Berry	0.01	103
		0.1	100

Methiocarb (total)	Bunches	0.01	102
		0.1	96
	Berry	0.01	99
		0.1	95

Residues of methiocarb and its metabolites in grapes (mg/kg) – 0.1 kg ai/hL (WP)

Trial no.	Sample	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 2001 0112/8	Bunches	0	<0.01	<0.01	0.10	0.11
Italy	Bunches	0	2.2	<0.01	0.23	2.4
0.1%	Bunches	21	0.06	0.01	0.18	0.24
	Berry	21	0.06	0.01	0.18	0.24
	Bunches	35	0.04	0.01	0.16	0.20
	Berry	35	0.02	<0.01	0.07	0.09
	Bunches	42	0.04	0.01	0.16	0.19
	Berry	42	0.01	<0.01	0.04	0.06
R 2001 0123/6	Bunches	00	0.59	<0.01	0.26	0.83
Portugal	Bunches	21	0.10	0.02	0.24	0.34
0.1%	Berry	21	0.10	0.02	0.20	0.31
	Bunches	35	0.03	0.01	0.15	0.18
	Berry	35	0.04	0.01	0.13	0.18
	Bunches	42	0.02	0.01	0.14	0.16
	Berry	42	0.03	0.01	0.12	0.15
R 2001 0329/8	Bunches	0	0.42	0.02	0.41	0.81
Spain	Bunches	0	0.84	<0.01	0.41	1.2
0.1%	Bunches	22	0.07	0.02	0.20	0.28
	Berry	22	0.10	0.02	0.23	0.33
	Bunches	35	0.04	0.01	0.14	0.19
	Berry	35	0.02	0.01	0.11	0.13
	Bunches	42	0.02	<0.01	0.09	0.10
	Berry	42	0.02	<0.01	0.07	0.10
R 2001 0330/1	Bunches	0	0.01	<0.01	0.05	0.07
Greece	Bunches	0	0.68	<0.01	0.13	0.81
0.1%	Bunches	21	0.04	<0.01	0.10	0.14
	Berry	21	0.04	<0.01	0.07	0.12
	Bunches	35	0.01	<0.01	0.04	0.06
	Berry	35	0.01	<0.01	0.04	0.06
	Bunches	42	<0.01	<0.01	0.04	0.06
	Berry	42	<0.01	<0.01	0.03	0.05
R 2001 0332/8	Bunches	0	0.92	<0.01	0.08	1.00
France	Bunches	21	0.04	<0.01	0.13	0.17
1%	Berry	21	0.03	<0.01	0.12	0.16
	Bunches	35	0.01	<0.01	0.06	0.08
	Berry	35	0.02	<0.01	0.08	0.11
	Bunches	42	0.02	0.01	0.10	0.13
	Berry	42	0.02	<0.01	0.08	0.10

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

4.2 Berry fruits

Reference: Bayer Australia Limited, Residue trials with Mesurol in Strawberries in Belgium, (from Bayer Australia Limited Submission 110, 22/12/78); Residue trials with Mesurol Snail Bait in Strawberries in Belgium, (from Bayer Australia Limited Submission 110, 22/12/80), Report numbers 2103/75, 2104/75.

Mesurol snail baits (4% methiocarb) were applied once to strawberries (var. Gorella) at 1.6 g ai/100 m^2 (0.16 kg ai/ha). Residues were determined in whole fruit using a GC method. It was stated that methiocarb sulfoxide and sulfone were included in the analyses.

Residues were non-detectable (<0.01 mg/kg) at 0, 4, 7 and 14 DAT in the two trials. The application rate corresponds to approximately one third of the maximum Australian label application rate for the 20 g/kg bait formulation.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Strawberries in Australia, (from Bayer Australia Limited Submission 110, 22/12/80), Report numbers 12/80. Trial location: NSW, Australia.

In this trial Mesurol 75% WP was applied to strawberries as a high volume spray at 150 g ai/100 L (1.95 kg ai/ha with spray volume of 1300 L/ha). Methiocarb residues were determined as the sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone using a GC method (*Determination of residues of Mesurol and its toxic metabolites in crops*, K. J. Strankowski and C., W. Stanley). Recovery of residues was reported as 68% with fortification at 1 ppm.

Rate	PHI (days)	Residues (mg/kg)
0.15 kg ai/100 L (1.95 kg ai/ha, spray volume 1300 L/ha)	1 3 5 7 10 14	26.5 21.5 18.0 10.0 8.5 7.0

Use of methiocarb WP formulation as a spray on strawberries or other berries is not approved in Australia.

Reference: JMPR (1981) Review of Methiocarb, pages 334 and 336.

Residue trials involving spray application of methiocarb WP formulation to blueberries and currants were reviewed by the JMPR in 1981 and are summarised below.

			Residues (mg/kg) / PHI (days)					
Crop, location	Rate (kg ai/ha)	No. applications	0	3-5	7-8	13-14	21	28-35
Blueberry (USA) 75 WP	1.7+1.7+2.2	3	3.3	5.2	5.4			
	2.2 (aerial)	2	5.4	3.4	3.6			
	2+2.2	2	3.1					
	2.2	2	25.6					
Currants, red (Germany) 50 WP	1.0	3	12.8, 21.7, 6.5			5.7, 7.4, 3.0	4.6, 6.0, 1.6	2.9, 2.8, 4.3, 1.5, 0.28

The use of methiocarb WP formulation as a spray on berry crops is not approved in Australia.

Reference: Seym, M. and Walz-Tylla, D. Determination of residues of methiocarb/methiocarb-sulfon/ methiocarb-sulfoxid in/on strawberry (fruit-wa, fruit, preserve, jam). Processing study. Bayer Ag. Report No. RA-2101/91, 9 December 1993. Includes study numbers 102016. NRA study no. 6311.

Methiocarb formulated as a 50% wettable powder was applied as a spray twice to strawberry crops at a rate of 2 kg product/ha using 1000 L water/ha. The concentration of methiocarb in the spray mixture was 0.1%. The application interval was 14 days and the last application was made 7 days before harvest. Samples of fruit were collected, washed and jam and preserve prepared using normal domestic practice. Fruit was washed in standing water under slow movement. Analyses were done on the unwashed and washed fruit, jam and preserve.

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00014. The method involves extraction of residues with dichloromethane, concentration of the extract and redissolving of the residue in HCl. After column cleanup residues are determined separately using HPLC with a fluorescence detector. The LOQs for each compound are 0.01 mg/kg in fruit, giving a total LOQ of 0.03 mg/kg. The maximum storage interval between sampling and analysis was approximately 7 months.

Recoveries were as follows:

Chemical	Sample	Fortification level (mg/kg)	Average recovery (%)
Methiocarb	Fruit	0.04	87
	Fruit-washed	0.4	77
	Preserve	0.04	64
	Jam	0.04	87
Methiocarb sulfone	Fruit	0.04	99
	Fruit-washed	0.4	98
	Preserve	0.04	104
	Jam	0.04	72
Methiocarb sulfoxide	Fruit	0.04	97
	Fruit-washed	0.4	98
	Preserve	0.04	93
	Jam	0.04	99

Average of 2 recovery experiments for each sample and fortification level.

Residues of methiocarb and metabolites in strawberries, jam and preserve (mg/kg) – 0.1 kg ai/hL (WP)

Trial no.	Sample	PHI (days)	Methiocarb	Processing factor	Methiocarb sulfoxide	Processing factor
102016 (UTC)	Fruit-washed	7	0.075	0.57	0.049	0.72
	Fruit	7	0.132		0.068	
	Jam	7	0.048	0.36	0.044	0.65
	Preserve	7	<0.040	0	<0.040	0
102016 treated	Fruit-washed	7	0.17	0.49	0.16	0.84
	Fruit	7	0.35		0.19	
		10	0.12		0.14	
		14	0.09		0.12	
	Jam	7	0.08	0.23	0.12	0.63
	Preserve	7	0.09	0.26	0.09	0.47

Significant residues of methiocarb and methiocarb sulfoxide were detected in some untreated control samples. Results for the treated samples are an average of two samples. Methiocarb sulfone residues were <0.04 mg/kg in all fruit and processed samples.

Methiocarb and methiocarb sulfoxide residues in fruit were reduced by washing and did not concentrate in jam or preserve.

4.3 Orchard crops

4.3.1 Citrus

Reference: Bayer Australia Limited, Residue trials with Mesurol in oranges in Australia, (from Bayer Australia Limited Submission 110, 22/12/78), Report number 19/78.

One orange tree was sprayed once with approximately 10 litres using a 0.15% spray solution of Mesurol 75% WP (*ca.* 3.3 kg ai/ha). Residues of methiocarb, its sulfoxide and sulfone were determined by GC with FID detection following extraction and oxidation. Recoveries of methiocarb were 100% and 97% for pith and skin, respectively, when fortified at 0.5 mg/kg. Results are corrected for recovery.

Report no., date	Location	Rate	PHI (days)	Residues (mg/kg)	
				Skins	Pith
Bayer 19/78 (9.11.78)	Griffith, NSW	0.15 kg ai/100 L (3.3 kg ai/ha)	1	1.5	<0.05
			7	0.2	<0.05
			14	0.05	<0.05
			21	<0.05	<0.05
			28	<0.05	<0.05

Only a summary of the residue trial was available. The application rate corresponds to twice the Australian label rate for the WP formulation. Flesh of fruit was not analysed and results were not reported on a whole fruit basis.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Oranges in Australia, Study numbers 33/83.

In two separate trials one orange tree (var. Valencia) was treated with Mesurol 75% WP spray at either 225 g ai/100 L (12 L/tree) or 450 g ai/100 L (12 L/tree). Residues of "methiocarb and metabolites" were determined by GC with FID detection (method: *"Determination of residues of BAY 37344 and metabolites in apples and pears by flame photometric gas chromatography"*, J. S. Thornton). Recovery of methiocarb residues from peel and pulp fortified at 0.5 mg/kg was 84 and 96%, respectively. Results are corrected for recovery.

Report no., date	Location	Rate	PHI (days)	Residues (mg/kg)	
				Pulp	Peel
Bayer 33/83a (28.11.83)	Griffith, NSW	0.225 kg ai/100 L (12 L/tree)	1	0.63	10.7
			3	1.4	10
			6	0.2	7
			10	0.3	5.7

			14	0.3	2.5
Bayer 33/83b (28.11.83)	Griffith, NSW	0.45 kg ai/100 L (12 L/tree)	1 3 6 10 14	2 1.1 0.5 0.2 0.36	16 14.5 16 3 4.8

Only a summary of the residue trials was available. The application rates in the two trials correspond to 3 and 6 times the Australian label rate of 0.075 kg ai/100 L for the WP formulation. Results were not reported on a whole fruit basis and the longest PHI was only 14 days (Australian GAP is 6 week PHI). It is not clear whether the analytical results reported include the methiocarb sulfone and sulfoxide metabolites.

Reference: JMPR (1981) Review of Methiocarb p. 317 – 367.

Four USA residue trials on citrus fruits carried out in 1975 were reviewed by the JMPR in 1981. In the two orange, one lemon and one grapefruit trials no residues (<0.01 mg/kg) were detected in peel or pulp of the fruits sampled 30 to 91 days after the last of 5 applications (1.1 kg ai/ha) using 2% baits. The use does not correspond to Australian GAP for orchard situations (0.44 kg ai/ha, PHI 7 days) because the application rate is higher (2.5×) and the PHI is longer.

4.3.2 Stone Fruit

Reference: Chemagro Corporation, Untitled residue experiments from Chemagro Corporation, Report numbers 30945, 31440, 39661, 39662, 39663, 39664, 39665, 39666, 39667, 39668, 39669, 40260 and 40261, Reports dated between 1971 and 1974.

Residue trials for cherries carried out in the USA were included in this reference. The trials all involved a single foliar spray application of methiocarb 75% WP.

Report number (date)	Trial location	Rate (g ai/100 L)	Spray volume (L)	PHI (days)	Residues (mg/kg)
30945 20 Sept 71	Michigan, USA	99.5	2730 – 3640	15	1.23
31440 16 Nov 71	Washington, USA	33.2 99.5	To runoff To runoff	26 26	7.81 1.39
39661 27 Feb 74	West Virginia, USA	99.5	1650	7 14 21	9.00 2.75 7.50
39662 27 Feb 74	Illinois, USA	99.5	1820	7 14 21	4.50 1.85 4.25
39663 27 Feb 74	Illinois, USA	99.5	455	0 3 7 14 21	11.00 6.50 6.25 1.50 1.15
39664 27 Mar 74	Illinois, USA	99.5	1650	7 14	1.00 1.30
39665 27 Mar 74	Illinois, USA	99.5	1650	7 14 21	15.00 2.75 0.65

39666 27 Mar 74	Illinois, USA	99.5	1480	7 14 18	1.15 0.30 0.40
39667 27 Mar 74	Illinois, USA	99.5	910	7 14 21	13.50 6.00 5.00
39668 15 Apr 71	Illinois, USA	99.5	1820	0 3 7 14 21	14.50 6.75 9.00 5.00 2.00
39669 27 Mar 74	Illinois, USA	99.5	2143	7 14 21	3.25 2.50 0.30
40260 20 May 74	Illinois, USA	99.5	1229	0 3 14	1.20 1.40 0.62
40260 20 May 74	Illinois, USA	99.5	1229	0 3 14 21	0.07 <0.04 1.20 0.60
40261 10 Apr 74	Illinois, USA	99.5	1820	0 3 7 14 21	11.50 4.00 5.00 1.55 5.00
22/76 (a) 28 Nov 76 (application date)	Burleigh, NSW	225	2250 (9 L/tree)	1 3 8 10	7.27 4.57 1.68 0.67

Details of the analytical method used to determine residues were not provided. It can therefore not be established whether the values reported include the parent methiocarb plus the sulfoxide and sulfone metabolites. The use patterns do not correspond to Australian GAP.

Reference: Bayer Australia Report No. 56/86a, 56/86b

The following Australian residue trials were provided for spray application of methiocarb 750 g/kg WP to cherries. Full details of the trials were not available. The use patterns do not correspond to GAP in Australia.

Total methiocarb residues in cherries (mg/kg)

Trial no.	Location	Application			PHI (days)	Total residues (mg/kg)
		Rate (g ai/100 L)	Volume (L/ha)	No.		
56/86a	Victoria	150	>4000	1	1 3 5 7 10 14	10.3 9.7 7.7 5.7 5.3 3.0
56/86b	Victoria	300	>4000	1	1 3 5 7 10 14	17.3 7.1 9.0 6.3 6.1 3.6
54/88a	South Australia	150	1800	1	13	0.62

54/88b	South Australia	150	1800	1	20	1.10
54/88c	South Australia	300	1800	1	3	0.74
54.88d	South Australia	300	1800	1	20	1.01
55/88a	South Australia	150	1800	1	13	0.64
55/88b	South Australia	150	1800	1	20	1.23
55/88c	South Australia	300	1800	1	13	0.83
55/88d	South Australia	300	1800	1	20	0.97

Reference: Chemagro division of Baychem Corporation Residue Experiments: 162-1612-73D, 521-1617-73D, 514-1618-73D, 661-1620-73D, 761-1621-73D, 761-1622-73D (27 February 1974), 461-1615-73D and 461-1616-73D (10 April 1974).

Mesurol 75% WP was applied 4 times to peaches as a foliar spray at a rate of 16 oz ai/100 gal (100 g ai/100 L). Samples were stored for approximately 6 months prior to analysis. Details of the analytical method were not provided. Results are summarised below.

Total methiocarb residues in peaches

Trial no.	Location	Application			PHI (days)	Total residues (mg/kg)
		Rate (g ai/100 L)	Volume (L/ha)	No.		
162-1612-73D	West Virginia (USA)	99.5	3360	4	7 14 21	5.44 3.30 4.20
521-1617-73D	Ontario (Canada)	99.5	560	4	7 14 21	20.50 13.50 4.65
514-1618-73D	British Colombia (Canada)	99.5	3360	4	7 14 21	6.60 3.75 2.33
661-1620-73D	Washington (USA)	99.5	5152	4	7 14 21	11.50 8.50 3.00
761-1621-73D	North Carolina (USA)	99.5	3360	4	7 14 21	11.00 7.20 2.55
761-1622-73D	South Carolina (USA)	99.5	2240	4	7 14 21	4.05 1.80 0.70
461-1615-73D	California (USA)	99.5	5600	4	0 3 7 14 21	14.00 18.00 11.50 10.00 10.00
461-1616-73D	California (USA)	99.5	4480	4	7 14 21	23.20 11.00 7.25

The use pattern does not correspond to GAP in Australia.

Reference: Bayer Australia Limited, Report no. 25/80, 19.12.80, Trial location Hanwood, NSW.

Apricots (2 trees) were sprayed once with Mesurol 750 g/kg WP at a rate of 150 g ai/100 L (200 g product/100 L, 3 L/tree). Residues of methiocarb, its sulfoxide and sulfone were determined by GLC. Residues in fruit at 1, 3, 7 and 14 DAT were 5.5, 4.5, 2.6 and 1.0 mg/kg respectively. The use pattern does not correspond to GAP in Australia.

4.3.3 Pome Fruit

Reference: Biologisches Institut der Farbenfabriken Bayer AG Leverkusen, Berichte Nr. 45/62 and 86/63.

Only an untranslated summary table of two trials were provided. Full details of the trial and analytical methods were not available. The use pattern does not correspond to GAP in Australia.

Trial no.	Location	Application			PHI (days)	Gross residues (mg/kg)
		Rate	Volume (L/ha)	No.		
45/62	Rowhill, England	0.1%	NS	3	0 14 21 28	1.0 <0.15 <0.15 NA
86/63	Rowhill, England	0.15%	NS	3	74	<0.2

4.4 Vegetables

4.4.1 Leafy Vegetables

Reference: Bayer Australia Limited, Residue trials with Mesurol in Spinach in Germany, (from Bayer Australia Limited Submission 140, 5/3/81), Report numbers 2138/76, 2127/76 and 2126/76.

Three trials were carried out in Germany in 1976 involving 2 foliar spray applications of Mesurol 500 WP (500 g/kg methiocarb) to spinach (var. kamentina) at 0.3 kg ai/ha (600 L/ha spray volume). Analyses include methiocarb sulfoxide and sulfone.

Report no., date	Crop	Location	Rate	PHI (days)	Residues (mg/kg)
Bayer, 2128/76 (8.9.76)	Spinach	Monheim, Germany	2×0.3 kg ai/ha (14 day interval) (500 g/kg WP)	0 7 14 21 28	22.75 1.31 0.19 0.11 0.09
Bayer, 2128/76 (8.9.76)	Spinach	Monheim, Germany	2×0.3 kg ai/ha (14 day interval) (500 g/kg WP)	0 7 14 21 28	27.16 1.56 0.49 0.24 0.17
Bayer, 2126/76 (8.9.76)	Spinach	Monheim, Germany	2×0.3 kg ai/ha (500 g/kg WP)	0 7 14 21 28	12.94 0.45 0.10 0.12 0.1

The use pattern does not reflect the Australian use of methiocarb. Only the 20 g/kg methiocarb baits are approved for use on leafy vegetables in Australia.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Lettuce in Australia, (from Bayer Australia Limited Submission 140, 5/3/81), Report numbers 22/79a, 22/79b.

Two Australian trials were provided (summaries only) in which Mesurol 75 WP (750 g/kg methiocarb) was applied to lettuce seedlings (var. Imperial 847) at 150 g ai/100 L (equivalent to 570 g ai/ha with spray volume of 380 L/ha). Lettuce was harvested when the heart was formed. Residues of methiocarb and its sulfoxide and sulfone were determined as the sulfone. Recoveries were reported as 100% when fortified at 0.5 mg/kg.

Following a single application residues in lettuce were <0.05 mg/kg at 49 DAT. Following two applications (59 day interval) residues in lettuce were 21 mg/kg at 7 days after the last application.

The use pattern is not consistent with Australian GAP. Only the 20 g/kg methiocarb pellets are approved for use on leafy vegetables in Australia.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Lettuce in Australia, Study numbers 23/79a and 23/79b.

Two trials were provided (summaries only) in which lettuce seedlings were treated with Mesurol 20 g/kg methiocarb pellets. The first application occurred when seedlings were 7 cm in height. Methiocarb residues were determined by GC with flame photometric detection. Residues of methiocarb, its sulfoxide and sulfone were determined in the analyses. Recoveries of 70 and 100% were reported for samples fortified at 0.5 ppm.

In the first trial crops were treated four times (14 day interval) at 40 mg ai/m^2 (400 g ai/ha), giving methiocarb residues of <0.1 mg/kg 7 days after the last application (49 days after first application). In the second trial, lettuce seedlings were treated once with Mesurol 20 g/kg pellets at 400 g ai/ha, giving methiocarb residues of <0.05 mg/kg at 49 days after application.

Reference: JMPR (1981) Review of Methiocarb p. 317 – 367.

A number of residue trials were reviewed by the JMPR in 1981. Results are summarised below.

Crop, country, year	Product	Application no., rate (kg ai/ha)	PHI	Sample			
				Whole	Head	Outer leaves	Other leaves
Lettuce, USA (TX), 1976	20 g/kg bait	5 (1.1)	1 3-4 7	2.3 2.6 3.7	0.01 0.03 0.03	0.1 11 1.1	8.3 1.3 12.2
Lettuce, USA (FL) 1976	20 g/kg bait	5 (1.1)	1 3-4 7	1.8			
Lettuce USA 1976-1980	20 g/kg bait	5-6 (1.1)	1 3-4 7	0.02-6.5 (mean 2.5, n=7) <0.02-30 (mean 2.5, n=6) <0.01-11 (mean 3.7, n=5)	<0.02-7.1 (mean 1.4, n=7) <0.01-2.1 (mean 0.5, n=6) <0.01-1.3 (mean 0.3, n=5)	0.1-12.7 (mean 4.1, n=7) 0.05-59 (mean 12.3, n=6) 0.03-14 (mean 0.3, n=5)	0.18-5.5 (mean 2.4, n=7) 0.05-20 (mean 5, n=6) 0.02-52 (mean 19, n=5)
Lettuce, Germany, 1975e	40 g/kg baits	1 (0.12)**	0 3-4 7-8 10 14	<0.05-0.24 (mean 0.1, n=7) <0.05-0.1 (mean 0.05, n=7) <0.05-0.1 (mean <0.05, n=6) <0.05-0.5 (mean 0.09, n=7) <0.05 (n=7)			

** Sample not specified – assume results expressed for whole commodity

The trials did not address Australian GAP, which involves application of 20 g/kg pellets at up to 0.44 kg ai/ha, with a 7 day PHI. Residues in the vegetables were highly variable. In the USA trials methiocarb residues in the whole commodity at 7 days after the last application ranged from <0.01 mg/kg to 11 mg/kg. The results were less variable in the German trial but the application rate was too low. The high variability in residues in the USA trials could be due to pellets becoming lodged within the leaves of the crop during application.

4.4.2 Brassica vegetables

Reference: Bayer Australia Limited, Residue trials with Mesurol in Cabbage in Australia, (from Bayer Australia Limited Submission 140, 5/3/81), Report numbers 25/79c, 25/79b, 25/79c.

Three trials were carried out in which cabbages were treated between 1 and 6 times with Mesurol 75% WP (750 g/kg methiocarb) at 150 g ai/100 L (570 g ai/ha, spray volume 380 L/ha).

Following a single application methiocarb residues of 0.05 mg/kg were detected in cabbage at 91 days after treatment. Following two applications (55 day interval) methiocarb residues of 1.98 and 1.12 mg/kg at 22 and 28 days after the last application, respectively. Following 6 applications (approximately 14 day intervals) methiocarb residues of 3.10 and 3.75 mg/kg were detected in cabbages at 7 and 14 days after the last application.

The use pattern does not correspond to Australian GAP. Only the 20 g/kg pellet formulation is approved for use in leafy vegetables in Australia.

Reference: JMPR (1981) FAO Plant Production and Protection Paper, 42. Evaluations. 23 November – 2 December 1981, Rome, 1982 (pages 317 – 367).

A number of residue trials were reported in the 1981 JMPR review of methiocarb. These are summarised below. The trials did not address Australian GAP, which involves application up to 0.44 kg ai/ha (PHI 7 days).

Residues of methiocarb (total) in brassica vegetables

Crop, country, year	Product	Application No., rate (kg ai/ha)	PHI (days)	Crop part analysed		
				Head	Leaves	Whole
Broccoli USA (KS), 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8	0.06 0.66 0.2	0.44 0.28 1.8	
Broccoli, USA (OR), 1975	20 g/kg bait	5 (1.1)	1 5 7-8	<0.01 0.02 0.03	<0.01 0.06 0.1	
Broccoli, USA (TX), 1976	20 g/kg bait	5 (1.1)	1 3-4 7-8	<0.02 <0.02 0.04	<0.05 0.04 0.05	
Broccoli, USA (CA), 1978	20 g/kg bait	5 (1.1)	1	0.26		
Brussel sprouts, USA (IN), 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8			0.02, 0.03 0.2, <0.01 0.06, <0.01
Brussel sprouts, USA (KS), 1974	20 g/kg bait	6 (1.1)	1 3-4 7-8			0.4 <0.01 0.3
Brussel sprouts, USA (CA), 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8			<0.01, <0.01 <0.01, <0.01 <0.01, 0.02
Brussel sprouts, Canada, 1975	20 g/kg bait	6 (1.1)	1 3-4			0.24 0.18
Cabbage, Canada, 1975	20 g/kg bait	5 (1.1)	1 3 7	0.2 0.4 0.04	10 1.1 0.8	3.1 0.6 0.3
Cabbage, USA, 1975	20 g/kg bait	5-6 (1.1)	1 3 7	<0.01-1.1 (mean 0.2, n=8) <0.01-0.17 (mean 0.06, n=7) <0.01-0.05 (mean 0.02, n=6)	0.2-5.1 (mean 1.7, n=8) 0.18-3.2 (mean 1.1, n=7) 1.3-15 (mean 8.5, n=6)	0.08-1.6 (mean 0.6, n=8) 0.08-1.0 (mean 0.4, n=7) 0.4-4.5 (mean 2.3, n=6)
Cabbage, Germany, 1978	20 g/kg bait	1 (0.12)	0 4 7 14 21	<0.05-0.34 (mean 0.13, n=3) <0.05-1.7 (mean 0.4, n=3) <0.05 (n=3) <0.05 (n=3) <0.05 (n=3)		
Cauliflower Canada, 1975	20 g/kg bait	5 (1.1)	1 3 7	0.03 0.05 0.05	0.12 0.60 0.08	0.05 0.16 0.06
Cauliflower USA, 1975-6	20 g/kg bait	5-6 (1.1)	1 3 7 8	<0.01-3.0 (mean 0.75, n=7) <0.01-2 (mean 0.49, n=6) <0.01-1.1 (mean 0.19, n=6) 0.29	0.06-6.8 (mean 2.5, n=7) 0.04-12.4 (mean 3, n=6) <0.01-0.3 (mean 0.09, n=6) 11.4	0.04-3.5 (mean 1.5, n=7) 0.08-4.0 (mean 1.0, n=6) <0.01-1 (mean 0.18, n=6) 2.4
Cauliflower Germany, 1980	40 g/kg bait	2 (0.12)	0 4 7 14 28	0.3-2.3 (mean 1.0, n=4) 0.1-0.27 (mean 0.18, n=4) 0.05-0.14 (mean 0.09, n=4) <0.05 (n=4) <0.05 (n=4)	0.07-0.8 (mean 0.41, n=4) 0.07-0.36 (mean 0.2, n=4) <0.05-1.3 (mean 0.42, n=4) <0.05 (n=4) <0.05 (n=4)	<u>Stem</u> 0.61-5.9 (mean 3.2, n=4) 0.2-1.6 (mean 0.82, n=4) 0.13-4.6 (mean 2, n=4) <0.05-0.2 (n=4) <0.05 (n=4)

Reference: Nüßlein, F. Determination of residues of Mesurol-Schneckenkorn 4 RB (a. s. Methiocarb) in/on Brussels sprouts in the field in the Netherlands, France, Great Britain and Germany. Report no. RA-2001/00, Bayer AG, 15 November 2001. Includes study numbers R 2000 0011/1, R 2000 0013/8, R 2000 0014/6 and R 2000 0015/4. NRA study no. 6302.

Methiocarb formulated as a 4% bait was applied to Brussels sprouts at 28 and 14 days before harvest at rates of 5.0 kg product per ha (0.2 kg ai/ha). Applications were made at growth stages between BBCH 42 and 48. Crops were harvested 14 days after the last application and analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The maximum storage interval between sampling and analysis was approximately 6 months.

Recoveries were as follows:

Chemical	Fortification level (mg/kg)	Recoveries (%)	Mean Recovery (%)
Methiocarb	0.01 0.1	90, 91, 91 82, 89	91 86
Methiocarb sulfone	0.01 0.1	84, 85, 87 80, 84	85 82
Methiocarb sulfoxide	0.01 0.1	92, 92, 93 66, 93	92 80
methiocarb (total)	0.03 0.3	89, 89, 89 76, 89	89 83

Residues of methiocarb and its metabolites in Brussels sprouts (mg/kg) – 0.2 kg ai/ha (RB)

Trial no.	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 2000 0011/1	0 14	<0.010 <0.010	<0.010 <0.010	<0.010 <0.010	<0.03 <0.03
R 2000 0013/8	0 14	<0.010 <0.010	<0.010 <0.010	<0.010 <0.010	<0.03 <0.03
R 2000 0014/6	0 14 35	0.144 <0.010 <0.010	<0.010 <0.010 <0.010	0.012 <0.010 <0.010	0.17 <0.03 <0.03
R 2000 0015/4	0 13	<0.010 <0.010	<0.010 <0.010	<0.010 <0.010	<0.03 <0.03

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

Reference: Schöning, R. and Sur, R. Determination of residues of Mesurol Schneckenkorn 4 RB (A.S. Methiocarb) on red cabbage and round cabbage in the field in Germany, Great Britain and Netherlands. Report no. RA-2140/99, Bayer AG, 6 June 2001. Includes study numbers R 1999 0577/7, R 1999 0578/5, R 1999 0579/3 and R 1999 0580/7. NRA study no. 6307.

Methiocarb formulated as a 4% bait was applied to cabbage crops twice, at 28 and 14 days before the expected harvest time at rates of 0.2 kg ai/ha. The last application

occurred when cabbage heads were approximately 50% of the maximum size. Samples were collected up to 28 days after the last application then analysed methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg, giving a total LOQ of 0.03 mg/kg. The maximum storage interval between sampling and analysis was approximately 13 months.

Recoveries were as follows:

Chemical	Sample	Fortification level (mg/kg)	Average recovery (round cabbage, %)	Average recovery (red cabbage, %)
Methiocarb	Heads	0.01 0.05 0.1	88 89 87	88 91 89
Methiocarb sulfone	Heads	0.01 0.05 0.1	93 86 86	85 85 83
Methiocarb sulfoxide	Heads	0.01 0.05 0.1	99 92 94	93 97 91
Methiocarb (total)	Heads	0.01 0.05 0.1	93 89 89	89 91 88

Residues of methiocarb and its metabolites in cabbage (mg/kg) – 0.2 kg ai/ha (RB)

Trial no.	Sample	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 1999 0557/7	Red cabbage (head)	0 7 14 21	0.039 <0.010 0.014 <0.010	<0.010 <0.010 <0.010 <0.010	<0.010 <0.010 <0.010 <0.010	0.06 <0.03 0.03 <0.03
R 1999 0578/5	Red cabbage (head)	0 7 14 21	0.040 <0.010 <0.010 <0.010	<0.010 <0.010 <0.010 <0.010	<0.010 <0.010 <0.010 <0.010	0.06 <0.03 <0.03 <0.03
R 1999 0579/3	Round cabbage (head)	-0 +0 7 10 14 21 28	0.052 0.145 0.034 0.063 0.052 0.058 0.037	<0.010 <0.010 <0.010 <0.010 <0.010 <0.010 <0.010	<0.010 0.013 0.040 0.023 <0.010 <0.010 <0.010	0.07 0.17 0.08 0.09 0.07 0.08 0.06
R 1999 0580/7	Round cabbage (head)	-0 +0 7 10 14 20 28	<0.010 <0.010 <0.010 <0.010 <0.010 <0.010 <0.010	<0.010 <0.010 <0.010 <0.010 <0.010 <0.010 <0.010	<0.010 <0.010 <0.010 <0.010 <0.010 <0.010 <0.010	<0.03 <0.03 <0.03 <0.03 <0.03 <0.03 <0.03

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

4.4.3 Pulse and legume vegetables

Reference: Bayer Australia Limited, Residue trials with Mesurol in Dwarf French Beans in Germany, (from Bayer Australia Limited Submission 140, 5/3/81), Report numbers 2121/76, 2120/76, 2122/76.

In these trials (summaries provided only) dwarf French beans were treated with Mesurol 500 g/kg WP (spray) at 0.3 kg ai/ha. Results are summarised below.

Crop, country, Report, no, year	Product	Application No., rate (kg ai/ha)	PHI (days)	Residues (mg/kg)
Dwarf French beans Monheim, Germany, 2121/76, 11.11.76	500 g/kg WP	2×0.3 kg ai/ha	0 7 14 21 28	0.10 <0.05 <0.05 <LOD <LOD
Dwarf French beans Monheim, Germany, 2120/76, 11.11.76	500 g/kg WP	2×0.3 kg ai/ha	0 7 14 21 28	0.39 0.06 <LOD <LOD <LOD

The use pattern does not correspond to GAP in Australia because the use of the WP formulation as a spray on beans is not approved in Australia.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Beans in Australia, (from Bayer Australia Limited Submission 140, 5/3/81), Report numbers 21/79.

Bush beans (seedlings) were treated once with Mesurol 750 g/kg WP at 150 g ai/100 L (570 g ai/ha with 380 L/ha spray volume). Residues of methiocarb its sulfoxide and sulfone were determined using a GC method. Recovery was 68% when fortified at 1 mg/kg. Beans contained methiocarb residues of 0.3 mg/kg at 39 DAT.

Reference: JMPR (1981) FAO Plant Production and Protection Paper, 42. Evaluations. 23 November – 2 December 1981, Rome, 1982 (pages 317 – 367).

Residue trials on snap beans and lima beans were reviewed by the JMPR in 1981 and are summarised below.

Crop, country, year	Product	Application No., rate (kg ai/ha)	PHI (days)	Crop part analysed		
				Beans	Vines	Pod
Beans, snap USA, (OR) 1977	20 g/kg bait	5 (1.1)	1	0.03		
Beans, snap USA (FL) 1975-6	20 g/kg bait	6 (1.1)	1 3-4 7-8	<0.01 0.02 <0.01	<0.01 <0.01 <0.01	
Beans, snap USA (NY) 1974-75	20 g/kg bait	5 (1.1)	1 3-4 7-8	0.5 0.02 0.02	0.5 0.06	

Beans, snap USA (IN) 1974-75	20 g/kg bait	5 (1.1)	1 3-4 7-8	0.03 <0.01 0.04	0.5 0.1 0.3	
Beans, snap Canada 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8	<0.01 <0.01 0.01	<0.01 0.1	
Beans, lima USA, (CA) 1975	20 g/kg bait	4 (1.1)	0			0.35
Beans, lima USA, (WI) 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8	<0.01 <0.01 0.02	0.03 0.6 0.04	0.03 0.01 0.03
Beans, lima USA, (NJ) 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8	<0.01 <0.01 <0.01	0.2	0.02 0.01 0.02
Beans, lima USA, (IN) 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8	<0.01 <0.01 <0.01	<0.01	<0.01 0.04 0.02
Beans, lima Canada 1975	20 g/kg bait	5 (1.1)	1 3-4 7-8	0.01 <0.01 <0.01	0.02 0.11	0.01 0.03 <0.01

Australian GAP for methiocarb pellets involves application at up to 0.44 kg ai/ha (PHI 7 days). The residue trials available for review involved 4-6 applications of methiocarb 20 g/kg baits at 1.1 kg ai/ha, 2.5 times the maximum application rate in Australia. At 7 days after the last treatment methiocarb residues in beans (of snap and lima beans) were, in rank order, <0.01 (4), 0.01, 0.02 (2) and 0.04 mg/kg (median underlined). Residues in pods (lima beans only) at 7 DALA were <0.01, 0.02 (2) and 0.03 mg/kg. Residues in bean vines were <0.01, 0.04, 0.06, 0.1 and 0.3 mg/kg.

4.4.4 Root and tuber vegetables

Reference: Bayer Australia Limited, Residue trials with Mesurol in Potatoes in Germany, (from Bayer Australia Limited Submission 140, 5/3/81), Report numbers 99/72, 98/72.

Potatoes (var. Grata) were sprayed once with methiocarb 500 g/kg WP at 0.57 kg ai/ha (150 g ai/100 L) and residues of methiocarb, its sulfoxide and sulfone were determined using a GC method. No detectable residues (<0.02 mg/kg) were found in potatoes in the two trials at 14, 21 or 28 days after application.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Carrots in Australia, (from Bayer Australia Limited Submission 140, 5/3/81), Report number 1/80.

Carrots (var. Top weight) were treated at the seedling stage with Mesurol 750 g/kg WP as a single spray application at 150 g ai/100 L (570 g ai/ha with 380 L/ha spray volume). Residues of methiocarb, its sulfoxide and sulfone were determined by GC. Recovery was stated as 116% when fortified at 0.5 mg/kg. Residues were below the limit of detection (0.1 mg/kg) at 42 days after treatment.

Reference: Nüßlein, F. Determination of residues of Draza 3 RB (a. s Methiocarb) on potato in the field in the Federal Republic of Germany and Great Britain. Report no. RA-2129/00, Bayer AG, 28 August 2001. Includes study numbers R 2000 0330/7, R 2000 0486/9, R 2000 0487/7 and R 2000 0488/5. NRA study no. 6301.

Methiocarb formulated as a 3% bait was applied to potato crops at 35 and 7 days before harvest at rates of 5.0 kg product per ha (0.15 kg ai/ha). Crops were harvested 7 days after the last application and analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The storage interval between sampling and analysis was approximately 7-8 months.

Recoveries were as follows:

Chemical	Fortification level (mg/kg)	Recoveries (%)	Mean Recovery (%)
Methiocarb	0.01 0.1	74, 77, 98, 106 91, 95, 96, 97	89 95
Methiocarb sulfone	0.01 0.1	76, 77, 92, 93 97, 97, 99, 100	85 98
Methiocarb sulfoxide	0.01 0.1	82, 85, 95, 103 93, 95, 97, 98	91 96
methiocarb (total)	0.03 0.3	78, 79, 95, 101 94, 96, 98, 98	88 97

Residues of methiocarb and its metabolites in potatoes (mg/kg) – 0.15 kg ai/ha (RB)

Trial no.	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 2000 0330/7	7	<0.010	<0.010	<0.010	<0.03
R 2000 0486/9	7	<0.010	<0.010	<0.010	<0.03
R 2000 0487/7	7	<0.010	<0.010	<0.010	<0.03
R 2000 0488/5	7	<0.010	<0.010	<0.010	<0.03

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

4.4.5 Fruiting vegetables

Reference: Bayer Australia Limited, Residue trials with Mesurol in Cucumber in Australia, (from Bayer Australia Limited Submission 140, 5/3/81), Report number 26/79.

Cucumbers (var. Crystal apple) were treated with Mesurol 750 g/kg WP as a single spray application at 150 g ai/100 L (570 g ai/ha). Residues of methiocarb its sulfoxide and sulfone were determined by GC. Recovery was stated as 96% when fortified at 1 mg/kg. No methiocarb residues were detected (<0.1 mg/kg) at 63 days after treatment.

The use pattern does not reflect Australian GAP, as there is no approved use of methiocarb as a spray on fruiting vegetables. Only a summary of the trial was available.

Reference: Bayer Australia Limited, Residue trials with Mesurol in Tomato in Australia, (from Bayer Australia Limited Submission 140, 5/3/81), Report number 27/79.

Tomatoes (var. Grosse Lisse) were treated with Mesurol 750 g/kg WP as a single spray application at 150 g ai/100 L (570 g ai/ha). Methiocarb residues were determined as methiocarb, its sulfoxide and sulfone. Recovery was reported as 51% with fortification at 0.5 mg/kg. No residues were detected (<0.1 mg/kg) in fruit harvested 91 days after application.

Reference: JMPR (1981) FAO Plant Production and Protection Paper, 42. Evaluations. 23 November – 2 December 1981, Rome, 1982 (pages 317 – 367).

Residue trials on fruiting vegetables (sweet corn, tomatoes) were reviewed by the JMPR in 1981 and are reproduced below.

Crop, country, year	Product	Application No., rate (kg ai/ha)	PHI (days)	Crop part analysed			
				Green forage	Kernel	Cob	Husk
Corn, sweet USA, 1977	20 g/kg bait	4 (1.1)	0 1 3 7	0.06-8.2 (mean 1.2, n=11) 0.07-1.4 (mean 0.4, n=11) 0.08-2.1 (mean 0.6, n=11) 0.07-3.4 (mean 0.8, n=11)	<0.01-<0.02 <0.01-<0.02 <0.01-<0.02 <0.01-<0.02	<0.01-0.1 <0.01-0.02 <0.01-0.03 <0.01-0.04	<0.01-0.4 (mean 0.13, n=11) <0.01-0.6 (mean 0.13, n=11) 0.06-0.5 (mean 0.11, n=11) 0.02-0.75 (mean 0.22, n=11)
Corn, field USA 1977	20 g/kg bait	4 (1.1)	9			<0.03	
				Fruit			
Tomato Canada 1975	20 g/kg bait	5 (1.1)	0 7	<0.01 0.05			
Tomato USA	20 g/kg bait	5-6 (1.1)	0 1 3-4 7	<0.01-0.42 (mean 0.06, n=8) <0.01-0.08 (mean 0.03, n=7) <0.01-0.07 (mean 0.02, n=8) <0.01-0.3 (mean 0.08, n=8)			
Tomato USA (CA) 1977	20 g/kg bait	6 (1.1)	0	<0.02 (fruit) <0.02 (dry pulp) <0.02 (puree) <0.02 (juice)			

The residue trials did not address Australian GAP. Methiocarb residues in sweet corn cobs were ≤0.04 mg/kg at 7 days after the last application at 1.1 kg ai/ha in the trials presented. Residues in tomatoes were ≤0.3 mg/kg at 7 days after the last treatment at 1.1. kg ai/ha.

Reference: Nüßlein, F. Determination of residues of Mesurol Schneckenkorn (4 RB) (A.S. Methiocarb) in/on corn following spread application in the field in Germany. Report no. RA-2049/01, Bayer AG, 10 September 2002. Includes study numbers R 2001 0124/4 and R 2001 0217/4. NRA study no. 6305.

Methiocarb formulated as a 4% bait was applied to corn crops after seeding (pre-emergent) and at growth stage BBCH 11-12 (1-2 leaves unfolded) at rates of 3.0 kg product per ha (0.12 kg ai/ha). Whole plants without roots and cobs without husks were sampled on day 119 or 122 after application and kernels were harvested on day 143 after the last application.

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg in plant, cobs and kernels, giving a total LOQ of 0.03 mg/kg. The maximum storage interval between sampling and analysis was approximately 5 months.

Recoveries were as follows:

Chemical	Sample	Fortification level (mg/kg)	Recoveries (%)	Mean Recovery (%)
Methiocarb	Plant without roots Cobs without husks	0.01 0.01	92, 84, 86, 84, 97, 90, 90 84, 80, 88	89 84
Methiocarb sulfone	Plant without roots Cobs without husks	0.01 0.01	97, 95, 94, 95, 94, 99, 90 94, 90, 98	95 94
Methiocarb sulfoxide	Plant without roots Cobs without husks	0.01 0.01	95, 95, 95, 95, 93, 96, 99 90, 87, 92	95 90
Methiocarb (total)	Plant without roots Cobs without husks	0.01 0.01	95, 91, 92, 91, 95, 95, 93 89, 86, 93	93 89

Residues of methiocarb and its metabolites in corn (mg/kg) – 0.12 kg ai/ha (RB)

Trial no.	Sample	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 2001 0124/4 Corn	Plant w/o roots	122	<0.010	<0.010	<0.010	<0.03
	Cobs w/o husks	122	<0.010	<0.010	<0.010	<0.03
	Kernels	143	<0.010	<0.010	<0.010	<0.03
R 2001 0317/4 Corn	Plant w/o roots	119	<0.010	<0.010	<0.010	<0.03
	Cobs w/o husks	119	<0.010	<0.010	<0.010	<0.03
	Kernels	143	<0.010	<0.010	<0.010	<0.03

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

Reference: Preu, M. Determination of residues of methiocarb in/on tomato following spread application of Mesurol-Schneckenkorn 4 RB (a.s. methiocarb) to tomato plants in the field in Portugal and Spain. Report no. RA-2164/01, Bayer AG, 27 May 2002. Includes study numbers R 2001 0424/3 and R 2001 0521/1. NRA study no. 6309.

Methiocarb formulated as a 4% bait was applied to tomato crops at growth stages BBCH 13-15 and 18-19. The interval between applications was 14 days and the last application was made 71-81 days before harvest. The application rates were 3.0 kg product per ha (0.12 kg ai/ha).

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg in fruit, giving a total LOQ of 0.03 mg/kg. The maximum storage interval between sampling and analysis was approximately 3 months.

Average recoveries were: methiocarb (90%), methiocarb sulfone (94%), methiocarb sulfoxide (94%) and total methiocarb 93% (n=7). Fortification levels were 0.01 mg/kg for the three compounds.

Residues of methiocarb, methiocarb sulfoxide and methiocarb sulfone were <0.01 mg/kg, giving a total methiocarb residue of <0.03 mg/kg in fruit for the two trials.

Reference: Seym, M. Determination of residues of Mesurol 50 WP on pepper, melon and tomato in Portugal and Spain. Bayer AG. Report no. 2087/93. 13 May 1997. Includes study numbers 304344, 304352, 304360, 304379, 304387, 304395, 304409, 304425 and 304433. NRA study no. 6312.

Methiocarb formulated as a 50% wettable powder was applied as a spray 2-3 times to tomato, peppers and melons using a spray concentration of 0.1 kg ai/100 L. Samples were collected from treated plots up to 28 days after the last application and analysed for methiocarb, its sulfoxide and sulfone. Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00014. The method involves extraction of residues with dichloromethane, concentration of the extract and redissolving of the residue in HCl. After column cleanup residues are determined separately using HPLC with a fluorescence detector.

Mean recovery of methiocarb, methiocarb sulfoxide and methiocarb sulfone (%)

Matrix	Fortification Level (mg/kg)	Methiocarb	Methiocarb Sulfoxide	Methiocarb sulfone
Pepper (fruit)	0.02 0.1 0.2 0.5	76 76 80 70	106 115 103 113	97 95 94 89
Washings	0.02 0.1 0.5	86 117 102	108 83 107	103 99 103
Melon (pulp)	0.02 0.1 0.5	88 82 93	101 113 108	96 98 89
Melon (pulp)	0.02 0.1	96 96	103 106	98 94
Melon (peel)	0.02 0.1 0.2 0.5	89 75 85 86	105 125 112 95	97 97 96
Melon (peel)	0.02 0.2	96 85	109 108	102 89
Tomato	0.02 0.1 0.2	88 89 87	102 107 108	93 96 99

Residues of methiocarb and its metabolites in various crops (mg/kg) – 0.1 kg ai/hL (WP)

Trial no.	Application No., rate (ai) (interval)	Spray volumes (L/ha)	Growth stage at appn (BBCH)	Sample	PHI (days)	M	MSO	MSO2	Total M
304344 Pepper	3x0.1 kg ai/hL (7, 11 days)	1000 1155 1000	71-73 71-75 75-79	Pepper	0 0 3 7 14 28	0.13 0.57 0.33 0.36 0.22 0.17	0.16 0.34 0.23 0.33 0.27 0.13	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.30 0.92 0.58 0.70 0.50 0.31
304352 Pepper	3x0.1 kg ai/hL (7, 9 days)	1173 1306 1306	69-75 69-81 69-89	Pepper	0 0 3 5 7 14 28	0.06 0.18 0.08 0.09 0.13 0.03 0.03	0.05 0.05 0.06 0.08 0.10 0.03 0.24	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.12 0.24 0.15 0.18 0.24 0.07 0.28
				Pepper (washed) Washings	7 14 7 14	0.06 <0.02 0.04 <0.02	0.09 0.05 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.16 0.07 0.06 0.03
304360 Melon	2x0.1 kg ai/hL (18 days)	1000 1062	65-75 69-85	Melon (pulp)	0 0 3 7 14 28	<0.02 0.07 <0.02 <0.02 <0.02 <0.02	0.05 0.12 0.05 0.06 0.04 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.07 0.20 0.07 0.08 0.06 0.03
				melon (peel)	0 0 3 7 14 28	0.07 1.70 0.74 0.96 0.41 0.19	0.20 1.20 0.64 0.55 0.32 0.16	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.28 2.91 1.39 1.52 0.74 0.36
				melon (whole)	0 0 3 7 14 28	0.03 0.53 0.20 0.29 0.14 0.06	0.10 1.43 0.21 0.20 0.13 0.05	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.14 0.97 0.42 0.50 0.28 0.12
304379 Melon	2x0.1 kg ai/hL (14 days)	1062 1137	80-85	Melon (pulp)	0 0 3 5 7 14 28	<0.02 <0.02 0.07 <0.02 <0.02 <0.02 <0.02	0.06 0.03 0.08 <0.02 0.06 0.04 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.08 0.05 0.16 0.03 0.08 0.06 0.03
				melon (peel)	0 0 3 5 7 14 28	0.51 0.39 1.70 0.68 0.63 0.33 0.15	0.45 0.46 0.74 0.33 0.59 0.25 0.17	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.97 0.86 2.45 1.02 1.23 0.59 0.33
				melon (whole)	0 0 3 5 7	0.15 0.14 0.41 0.13 0.11	0.17 0.18 0.22 0.07 0.15	<0.02 <0.02 <0.02 <0.02 <0.02	0.33 0.33 0.64 0.21 0.27

					14 28	0.09 0.05	0.09 0.06	<0.02 <0.02	0.19 0.12
304387 Tomato	2x0.1 kg ai/hL (15 days)	1000 1000	69-79 80-89	Tomato	0 0 3 5 7 14 21	0.33 0.99 0.97 0.72 0.59 0.34 0.26	0.24 0.23 0.28 0.25 0.22 0.26 0.08	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.58 1.23 1.26 0.98 0.82 0.61 0.35
304395 Tomato	3x0.1 kg ai/hL (13, 16 days)	1209 1416 1416	1.9 m 2.3 m 2.3 m	Tomato	0 0 3 5 7 14	0.03 0.48 0.30 0.13 0.13 0.08	0.07 0.09 0.12 0.07 0.10 0.10	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.11 0.58 0.43 0.21 0.24 0.19
304409 Tomato	3x0.1 kg ai/hL (14, 14 days)	1500 1407 1500	75 77 79	Tomato	0 7 14	0.70 0.45 0.42	0.17 0.13 0.17	<0.02 <0.02 <0.02	0.88 0.59 0.60
304425 Melon	2x0.1 kg ai/hL (14 days)	1000 1000	67-79 67-85	Melon (pulp) melon (peel) melon (whole)	0 0 3 5 7 0 0 3 5 7 0 0 3 5 7	<0.02 0.02 <0.02 <0.02 <0.02 0.02 1.20 0.26 0.38 0.29 <0.02 0.37 0.09 <0.02 0.09	<0.02 <0.02 <0.02 <0.02 <0.02 0.06 0.40 0.15 0.21 0.22 0.03 0.13 0.06 0.07 0.07	<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 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 0.08 1.61 0.42 0.60 0.52 0.05 0.51 0.15 0.21 0.17
304433 Melon	2x0.1 kg ai/hL (14 days)	1000 1000	61-81	Melon (pulp) melon (peel) melon (whole)	0 7 0 7 0 7	<0.02 <0.02 0.22 0.05 0.08 0.02	<0.02 <0.02 0.16 0.14 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 0.39 0.20 0.15 0.08

Residues in untreated control samples were <0.02 mg/kg for each chemical except for trial 304379 where residues of 0.12 mg/kg were detected in melons. In calculating the total methiocarb residues <0.02 mg/kg results are assumed to be 0.01 mg/kg (ie ½ LOQ). Results are not corrected for recovery values or moisture contents in the samples. M = methiocarb. MSO = methiocarb sulfoxide. MSO2 = methiocarb sulfone.

4.4.6 Stalk and stem vegetables

Reference: Bayer Australia Limited, Residue trials with Mesurol in Celery in Australia, (from Bayer Australia Limited Submission 140, 5/3/81), Report number 4/80.

In this trial celery was treated once with Mesurol 750 g/kg WP as a single spray application at 150 g ai/100 L (570 g ai/ha). Residues of methiocarb, its sulfoxide and

sulfone were determined by GC. Recovery was reported as 78% with fortification at 1 mg/kg. Methiocarb residues of 0.1 mg/kg were detected in celery at 99 days after treatment.

Reference: JMPR (1981) FAO Plant Production and Protection Paper, 42. Evaluations. 23 November – 2 December 1981, Rome, 1982 (pages 317 – 367).

Residue trials in artichokes were reviewed by the JMPR in 1981. Results are presented below.

Crop, country, year	Product	Application No., rate (kg ai/ha)	PHI (days)	Residues (mg/kg)
Artichokes USA (CA), 1975	20 g/kg bait	5 (1.1)	1 3 7-8 13-14	0.03 0.03 0.05 <0.01
Artichokes USA (CA), 1977	20 g/kg bait	5 (1.1)	1	<0.01
Artichokes USA (CA), 1975	75% WP	5 (1.1)	0 1 3 7-8 13-14	8.9 4.1 3.8 1.5 0.9

The trials did not address Australian GAP (20 g/kg baits, max. rate 0.44 kg ai/ha, PHI 7 days).

4.5 Broadacre crops

4.5.1 Cereals

Reference: JMPR (1981) FAO Plant Production and Protection Paper, 42. Evaluations. 23 November – 2 December 1981, Rome, 1982 (pages 317 – 367).

One German residue trial on barley was reviewed by the JMPR in 1981. In this trial, a 40 g/kg bait formulation was applied to barley three times at 0.12 kg ai/ha. No methiocarb residues were detected (<0.05 mg/kg) in barley grain or straw at 76-92 days after the last application. This trial did not address the maximum Australian use pattern (0.44 kg ai/ha, PHI 7 days).

Three trials on rice were also reviewed. One involved a seed treatment application at 0.5 lb/100 lb seed (0.5 kg ai/100 kg seed). The other two trials involved application of methiocarb 750 g/kg WP as an aerial post-emergent spray at 2.2 kg ai/ha (2 applications). Results are as follows.

Crop, country, year	Product	Application No., rate (kg ai/ha)	PHI (days)	Residues (mg/kg)	
				Processed grain	Hulls
Rice USA (MN), 1977	75% WP	2 (2.2)	7-10 14 untreated	0.06 0.08 0.14	1.2 0.11 0.04-0.09
				Grain, green	Straw

Rice USA (MN), 1977	75% WP	2 (2.2)	0 1 3 7 10 untreated	21-48 25-89 12-18 6.6-18 6.8-23 0.1-1.6	4.6-20 9.4-11 5-6.2 3.9-10 0.6-8.4 0.04-0.05
				Grain	Straw
Rice USA 1977	75% ST (seed treatment)	1 (0.5 kg ai/100 kg seed)	105 119 141 147 untreated	0.03 0.24 0.01 0.11 0.02-0.4	0.14 0.84 0.32 <0.01 0.05-0.9

There are no approved uses of methiocarb as a seed treatment or as a foliar spray to cereal crops.

Reference: Nüßlein, F. Determination of residues of Mesurol-Schneckenkorn 4 RB (a. s. Methiocarb) in/on spring barley and spring wheat in the field in Germany and France. Report no. RA-2132/00, Bayer AG, 25 February 2002. Includes study numbers R 2000 0337/4, R 2000 0339/0, R 2000 0405/2 and R 2000 0407/9. NRA study no. 6303.

Methiocarb formulated as a 4% bait was applied to cereal crops at seeding and at growth stage BBCH 12 (2 leaves unfolded) at rates of 3.0 kg product per ha (0.12 kg ai/ha). Green plants were sampled at growth stages 29 and 51, which were 14 and 64 days after the last application. Grain and straw samples were collected at crop maturity 105-120 days after the last application.

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg for grain and 0.05 mg/kg for green plant material, giving a total LOQ of 0.03 mg/kg for grain and 0.15 mg/kg for green plant. The maximum storage interval between sampling and analysis was approximately 14 months.

Recoveries were as follows:

Chemical	Sample	Fortification level (mg/kg)	Recoveries (%)	Mean Recovery (%)
Methiocarb	Wheat Straw	0.05	80, 83, 87, 88	85
	Wheat Grain	0.01	79, 82, 84, 87	83
	Wheat Green material	0.01	76, 78, 83, 94	83
Methiocarb sulfone	Wheat Straw	0.05	85, 88, 89, 89	88
	Wheat Grain	0.01	81, 82, 84, 85	83
	Wheat Green material	0.01	80, 84, 92, 103	90
Methiocarb sulfoxide	Wheat Straw	0.05	85, 88, 91, 92	89
	Wheat Grain	0.01	73, 84, 86, 90	83
	Wheat Green material	0.01	77, 83, 93, 93	87
Methiocarb (total)	Wheat Straw	0.15	83, 88, 90, 97	90
	Wheat Grain	0.03	83, 85, 88, 78	84
	Wheat Green material	0.03	78, 82, 89, 97	87
Methiocarb	Barley Straw	0.05	82, 89, 91, 98	90
	Barley Grain	0.01	86, 87, 91, 94	90
	Barley Green material	0.01	76, 84, 94, 94, 96	89
Methiocarb	Barley Straw	0.05	96, 97, 97, 97	97

sulfone	Barley Grain	0.01	96, 98, 98, 102	99
	Barley Green material	0.01	69, 78, 90, 91, 93	84
Methiocarb sulfoxide	Barley Straw	0.05	80, 88, 90, 102	90
	Barley Grain	0.01	99, 100, 104, 106	102
	Barley Green material	0.01	63, 74, 85, 85, 90	79
Methiocarb (total)	Barley Straw	0.15	88, 89, 93, 99	92
	Barley Grain	0.03	94, 96, 97, 99	97
	Barley Green material	0.03	72, 76, 90, 91, 92	84

Residues of methiocarb and its metabolites in cereals (mg/kg) – 0.12 kg ai/ha (RB)

Trial no.	Sample	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 2000 0337/4	Forage	14	<0.010	<0.010	<0.010	<0.03
Spring barley	Forage	36	<0.010	<0.010	<0.010	<0.03
	Grain	106	<0.010	<0.010	<0.010	<0.03
	Straw	106	<0.050	<0.050	<0.050	<0.15
R 2000 0339/0	Forage	16	<0.010	<0.010	<0.010	<0.03
Spring wheat	Forage	51	<0.010	<0.010	<0.010	<0.03
	Grain	113	<0.010	<0.010	<0.010	<0.03
	Straw	113	<0.050	<0.050	<0.050	<0.15
R 2000 0405/2	Forage	18	<0.010	<0.010	<0.010	<0.03
Spring barley	Forage	43	<0.010	<0.010	<0.010	<0.03
	Grain	105	<0.010	<0.010	<0.010	<0.03
	Straw	105	<0.050	<0.050	<0.050	<0.15
R 2000 0407/9	Forage	26	<0.010	<0.010	<0.010	<0.03
Spring wheat	Forage	64	<0.010	<0.010	<0.010	<0.03
	Grain	120	<0.010	<0.010	<0.010	<0.03
	Straw	120	<0.050	<0.050	<0.050	<0.15

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

Reference: Nüßlein, F. Determination of residues of methiocarb, methiocarb sulfone and methiocarb sulfoxide in/on spring barley and spring wheat following spread application of Mesurol Schneckenkorn (4 RB) in the field in Greece, Portugal and Southern France. Report no. RA-2133/00, Bayer AG, 26 September 2002. Includes study numbers R 2000 0338/2, R 2000 0340/4, R 2000 0406/0 and R 2000 0408/7. NRA study no. 6304.

Methiocarb formulated as a 4% bait was applied to cereal crops at seeding and at growth stage BBCH 12-13 (2-3 leaves unfolded) at rates of 3.0 kg product per ha (0.12 kg ai/ha). The last application was at 91-141 days before harvest. Green plants were sampled between 23-71 days after the last application. Grain and straw samples were collected at crop maturity 91-141 days after the last application.

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg for grain and 0.05 mg/kg for green plant material, giving a total LOQ of 0.03 mg/kg for grain and 0.15 mg/kg for green plant. The maximum storage interval between sampling and analysis was approximately 14 months.

Recoveries were as follows:

Chemical	Sample	Fortification level (mg/kg)	Recoveries (%)	Mean Recovery (%)
Methiocarb	Barley Straw	0.05	83, 84, 84	84
	Barley Grain	0.01	75, 75, 76	75
	Barley Green material	0.01	71, 73, 76, 74	74
Methiocarb sulfone	Barley Straw	0.05	89, 89, 87	88
	Barley Grain	0.01	90, 86, 94	90
	Barley Green material	0.01	87, 90, 91, 91	90
Methiocarb sulfoxide	Barley Straw	0.05	90, 89, 85	88
	Barley Grain	0.01	90, 91, 94	92
	Barley Green material	0.01	82, 90, 87, 90	87
Methiocarb (total)	Barley Straw	0.15	88, 87, 85	87
	Barley Grain	0.03	85, 84, 88	86
	Barley Green material	0.03	80, 84, 85, 85	84

Residues of methiocarb and its metabolites in cereals (mg/kg) – 0.12 kg ai/ha (RB)

Trial no.	Sample	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 2000 0338/2 Spring barley	Forage	43	<0.010	<0.010	<0.010	<0.03
	Forage	64	<0.010	<0.010	<0.010	<0.03
	Grain	141	<0.010	<0.010	<0.010	<0.03
	Straw	141	<0.050	<0.050	<0.050	<0.15
R 2000 0340/4 Spring wheat	Forage	23	<0.010	<0.010	<0.010	<0.03
	Forage	41	<0.010	<0.010	<0.010	<0.03
	Grain	91	<0.010	<0.010	<0.010	<0.03
	Straw	91	<0.050	<0.050	<0.050	<0.15
R 2000 0406/0 Spring barley	Forage	28	<0.010	<0.010	<0.010	<0.03
	Forage	57	<0.010	<0.010	<0.010	<0.03
	Grain	114	<0.010	<0.010	<0.010	<0.03
	Straw	114	<0.050	<0.050	<0.050	<0.15
R 2000 0408/7 Spring wheat	Forage	28	<0.010	<0.010	<0.010	<0.03
	Forage	71	<0.010	<0.010	<0.010	<0.03
	Grain	119	<0.010	<0.010	<0.010	<0.03
	Straw	119	<0.050	<0.050	<0.050	<0.15

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

4.5.2 Oilseeds

Residue trials on sunflower and rapeseed crops were provided. Additional trials on rapeseed were reviewed by the JMPR in 1999, however the trials did not address the Australian use pattern.

Reference: Schöning, R. and Sur, R. Determination of residues of Mesurol Schneckenkorn 4 RB (A.S. Methiocarb) in/on winter rape in the field of Belgium, France, Great Britain and in Germany. Report no. RA-2169/99, Bayer AG, 11 July 2001. Includes study numbers R 1999 0711/7, R 1999 0712/5, R 1999 0713/3 and R 1999 0714/1. NRA study no. 6306.

Methiocarb formulated as a 4% bait was applied to rape (canola) crops at growth stages 12-14 and then 14 days later. Samples of green plant were collected between 0 and 154 days after the second application and seeds were collected at crop maturity 266-286 days after the last application. The application rates were 3.0 kg product per ha (0.12 kg ai/ha).

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg for seed and green plant, giving a total LOQ of 0.03 mg/kg. The maximum storage interval between sampling and analysis was approximately 19 months.

Recoveries of methiocarb and its metabolites in rape (mg/kg)

Chemical	Sample	Fortification Level (mg/kg)	Recovery (%)	Average (%)
Methiocarb	Green plant	0.01	83, 86, 86	
		0.01	87, 91, 76	85
		0.1	96	96
	Seed	0.01	86, 90, 87	
		0.01	73	84
Methiocarb sulfone	Green plant	0.01	90, 91, 96	
		0.01	94, 96, 85	92
		0.1	88	88
	Seed	0.01	92, 97, 92	
		0.01	99	95
Methiocarb sulfoxide	Green plant	0.01	90, 96, 95	
		0.01	100, 105, 92	96
		0.1	97	97
	Seed	0.01	87, 89, 90	
		0.01	91	89
Total methiocarb	Green plant	0.03	88, 91, 92	
		0.03	94, 97, 84	91
		0.3	94	94
	Seed	0.03	88, 92, 90	
		0.03	88	90

Residues of methiocarb and its metabolites in rape (mg/kg) – 0.12 kg ai/ha (RB)

Trial no.	Sample	PHI (days)	Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide	Total methiocarb
R 1999 0711/7	Green plant	0	<0.010	<0.010	0.018	0.04
		69	<0.010	<0.010	<0.010	<0.03
		145	<0.010	<0.010	<0.010	<0.03
	Seed	266	<0.010	<0.010	<0.010	<0.03
R 1999 0712/5	Green plant	0	<0.010	<0.010	<0.010	<0.03
		11	<0.010	<0.010	<0.010	<0.03
		154	<0.010	<0.010	<0.010	<0.03
	Seed	280	<0.010	<0.010	<0.010	<0.03
R 1999 0713/3	Green plant	0	0.037	<0.010	<0.010	0.06
		34	<0.010	<0.010	<0.010	<0.03
		141	<0.010	<0.010	<0.010	<0.03
	Seed	286	<0.010	<0.010	<0.010	<0.03
R 1999 0714/1	Green plant	4	0.051	<0.010	<0.010	0.07
		7	<0.010	<0.010	<0.010	<0.03
		14	<0.010	<0.010	<0.010	<0.03
		28	<0.010	<0.010	<0.010	<0.03
	Seed	284	<0.010	<0.010	<0.010	<0.03

Residues were <0.010 mg/kg for each metabolite in all control samples. Results are expressed on a fresh weight basis and are not corrected for recoveries.

Reference: Heinemann, O. and Preu, M. Determination of residues of Mesurol Schneckenkorn (4 RB) in/on sunflower after spread application in the field in Northern France. Report no. RA-2146/01, Bayer AG, 12 February 2002. Includes study numbers R 2001 0116/3 and R 2001 0117/1. NRA study no. 6308.

Methiocarb formulated as a 4% bait was applied to sunflower crops 98 and 84 days before harvest when crops were 0.15-0.2 m or 0.38-0.5 m in height. The interval between applications was 14 days. Samples of seeds were collected at crop maturity 84 days after the last application. The application rates were 3.0 kg product per ha (0.12 kg ai/ha).

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with aqueous acetonitrile and column cleanup. Residues of methiocarb and its metabolites are determined separately. The LOQs for each compound are 0.01 mg/kg for grain, giving a total LOQ of 0.03 mg/kg. The maximum storage interval between sampling and analysis was approximately 3 months.

Average recoveries were: methiocarb (98%), methiocarb sulfone (96%), methiocarb sulfoxide (97%) and total methiocarb 97% (n=7). Fortification levels were 0.01 mg/kg for the three compounds.

Residues of methiocarb, methiocarb sulfoxide and methiocarb sulfone were <0.01 mg/kg, giving a total methiocarb residue of <0.03 mg/kg in seed for the two trials.

4.5.3 Pastures

No residue data were available for pastures.

4.6 Rotational crops

Reference: Murphy, JJ, Morris, RA, Residues of ^{TM}Mesurol in Rotational crops, Study number MR66926, 1 February 1979.

Several pages were missing from this report, however the following information was available for review. Mesurol 75 WP was applied to bare soil at rates of 20, 40, 80 and 160 oz ai/acre (equivalent to approximately 1.4, 2.8, 5.6 and 11.2 kg ai/ha). Representative cereal, legume and root crops were planted on these plots at 30, 60, 90, 120 and 365 days after treatment.

Residues in corn green forage were <0.02 mg/kg when planted 30 days after treatment to bare soil at the 2.8 and 5.6 kg ai/ha rates, and 0.14 mg/kg at the 11.2 kg ai/ha rate. Residues in corn kernel were <0.02 mg/kg for all treatment rates when planted from 30 days after treatment.

In black eyed peas, residues in green vines were found at 0.15 mg/kg for the 30 DAT planting at 5.6 and 11.2 kg ai/ha treatment group, and at 0.07 mg/kg for the 90 DAT

planting at 11.2 kg ai/ha treatment group. Residues in peas and pods were <0.02 mg/kg for all treatment rates from 30 DAT planting.

Finite residues at 0.29 mg/kg were found in turnip tops for the 11.2 kg ai/ha rate for 30 DAT planting.

4.7 Animal Feeding Studies

Summaries and results from three animal feeding studies were made available to APVMA reviewers to support the review of methiocarb. The complete poultry study was provided however the complete cow transfer studies were not submitted for review. The same studies were evaluated by the JMPR in 1999. The JMPR evaluation of these studies is reproduced below.

Reference: JMPR (1999) FAO Plant Production and Protection Paper, 157. Evaluations. Part 1-Residues. Volume 1. 20-29 September 1999, Rome, 2000.

The following is reproduced from the JMPR (1999) periodic review of methiocarb.

"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

Poultry commodities and milk were stored for less than 1 month prior to analysis, and tissues from the cattle feeding study were stored for less than 3 months prior to analysis.

The above poultry study was provided to the NRA for assessment in this review.

5 Fate of residues during processing and storage

5.1 In processing

The effect of the vinification process on methiocarb residues was investigated by Miller et al. (1985). This study is presented in 4.1.

Processing studies in which the effect on methiocarb residues from washing, peeling and cooking of potatoes, and washing and preserving strawberries and jam was investigated were reviewed by the JMPR in 1999. These studies were not made available to the NRA.

Reference: Beier, C. and Babczinski, P. Aqueous hydrolysis of Mesurol® (methiocarb) under conditions of processing studies. Bayer AG report: MR-543/00, 2001-12-04. Laboratory project ID M1771089-3. NRA study no. 6313.

This study investigates the hydrolysis of ^{14}C-methiocarb in water at various pHs and temperatures. Buffered water at pHs of 4, 5 and 6 and containing 0.5 mg ai/L were prepared with *ca.* 1% acetonitrile for solubilisation of the methiocarb. The pH 4 solution was incubated for 20 minutes at 90°C. The pH 5 solution was incubated for 60 minutes at 100°C and the pH 6 solution was incubated at 120°C (autoclave) for 20 minutes.

Recovery of radioactivity was 100.0-103.4% of the initial radioactivity.

	Methiocarb		Methiocarb phenol		M1	
Conditions	T=0	Termination	T=0	Termination	T=0	Termination
PH 4, 90°C, 20 mins.	99.6	98.1	<0.2	0.5	<0.2	0.4
PH 5, 100°C, 60 mins	99.6	47.3	<0.2	46.6	<0.2	7.5
PH 6, 120°C, 20 mins	98.0	2.3	1.2	92.7	0.6	4.7

Degradation of methiocarb was greatest at higher pH. Little degradation was observed at pH 4.

5.2 In storage

Two storage stability studies were available for review, including one published review of stability of various carbamate residues in animal tissues and one study which investigated the stability of residues in various plant commodities. The stability of methiocarb, methiocarb sulfoxide and methiocarb sulfone were also reviewed by the JMPR (1999). Articles referred to in the JMPR report were not available for review.

Reference: Ali, M.S, White, J.D, Bakowski, R.S, Philippo, E.T., Ellis, R.L, Analyte Stability Study of N-Methylcarbamate Pesticides in Beef and Poultry Liver tissues by

Liquid Chromatography, *Journal of AOAC International*, 76(6), 1993, p. 1309 – 1316.

The stability of residues of various carbamate pesticides, including methiocarb and methiocarb sulfoxide, were determined in beef, duck and poultry livers. The results for beef liver fortified with methiocarb and methiocarb sulfoxide at 200 μg/kg and stored for 6 months at -4°C are summarised below.

	Residues (μg/kg) / Storage period (months)								
Analyte	Initial	0.5	1	1.5	2	3	4	5	6
Methiocarb sulfoxide	24.8	43.0	70.5	38.4	53.3	60.6	33.3	37.0	43.7
Methiocarb	293.9	262.1	273.1	278.7	319.7	317.4	372.0	351.4	301.0
Methiocarb sulfoxide[1]	126.7	147.2	118.4		119.8	82.1			88.0

[1] Stability of methiocarb sulfoxide residues was redetermined after initial results showed variability in residues.

The results are highly variable for both methiocarb and methiocarb sulfoxide over the 6-month storage period.

Reference: Preu, M. Storage stability of methiocarb, methiocarb sulfoxide and methiocarb sulfone in/on canola (seed), grapes (bunch of grapes), potato (tuber) and field pea (seed) during freezer storage for 24 months. Bayer CropScience AG, Report no. MR-451/01, 7 November 2002. Study identification P 642001005. NRA study no. 6314.

Samples were fortified with methiocarb, methiocarb sulfoxide and methiocarb sulfone at a level of 0.2 mg/kg then stored at -18°C for up to 24 months. Samples were analysed at several time points during the storage period.

Samples were analysed for methiocarb, methiocarb sulfone and methiocarb sulfoxide residues using HPLC-MS/MS method 00616. The method involves extraction of residues with acetonitrile/water (low fat matrices) or acetonitrile/hexane (high fat matrices). Following concentration of the extract and addition of acetic acid the raw extract is cleaned up by solid phase extraction on a non-polar column. Analysis is by reverse phase HPLC with ESI ionisation and MS/MS detection.

The maximum storage interval between sampling and analysis was approximately 18 months.

Mean recovery of methiocarb, methiocarb sulfoxide and methiocarb sulfone (%)

Matrix	Fortification Level (mg/kg)	Methiocarb	Methiocarb Sulfoxide	Methiocarb sulfone	Total methiocarb
Potato tuber	0.01	88	95	94	93
Grapes (bunch)	0.01	88	97	94	93
Field pea seed	0.01	89	94	94	92
Canola seed	0.01	82	92	93	89

Recovery of residues after frozen storage (-18°C) for up to 24 months

Matrix	Storage interval (days)	Methiocarb	Methiocarb sulfone	Methiocarb Sulfoxide	Total methiocarb
Potato tuber	0	93	99	97	96
	27	91	93	93	92
	91	88	99	102	96
	181	85	99	101	95
	362	88	106	100	98
	540	85	97	102	94
	733	78	92	99	89
Grapes (bunch)	0	86	94	97	92
	27	85	93	95	91
	91	85	97	104	95
	181	76	92	106	91
	362	66	100	115	93
	540	67	95	115	92
	733	62	91	119	90
Field pea seed	0	84	88	91	87
	27	87	94	99	93
	89	88	96	100	94
	181	88	96	101	95
	362	81	88	88	85
	538	81	96	98	91
	734	79	93	96	89
Canola seed	0	88	91	93	90
	27	78	83	83	81
	91	97	96	95	96
	181	75	72	73	73
	358	67	71	66	68
	540	75	78	76	76
	733	70	77	78	75

Potato tubers – there was a gradual decline of methiocarb residues over the 2 year storage period. Methiocarb sulfoxide and sulfone residues were fairly constant and there was no significant decline or change in total methiocarb residues.

Grapes – Methiocarb residues declined to as low as 62% during the storage period. Methiocarb sulfone residues increased and no significant change in total methiocarb residues was observed indicating residues of total methiocarb are stable in grapes.

Field pea seed – residues of methiocarb, the sulfoxide and sulfone were variable over the storage period but were between 90-110% of the initial value. Total methiocarb residues also ranged between 90-110% of the initial level.

Canola seed – residues of methiocarb, the sulfoxide and sulfone were variable over the storage period but were between approximately 70-100% of the initial value. Concurrent recoveries ranged from 70-90% with an average concurrent recovery of 83%.

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Appendix 1

PACC decisions concerning methiocarb (residue implications)

March 1979 recommend MRL for grapes (25 mg/kg), cherries (15 mg/kg) and oranges (5 mg/kg)

February 1981 recommend MRL for berry fruit (P30 mg/kg)

May 1981 recommend MRL for stone fruit (15 mg/kg) and vegetables (0.1 mg/kg)

February 1982 delete cherry MRL (15 mg/kg)

December 1985 amend MRL for stone fruit (P15 mg/kg), berry fruit (P5 mg/kg) and grapes (P5 mg/kg)

November 1986 recommend MRL for wine (0.1 mg/kg)

June 1987 delete MRL for oranges (5 mg/kg), berry fruits (P5 mg/kg), grapes (P5 mg/kg) and stone fruit (P15 mg/kg). Recommend MRL for fruit (P0.1 mg/kg)

August 1988 recommend MRL for grapes (0.5 mg/kg) and citrus fruit (0.1 mg/kg). Amend "fruit" MRL to "fruit, except grapes and citrus fruits" (P0.1 mg/kg).

Appendix 2

NEDI calculation for methiocarb

Methiocarb

Calculation of NEDI (ADI for Methiocarb = 0.002 mg/kg of body weight)

Commodity	Food Consumption g/kg bw/day		MRL mg/kg	expected residue	NEDI mg/kg bw/day	% of ADI	
Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead cabbages	0.3249	T	5	2	6.498E-04	32.5%	estimated HR
Cereal grains	2.5686	T	0.1	0.1	2.569E-04	12.8%	CF+CM+GC
Edible offal (mammalian)	0.0157	T	0.2	0.1	1.570E-06	0.1%	estimated HR
Eggs	0.2228	T*	0.02	0	0.000E+00	0.0%	assume nil residues
Fruits (except grapes)	4.4089	T	0.1	0.1	4.409E-04	22.0%	all fruits except grapes, wine
Grapes (excluding wine)	0.1199	T	0.5	0.5	5.995E-05	3.0%	
Leafy vegetables	0.1716	T	5	2	3.432E-04	17.2%	estimated HR
Milks	8.9933	T	0.1	0.03	2.698E-04	13.5%	estimated HR
Meat (mammalian)	1.7276	T*	0.05	0	0.000E+00	0.0%	assume nil residues
Oilseed	0.0542	T	0.1	0.1	5.420E-06	0.3%	
Poultry meat	0.5596	T*	0.02	0	0.000E+00	0.0%	assume nil residues
Poultry, Edible offal of	0.0024	T	0.5	0.28	6.720E-07	0.0%	
Vegetables [except Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead cabbages; Leafy vegetables]	3.5651	T	0.1	0.1	3.565E-04	17.8%	All veg except brassicas, leafy
Wine	0.6766	T	0.1	0.04	2.706E-05	1.4%	PF 0.4
Total					0.00241	mg/kg bw/day	
					0.16159	mg/person/day	

* At or about the limit of determination
** Equivalent to 121 % of the ADI

These calculations have been made in accordance with 'Guidelines for Predicting Dietary Intake of Pesticide Residues' (World Health Organization)

NEDI - National Estimate of Dietary Intake
ADI - Acceptable Daily Intake
MRL - Maximum Residue Limit
Using consumption figures from 1995 Total diet survary data for people aged 2 yeas and above.