PART D

ENVIRONMENT

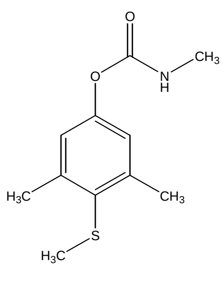
1 Introduction

Methiocarb is a carbamate that has been used as an insecticide, molluscicide, and bird repellent. Three registered products contain methiocarb, with a single registrant (Bayer CropScience Pty Ltd). Two products are pelletised and the third a wettable powder that is sprayable after mixing. Baysol Snail & Slug Bait (product number 51851) is used for the control of slugs and snails in home gardens. Mesurol Snail and Slug Bait (product number 33274) is used in a range of cropping situations, including sunflowers, canola, berry crops, vegetables, vineyards, greenhouses, citrus and ornamentals (including nurseries and cut flower production). Mesurol 750 Bird Repellent and Snail and Slug Spray (product number 33276) is used as a cover spray for snail, slug, insect and bird control. It is also used under permit (PER4408) to control western flower thrips in ornamentals.

Methiocarb does not appear to have been subjected to regulatory action in overseas jurisdictions. However, all food uses were voluntarily withdrawn in the USA between 1989 and 1992 after the registrant made a commercial decision not to generate the data necessary to support them. A reregistration eligibility decision (RED) document was prepared y the US EPA in 1994. The RED and the associated fact sheet (dated February 1994) can be downloaded from the US EPA's website (http://www.epa.gov/ebtpages/pesticides.html). UK authorities reviewed methiocarb in 1998 (Ministry of Agriculture, Fisheries and Food, 1998). Methiocarb has not been specifically reviewed by international organisations, but a general review of the carbamate insecticides is available (IPCS, 1986).

2 Chemical Identity

Name (CAS):	3,5-dimethyl-4-(methylthio)phenyl methylcarbamate
Common name:	methiocarb
CAS number:	2032-65-7
Molecular formula:	$C_{11}H_{15}NO_2S$
Molecular weight:	225.3
Structural formula:	



3 Physico-chemical Properties

Melting Point:	119^{o}C
Vapour Pressure:	0.015 mPa at 20^{o}C
Water Solubility:	27 mg/L at 20^{o}C
Partition Coefficient:	logP = 3.08
Dissociation constant:	no readily dissociable functionality

4 Environmental Exposure

4.1 Environmental Release

4.1.1 Volume

Bayer provided information on the quantity of methiocarb used during 1997. Information on agricultural uses can only be indicative as the scale of use depends on pest pressure, which can be highly variable between seasons. Use of the wettable powder product (Mesurol 750 Bird Repellent and Snail and Slug Spray) was relatively minor at about 3 tonnes. Snail and slug baits were the main products used, with 393 tonnes methiocarb in the home garden product (Baysol Snail & Slug Bait) and 134 tonnes in cropping situations (Mesurol Snail and Slug Bait). The wettable powder products contain 750 g/kg methiocarb; both the snail baits contain 20 g/kg methiocarb.

Applying the above information to the application rates indicated on approved labels suggests that Mesurol Snail and Slug Bait could have been applied at the low rate of 5.5 kg/ha (110 g/ha methiocarb) across some 1.2 million hectares of cropland. Sales of the spray formulation would cover a few thousand hectares. Large volumes are used in home garden situations, with application likely to occur much more frequently than in agriculture.

As noted in the agriculture assessment, there has been a general increase in the use of methiocarb overall, due mainly to an expansion of the areas planted to crops (for example canola) in which it is used. In addition, there has been an extension of the range of some of the snail pests in recent seasons. The general move toward conservation tillage practices in broadacre cropping has also seen an increase in numbers of snail and slug pests because of their use of dead plant material as harbourages. These pests can cause considerable crop damage in seasons that favour their development. The use of the wettable powder formulation against western flower thrips is a relatively recent development. Methiocarb forms part of the ornamental plant industries resistance strategy for this pest.

4.1.2 Application and use pattern

As noted in the agriculture assessment, registered products containing methiocarb are used in home gardens and in the production of broadacre crops (including cereals, oilseeds and pastures), ornamentals (including nurseries and cut flower production), greenhouses, vineyards, vegetables, berry crops and citrus. The pests controlled include snails, slugs, false wireworm beetles, fungus gnats, birds and western flower thrips, as outlined below. Approved labels provide instructions for application by ground-based equipment only. In terms of methiocarb, application rates for the bait formulations are about an order of magnitude (ten times) lower than for the cover sprays.

Mesurol 750 Bird Repellent and Snail and Slug Spray

Only the wettable powder product (Mesurol 750 Bird Repellent and Snail and Slug Spray) is used as a bird repellent. It is applied through boom spray or air mist equipment as a full cover spray (200 g/100 L) when birds begin attacking plants. Ornamentals are specified on the label, but one grower reported use as a cover spray (2000 L/ha, equivalent to 3 kg/ha methiocarb) for bird control in cherries. Another reported use in blueberries by spot spraying potted trees and moving them to hot spots in blueberry orchards where they protect surrounding production trees. Victorian agricultural authorities include methiocarb as a bird repellent in spray programs for canola. Pest bird species identified on the label (blackbirds, sparrows, starlings and Indian mynas) are all introduced to Australia. Spray volumes for high volume ornamental spraying may reach 500-1000 L/ha, equivalent to 0.75-1.5 kg/ha methiocarb.

This product is also used:

- as a cover spray (100 g/100 L) for snail and slug control in grapevines, oranges, ornamentals and poppies;
- as a soil drench (300 g/100 L) for control of glasshouse sciarids (fungus gnats); and more recently
- as a cover spray (200 g/100 L) for control of western flower thrips in ornamentals (under permit – PER4408).

The approved label also provides a double rate (200 g/100 L) for the control of garden weevils at or before flowering (before the establishment of foliage) with a repeat application after 3 weeks if required. The specified application rate for poppy seedlings is 5.5 kg/ha (4.1 kg/ha methiocarb).

Orchard-type spraying equipment would be used in grapes and citrus, boomspray equipment in canola and strawberries, with boomspray or handwands used for ornamentals.

Baysol snail & Slug Bait

Users (home gardeners) are instructed to distribute this product evenly at 100 pellets/m^2 (equivalent to 25 kg/ha product, or 500 g/ha methiocarb) for control of snails, slugs, slaters and millipedes. Application would generally be by hand. The frequency of application remains undefined. Frequent use may be expected in the home garden, particularly in the spring when snails and slugs are active and newly planted seedlings are vulnerable to attack.

Mesurol Snail and Slug Bait

Agricultural users generally apply this product once or twice per season for snail and slug control, although use is not required every season because of variable pest pressure. Environmental exposure to methiocarb is likely to be widespread as approved labels provide instructions for use in crops including cereals, oilseeds, orchards, pastures and vegetables, which together are planted across substantial areas. Baits are to be scattered evenly where snails and slugs occur, either by hand or using such equipment as fertiliser spinners, combines or sod seeders. Some growers report successful crop protection using perimeter baiting techniques. Application rates for snail and slug control are 5.5 kg/ha (110 g/ha methiocarb) for most infestations, but increase to 11-22 kg/ha for heavy infestations or tall and dense vegetation. False wireworms are also controlled (in sunflowers) by baiting at 2.5 kg/ha 1-3 days after sowing. Some minor crops such as culinary herbs receive the same rate as recommended for home gardens.

4.1.3 Environmental monitoring

Only limited information is available on the environmental occurrence of methiocarb. Case studies of pesticide contamination have been conducted in the Ebro River estuary in northeast Spain and an aquifer in Almeria (southeast Spain) using automated on-line solid phase extraction followed by liquid chromatographic techniques. The Ebro River basin occupies some 84000 km^2, within which wheat, corn and vineyards are the main crops. Rice is grown in the delta region. Almeria is a major centre for vegetable production (peppers, tomatoes, melons and cucumbers). Most production occurs in glasshouses, with extensive irrigation because of the hot, dry climate. Methiocarb is used as a foliar spray.

Surface waters remained free of methiocarb, which was not much used in the Ebro River region. Methiocarb, used at an estimated 2 tonnes/year in the Almeria area, was a common contaminant of groundwater's, particularly during the summer months but also into the winter in some wells. Concentrations detected ranged up to about 0.4 µg/L. Investigations at one well found that methiocarb was accompanied by roughly equal amounts of its sulfone, thought to arise by microbial oxidation in the unsaturated soil layer. Separate investigations found this hydrophilic metabolite to be unstable under simulated aquifer conditions, suggesting that its detection in groundwater reflects continuous loading from the overlying soil. The authors note that methiocarb has also been detected in Nebraska groundwater, at concentrations below 0.5 µg/L.

Carbamate contamination occurred very quickly in response to winter and spring furrow irrigations, notwithstanding that the silt loams characteristic of the area should have been able to retain residues near the surface. The authors suggest that this may reflect preferential flow through macropores, a phenomenon known to be favoured in non-tillage soils such as those of the study region (Barcélo *et al*, 1996).

The US Geological Survey collects data on pesticide contamination of surface and groundwater's under the National Water-Quality Assessment (NAWQA) Program. Results from the first cycle of NAWQA water-quality data collection during 1992-1996 include analyses of 76 pesticides and 7 selected pesticide degradation products in about 8,500 samples of ground water and surface water in 20 major watersheds (NAWQA study units) across the US. The 76 herbicides, insecticides, and fungicides targeted in the study account for approximately 75 percent of agricultural pesticide use in the U.S. and a substantial portion of urban and suburban use. Note that food uses for methiocarb were phased out before the start of this monitoring period.

In May 2000, results were available on the USGS website for 16 study units. Methiocarb residues were detected in only one study unit, with a 1% rate of detection at concentrations in the order of 0.1 µg/L in surface waters of the Willamette Basin, Oregon.

4.2 Environmental Chemistry and Fate

Carbamate insecticides vary in their properties, particularly water solubility, but generally have low vapour pressure. Atmospheric redistribution is usually insignificant, but residues can be transported in aqueous solution. These compounds are usually unstable with respect to hydrolysis in both aqueous and soil environments, particularly under alkaline conditions. Sulfoxidation is also a common reaction for carbamates with sulfide functionality. The bioaccumulation potential is usually slight (IPCS, 1986).

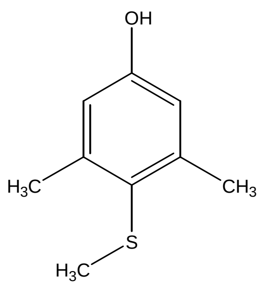
Methiocarb conforms to the above profile and behaves as a typical carbamate insecticide. The US EPA fact sheet notes that methiocarb appears to be moderately persistent and relatively immobile in soil, and is not likely to contaminate ground water. The registrant has provided reports for a range of tests that have been conducted to confirm this, as described below. Except where specifically noted, it would appear that tests have been conducted satisfactorily according to accepted international guidelines such as those of the US EPA (Hitch, 1982a, and subsequent revisions) and OECD. Unless otherwise indicated, radiolabels were at the oxygen-bearing ring carbon.

4.2.1 Hydrolysis

Two studies were submitted. Results indicate that methiocarb is susceptible to hydrolysis about the carbamate linkage, which detoxifies the molecule. The half-life is about a month at neutral pH, extending to around a year under acidic conditions (pH 4-5) but decreasing to a few hours in alkaline solution (pH 9). Hydrolysis is likely to be a significant pathway for degradation of methiocarb under neutral to alkaline conditions.

Hydrolysis of radiolabelled methiocarb (10 mg/L) in phosphate buffer solution (pH 5, 7 and 9) was studied in sterilised glass tubes for 30 days at 25^{o}C, with samples taken periodically for radioassay and TLC analysis.

Methiocarb remained stable in the acidic buffer, with 90% remaining after an extended incubation time of 51 days. Degradation proceeded more rapidly at neutral to alkaline pH with the formation of 3,5-dimethyl-4-(methylthio)phenol. The extrapolated half-life was 321 days in the acidic buffer, decreasing to 24 days at neutral pH and 0.21 days in the alkaline buffer. Small amounts of the corresponding sulfoxides were seen in all samples, apparently due to aerial oxidation during chromatography (Saakvitne *et al*, 1981).



3,5-dimethyl-
4-(methylthio)phenol

Summary results from a second study, conducted at 22°C and monitored by reverse phase HPLC, show similar trends. The extrapolated half-life at pH 4 exceeded a year, and remained more than a month at neutral pH. In alkaline buffer solution, hydrolysis proceeded rapidly with a half-life of 6 hours. 3,5-Dimethyl-4-(methylthio)phenol was the only hydrolysis product identified (Wilmes, 1983).

4.2.2 Photolysis

Two unpublished studies on the photodegradation of methiocarb were presented, one in aqueous solution and one on the soil surface. A published paper confirming the results on soil surfaces was also submitted. Methiocarb undergoes relatively slow photo oxidation to its sulfoxide, probably through reaction with singlet oxygen. Note that this reaction leaves the carbamate linkage intact, so that the degradation product is likely to retain the toxic properties of the parent. Half-lives for photodegradation in aqueous solution and on the soil surface are likely to be in the order of 1-2 months.

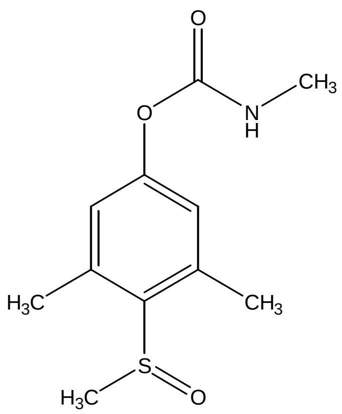
Water

Photolytic half-lives in surface waters were estimated from the ultraviolet spectrum (maximum at 199 nm extending to 211 nm, with secondary maximum at 262 nm and limited absorbance at 295-316 nm) and quantum yield (0.2825 based on kinetic results from two photodegradation experiments in a merry-go-round irradiation apparatus) to range from 5 to 1340 days, depending on latitude and season. Predicted half-lives for the typical use period (spring-summer) were 6-16 days, but with a cautionary note that the artificial light source is likely to have delivered more UV radiation than is naturally present in sunlight close to the ground (Hellpointner, 1991).

Predictions that are more conservative were obtained by exposing radiolabelled methiocarb in acidic buffer solution (pH 5) to Kentucky winter sunlight for 30 days at 25°C. Degradation products were characterised by HPLC with confirmation by TLC. Methiocarb remained largely unchanged (84% in irradiated samples and 95% in dark control) with the main degradation product identified as methiocarb sulfoxide. Extrapolated half-lives in irradiated and dark samples were 88 and 238 days, respectively, with a net half-life of 128 days due to photolysis. The authors conclude that a half-life in the order of 2 months would be typical during the growing season (Kesterson *et al*, 1988).

Soil

Photolysis on a soil surface was investigated in tandem with the aqueous study described above. Radiolabelled methiocarb was dispensed in ethyl acetate solution over the surface of a 0.5 mm layer of autoclaved sandy loam soil (pH 6.6, 1.45% organic matter) to provide a concentration of 9.1 mg/kg. Samples were exposed to natural sunlight in stainless steel exposure chambers with quartz lids and exhaust extraction through ethylene glycol traps. Estimated half-lives in irradiated samples and dark control were 28 and 81 days, respectively, with a net half-life of 53 days due to photodegradation. Methiocarb sulfoxide (23% after 30 days) was the main degradation product in irradiated samples. The authors conclude that a half-life in the order of 21 days would be typical during the growing season (Jackson *et al*, 1988).



methiocarb sulfoxide

The susceptibility of methiocarb to photo oxidation at the soil surface is described in the published literature (Gohre and Miller, 1986). Autoclaved soils were treated at 50-200 mg/kg with a methylene chloride solution of methiocarb by one of two methods. Soils were sprayed using an atomiser, mixed and exposed in stoppered Kimax flasks to summer sunlight for about 10 days, or surface treated using a syringe and exposed to sunlight in open Petri dishes. Three sprayed soils (pH 6.5-7.5) lost around 30-60% of the parent material with the formation of methiocarb sulfoxide as main product, probably through reaction with singlet oxygen. Loss was inversely correlated with the organic matter content of the soil. Photodegradation of surface residues proceeded more rapidly in the one soil tested, with more than 30% of applied methiocarb lost within 36 hours, mainly through photo oxidation to the sulfoxide (63% yield).

4.2.3 Metabolism

Four test reports were submitted, describing the aerobic and anaerobic degradation of methiocarb in soils and water. Methiocarb can be persistent in acidic soils, but degrades with initial half-lives of a few days or weeks in neutral to alkaline soils. In each case, detoxification follows an hydrolytic pathway, but proceeds by a slower oxidation to methiocarb sulfoxide in acidic soils. Chemical catalysis or microbial metabolism may intervene. Sulfoxide metabolites revert to sulfides under anaerobic conditions. Methiocarb degrades completely in a matter of days in alkaline waters but is likely to be more persistent in acidic media, although this has not been tested.

Aerobic degradation in three soils

Soils used in these early investigations were prepared from a silt loam (pH 5.5, 1.8% organic matter) by amendment with brick sand to form a sandy loam (pH 6.4, 1.4% organic matter) or enrichment to 4.6% organic matter using peat. Methiocarb (12.5 mg as a coating on 5 g sand) was added to 50 g samples, followed after 10 days by radiolabelled methiocarb (255 µg on 1 g sand). A mixture (1:11, located at methylthio and carbonyl positions respectively) of ^{3}H and ^{14}C labels was used. Samples were extracted with chloroform/methanol at 2, 7 and 17 days after treatment, and the extracts were washed with water. Aqueous and solvent phases were analysed by TLC-autoradiography.

Recoveries based on tritium declined to around 60-80% of applied during the study, compared with soil that had been denatured with chloroform, in which recoveries through 12 days remained above 90% for methiocarb and 80% for its sulfoxide. Degradation includes a biological component. Most of the extracted radiolabel remained organosoluble, and appeared to retain the carbamate linkage based on the lack of significant variation in the $^{3}H/^{14}C$ ratio. Phenolic activity in the water fraction increased slowly. Chromatography of organic extracts revealed mostly unchanged methiocarb, with its sulfoxide reaching around 15% of applied after 17 days (Church and Flint, 1971).

Aerobic degradation in six soils

Aerobic degradation was studied in six different soils, the microbial activity of which had been maintained by growing corn plants, over a 6-week period in growth chambers at 30°C. Methiocarb, radiolabelled at the carbonyl position, was surface applied at 10 mg/kg or 100 mg/kg to six soils (see table). The progress of the degradation was monitored by TLC-autoradiography of acetone extracts.

Soil type	pH	Organic matter	Half-life (days)
Loamy sand	7.8	2.9%	10
Loam	7.7	4.0%	14
Sandy clay loam	7.6	1.9%	4
Loam	5.8	2.9%	56
Loam	5.6	5.0%	52
Loam	4.1	1.4%	>> 56

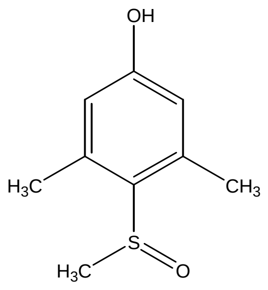
Mineralisation of the carbonyl carbon-to-carbon dioxide was relatively slow in the most acidic loam (8% evolution) and rapid in the sandy clay loam (99% evolution). Mineralisation of the less labile ring carbons is likely to have been slower. Hydrolysis was the main degradation route in alkaline soils and proceeded rapidly, while relatively slow oxidation to the sulfoxide preceded hydrolysis in acidic soils.

Preliminary investigations found a rapid hydrolysis in aerated, soil-perfused water (pH 7.5) treated at 1 mg/L, with 1.5% degradation after 4 hours and 90.1% after 14 days. This compares with half-lives of about a month at neutral pH under sterile conditions. The degradation product was stable as indicated by work with ring-labelled material (Starr and Cunningham, 1973).

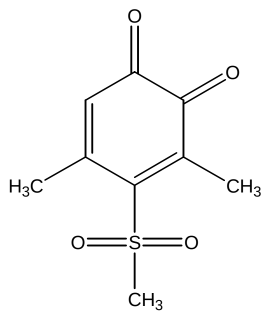
Aerobic/anaerobic degradation in sandy loam soil

Chromatographic analysis revealed that methiocarb (1.5 mg/kg) degraded to a range of metabolites when incubated under aerobic conditions with sandy loam soil (pH 6.7, 1.9% organic carbon) for 217 days at 24°C, with only 3% of applied remaining unchanged. Degradation followed a biphasic pattern, with a half-life of 17.7 days over the initial 2 months and 111 days for the remainder. Methiocarb sulfoxide was the main product identified in the soil, reaching 30% of applied after 29 days before declining to 2% at the final sampling. Its hydrolysis product, 3,5-dimethyl-4-(methylsulfinyl)phenol, reached 18% of applied after 64 days before declining to 7% at the final sampling. The corresponding sulfones were seen in smaller amounts, and were in decline at the final sampling. Only one of the metabolites identified in the soil (8% of the quinone) was still increasing at the final sampling. Evolution of carbon dioxide was first detected at 14 days and increased steadily to 34% of applied.

Bound residues represented 43% of applied at the final sampling, when the material balance was 98%.



3,5-dimethyl-4-(methylsulfinyl)phenol



3,5-dimethyl-4-(methylsulfonyl) -1,2-benzoquinone

Anaerobic degradation was studied after flooding 14 day old samples with pH 5 water and maintaining them under a nitrogen atmosphere. Extractability declined from 87% to 76% after 50 days of anaerobic incubation, and methiocarb from 55% to 27% of total radioactivity. Anaerobic degradation followed pseudo first order kinetics with an apparent half-life of 64 days and formation of a different metabolite, the hydrolysis product 3,5-dimethyl-4-(methylthio)phenol. This metabolite, small amounts of which were recovered from volatile traps, formed in greater quantity than could be accounted for by methiocarb degradation, suggesting sulfoxide reduction. This was confirmed by the observation that the sulfoxide metabolites formed in the initial aerobic period were present in only trace amounts after the anaerobic period (Minor and Freeseman, 1989).

Aquatic metabolism

Radiolabelled methiocarb (2 mg/L) was degraded within 3 days when incubated for 32 days in the dark in aerobic pond water (pH 8) without sediment under greenhouse conditions (mean temperature 26^{o}C). 3,5-Dimethyl-4-(methylthio)phenol was the main compound present at 3 days, but declined from this peak of 80% to 34% after 14 days, at which time 3,5-dimethyl-4-(methylsulfinyl)phenol represented 63% of applied radioactivity.

Anaerobic conditions were created by flooding soil (a silty clay loam from the same pond) with an equal weight of pond water containing 2 mg/L glucose. The aqueous phase was refreshed with unadulterated pond water prior to introduction of radiolabelled methiocarb (2 mg/L), which degraded with a half-life of less than 3 days. Most of the radiolabel partitioned to the soil phase (30% after 3 days, increasing to 50% after a week) and eventually formed unextractable residues (72% after 112 days). The only extractable metabolite identified during the incubation was 3,5-dimethyl-4-(methylthio)phenol (Minor and Atwell, 1979).

4.2.4 Mobility

Two conventional batch adsorption studies with methiocarb were submitted, together with additional studies on the sulfoxide metabolite and the phenol derived from its hydrolysis. Two column leaching studies, one following prior incubation, confirmed the batch adsorption results.

Methiocarb sorbs strongly to soils and has low mobility. However, the main metabolites (methiocarb sulfoxide and the corresponding phenol) are highly mobile in soils, although methiocarb sulfoxide is unstable with respect to hydrolysis. Sulfone metabolites are likely to share these properties, but this has not been specifically tested.

Adsorption/desorption of methiocarb on loam soil

The sorption of radiolabelled methiocarb (0.25-4.8 mg/L in the aqueous phase) was studied on a loam soil (pH 5.9, 4.2% organic matter) over a 16-hour period with 5 volumes of water. Results correlated well with the Freundlich isotherm, with a soil organic carbon partition coefficient of 530 indicative of strong sorption and low mobility, according to the McCall scale (McCall *et al*, 1980). A subsequent desorption released 17-22% of the sorbed material (Atwell and Murphy, 1978).

Adsorption/desorption of methiocarb on various soils

The adsorption of radiolabelled methiocarb (0.4-4 mg/L) from 4-20 volumes of 0.01 M $CaCl_2$ solution onto four soils (see table) was studied over a 24-hour equilibration period. Preliminary investigations found methiocarb to be stable over this period and to reach sorptive equilibrium. Data obtained correlated well with the Freundlich equation, with exponents of less than unity indicating declining sorption with increasing concentration, and soil organic carbon partition coefficients generally indicating strong sorption and low mobility.

Soil type	pH	organic matter	sand/silt/clay	Koc	
				Adsorption	Desorption
Sand	4.3	1%	88/7/5%	1000	1550
Sandy loam	4.9	1.3%	72/21/7%	630	990
Silt loam	5.9	2.9%	17/66/17%	600	1080
Clay loam	6.3	2.2%	20/50/30%	410	680

For the desorption step, significant degradation was observed during the required equilibrium period of 48 hours, amounting to 8-22% even with such precautions as denaturing the soil and degassing the supernatant. Degradation formed methiocarb sulfoxide (solubility 7000 mg/L) and smaller amounts of the corresponding phenol, both of which were partitioned to the aqueous phase. Equilibrium concentrations of methiocarb were calculated on the assumption that this was the sole analyte in the soil phase. Desorption correlated well with the Freundlich equation, with exponents of less than unity indicating increased desorption from higher sorbed concentrations. Soil organic carbon desorption coefficients were higher than those for adsorption (Ridlen and Pfankuche, 1987a).

Adsorption/desorption of methiocarb sulfoxide on various soils

Attempts to repeat the above experiment using methiocarb sulfoxide were compromised by its hydrolysis to the corresponding phenol. The average soil organic carbon partition coefficient for methiocarb sulfoxide was less than 31. Estimates based on water solubility (0.7%) and octanol/water partition coefficient (4) were less than 10. Methiocarb sulfoxide is very highly mobile in soils, but hydrolytically unstable (Ridlen and Pfankuche, 1987b).

Adsorption/desorption of phenol metabolite on various soils

An analogous study with 3,5-dimethyl-4-(methylsulfinyl)phenol required 24 hours to reach equilibrium with four German soils (see table) found high to very high mobility, with desorption coefficients again higher than those for adsorption (Fent, 1981).

Soil type	pH	organic carbon	sand/silt/clay	Koc	
				Adsorption	Desorption
Loamy sand	6.3	2.48%	80/13/7%	27	62
Sand	5.9	0.7%	89/11/0%	27	106
Silt loam	8.1	0.9%	36/53/11%	48	154
Silty clay	7.6	0.64%	15/45/40%	101	257

Column leaching of methiocarb

Radiolabelled methiocarb (1.9 mg on 5 g soil) was added to the surface of soil columns (diameter 7.5 cm and length 30 cm) and slowly eluted with water. This study is poorly reported, with elution rates expressed only as an upper limit (2.5 cm/hour) and quantities reported ambiguously as 15 or 50 cm. Leachate was only contaminated for the sandy loam (Houseworth and Tweedy, 1979). No analyses were conducted on leachates, but it appears likely that the more mobile hydrolysis product [3,5-dimethyl-4-(methylthio)phenol] was eluted from this alkaline soil.

Soil type	pH	Organic matter	Residues (%) in the following segments (cm)				
			0-7.5	7.5-15	15-22.5	22.5-30	Leachate
Sandy loam	8.0	0.6%	19.5	17.8	38.3	12.2	12.2
Loam	6.1	0.7%	31.2	60.6	8.1	0	0
Muck	5.1	77%	98.7	0.4	0.8	0	0
Clay	6.2	5.2%	84.9	7.6	5.3	2.1	0
Sand	4.8	1.5%	91.1	5.8	2.2	0.8	0

Column leaching of methiocarb and metabolites

In this study, radiolabelled methiocarb (37 mg/kg) was incubated on sandy loam soil for 30 days before application (20 g) to soil columns (diameter 5.5 cm and length 30 cm) of three soils (see table). Columns were eluted with 50 cm 0.01 M $CaCl_2$ over a 5-day period.

Soil type	pH	Organic matter	Residues (%) in the following segments (cm)				
			Soil	0-10	10-20	20-30	Leachate
Sand	4.3	0.8%	10	18	29	14	23
Sandy loam	5.0	2.3%	14	44	26	8	7
Silt loam	5.9	2.2%	13	50	24	6	3

Methiocarb remained the main analyte (80% of applied radiolabel) after the initial incubation, accompanied by its sulfoxide and the corresponding phenol in roughly equal proportions. The main variable affecting leaching in these acidic soils appears to be texture, with the sand column proving the least retentive. Parent methiocarb was only found in sand and sandy loam leachates, at less than 2% of applied. The more mobile oxidation product, methiocarb sulfoxide, leached through the sand column in greater quantities than could be accounted for by pre-incubation (12% of applied, compared with 7% before elution) and was accompanied by 7% of the corresponding phenol, indicating continuing oxidation on the sand. Small amounts of the phenols derived from methiocarb and its sulfone were also detected in leachate (Ridlen, 1987).

Simple model predictions

The potential for pesticides to leach can be estimated from the nomogram of Gustafson (1989) if soil adsorption and persistence data from the field are available. Application of the above soil organic carbon partition coefficients (410-1000) and a field half-life of 2 months places methiocarb in the transition between probable and improbable leachers. For half-lives in the order of a week, the nomogram identifies methiocarb as an improbable leacher.

The leaching potential of methiocarb sulfoxide and methiocarb sulfone is difficult to predict because information on their persistence is not available, other than that these metabolites are likely to be more susceptible to hydrolysis than is methiocarb. Similarly, information on the persistence of the phenolic metabolites is not available. Their mobility is likely to be high, however, and leaching likely under certain conditions.

4.2.5 Field dissipation

Only very limited and rather old information was presented on the dissipation of methiocarb under field conditions. Residue analysis in a range of soils found half-lives ranging from a week to 2 months, in the same order as those obtained from laboratory investigations and with no obvious distinction between spray and bait formulations. Small plot studies with spray formulations indicated that runoff losses should remain below 10% of applied methiocarb, although large storms soon after treatment may cause greater losses (26% of applied). When applied as the pelletised formulation, methiocarb would be expected to be less mobile, but this has not been investigated. Leaching potential appears low based on the limited information presented, but monitoring studies in Spain indicate that residues of methiocarb and metabolites can leach through no-till soils to contaminate groundwater.

Field persistence

Limited information is available from a Bayer review (Timme, 1982). One study entailed application of a wettable powder formulation at 22.4 kg/ha methiocarb with incorporation to 10-15 cm. The half-life for methiocarb residues was 15 days in silt loam and 45 days in clay. Further studies found half-lives of 15-50 days in two sandy loams and a silt loam. Residues found in the surface 15 cm of soil immediately after treatment were highly variable (4.4-28 mg/kg). The reasons for this variability are unclear and the company was requested to provide original reports for these studies to assist in understanding the data. Bayer Germany has advised that a field dissipation study is not required in the EU as the DT_{50} in the laboratory is less than 60 days. A paper by T Schad (1998) calculates the DT_{50} to be between 1.0 and 1.6 days based on data from the aerobic degradation studies of Brumhard (1998). The Brumhard paper, which also allowed calculation of the DT_{50}s for methiocarb sulfoxide as well as methiocarb phenol sulfoxide and sulfone, has not been provided for assessment.

In spite of this advice, the UK assessment report (Ministry of Agriculture, Fisheries and Food, 1998) describes a series of field dissipation trials carried out at 6 sites in Germany in 1989, with the FS formulation of methiocarb applied as a spray formulation to bare soils plots in late spring/early summer. The DT50 values in the 0-10 cm layer were found to be in the range of 4.5-50 days, with methiocarb only detectable in the 10-20 cm soil layer in one or two instances. Reference details are not available.

Studies with baits applied at 5.6 kg/ha methiocarb found half-lives of 6-64 days in 7 soils, with most residues confined to the surface 15 cm. Residues in time zero samples were again highly variable (0.58-5.69 mg/kg as sum of methiocarb and sulfoxide and sulfone metabolites). The sulfoxide and sulfone metabolites could be detected for up to a year in some soils, but concentrations were declining by this time. Original reports for this testing should be provided.

Field mobility

Methiocarb was spray applied at 4.5 kg/ha to gently sloping plots (10 m^2) of freshly tilled soil (slightly acidic loam and clay loam). After a 24-hour delay, a total of 11 cm of irrigation/rainfall was applied to the plots over a 14 days. High losses in the initial 24 hours were attributed to wash-off of the wettable powder formulation by irrigation water. The concentration in runoff water leaving the loam plot was 17.2 mg/L in this initial event, which involved 2.5 cm irrigation over a 15 minutes. This high rate of watering reflects an intense storm event rather than normal irrigation practice. The loam plots lost more than 26% of applied methiocarb at an average concentration of 7.4 mg/L, but most losses (23.4%) occurred in the initial event. The clay loam was more retentive, losing a little fewer than 6% at an average 1.04 mg/L (Church, 1970).

A second study (Flint and Shaw, 1974) was provided as an abstract only. A wettable powder formulation was applied to freshly tilled soils at 4.5 kg/ha methiocarb. Losses in runoff water from sandy loam, silty clay and high organic silty clay plots were 1.5, 3.9 and 4.5%, respectively, following a total of 40-48 cm rainfall/irrigation in seven events. Leaching of residues was also evident, particularly in the sandy soil.

These results indicate that runoff losses are likely to remain below 10%, unless a large storm occurs soon after application of the wettable powder formulation.

4.2.6 Bioaccumulation

A single test was submitted, confirming that methiocarb is a typical carbamate insecticide in having limited bioaccumulation potential.

Uptake of methiocarb by and depuration from bluegill sunfish required about a week to reach steady state. During 34 days of continuous exposure to 0.01 mg/L radiolabelled methiocarb, bluegills accumulated 0.25 mg/kg in the first hour, and reached residue levels of 0.6-0.9 mg/kg (bioconcentration factor 60-90) from the fourth day onwards. Only 6% of whole body residues were recovered as carbamates (methiocarb and its sulfoxide and sulfone). On return to clean water, residues declined to 0.25 mg/kg within 24 hours, further to 0.07 mg/kg by day 7, and below the limit of detection (0.05 mg/kg) by day 14 (Lamb, 1974).

4.2.7 Summary of environmental fate

Information has been presented in the following areas to determine the environmental fate of methiocarb.

Hydrolysis

Two studies were submitted. Results indicate that methiocarb is susceptible to hydrolysis about the carbamate linkage, which detoxifies the molecule. The half-life is about a month at neutral pH, extending to around a year under acidic conditions (pH 4-5) but decreasing to a few hours in alkaline solution (pH 9). Hydrolysis is likely to be a significant pathway for degradation of methiocarb under neutral to alkaline conditions.

Photolysis

Two unpublished studies on the photodegradation of methiocarb were presented, one in aqueous solution and one on the soil surface. A published paper confirming the results on soil surfaces was also submitted. Methiocarb undergoes relatively slow photo oxidation to its sulfoxide, probably through reaction with singlet oxygen. Note that this reaction leaves the carbamate linkage intact, so that the degradation product is likely to retain the toxic properties of the parent. Half-lives for photodegradation in aqueous solution and on the soil surface are likely to be in the order of 1-2 months.

Metabolism

Four test reports were submitted, describing the aerobic and anaerobic degradation of methiocarb in soils and water. Methiocarb can be persistent in acidic soils, but degrades with initial half-lives of a few days or weeks in neutral to alkaline soils. In each case, detoxification follows an hydrolytic pathway, but proceeded by a slower oxidation to methiocarb sulfoxide in acidic soils. Chemical catalysis or microbial metabolism may intervene. Sulfoxide metabolites revert to sulfides under anaerobic conditions. Methiocarb degrades completely in a matter of days in alkaline waters but is likely to be more persistent in acidic media, although this has not been tested.

Mobility

Two conventional batch adsorption studies with methiocarb were submitted, together with additional studies on the sulfoxide metabolite and the phenol derived from its hydrolysis. Two column leaching studies, one following prior incubation, confirmed the batch adsorption results.

Methiocarb sorbs strongly to soils and has low mobility. However, the main metabolites (methiocarb sulfoxide and the corresponding phenol) are highly mobile in soils, although methiocarb sulfoxide is unstable with respect to hydrolysis. Sulfone metabolites are likely to share these properties, but this has not been specifically tested.

Field dissipation

Only very limited and rather old information was presented on the dissipation of methiocarb under field conditions. Residue analysis in a range of soils found half-lives ranging from a week to 2 months, in the same order as those obtained from laboratory investigations and with no obvious distinction between spray and bait formulations. Small plot studies with spray formulations indicated that runoff losses should remain below 10% of applied methiocarb, although large storms soon after treatment may cause greater losses (26% of applied). When applied as the pelletised formulation, methiocarb would be expected to be less mobile, but this has not been investigated. Leaching potential appears low based on the limited information presented, but monitoring studies in Spain indicate that residues of methiocarb and metabolites can leach through no-till soils to contaminate groundwater.

Bioaccumulation

A single test was submitted, confirming that methiocarb is a typical carbamate insecticide in having limited bioaccumulation potential.

Synopsis

Methiocarb is transformed in the environment through hydrolytic and oxidative reactions. Hydrolysis predominates in alkaline media, but is preceded by oxidation under acidic conditions. Hydrolytic pathways detoxify the molecule, while oxidative reactions transform methiocarb to its sulfoxide and sulfone, both of which are likely to retain biological activity but to be unstable with respect to hydrolysis. Microbial activity or chemical catalysis may intervene in both pathways. The rate of degradation is influenced by numerous factors, including temperature, pH, soil texture, redox potential, moisture and microbial activity. Typical half-lives in surface soils for methiocarb are in the range of a week to 2 months. Methiocarb has low mobility but its metabolites are highly mobile in soils and likely to move with soil water.

5 ENVIRONMENTAL EFFECTS

The toxicity of carbamate insecticides arises because of their ability to inhibit acetylcholinesterase. Carbamylation of this enzyme is unstable and regeneration relatively rapid compared with the phosphorylated enzyme. Carbamate insecticides tend to be less dangerous than the organophosphate insecticides because of this reversibility, having a wider margin between doses that cause mortality and those that elicit the onset of symptoms (IPCS, 1986). Enzyme activity assays with acetylcholinesterase of bovine erythrocytes and butyrylcholinesterase of equine plasma demonstrate a much lower affinity of carbamates for cholinesterases compared with organophosphates, and show methiocarb to have only a small effect on these enzymes compared with pirimicarb, carbofuran and oxamyl (Barthovä *et al*, 1989).

The US EPA fact sheet notes that methiocarb is toxic to terrestrial mammals. It is very highly toxic to birds on an acute oral basis. In subacute studies, it is slightly toxic to waterfowl and practically non-toxic to upland game birds. Methiocarb is highly toxic to cold- and warm-water fish. It is very highly toxic to aquatic invertebrates. It also is very highly toxic to honey bees.

Most of the studies reviewed below, particularly the unpublished ones, were provided by the registrant. Data gaps have been filled with information from the published literature or by reference to the US EPA's draft database of presently known ecotoxicity endpoints judged acceptable for use in the ecological risk assessment process, as compiled by the US EPA's Ecological Effects Branch. Except where specifically noted, it would appear that tests have been conducted satisfactorily according to accepted international guidelines such as those of the US EPA (Hitch, 1982b, and subsequent revisions) and OECD.

Toxicity classifications used by the US EPA for inter-chemical comparison are adopted for birds and aquatic organisms. For terrestrial invertebrates, the classifications of Mensink *et al* (1995) are used.

5.1 Avian Toxicity

Acute oral toxicity data are available for a wide range of birds. Most of the data are old and poorly described, but results are consistent with those from more recent, well reported studies. Methiocarb is highly to very highly toxic to birds by the acute oral route of exposure, with most LD_{50}s in the 5-15 mg/kg range. Intoxication is characterised by a rapid onset of paralysis, progressing to mortality within a few hours. Remission is fairly rapid in sublethally dosed birds. Methiocarb sulfoxide appears to be even more toxic than methiocarb. Methiocarb sulfone appears less toxic and has an immobilising effect on birds at doses an order of magnitude below those that cause death.

Data on dietary toxicity are more limited. Dietary toxicity is variable, ranging from slightly to highly toxic. Testing is compromised in most species by strong repellent effects. Mortality tends to be delayed for some days as birds starve to death.

Reproductive testing with quail and ducks found that these species could tolerate dietary concentrations of 50-100 ppm without adverse effects on health or food consumption. Higher doses in Japanese quail led to anorexia and impaired reproductive capacity.

Palatability tests were also conducted in order to investigate further the anorexic effects apparent in dietary studies. Most of the tests are rather old, but both old and newer studies provide consistent evidence for a strong repellent effect of methiocarb to birds, whether mixed with normal feed or scattered as baits at typical rates of use. Quail were able to discriminate between clean and contaminated food, under both laboratory and simulated field conditions, with feed offered in separate hoppers or mixed together. Mild symptoms such as weight loss and apathy were seen in some quail when only limited amounts of clean food were offered. Blackbirds and starlings that were offered contaminated earthworms or cutworms displayed similar discrimination. Some consumption occurred when clean food was in short supply, but without causing any obvious harm. Methiocarb has been registered by the US EPA for aversive conditioning of corvids predating on eggs. This apparent safety does not extend to small and sensitive species. Captive canaries suffered heavy mortality on exposure to treated oat seeds, each of which may have contained a lethal dose.

Field studies also returned favourable results, with most reporting neither mortality nor aberrant behaviour. One detailed study in English cherry orchards sprayed for bird control found a limited number of non-target casualties but could not detect any impacts on overall numbers or breeding success.

5.1.1 Acute oral

Limited data indicate that methiocarb is likely to be highly to very highly toxic to birds exposed via the acute oral route.

Testing with Japanese quail used six groups of 10 birds (5 males and 5 females) dosed via gelatine capsule with 0.7-22.5 mg/kg methiocarb (500 SC formulation). Doses were spaced by a factor of 2, slightly above the recommended maximum of 1.67. Symptoms of intoxication (apathy, incoordination, salivation) were seen within 1-2 hours of dosing in affected birds but subsided within 24 hours in survivors. Mortalities only occurred at the two highest doses, affecting 70-80% of birds within 2.5 hours of dosing. Ideally, at least three levels should result in mortality between, but not including, 0% and 100%; at least one level should kill more than 50%, and at least one level should kill less than 50% of the birds in a group. Gross pathological observations found no treatment related abnormalities in these casualties. No adverse effects on feed consumption or body weight were noted during a 14-day observation period after dosing. The LD_{50} was 11.7 (8.5-16.5) mg/kg, and the NOEL 0.7 mg/kg (Schmuck, 1997). This study is reported in detail and can be considered reliable, notwithstanding that the slightly excessive spacing between doses resulted in only two dose levels causing mortality. Older studies are less well reported but provide consistent results, as outlined below.

Short summaries of some older acute oral tests were also presented, but without the detail necessary for their full evaluation. The following LD_{50s} were obtained: 5-10 mg/kg in female Japanese quail (Hermann, 1983a); 10 mg/kg in male Japanese quail (Hermann, 1983b); and 270 mg/kg in ring-necked pheasant hens (Hudson, 1972). Another researcher (Schafer, 1968) found an approximate LD_{50} of 1000 mg/kg in ring-necked pheasants.

Summary data sheets are also available for a range of birds administered alcoholic solutions of methiocarb via stomach tube after 4 hours fasting. A rapid onset of paralysis was noted, within 5 minutes at higher doses. Mortality occurred within half an hour at higher doses. The approximate acute oral LD_{50s} in starlings, red-winged blackbirds, pigeons and ringbill gulls were 12-15, 11-20, 50 and 5-10 mg/kg, respectively. Corresponding doses causing sedation were 2-10, > 2, 11-50 and 2.5-5 mg/kg (DeCino, 1964).

Results from the tests submitted are consistent with those published in the literature. For example, the LD_{50s} of methiocarb to starlings and red-winged blackbirds are 13 and 4.6 mg/kg, respectively. As expected for derivatives with an intact carbamate linkage, oxidative metabolites retain the toxicity of methiocarb, as indicated by LD_{50s} in red-winged blackbirds of 42 mg/kg for methiocarb sulfoxide and 1.8 mg/kg for methiocarb sulfone (Schafer, 1972). These published data contradict the unpublished reports (see below) and are inconsistent with mammalian data. The sulfoxide is also identified by the company code Bay 41791, and the sulfone by Bay 41790. It appears that these metabolite toxicity results are incorrectly assigned, which would be easy to overlook, as the two chemical names are identical except for a single letter. The company was asked to confirm that the sulfoxide is the more toxic metabolite, and provided a later paper (Schafer et al, 1983) where this error had been corrected.

Data sheets in the submission provide more detail on the metabolite studies (Schafer, 1968). The studies aimed to determine whether compounds might be useful as bird repellents, by comparing the LD_{50} with the ED_{50} based on immobilisation. For the sulfone, birds suffered complete mortality within half an hour of dosing at 56 mg/kg, but survived dosing at 32 mg/kg. Birds were rapidly immobilised (within 6-27 minutes) for up to 1.5 hours, at all but the lowest dose of 1.8 mg/kg. The LD_{50} exceeded the ED_{50} by a factor of 16, indicating potential as a stupefacient. For the sulfoxide, toxicity was very high and the ratio only 3. The author notes that methiocarb itself is the most consistently repellent compound among those he has investigated.

The repellent effects of methiocarb are highlighted in a literature review (Dolbeer *et al*, 1994) that compares LD_{50}s with TI_{50}s (the median acute oral dose causing temporary immobilisation). The LD_{50}s in 36 species range from 1.3 mg/kg in budgerigars to 1000 mg/kg in ring-necked pheasants, with 19 species between 5 and 15 mg/kg. Sparrows, finches, doves and blackbirds are sensitive with many LD_{50}s below 10 mg/kg. For the 16 species with available data, lethal doses exceed those causing temporary immobilisation by factors ranging from 1 to 5.7.

An LD_{50} of 16.8 mg/kg is reported for rose-ringed parakeets intubated with methiocarb in aqueous solution. Birds could detect methiocarb at 0.1-0.2% on food even with no prior exposure, and discriminated in favour of clean feed (Hussain *et al*, 1992).

The acute oral toxicity, repellency and hazard potential have been calculated for methiocarb (Schafer et al,1983). The repellency value (R_{50}) for redwinged blackbirds is 6.85 mg/kg. The LD_{50} for starlings and coturnix quail were 11.3-50.0 mg/kg and 8.84-10.4 mg/kg respectively.

5.1.2 Acute dietary

Unpublished dietary studies were not submitted, but a published paper (Kenaga, 1979) in the submission provides some information. The LC_{50} in Japanese quail is reported to be 1427 ppm, indicative of slight toxicity. The contrast with the LD_{50} indicates that birds find food laced with this intoxicant unpalatable, consistent with the use of methiocarb as a bird repellent.

The LC_{50} in Japanese quail has been reported elsewhere as 1457 ppm, but with wide confidence intervals (0-infinity) because of a single death at 501 ppm. All mortality occurred between 3 and 6 days after the contaminated food was first offered. The toxic dose was much higher than the discrimination threshold (the concentration above which birds choose more untreated than treated food) of 222-224 ppm (obtained using 5:5 or 1:1 ratios of feeders). Only one death occurred in these discrimination tests, the smallest bird 3 days after being offered food spiked at 2000 ppm. Little or no discrimination was evident when only one of ten feeders contained untreated food, except at the highest dose of 2000 ppm when 42% of consumption was untreated. One bird died on the first day, and four more on days 3-5 after losing an average 37% of their body weight. Overall percent mortality was inversely related to food consumption (Bennett, 1989).

Results from longer-term (30-day) dietary studies confirm that methiocarb-laced food is repellent to some birds. Mortalities in these studies were apparently due to ingestion of an acute lethal dose within a single feeding period, but the effects of intoxication and food deprivation were difficult to distinguish. Deaths under field conditions were considered unlikely.

Food was treated at 100, 316 and 1000 ppm methiocarb in a study with mourning doves (*Zenaidura macroura*). Consumption was reduced dose-responsively compared with controls, particularly in the high dose group during the initial 2 weeks of exposure. Notwithstanding the decreased food consumption, birds were exposed to increasing levels of methiocarb, estimated at 1.3, 2.8 and 11.6 LD_{50s}/day respectively. Mortalities only occurred at the highest dose, leaving a single survivor that exhibited only minor nervous symptoms. Deaths occurred in the initial 2 weeks, preceded by typical symptoms of acute methiocarb intoxication. The estimated LC_{50} was 630 ppm.

The repellent effects do not appear universal, however. Common grackles, a sensitive species (LD_{50} 10 mg/kg), suffered 25% mortality at 100 ppm, with food intake equivalent to 1.9 LD_{50}s/day (Schafer *et al*, 1975).

The shortage of dietary toxicity data for methiocarb has been noted by others (Dolbeer *et al*, 1994) with the observation that the limited data available show a low risk to birds. Thus, the most sensitive LC_{50} referred to by these authors is that determined for mourning doves (630 ppm, as described above – note that common grackles appear more sensitive, but the LC_{50} in this species has not been determined). LC_{50s} in other species are generally above 1000 ppm, compared with typical residues of less than 10 ppm on fruit. The authors calculated that birds would need to feed exclusively on contaminated fruit for several hours to reach a lethal dose, even if satiation or immobilisation did not intervene.

The limited number of acute dietary studies in the submission is acceptable, as numerous studies on avian acceptance and palatability have been submitted, as described below. Dietary studies with repellent compounds can be uninformative, as effects tend to occur from starvation rather than intoxication.

5.1.3 Reproduction

Pen-reared quail, previously untreated and phenotypically indistinguishable from wild birds, were 21 weeks old and weighed 160-215 g when this study was initiated. Each dose level used 24 cages with a pair of birds in each cage. Food consumption was checked weekly and body weights at 0, 2, 4, 6, 8 and 25 weeks. Gross post mortem examinations were conducted on casualties.

No effects were observed on adult survival, body weight, feed consumption, brain cholinesterase or reproduction in bobwhite quail exposed for 10 weeks before and during egg laying to 2, 10 or 50 ppm methiocarb in the feed. Two females died in the low dose group, but no treatment related lesions were apparent at post mortem. A slight reduction in chick survival at 14 days was not considered to be compound related as it only affected the low and high dose groups, and was not consistent from week to week (Lamb and Carsel, 1982a).

A similar study with mallard ducks exposed for 19 weeks to dietary concentrations of 25, 50 or 100 ppm found no significant effects on survival, feed consumption or body weight. Pen-reared ducks, previously untreated and phenotypically indistinguishable from wild birds, were 19 weeks old and weighed 1020-1595 g (males) or 900-1400 g (females) when this study was initiated. Each dose was tested in 14 individually caged pairs of ducks. Food consumption was checked weekly and body weights at 0, 2, 4 and 6 weeks, and at termination.

There was an apparent increase in net reproduction, reaching 170% at 100 ppm compared with controls. Brain cholinesterase was 22% less than controls in females from this group. The NOEL was 50 ppm based on brain cholinesterase and 100 ppm based on chick survival at 14 days (Lamb and Carsel, 1982b).
Studies with coturnix quail used higher exposures (100, 316 and 1000 ppm) for 4 weeks. The estimated LC_{50} in this well conducted study was slightly above 1000 ppm, based on 33% mortality (days 7-26) at this dose with typical symptoms of acute intoxication. Weight gain and food consumption were not significantly affected at the lower doses during the dosing period, but subsequent food intake was depressed at 316 ppm. Food consumption was depressed during the dosing period in the high dose group. Mean daily methiocarb consumption exceeded the LD_{50} by factors of 1.5, 3.7 and 7.9, notwithstanding the anorexic effects. Chick survival at 10 days was significantly reduced at the two higher doses, and egg production at the highest dose (Schafer *et al*, 1975).

5.1.4 Bait palatability to bobwhite quail

A laboratory study used caged groups of ten bobwhites offered control feed, 2% methiocarb baits or an equal mixture of the two for four days. Three groups had access to a single feeder containing one of these preparations, and the other two were provided with two feeders, one containing control feed.

Birds fed primarily on control feed when this was available to them. Even when it was mixed with baits, birds were quite successful in consuming only the control feed. Bait lost from feeders did not appear to be consumed, but rather dropped in the litter pan. Significant weight loss occurred only in birds with no access to control feed and was mostly regained during a 3-day recovery period. The only symptoms seen at necropsy were fatty livers, attributed to food deprivation, in the birds offered only bait material (Carlisle and Carsel, 1982).

Results were similarly favourable when bobwhite quail were exposed outside on turf in small pens to a broadcast application of 2% baits at 60 kg/ha. Birds also had access to sunflower seeds. No mortalities occurred and there were no significant differences in body weight or brain cholinesterase activity between control and exposed birds (Carlisle and Toll, 1982).

5.1.5 Bait palatability to sparrows and Japanese quail

A study with sparrows and Japanese quail was conducted under aviary conditions with a 4% bait formulation containing Bitrex. Each aviary contained 10 sparrows and 8 quail, and a prepared experimental bed planted with lettuce, to which 1.4 g of bait was applied at the recommended rate (3 kg/ha, comparable to the general agricultural rate in Australia of 5.5 kg/ha pellets containing 2% methiocarb) together with 160 g feed, replenished daily for 4 days. Birds had previously been acclimatised to feed, and to each other, for 14 days. Preliminary calculations indicated that a single bait pellet may kill a sparrow, and that two pellets may be enough to kill Japanese quail. Birds pecked at the treated soil surface for several hours each day, and consumed the lettuce seedlings within 2 days. However, no behavioural abnormalities or symptoms of intoxication were observed during the 4-day exposure period and a subsequent 14 days of observation (Grau, 1983).

A second aviary study used groups of eight Japanese quail exposed to a 2.1% bait formulation scattered over the floor with untreated feed. Four groups were offered a ration of 12 g bait and 4 g food per bird, and another four 1.5 g bait and 14.5 g food, for an 8-hour period after fasting for 15 hours. No birds died, but mild symptoms (ptosis, giddiness, apathy) occurred in 15 of the more highly exposed birds and 6 in the lower exposure groups. Symptoms subsided rapidly (mostly within the hour) but interest in the bait material was not renewed. No symptoms were observed during a 14-day observation period, and there was no distinct loss of weight in any bird (Grau, 1987a).

5.1.6 Bait palatability to free-range hens

Mesurol Snail and Slug Bait was distributed at 22 kg/ha over bare ground in fowl yards at Dural NSW. Hens were introduced after having been penned for 24 hours to encourage scratching and foraging on release. Most of the hens pecked around the baits, but some picked them up and either dropped or swallowed them. By one day after treatment, there was no further interest in the baits, which remained distributed on the ground. Two sacrificed hens showed no evidence of bait consumption. Similar conditions prevailed 5 days after treatment, with all hens in healthy condition (Fullerton, 1971)

5.1.7 Treated seed palatability to songbirds

This study used 6 groups of 5 aviary housed canaries (*Serinus canarius*) exposed after 1 hour without food to broadcast shelled oat seeds dressed with Mesurol FS 500 at 1.14 kg/dt. The low LD_{50} in this species (3-5 mg/kg) means that a single seed may contain a lethal dose. No effects were seen in unfed controls or in birds fed untreated oat seeds. In contrast, exposed birds suffered heavy mortality (9/30) with sub-lethal effects (apathy) in survivors. Results show that small, sensitive birds may be killed by methiocarb seed dressing under actual use conditions (Schmuck, 1992a).

5.1.8 Effect of colour on bait acceptance by birds

Captive starlings and house sparrows were offered a choice between untreated turkey crumbs and similar food treated at about 0.7% with a range of repellents including methiocarb, with or without the addition of a blue dye. Untreated food was offered in two dishes and a hopper for 9 days before introduction of the toxicant to one of the dishes for 7 days. A final 6-day period studied the response to coloured but uncontaminated food.

Consumption of food from the methiocarb treated dish was dramatically reduced, regardless of colour. Birds also avoided coloured food, even without added toxicants. Methiocarb is thought to act as a bird repellent through learnt aversion to the illness it induces, and also to having a noxious taste. Starlings appeared to develop an aversion to methiocarb more rapidly than did sparrows (Greig-Smith and Rowney, 1987).

5.1.9 Avian responses to contaminated invertebrates

Earthworms (a mixture of *Lumbricus terrestris* and *Eisenia foetida*) were contaminated with methiocarb by exposing them in trays of soil to a surface application of 1000 kg/ha 4% bait formulation. Dead and injured earthworms were collected from the soil surface after 4 days and presented to captive blackbirds (*Turdus merula*) after 2 hours fasting. In the absence of untreated earthworms, blackbirds consumed the occasional dead or affected specimen. When freshly caught earthworms were available, these were readily consumed. In addition, less affected earthworms collected from the subsoil in the exposure chamber rather than the surface were fully consumed within 2 hours. Contaminated worms were accepted in larger numbers over extended periods without alternative food, but without the birds suffering any disadvantageous consequences (Hermann, 1968).

A similar study was conducted with captive starlings and cutworms allowed access to moistened baits as the only food for 24 hours. Significant avoidance behaviour was said to be observed, even though no alternative food was offered. Preliminary laboratory tests had found that contaminated cutworms induced severe regurgitation in starlings, as did the bait itself (Hermann, 1983c).

5.1.10 Aversive conditioning of egg predators

The repellency of methiocarb to avian predators and scavengers has been exploited to protect colonies of endangered California least terns, by using aversive conditioning of offending birds that predate on eggs. The technique involves exposing ravens to Coturnix quail eggs that have been injected with methiocarb. The toxicant causes ravens that eat the treated eggs to become sick, and they learn to avoid small spotted eggs. Because of their territorial behaviour, ravens trained to avoid eggs actively exclude untrained ravens from the area (USDA, 1995).

The U.S. Department of Agriculture's National Wildlife Research Center indicates on its website that the 75% wettable powder formulation has recently been registered by the US EPA for conditioning of common ravens, white-necked ravens and common crows. Eggs are treated with 30 mg methiocarb, making them somewhat toxic to animals that feed upon them. Treated areas must be observed, at least periodically. The label notes that aversive conditioning may be most effective when predatory corvids are territorial or resident birds, and that avoidance responses may be acquired over a period of time and may require repeated exposures for maintenance. Birds may die occasionally after eating treated eggs, but most are said to survive.

5.1.11 Field studies

An intensive trial was conducted in a 6.4 ha cherry orchard in Kent, which received three fortnightly air blast applications as a 0.2% aqueous spray mixture at 4.3 kg/ha methiocarb, a rate commercially recommended for bird control in the USA. Trees were planted on an 11 m grid and were between 2 and 6 m high. Measurement of ground deposition found around 40% on the ground between the trees. There were said to be negligible losses to drift (estimated at 0.1%) as spray deposits outside the treated area were relatively low. Peak concentrations occurred between 0.8 and 4 m elevation but with significant residues captured to 11 m on vertical targets. Residues on cherries immediately after treatment declined from 26 ppm to 8 ppm as the fruit swelled, and remained above 1 ppm for less than a week following each treatment.

Extensive mist netting caught 2935 birds (2403 ringed individuals) from 42 species, considered an unusually varied bird fauna for orchards in this area. Sparrows, blackbirds, thrushes, starlings and greenfinches were dominant. Most of the damage to ripening fruit was caused by blackbirds and thrushes, but greenfinches and gulls were also observed feeding on cherries. Short-term declines in capture rates were observed for some species immediately after treatment, possibly resulting from disturbance, but the commonest species showed no major changes. Breeding success in nest boxes and natural nests found in the area remained high.

Systematic searches for affected wildlife occurred before treatment, immediately after application, and 1, 3 and 5 days later, both within the orchard and in surrounding hedgerows. Although search efficiency was not tested, it was believed to be high because of the simple habitat, assistance by trained dogs, the apparent low level of scavenging activity, and the discovery of mortality from natural causes or trauma. Only 15 dead and 3 incapacitated birds were found, many being recently fledged juveniles. Poisoning was suspected in 12 individuals, and trauma in two. Six of the suspected methiocarb casualties (blackbirds, greenfinches, a house sparrow and a linnet) had biochemical measurements consistent with exposure and four showed no esterase depression. Esterase assays were not conducted in the remainder.

To investigate possible sub-lethal effects, biochemical measurements of esterase activity in blood and tissue samples of trapped birds were conducted. Mean plasma acetylcholinesterase activities were significantly depressed in house sparrows, starlings, blackbirds and thrushes after each treatment. Methiocarb residues (parent compound only) were also detected in starling and house sparrow breast tissue (median 0.016 mg/kg in both species).

In summary, birds were exposed to methiocarb from this use pattern, with a few individuals receiving lethal exposures but most effects transient and sub-lethal. There were no apparent impacts on overall numbers and breeding success (Greig-Smith *et al*, 1981; Hardy *et al*, 1993).

The above study is included among 33 field studies from various countries that have been reviewed. Methiocarb was applied to fruit and other crops as an aqueous spray for bird control, generally at around 2 kg/ha but reaching an estimated 10.9 kg/ha in one trial. None of the other studies reported any avian mortality in methiocarb treated areas, but two studies reported dead birds in control fields and seven reported temporarily aberrant avian behaviour (in 28 individual birds) that may have resulted from methiocarb exposure. The average estimated crop loss across 26 sites (47.7 ha) was 15%, compared with 36% for nearby untreated plantings, indicating that the aversive effects observed in the laboratory also operate in the field (Dolbeer *et al*, 1994).

5.1.12 Home gardens

Questionnaires were returned by 17 of 40 English amateur gardeners supplied with methiocarb slug pellets (concentration not disclosed) for application at around 1-2 g/m^2(10-20 kg/ha). Most of the applications were to wet soil in autumn, during a period of exceptionally high rainfall. Situations of use included lettuces in frames, gravel drives, lawns, soft fruit, vegetables, shrubs, roses and herbaceous borders. Pellets disintegrated in 1-6 days but remained visible for up to a month. Wild and domestic animals present included 15 bird species, 5 mammals and an amphibian, none of which showed any adverse reactions. Snails and slugs were well controlled, but impacts were observed on other invertebrates, mainly earthworms but also beetles, millipedes and woodlice. One thrush was observed eating three affected earthworms, and a regurgitated slug was reported (Ford, 1968).

5.1.13 Incident reports

In the UK, the Wildlife Incident Investigation Scheme provides a major source of information about incidents (mainly mortality) arising from pesticide use or, predominantly, misuse as well as for other types of pesticide incident affecting certain groups of vertebrates and bees. Classes of chemicals most frequently involved in these incidents include the anti-cholinesterase carbamate and organophosphate insecticides, rodenticides and the molluscicides metaldehyde and methiocarb. Incidents involving other chemicals such as paraquat are occasionally reported but usually resulting from abuse. Whilst mostly the result of abuse or misuse, these incidents provide some evidence for the potential sub-lethal or chronic impacts of certain classes of pesticides which may arise out of approved use.

Carbofuran (29 confirmed incidents) was identified as the main cause of death in non-target animals based on investigation of suspected pesticide poisoning incidents during 1998, followed by metaldehyde, which was implicated in 24 confirmed incidents. Methiocarb was involved in 11 incidents, mostly to companion animals. Dogs were poisoned by uncleared spills (3 incidents), improper disposal of treated seed (1 incident), deliberate poisoning (2 incidents) and indeterminate (2 incidents). Deliberate poisoning was involved in two separate incidents involving a cat and a badger. No avian incidents were linked to methiocarb, although numerous pesticide-related incidents were reported. Only one incident, an earthworm kill described later in this report, was linked to authorised use of methiocarb (Fletcher *et al*, 1999). The relatively low profile of methiocarb is consistent with the home garden observations outlined above.

5.2 Aquatic Toxicity

Static testing with three species of fish found methiocarb to be moderately to highly toxic (96 hour LC_{50s} typically in the order of 1-5 mg/L based on nominal concentrations). Life cycle studies found significant toxic effects at 0.1 mg/L. Tadpoles appear to share similar acute sensitivity. Available data indicate that methiocarb is very highly acutely toxic to aquatic invertebrates. The 48-hour LC_{50} to

Daphnia magna was 19 µg/L. Reproductive impairment in this species occurred at concentrations below 1 µg/L. Limited data indicate that methiocarb is moderately to highly toxic to molluscs and moderately toxic to algae.

5.2.1 Fish acute toxicity

Test reports were submitted for a variety of static tests as tabulated below. Most of the tests are old and only briefly reported. Results are variable and generally not confirmed by analysis, and should be regarded as unreliable because the actual level of exposure is unclear. Where analysis occurred, test concentrations were found to decline markedly with time, consistent with the hydrolytic instability of methiocarb under the slightly alkaline test conditions. However, given that a similar rate of decline is likely in natural surface waters, it can be argued that the nominal test results offer an acceptable basis for deterministic hazard assessments based on predicted initial exposure concentrations.

Test	Species	LC_{50} (95% CI)	Reference
96 hour static	Rainbow trout	5.1 (4.6-5.6) mg/L	Grau, 1984a
96 hour static	Rainbow trout	4.7 (3.8-8.1) mg/L	Hermann, 1980a
96 hour static	Rainbow trout	0.44 (0.36-0.54) mg/L	Lamb, 1981
96 hour static	Rainbow trout	1.1 (0.9-1.2) mg/L	Lamb and Roney, 1973
96 hour static	Golden orfe	7.5 (7.0-8.5) mg/L	Grau, 1984b
96 hour static	Golden orfe	3.8 (3.0-4.7) mg/L	Hermann, 1980b
96 hour static	Bluegill sunfish	0.75 (0.64-0.89) mg/L	Lamb, 1981
96 hour static	Bluegill sunfish	1.5 (1.2-1.8) mg/L	Lamb and Roney, 1973

The rainbow trout tests were conducted using a 50% WP formulation, technical active (two tests) and 75% WP, respectively. Formulations were dispersed in water, and the technical active was solubilised with acetone. All concentrations refer to active ingredient and are nominal.

The golden orfe tests were conducted using a 50% WP formulation and technical active/acetone, respectively. Analysis of a blank test solution of technical active using a method that also detects the toxicologically relevant sulfoxide and sulfone metabolites found concentrations declined from an initial 97% through 53% at 48 hours to 28% at the end of the exposure period.

The bluegill tests were conducted on acetone solubilised technical active and 75% wettable powder, respectively, with results reported as nominal concentrations of methiocarb.

5.2.2 Fish early life stage toxicity

Rainbow trout were exposed for 56 days from the egg stage to methiocarb (25, 50, 100, 200 and 400 µg/L) under analytically verified flow-through conditions. Embryo survival was unaffected by methiocarb exposure but larvae became intoxicated above about 100 µg/L, with significant mortality, weight reduction and effect on swimup development at the two highest doses. The 56 day LC_{50} was 0.55 (0.44-1.00) mg/L with a NOEC of 50 µg/L (Carlisle, 1985). Results from this test can be considered reliable as concentrations were analytically verified.

5.2.3 Tadpole acute toxicity

Results are available from static testing at 16°C with southern leopard frogs, exposed as egg clusters until they hatched or development ceased (Marking and Chandler, 1981). The nominal 96-hour LC_{50} was 8.7 mg/L, and did not differ greatly over shorter timeframes. Hatch success exceeded 95% at 15 mg/L but dropped below 5% at 25 mg/L. Corresponding concentrations for larval survival were 2 and 8 mg/L. Tadpoles and fish appear to share similar sensitivity to methiocarb.

5.2.4 Aquatic invertebrate acute toxicity

Exposure of *Daphnia magna* to several concentrations of technical methiocarb in reconstituted water (pH 7.6) under standard static conditions found a dose-dependent increase in mortality. The nominal 48-hour LC_{50} was 19 (13-26) µg/L. This result should be treated with caution as exposure concentrations were not analytically verified, although there is some indirect evidence for the stability of methiocarb in this test as most mortalities occurred between 24 and 48 hours (Nelson, 1979).

Toxicity data (96 hour LC_{50s}) obtained in standard static tests with other invertebrates are available in the published literature (Marking and Chandler, 1981) as follows: juvenile glass shrimp, 110 µg/L; juvenile crayfish, 1300 µg/L; mayfly nymph, 7 µg/L; and caddisfly larvae, 14 µg/L. Test media were dosed with a stock solution of technical methiocarb. Concentrations were not verified analytically.

5.2.5 Aquatic invertebrate reproduction

Life cycle toxicity of radiolabelled methiocarb to *Daphnia magna* was studied in a 21-day test under flow-through conditions with analytically verified concentrations, which were 106-131% of nominal on average. Survival remained unaffected up to the highest mean-measured concentration tested of 1.3 µg/L, but daphnid lengths were significantly different at 0.32 µg/L and above. Production of young was significantly affected at 0.10 µg/L and above. Results can be considered reliable as concentrations were analytically verified (Forbis, 1987).

5.2.6 Toxicity to molluscs

Static testing was conducted with adults of the gastropod mollusc *Pottomydus cingulatus*, collected from Karachi beaches and acclimatised for a week before testing. The 24-hour LC_{50} was 28 mg/L, and mortality was complete at 62 mg/L (Jahan *et al*, 1995).

The US EPA draft database lists a 96-hour EC_{50} of 1 mg/L for shell growth in eastern oysters (*Crassostrea virginica*) and 96-hour LC_{50}s of 0.1 mg/L for adult river horn snails (*Oxytrema catenaria*) and 8.8 mg/L for Asiatic clams (*Corbicula manilensis*).

5.2.7 Algal toxicity

A single study with the green alga *Scenedesmus subspicatus* was submitted. Methiocarb was moderately toxic, with a nominal 96-hour EC_{50} of 1.15 mg/L in the alkaline (pH 8-8.5) nutrient solution used (Anderson, 1984).

5.3 Non-target Terrestrial Invertebrates

Methiocarb is acutely toxic to bees by contact and oral exposure routes. However, exposure of bees will be low when the snail bait formulation is used.

The acute and reproductive effects of methiocarb on earthworms were studied in three artificial soil tests and in four field studies. Methiocarb is slightly to moderately toxic to earthworms when distributed through the soil, with LC_{50s} in the order of 100 mg/kg. Toxicity is moderated when the snail bait formulation is used, except for surface feeding species. Effects on cocoon production are evident at concentrations an order of magnitude lower than those that cause mortality. Reproductive success is impaired when earthworms are tested in boxes at typical application rates, but major population effects do not appear to occur in the field, notwithstanding the deaths of litter feeding species.

A range of laboratory and field tests were conducted with carabid and rove beetles, and effects on numerous other arthropod fauna were studied in the field. These tests generally did not follow established protocols. Predatory insects as represented by carabid beetles feed on pellets and suffer heavy mortality when snail baits are applied under laboratory conditions. Population reductions occur under field conditions. In contrast, rove beetles do not feed on pellets, but suffer heavy mortality through contact under highly exposed laboratory conditions when no refuge is available. Predatory fauna are not expected to be adversely affected in the field by single applications of methiocarb for snail and slug control. Any effects on the function of the decomposer community are expected to be small.

Methiocarb does not appear to impair soil microbial functions.

5.3.1 Bees

Contact toxicity was studied by dosing young worker honeybees (*Apis mellifera*) with varied concentrations of an acetone solution of methiocarb. Teams of ten bees supplied with methiocarb in aqueous sucrose solution were used to determine oral toxicity. Control mortality remained well below the validity criterion of 15%. The 48-hour acute oral LD_{50} was 0.47 µg/bee, and the contact LD_{50} was 0.23 µg/bee, indicating that methiocarb is toxic to bees. Most deaths occurred within 24 hours of dosing. Affected bees were restless and irritable, with uncontrolled motions. Survivors were asymptomatic at the conclusion of the test (Heimbach, 1995a).

5.3.2 Earthworms

Laboratory toxicity studies

Toxicity of a wettable powder formulation to groups of 6 earthworms (*Eisenia foetida*) was studied in quartz sand amended with 5% bentonite, 1% calcium carbonate, 0.5% cattle manure (replenished weekly) and peat. The effects of varying peat content (2.5, 5 and 10%) were investigated. Mean earthworm weight varied inversely with peat content, from 321 mg at 2.5% to 282 mg at 10% peat. The 28-day LC_{50s} were 60.7, 107.5 and 129.2 mg/kg methiocarb, with toxicity clearly ameliorated by the addition of peat. These results indicate slight to moderate toxicity to earthworms. Weight reduction was evident at 10 mg/kg, the lowest dose tested. There was essentially no cocoon production in test vessels, compared with around 20 cocoons in each control vessel (Heimbach, 1982a). This test followed an early proposal for an OECD guideline, but differs from the accepted guideline in some minor aspects such as soil composition and in the observations regarding cocoon production. Results are considered reliable, but the sensitivity of earthworms to methiocarb clearly depends on soil organic matter content.

It is recognised that the results of such testing are sufficient to determine relative toxicity of chemicals but have limited ecological relevance as they examine effects on individual worms rather than on populations or communities. Factors such as predator-prey relationships, fecundity, changes in egg fertility, growth or behaviour exert strong influences on earthworm ecology. Furthermore, earthworms represent only one facet of soil ecosystems (Reinecke, 1992).

An analogous study was conducted with a slug bait formulation, which was ground up before distribution through an artificial soil containing 10% peat. The LC_{50} was 195 mg/kg methiocarb, with symptoms (body weight and cocoon production) apparent at 10 mg/kg but no mortalities below 100 mg/kg. Testing with intact baits found only isolated mortality at 178 and 316 mg/kg (Heimbach, 1982b).

Reproduction

Effects on reproduction were studied in test boxes containing artificial soil and 10 earthworms, with fortnightly addition of cattle manure as food. Survivors were removed and weighed after 28 days exposure. Numbers and weights of offspring were determined after a further 28 days. Body weights were reduced at all concentrations (2, 4, 8 and 10 kg/ha of a 50% wettable powder) and some earthworms came to the surface at the three highest doses. Numbers of offspring were reduced dose responsively by 81, 94, 97 and 95%, with corresponding reductions (77, 91, 95 and 95%) in total biomass (Heimbach, 1995b).

Field studies and observations

Field studies were conducted in Germany on pasture treated twice during summer with 4% pellets at 3 kg/ha, comparable to the general Australian agricultural rate of 5.5 kg/ha 2% pellets. Some dead earthworms were found at the surface after treatment, particularly of the surface feeders *Lumbricus terrestris* and *L. rubellus*, but affected less than 2% of the population. Remaining worms were counted by hand sorting and formalin extraction, which revealed the presence of six species (*L.*

terrestris, *L. rubellus*, *L. castaneus*, *Allolobophora rosea*, *A. calignosa* and *A. chlorotica*). No differences in numbers or biomass were noted between control and treated plots in autumn or the following spring, except for lower numbers of *A. rosea* in the spring. This observation could not be interpreted as a response to methiocarb given the absence of effect in the preceding autumn and the relatively low and variable population densities in controls (Heimbach, 1985, 1990a).

An analogous study at the same site with a WP formulation applied at 1 or 4 kg/ha methiocarb returned similar results. Some earthworms were found dead or incapacitated at the surface after treatment, but were too few in number to affect populations. The same six species were identified as present in the soil, together with another, *A. terrestris longa*. One species (*A. calignosa*) was reduced in number for a few weeks at the fourfold rate but populations had recovered by autumn (Heimbach, 1986).

Field observations from New Zealand are also available. Methiocarb was applied to pasture at 0.5 and 1 kg/ha, either as spray or 2% bait formulation. Moribund earthworms came to the surface of the test plots, and subsequently died. The litter feeding species *Lumbricus terrestris* Hoffmeister was most affected, as both adults and juveniles, although bait formulations appeared not to affect adult populations. The topsoil mixing species *Allolobophora calignosa* Savigny was only slightly affected, with the greatest population reduction of 29% occurring in the high rate spray plot. Juvenile populations did not appear to be affected by either treatment. The author concludes that methiocarb can kill earthworms under field conditions, but that kill rates and species affected will depend on the mode of application and the season. Single spray applications would cause a small and transient earthworm decline, but frequently repeated applications may have a greater deleterious effect on populations (Barker, 1982).

Limited details are available of an Australian trial conducted in spring 1970 at Dural NSW. Mesurol snail baits were applied at 5.6 or 22.4 kg/ha shortly after a substantial rainfall when the worm population was active quite near to the soil surface. Worm populations were enumerated by formalin extraction before and one week after treatment. The species present were *Allolobophora calignosa* and *Megascolex* sp. No dead worms were seen at the surface, and there was no indication of an effect on populations. Formalin treatment released an average 8.2 worms/m^2 before treatment, and 5.8 and 6.6 worms/m^2, respectively, after low and high rate treatments (Fullerton, 1970).

Earthworm impacts are reported in a 1994 letter from a West Australian home gardener to the National Registration Authority. The correspondent reported that earthworms died in large numbers beneath garden mulch and in an adjacent worm farm following use of methiocarb snail baits according to label.

A similar incident arising from agricultural use has been reported from the UK (Fletcher *et al*, 1999). The incident occurred in October 1998 after pellets had been applied at the approved rate using a fertiliser spreader. Soil (clay with flint overlying chalk) was described as moist but not waterlogged at the time of treatment. Application was followed by several days of wet weather, with light rain falling on most days. Chemical analysis of dead earthworms revealed methiocarb residues of 8-

12 mg/kg. The report acknowledges that such incidents may occasionally occur, but that it is unlikely that populations would be adversely affected. Residues detected were considered too low to present a secondary poisoning risk to birds and small mammals.

5.3.3 Carabid beetles

Snail baits

Two European species of wild caught carabid beetle (*Calathus fuscipes* and *Pterostichus melanarius*) were housed in groups of twenty in plastic containers with a 5 cm layer of damp peat. Methiocarb baits were scattered on the surface as the only food for 2 weeks, with supplementation by mealworms for a further 3 weeks. Three bait concentrations (1%, 2% and 4%) were used, at normal and twofold rates of 75/150, 50/100 and 33/65 pellets/m^2. By way of comparison, the Australian home garden rate of 25 kg/ha 2% baits equates to 100 pellets/m^2. Survival of control beetles was good, but exposed beetles suffered 50-90% mortality, particularly in the first 1-2 weeks. Not all bodies were recovered, with the discovery of remains indicating consumption by surviving beetles. Both species responded similarly, and independently of treatment rate. Pellets showed evidence of feeding (Heimbach, 1988).

A second study tested the effect of 4% methiocarb snail baits on one month old laboratory reared imagines of *Poecilus cupreus*, and on wild caught *Carabus granulatus*, *Pterostichus melanarius* and *Harpalus rufipes*. Beetles were tested in groups of two males and two females in test vessels (170 cm ground area) containing 1 cm of wet sandy soil, with chopped fly pupae provided twice weekly as food. A single bait pellet was placed on the soil surface, exceeding the recommended rate of 3 kg/ha several times over. High mortality (66-100%) occurred in all species except the relatively insensitive *Pterostichus melanarius* in which mortality reached 25%. Semi-field observations from enclosures on clay loam soil in which canola had recently germinated were consistent with the laboratory results. Mortality of *Poecilus cupreus* reached 60% after 6 days. Similarly, 90% of *Carabus granulatus* beetles were dead within 7 days. The less sensitive *Pterostichus melanarius* suffered only 20% mortality (Büchs *et al*, 1989).

Treated seeds

A third study exposed laboratory raised *Poecilus cupreus* at 10-12 weeks of age to treated wheat seeds (0.1% methiocarb) planted at 200 kg/ha into sand or sandy loam soil, with grains buried to 1 cm or left partly uncovered. Fly pupae were also offered as food. With the exception of seeds left exposed on sand, mortality rates did not differ from controls. Consumption of fly pupae was significantly reduced where seeds were only partly covered. When coated seeds were placed on the sand surface, mortality reached 90% (Heimbach, 1990b).

Larvae of this species were also tested, in individual cups containing a single treated maize seed planted at a depth of 2 cm in soil. Exposure was an order of magnitude higher than would occur in the field. Bisected mealworm larvae were provided as food. Development of control larvae was 90% successful, with larvae entering the pupal stage at day 26 and completing metamorphosis 13 days later. Larval development was arrested in the treated chambers, with none pupating (Schmuck, 1992b).

Field study

A 4-year field study examined the effects of methiocarb slug pellets on surface predator activity, particularly carabid beetles, using pitfall traps. Baits (probably containing 4% methiocarb) were either drilled with the seed (winter cereals) or scattered on the surface after sowing in autumn, at a rate of 5.5 kg/ha. All common late autumn/winter populations were much reduced in abundance by both forms of treatment. At least one species (*Bembidion obtusum*) did not recover in the following growing season. Late spring and early summer active species showed a variable response, thought to be due to complex behavioural differences rather than direct toxicity, and perhaps a reflection of secondary effects on prey density (Purvis and Bannon, 1990, 1992).

5.3.4 Staphylinid (Rove) beetles

These staphylinid beetles were tested in groups of ten males and ten females for 37 days in boxes containing natural soil (sandy loam, 0.75% organic carbon). Treated corn seeds (0.05% methiocarb) were planted 2 cm deep in the soil at a rate twenty times higher than would occur in practice. Host fly pupae were added weekly after the second week. Emerging offspring were counted daily. Adult mortality was difficult to determine precisely as the small black beetles provided little contrast with the surrounding soil, but appeared low. Emergence rates were essentially unaffected at 98% of control levels, compared with 28% for the reference substance (carbofuran). The author notes that soil is a more realistic test medium for seed dressing formulations than the suggested quartz sand, which allows active constituents to rapidly contaminate the entire test chamber (Schmuck, 1993).

Another test used 1-2 week old adult females housed individually in glass cells (3.5 cm diameter) on moist sand with fresh food provided daily. Beetles were each exposed to a single pellet for 4 days, a much higher level of exposure than would occur in the field. Survival, egg production and egg hatch were measured. Feeding on pellets was not observed. Survival was reduced by 78%, and egg production by 86%, but egg hatch remained unaffected. Prior grinding and mixing of the pellets with the sand left the beetles with no refuge and caused even more pronounced effects, with all females dead before any eggs had been laid (Samsøe-Petersen *et al*, 1992).

5.3.5 Field studies

The effects of methiocarb treatment on resident arthropod fauna were studied in Ireland on a poorly drained silty clay loam. Seed dressing (0.05%) represented the control treatment. Methiocarb was applied to test plots as a 4% granule, either scattered on the surface or drilled with the seed at 5.6 kg/ha product in autumn. Surface fauna were sampled with pitfall traps, and soil dwellers using a funnel method.

Among the soil dwellers, no significant effects were seen on earthworm, acarine or dipteran numbers. Beetles occurred sporadically, with hydrophilid and staphylinid larvae showing significant responses on one sampling date each. Onchiurid collembola were less abundant in seed treatment plots the following spring and summer, suggesting an attraction of these organisms to germinating seedlings.

Pitfall trap results found no significant effects on surface collembola. Carabid numbers were depressed in autumn and spring on the surface treated plots, when adults and larvae, respectively, are usually most abundant. Some effects were also seen on diptera, with Cecidomycae larvae affected in autumn and adult Sciaridae in spring. Spring Diplopoda populations were depressed by the surface treatment and to a lesser extent by the seed dressing.

The authors conclude that predatory fauna, which can play a key role in preventing early season build up of aphid populations, should not be adversely affected by a single surface treatment of methiocarb for slug control, and that any effects on the function of the decomposer community will be small (Kelly and Curry, 1985).

A 30 day small plot trial in Swiss meadows examined the effects of 5% metaldehyde and 4% methiocarb pellets, applied at 3 or 30 kg/ha (120 or 1200 g/ha methiocarb), on summer populations of surface dwelling soil fauna such as carabids, staphylinids, spiders, isopods and millipedes. Invertebrate fauna were enumerated using a single pitfall trap in the centre of each plot. At the higher application rate, there was a significant impact of methiocarb on staphylinids, compared with control and metaldehyde treatments. Smaller carabids were also reduced, but the effect was not significant. The dominant carabid species, *Pterostichus melanarius*, remained unaffected, as did other invertebrate groups (Bieri *et al*, 1989).

5.3.6 Soil micro-organisms

Effects of methiocarb (50 or 250 mg/kg) on microbial populations were studied in clay loam and silt loam soils maintained at 50% field capacity for 56 days. Soil samples were assayed at intervals for populations of fungi, bacteria and actinomycetes. No significant effects were seen (Houseworth and Tweedy, 1972).

Minimal inhibition of nitrification and denitrification processes occurred over a 28-day period in sandy loam soil treated with methiocarb at 2.25 or 22.5 mg/kg (Atwell, 1978).
Exposures in the above studies are representative of recommended application rates. For example, application of methiocarb at the high rate of 4 kg/ha would leave residues of about 65 mg/kg if evenly dispersed through 5 cm of soil with a density of 1.2.

5.4 Mammals

Available data indicate that methiocarb is highly toxic to mammals by the acute oral route, but that aversive effects moderate the dietary hazard as occurs for birds. Methiocarb sulfoxide is more toxic than methiocarb, and methiocarb sulfone much less toxic. Kills of rodents have been reported from the field, including one Australian trial investigating the potential of methiocarb pellets for controlling plague mice, but no significant population impacts have been recorded.

5.4.1 Acute toxicity

Acute oral LD_{50s} in rats, mice, and dogs are about 20, 52-58 and 25 mg/kg, respectively (Tomlin, 1997). Another reference cites a rat LD_{50} of 100-135 mg/kg for methiocarb, and 42 mg/kg for methiocarb sulfoxide. Methiocarb sulfone and the three phenolic metabolites have LD_{50s} above 1000 mg/kg (Gras *et al*, 1981). Similar trends are reported in an old company review (Timme, 1982) with rat LD_{50s} of 13, 6 and > 1000 mg/kg, respectively, for methiocarb, methiocarb sulfoxide and methiocarb sulfone.

As for birds, the toxicity of methiocarb is likely to be moderated by aversive effects in sub-lethally dosed individuals. There is some evidence to support this, as outlined below.

5.4.2 Acceptance tests

Acceptance of 2% methiocarb slug baits by groups of 10 field mice was studied in small enclosures to which baits had been applied at 3 or 6 kg/ha. One dead mouse was found in each treated area the day after treatment, and another mouse in each area at the end of the study. Residue analysis using a method that also detects methiocarb sulfoxide and methiocarb sulfone found no detections above the limit of 1 mg/kg (Grau, 1989).

Methiocarb pellets were also mixed with pelleted rabbit food and offered to captive hares, after removal of the pellets and carrots on which they had been maintained. Video observations revealed that one hare consumed 20% of bait pellets and 51% of the food offered (a mixture of 1.5 g bait and 13.5 g food) over an 8 hour period. No adverse symptoms were apparent. A second hare that had been fasted for 24 hours consumed 23% of the bait and 74% of the food within 2 hours, again with no apparent effect. Both hares were then offered a mixture of 50 g bait and 450 g food. Bait consumption over the following day was very limited, with the first hare declining baits completely (Grau, 1987b).

5.4.3 Field studies on English winter cereals

Effects on small mammals living in a winter barley field (8 ha) were evaluated by live trapping before and after surface application of 4% baits at 5.5 kg/ha. Capture rates were not strongly affected by treatment, and numerous individuals were recaptured after baiting. No evidence of feeding on pellets was discovered at post-mortem examination, but brain acetylcholinesterase activity was reduced in 8 out of 20 wood mice examined. Residue analysis of stomach contents found between 0.57 and 121.8 mg/kg methiocarb in eight wood mice, including all five mice found dead in traps. Only two mice had sufficiently high residues to indicate methiocarb poisoning as the cause of death. Dead earthworms found on the surface, particularly in wet conditions, contained 2.15-77.2 mg/kg methiocarb. Their presence on the surface coincided with depression of brain acetylcholinesterase in mice (Greig-Smith, 1989).

A second trial in which 4% baits were applied at 5.5 kg/ha in autumn to English winter cereals provided contrasting results. Farm workers reported a number of dead wood mice in treated fields, and subsequent line trapping found a large and statistically significant decline in mouse numbers in the few days after baiting, including a failure to trap any mice in two fields sampled 2-4 days after treatment. Subsequent catch rates recovered after a week to levels obtained pre-treatment, but most were juveniles and only one marked individual was recaught. Results indicate a sharp reduction in survival that was rapidly compensated for by juveniles dispersing at this time of the year (Johnson *et al*, 1992).

A third capture-mark-release study compared autumn and spring applications (4% baits at 5.5 kg/ha) and found decreases of 78% and 33%, respectively. Recapture rates were much lower in the autumn than in the spring. The autumn impact was larger notwithstanding that mouse activity was higher in untreated hedgerows during this season. Unlike the previous study, the proportion of juveniles in the population did not increase, but was already high at 54% pre-treatment. Survivors captured after treatment showed no cholinesterase depression (Shore *et al*, 1997).

5.4.4 Australian field observations

Investigations were conducted in the early 1990s to determine whether methiocarb snail baits would be effective in controlling plague mice, and conversely whether consumption of the baits by mice would compromise snail control. Baits were deployed in trails or broadcast. The effects of methiocarb and strychnine as toxicants on wheat were compared.

Bait trails laid in a paddock with very high mouse activity killed more than 20% of marked mice as well as large numbers of unmarked mice. Populations did not appear to be affected, with trap success remaining above 100%. No dead mice were found after perimeter broadcast treatment. A comparative study with broadcast laced wheat found 86-94% mortality from strychnine but only 39-46% from methiocarb. The authors conclude that methiocarb is unlikely to be effective as a rodenticide because of the aversion that develops in many mice before ingesting a lethal dose (Mutze and Hubbard, 1994).

5.5 Reptiles

No data have been provided, but high toxicity must be assumed given the broad spectrum of activity.

5.6 Phytotoxicity

No data were presented. The label for Mesurol 750 indicates that it has been used without damage on a wide range of ornamental plants, but that phytotoxicity should always be tested on a small number of plants in case local conditions favour adverse reactions.

5.7 Summary of Environmental Toxicity

Toxicity tests with methiocarb have been conducted in the following organisms.

5.7.1 Birds

Acute oral toxicity data are available for a wide range of birds. Most of the data are old and poorly described, but results are consistent with those from more recent, well reported studies. Methiocarb is highly to very highly toxic to birds by the acute oral route of exposure, with most LD_{50s} in the 5-15 mg/kg range. Intoxication is characterised by a rapid onset of paralysis, progressing to mortality within a few hours. Remission is fairly rapid in sublethally dosed birds. Methiocarb sulfoxide appears to be even more toxic than methiocarb. Methiocarb sulfone appears less toxic and has an immobilising effect on birds at doses an order of magnitude below those that cause death.

Data on dietary toxicity are more limited. Dietary toxicity is variable, ranging from slightly to highly toxic. Testing is compromised in most species by strong repellent effects. Mortality tends to be delayed for some days as birds starve to death.

Reproductive testing with quail and ducks found that these species could tolerate dietary concentrations of 50-100 ppm without adverse effects on health or food consumption. Higher doses in Japanese quail led to anorexia and impaired reproductive capacity.

Palatability tests were also conducted in order to further investigate the anorexic effects apparent in dietary studies. Most of the tests are rather old, but both old and newer studies provide consistent evidence for a strong repellent effect of methiocarb to birds, whether mixed with normal feed or scattered as baits at typical rates of use. Quail were able to discriminate between clean and contaminated food, under both laboratory and simulated field conditions, with feed offered in separate hoppers or mixed together. Mild symptoms such as weight loss and apathy were seen in some quail when only limited amounts of clean food were offered. Similar discrimination was displayed by blackbirds and starlings offered contaminated earthworms or cutworms. Some consumption occurred when clean food was in short supply, but without causing any obvious harm. Methiocarb has been registered by the US EPA for aversive conditioning of corvids predating on eggs. This apparent safety does not extend to small and sensitive species. Captive canaries suffered heavy mortality on exposure to treated oat seeds, each of which may have contained a lethal dose.

Field studies also returned favourable results, with most reporting neither mortality nor aberrant behaviour. One detailed study in English cherry orchards sprayed for bird control found a limited number of non-target casualties but could not detect any impacts on overall numbers or breeding success.

5.7.2 Aquatic organisms

Static testing with three species of fish found methiocarb to be moderately to highly toxic (96 hour LC_{50s} typically in the order of 1-5 mg/L based on nominal concentrations). Life cycle studies found significant toxic effects at 0.1 mg/L. Tadpoles appear to share similar acute sensitivity. Available data indicate that methiocarb is very highly acutely toxic to aquatic invertebrates. The 48-hour LC_{50} to *Daphnia magna* was 19 µg/L. Reproductive impairment in this species occurred at concentrations below 1 µg/L. Limited data indicate that methiocarb is moderately to highly toxic to molluscs and moderately toxic to algae.

5.7.3 Non-target terrestrial invertebrates

Methiocarb is acutely toxic to bees by contact and oral exposure routes. However, exposure of bees will be low when the snail bait formulation is used.

The acute and reproductive effects of methiocarb on earthworms were studied in three artificial soil tests and in four field studies. Methiocarb is slightly to moderately toxic to earthworms when distributed through the soil, with LC_{50s} in the order of 100 mg/kg. Toxicity is moderated when the snail bait formulation is used, except for surface feeding species. Effects on cocoon production are evident at concentrations an order of magnitude lower than those that cause mortality. Reproductive success is impaired when earthworms are tested in boxes at typical application rates, but major population effects do not appear to occur in the field, notwithstanding the deaths of litter feeding species.

A range of laboratory and field tests were conducted with carabid and rove beetles, and effects on numerous other arthropod fauna were studied in the field. These tests generally did not follow established protocols. Predatory insects as represented by carabid beetles feed on pellets and suffer heavy mortality when snail baits are applied under laboratory conditions. Population reductions occur under field conditions. In contrast, rove beetles do not feed on pellets, but suffer heavy mortality through contact under highly exposed laboratory conditions when no refuge is available. Predatory fauna are not expected to be adversely affected in the field by single applications of methiocarb for snail and slug control. Any effects on the function of the decomposer community are expected to be small.

Methiocarb does not appear to impair soil microbial functions.

5.7.4 Mammals

Available data indicate that methiocarb is highly toxic to mammals by the acute oral route, but that aversive effects moderate the dietary hazard as occurs for birds. Methiocarb sulfoxide is more toxic than methiocarb, and methiocarb sulfone much less toxic. Kills of rodents have been reported from the field, including one Australian trial investigating the potential of methiocarb pellets for controlling plague mice, but no significant population impacts have been recorded.

6 PREDICTION OF ENVIRONMENTAL HAZARD

Methiocarb is transformed in the environment through hydrolytic and oxidative reactions. Hydrolysis predominates in alkaline media, but is preceded by oxidation under acidic conditions. Hydrolytic pathways detoxify the molecule, while oxidative reactions transform methiocarb to its sulfoxide and sulfone, both of which are likely to retain biological activity but to be unstable with respect to hydrolysis. Microbial activity or chemical catalysis may intervene in both pathways. The rate of degradation is influenced by numerous factors, including temperature, pH, soil texture, redox potential, moisture and microbial activity. Typical half-lives in surface soils for methiocarb are in the range of a week to 2 months. Methiocarb has low mobility but its metabolites are highly mobile in soils and likely to move with soil water.

Methiocarb has high to very high toxicity to birds, mammals, aquatic organisms and non-target invertebrates. In addition, the main formulation used is a grain-based pellet that can be consumed by birds, mammals and non-target invertebrates. These properties indicate a potential hazard to birds, mammals and non-target invertebrates exposed to methiocarb at the site of application, and to aquatic fauna exposed to residues in water draining treated areas.

The environmental hazard of methiocarb is assessed below. The approach used is essentially that of the US EPA and involves determining the ratio of concentration to toxicity, a parameter known generally as the risk quotient (Q) and more correctly as the hazard quotient. According to methodology used by the US EPA for its reregistration program (US EPA, 1994), a Q of less than 0.2 (for terrestrial species) or 0.1 (for aquatic species) indicates that acute risk is minimal and no further assessment is needed. The US EPA considers that the potential for acute risk is high where quotients exceed 0.5, and that regulatory action may be warranted in addition to restricted use classification. The risk quotient is an essentially qualitative parameter rather than a highly quantitative measure of ecological risk, particularly as exposure and environmental fate are currently excluded from its derivation. Environmental concentrations used to derive the risk quotient are simply estimated from the application rate.

6.1 Terrestrial hazard

Birds and mammals may be exposed to methiocarb by direct consumption of granules, contaminated invertebrates or plant material. Arthropods will be exposed by direct granule consumption or indirectly to residues in invertebrates or vegetation. Risks from these exposures are discussed below.

6.1.1 Birds

Birds may ingest granular pesticide formulations when foraging for food or grit. They also may be exposed by other routes, such as walking on exposed granules, drinking water contaminated by granules, or consuming contaminated prey.

The US EPA has adopted a level of concern of 1 LD_{50} per square foot (roughly equivalent to 10 LD_{50s}/m^2) as a screening tool to identify low risk granular pesticides for which no further work is needed. Again, this procedure assesses hazard rather than risk, as it measures only the number of granules potentially available to birds, with no information on the likelihood of consumption. This is a major shortcoming for chemicals such as methiocarb with recognised aversive effects in birds.

Potential exposure based on an avian LD_{50} of 1 mg/kg for a small bird weighing 20 g (that is, an LD_{50} of 20 µg/bird) equates to 2500 LD_{50s}/m^2 for the home garden rate of 25 kg/ha product (50 mg/m^2 methiocarb). Furthermore, the average pellet contains 500 µg methiocarb, or 25 LD_{50s} for a sensitive small bird. Methiocarb pellets are clearly hazardous to sensitive small birds, as they are readily available at the soil surface and each contains multiple lethal doses. Heavy mortality of canaries offered

treated oat seeds in the laboratory supports this analysis, but field evidence to confirm it is very limited.
Hazard to larger and less sensitive birds is less clear cut. The LD_{50} for a 200 g bird with a sensitivity of 5 mg/kg is 1 mg, or two average pellets. The US EPA's screening tool still identifies a potential hazard to birds, as the home garden rate of 25 kg/ha equates to 50 LD_{50s}/m^2. However, the hazard is moderated by aversive effects. This larger but still relatively sensitive bird would probably survive consumption of a single pellet, provided that the subsequent aversion is strong enough to deter further consumption. Available data indicate that birds are likely to be temporarily immobilised by sub-lethal doses of methiocarb. The general agricultural rate of 5.5 kg/ha pellets only marginally exceeds the US EPA threshold of 10 LD_{50s}/m^2, indicating that field use is unlikely to be hazardous to larger birds.

This hazard analysis suggests that most birds should survive exposure to methiocarb snail bait formulations, even if there is some initial attraction. Mortality may occur in small, sensitive species if they are attracted to the baits. Experience with the use of snail baits suggests that this would be an unlikely occurrence. No avian incidents have been linked to use of methiocarb pellets in Australia, notwithstanding their widespread use in home gardens and in agriculture. Methiocarb was not involved in any of the avian incidents described in the most recent incident report from the UK.

For spray applications, maximum residues may be estimated using the updated Kenaga nomogram (Fletcher *et al*, 1994). The approach is conservative as it assumes that birds obtain all their dietary requirements from food that has just been contaminated and contains the highest possible residue. Use at 4.1 kg/ha to protect poppy seedlings would leave maximum residues in the order of 500-900 ppm on foliage, and around 50 ppm on insects. Similarly, use at 1.5 kg/ha on ornamentals would leave maximum residues of around 200 ppm on the crop and 20 ppm on insects. Maximum residues measured on cherries are 26 ppm following spray application at 4.3 kg/ha methiocarb. These residues are much lower than those in pellets, suggesting a greater margin of safety. The rate of ingestion of methiocarb residues will be slower, and the opportunity for immobilisation to intervene correspondingly greater. Predicted and measured residues are generally well below all recorded LC_{50s}, most of which exceed 1000 ppm.

Experience with the use of methiocarb tends to confirm the above analysis. Even when the field use of methiocarb for bird control (a high rate use) is intensively monitored, only a few small birds are discovered dead as a result, and impacts on populations or breeding success remain undetectable.

6.1.2 Mammals

Mammals appear to respond to methiocarb exposure in a similar way to birds, with toxicity moderated by aversive effects. Field studies indicate that some rodents consume methiocarb snail baits with fatal consequences, but have been unable to demonstrate a significant effect on populations even when the intention was to control plague mice in Australia.

6.1.3 Invertebrates

Laboratory studies can be used to assess hazard to earthworms. The highest rate of bait application for methiocarb (500 g/ha) would leave residues of 8.3 mg/kg if evenly distributed through 5 cm soil (density 1.2). This prediction is well below 100 mg/kg, a concentration that caused no earthworm mortality in laboratory exposures, but approaches the concentration of 10 mg/kg at which weight reduction and effects on cocoon production were evident. Spray application at the high rate of 4 kg/ha would leave initial soil residues of about 65 mg/kg in the surface 5 cm. These simple calculations indicate that methiocarb residues dispersed through the soil should not exert lethal influences on earthworms, but may give rise to sub-lethal effects. Some mortalities may occur among surface or litter feeding species where baits are laid.

Field observations confirm the above analysis. In general, earthworms appear unaffected by methiocarb treatments. Some individuals of some species are killed, apparently by feeding on baits rather than contact with contaminated soil, but numbers involved appear too low to affect populations. Short-term population declines are apparent in some species, but populations then recover.

Laboratory studies with carabid and staphylinids (rove) beetles indicate that these organisms also can be lethally affected by methiocarb treatment. Carabids die after eating methiocarb baits, but rove beetles appear unaffected by this exposure route. Their survival and reproduction can, however, be affected by residues dispersed in the soil at exaggerated rates.

Field evaluations of the effects on invertebrate communities at application rates typical of Australian agricultural uses have shown that methiocarb causes short-term disruption, particularly to beetles, but that most species recover by the following season. Surface feeding predators such as carabids have been shown to be particularly sensitive, with sensitive species eliminated in overseas field trials. However, the ecological function of these predatory organisms should not be significantly impaired as only a small minority of species is affected in this way.

6.1.4 Reptiles

No information was submitted, but a toxic hazard to reptiles must be assumed to exist. Toxicity data for methiocarb to reptiles are not available from Bayer Germany, which submitted that a literature search on various databases did not produce any information.

Bayer Australia has also stated that no reports of reptile deaths or toxic effects from the use of pelleted methiocarb have been received during the 30 years of use in Australia.

6.2 Aquatic hazard

Aquatic exposure to methiocarb and its toxic metabolites may arise via spray drift or when drainage water enters natural bodies of water.

For drift, screening level risk assessments assume transfer of 10% of the application rate to 15 cm water. Resultant concentrations would be 1 mg/L for spray application at 1.5 kg/ha to ornamentals, and 2.8 ppm for application at 4.1 kg/ha to poppy seedlings.

The standard runoff scenario used for risk assessment by the US EPA entails a treated area of 10 acres draining into a 1 acre pond with a depth of 6 feet (Urban and Cook, 1986). A generalised maximum runoff figure of 1.5% is used, based on earlier findings that runoff losses of water-soluble pesticides range from less than 0.5% to a maximum of 1.5% if a large, early runoff event occurs. Predicted concentrations of methiocarb in a 2 m pond, based on this model, would be 3.75 µg/L following bait application at 25 kg/ha (500 g/ha methiocarb), or 28 µg/L following spray application at 4.1 kg/ha to poppy seedlings. Predicted environmental concentrations in a shallow (20 cm) wetland contaminated in this way would be 37.5 and 280 µg/L, respectively.

6.2.1 Vertebrates (fish and tadpoles)

The most sensitive acute LC_{50} for fish is 440 µg/L in rainbow trout. Predicted concentrations in deeper water from runoff remain below 44 µg/L (10% of the LC_{50} for rainbow trout). Shallow water predictions remain below the LC_{50} for rainbow trout. Toxicity data are available only as nominal concentrations, and the toxicant is known to decline in concentration under laboratory conditions. However, this screening level assessment is considered robust enough to exclude hazard to fish from methiocarb-contaminated runoff, as dissipation processes for methiocarb in the laboratory should be at least as efficient under field conditions. Laboratory studies found complete degradation in a few days in alkaline aerobic pond water.

Concentrations from spray drift exceed those calculated for runoff. Predicted concentrations arising from 10% drift to shallow (15 cm) water extend into the low ppm range for higher rate spray treatments, which would be lethal to more sensitive fish based on laboratory results for rainbow trout and bluegill sunfish. This screening level assessment highlights the importance of avoiding insecticide drift to waterways. However, drift of 10% to water is an unlikely occurrence that would reflect poor agricultural practice, given that methiocarb is applied using ground-based equipment. The US EPA currently assumes a fixed amount (1%) of drift to aquatic habitats from ground hydraulic boom pesticide applications. This level of drift from boomspray application at the high rate of 4.1 kg/ha as used in poppy seedlings would leave an estimated 0.28 mg/L in 15 cm water, for a hazard quotient of 0.6 based on the LC_{50} of 0.44 mg/L for rainbow trout. Water depth would have to increase to nearly a metre in order to reduce the hazard quotient below 0.1 and allow confidence that acute risk to fish is low.

Provided that care is taken to avoid drift off-target, significant impacts on fish populations are not expected as methiocarb degrades rapidly in aerobic aquatic environments, most fish will inhabit deeper water, and use of the spray formulation will be localised. Spray application is not common for methiocarb, with most product used having a very low drift potential because it is pelletised for snail control.

Use of more sophisticated computer modelling techniques provides less conservative exposure predictions, as outlined below, which essentially eliminate concerns for fish.

6.2.2 Invertebrates

For invertebrates, the usual indicator organism is *Daphnia magna*. Some other invertebrates (mayfly nymphs and caddisfly larvae) appear to share the high sensitivity of daphnids to methiocarb. Predicted concentrations from drift and runoff remain well above the acute LC_{50} of 19 µg/L for *Daphnia magna*, except for the snail bait formulation.

Predicted concentrations from runoff to deeper water only marginally exceed the above LC_{50}, even at the high rate of 4.1 kg/ha for poppy seedlings, and significant ecological impacts from runoff contamination are not expected given the low volumes of use and consequent infrequency of such events, and the ready regeneration of invertebrate populations by immigration or reproduction. Runoff to shallow wetlands may be expected to exert more significant ecological effects, particularly following high rate treatments. However, this risk will decline with time since application as methiocarb residues become less prone to transport in runoff.

Predicted concentrations from drift to shallow water extend into the low ppm (mg/L) range, considerably above the LC_{50} of 19 µg/L for *Daphnia magna*. Based on these simple worst-case calculations, drift contamination would be expected to have a short-term impact on invertebrate populations where drift enters the water body. More broad scale ecological consequences would not be expected given the low volumes of use and consequent infrequency of such events, lack of aquatic persistence, and the ready regeneration of invertebrate organisms by immigration or reproduction. However, every effort should be made to avoid localised disruptions likely to result from drift contamination.

6.2.3 Computer modelling

Predictions of aquatic exposure can be obtained from the AgDRIFT™ model. AgDRIFT is a computer code that models the aerial application of pesticides, with a validated solution technique against a series of studies conducted by the Spray Drift Task Force (SDTF). The estimates are for a pond or stream 60 m wide with an average depth of 2 m situated with the near edge 30 m downwind from the site of application, or for a wetland with the same dimensions apart from shallow water depth of 15 cm. Accordingly, buffers of 0 m in the model are equivalent to a distance of 30 m between the edge of the crop and the edge of the water body. Deposition is integrated across the water body to provide an estimated average concentration.

Note that the concentrations are estimated directly from deposition data with no recognition of the dissipation losses that would be expected to occur, particularly in alkaline waters. Therefore, a prediction that aquatic exposures will exceed toxic levels does not infer that biological consequences will inevitably occur.

The model predicts that initial concentrations in wetland and pond environments following application of methiocarb at 4.1 kg/ha (the highest rate use for slug and snail control in poppy seedlings) by low boomspray would be 29.3 and 2.2 µg/L, respectively. Application to ornamentals by orchard air blast at the high rate of 2 kg/ha would give rise to initial predictions of 2.6 and 0.2 µg/L. These more realistic predictions indicate that aquatic invertebrates inhabiting shallow wetlands may be adversely affected by spray drift from high rate application as occurs for poppy seedlings. However, the hazard appears relatively low, and longer-term effects on these organisms would not be expected given their high capacity for recovery. These more realistic predictions indicate that fish are very unlikely to be affected, as noted above.

In Germany and some other EU member States, basic drift values are used for predicting aquatic exposure. Outdoor drift trials with conventional equipment have been used to complete basic drift values for field crops (50 trials), grapes (56 trials), orchards (78 trials) and hops (31 trials). Estimates for drift are given as the 95th percentile of mean values, quoted as percentage of the application rate (Ganzelmeier and Rautmann, 2000).

In Australia, spray formulations of methiocarb are applied to field crops (canola and poppies, up to 4.1 kg/ha), orchards (oranges are listed on the label, but the only reported use is for bird control in cherries at 1.5 kg/ha), grapevines (early season use, not expected to exceed 750 g/ha) and ornamentals (typically 1.5 kg/ha). The basic drift values can be used to determine buffer zone distances for protection of fish and invertebrates. The following hazard quotients are obtained for shallow water, based on toxicity results of 0.44 mg/L for fish and 19 µg/L for invertebrates.

Crop	Application rate	Buffer	Concentration in 15 cm water	Hazard quotient	
				Fish	Invertebrates
Field	4100 g/ha	3 m	0.32 mg/L	0.73	16.8
		5 m	0.19 mg/L	0.43	10
		10 m	0.10 mg/L	0.23	5.3
		30 m	0.034 mg/L	0.08	1.8
Orchard (late season treatment)	1500 g/ha	3 m	0.14 mg/L	0.31	7.4
		5 m	0.09 mg/L	0.20	4.7
		10 m	0.05 mg/L	0.11	2.6
		30 m	0.0097 mg/L	0.022	0.5
Grapevines (early season treatment)	750 g/ha	3 m	0.018 mg/L	0.041	0.95
		5 m	0.008 mg/L	0.018	0.42
		10 m	0.0015 mg/L	0.0034	0.079

The Ganzelmeier prediction of 0.034 mg/L at 30 m for field crops sprayed at 4.1 kg/ha aligns well with the AgDRIFT prediction of 0.029 mg/L, with the standard 30 m distance to the edge of the pond. The AgDRIFT data were obtained under conditions more conducive to drift, with some SDTF trials conducted under higher wind speeds, higher temperatures, and lower humidity. For orchard applications, the Ganzelmeier data indicate higher levels of drift than do the SDTF data. The SDTF data are pooled from grapes (both conventional and wrap around sprayers) and apple orchards, while the Ganzelmeier results for grapevines show a lower drift compared to orchards. Therefore, the Ganzelmeier results are considered more reliable.

The Ganzelmeier predictions remain conservative in making no allowance for dissipation processes. They indicate that fish inhabiting shallow water should not be adversely affected by spray application of methiocarb, with hazard quotient values only exceeding 0.5 for application within 3 m of the water's edge. Invertebrates are at higher risk because of their greater sensitivity, but populations of these organisms tend to be more resilient because of their rapid regeneration times. Based on the limited use of methiocarb as a spray (see Environmental Exposure), mitigation of these hazards is not required.

As noted above, spray application is not commonly used for methiocarb, with most product used having a very low drift potential because it is pelletised for snail control.

7 CONCLUSIONS

Methiocarb is a carbamate insecticide/acaricide/molluscicide/bird repellent that is mainly used in pelletised form for control of slugs and snails in agricultural and home garden situations. Application occurs when pests become active, for example when rain occurs or when newly sown seedlings are watered in. The pellets begin to disintegrate through weathering within a week but are likely to remain visible for up to a month unless consumed. Smaller amounts are formulated for spray application to control slugs, snails, hibiscus flower beetles, garden weevils, western flower thrips and glasshouse sciarids in various crops (grapevines, hibiscus, ornamentals and poppies) and to repel birds attacking ornamentals and canola seedlings.

Methiocarb is transformed in the environment through hydrolytic and oxidative reactions. Hydrolysis predominates in alkaline media, but is preceded by oxidation under acidic conditions. Hydrolytic pathways detoxify the molecule, while oxidative reactions transform methiocarb to its sulfoxide and sulfone, both of which are likely to retain biological activity but to be hydrolytically unstable. Microbial activity or chemical catalysis may intervene in both pathways. The rate of degradation is influenced by numerous factors, including temperature, pH, soil texture, redox potential, moisture and microbial activity. Typical half-lives for methiocarb in surface soils are in the range of a week to 2 months. Methiocarb has low mobility but its metabolites are highly mobile in soils and likely to move with soil water.

Testing indicates that methiocarb has high to very high toxicity to birds, mammals, aquatic organisms and non-target invertebrates. As a carbamate insecticide with a broad spectrum of activity, methiocarb is likely to be highly toxic to other organisms such as reptiles. In addition, the main formulation used is a grain-based pellet that can be consumed by a broad range of non-target organisms such as birds, mammals, reptiles, earthworms and beetles. Metabolites with an intact carbamate linkage may be expected to retain toxic properties. Methiocarb sulfoxide appears more toxic than methiocarb.

Hazard assessment using deterministic methods suggests likely impacts from the snail bait formulations on non-target organisms that consume them. Small birds, reptiles, and invertebrate fauna such as beetles and earthworms appear to be the main concerns. While methiocarb appears potentially hazardous to these organisms, it should be emphasised that no avian incidents have been linked to methiocarb pellets in Australia, notwithstanding their widespread use in home gardens and in agriculture. One user has reported impacts on earthworms. The spray formulation has a similar hazard profile, but less pronounced, as the toxicant is not concentrated into edible pellets, and also represents a potential hazard to aquatic invertebrates exposed in shallow water to spray drift if care is not taken in application.

Overseas monitoring and incident reports largely confirm the above assessment. In terrestrial situations, mortality of small birds has been reported from some field trials, but with a relatively low incidence. Aversive effects appear to greatly limit avian mortality. Rodents may also consume the baits, but mortality rates are again relatively low because of aversive effects. Similar impacts on reptiles have not been documented, but neither have they been investigated. The most commonly reported non-target impacts are to invertebrates that consume baits, notably carabid beetles and surface feeding earthworm species. Although individual carabids and earthworms may be killed in large numbers by methiocarb treatment, particularly at higher rates, longer-term impacts on populations generally do not arise. Sensitive species of carabid beetle can be eliminated from treated areas, particularly with repeated applications of methiocarb, but the overall function of the predator community does not appear to be compromised.

Methiocarb is seldom detected in aquatic environments, either in Australia or overseas. Although it has the potential if not used carefully to produce localised harmful effects in aquatic fauna, particularly invertebrates, no such incidents have been recorded from field use.

The continued use of methiocarb is not expected to lead to significant environmental contamination or broad scale impacts on populations of non-target organisms. Some invertebrate species, particularly sensitive ground beetles, are likely to be killed where snail baits are applied, but effects will be localised and the ecological function performed by these organisms should not be impaired. Frequent use as occurs in home gardens is likely to be ecologically disruptive, with impacts expected on some beetle species as well as the target snails, slugs, slaters and millipedes. Some earthworms are also likely to be killed, but any impacts are expected to be localised. Small lizards are also likely to be killed if they consume baits.

Similar predictions may be made for agricultural situations. Small birds, mammals and reptiles in cropping areas are likely to be killed if they consume baits, but numbers involved would be expected to remain relatively low and overall populations would not be affected. Impacts on the invertebrate ecology of agricultural fields would be less pronounced than in the home garden because of the lower rates and relative infrequency of use. Short term, localised disruption to aquatic communities may occur in agricultural situations when spray drifts to water, but any such disruption would affect only small areas with no lasting ecological consequences.

Sufficient information has been presented to allow assessment of the likely environmental impact associated with the use of methiocarb, with the exception of modern field dissipation data, and no information on toxicity to reptiles (a deficiency not specific to methiocarb but common to all agricultural chemicals). Assessment indicates that methiocarb should not persist in the environment but that it has a very broad spectrum of biological activity consistent with its ability to inhibit acetylcholinesterase. Non-target organisms such as birds, mammals, reptiles, earthworms and beetles are likely to be killed by use of methiocarb, particularly the snail bait formulations. Populations of these organisms are not expected to be affected by such impacts, but some sensitive beetle species may be eliminated from treated areas by frequently repeated applications.

8 ADEQUACY OF LABELS

8.1 Mesurol 750 Bird Repellent and Snail and Slug Spray

The label for Mesurol 750 contains the following warnings of toxicity to bees and fish:

> "Dangerous to bees. Do not spray any plants in flower while bees are foraging."
>
> "Dangerous to fish. Do not contaminate dams, rivers, ponds, waterways or drains with the chemical or used containers."

The hazard assessment has confirmed the toxicity of methiocarb to bees. The warning and accompanying instruction not to spray when bees are actively foraging are adequate.

The hazard assessment has concluded that the toxicity of methiocarb to aquatic invertebrates is much higher than to fish. It is considered that the current label's warning in respect of hazard is inadequate and should be varied to read:

> "Dangerous to fish and aquatic invertebrates. Do not contaminate dams, rivers, ponds, waterways or drains with the chemical or used containers".

8.2 Mesurol Snail and Slug Bait

The label for Mesurol Snail and Slug Bait contains the following instruction aimed at minimising harmful effects to aquatic organisms: "Do not contaminate dams, rivers, ponds, waterways or drains with the chemical or used containers". Instructions to "clean up spilled pellets so that they are not eaten by animals and birds" are also included, as are instructions to scatter bait pellets evenly and not to heap pellets. It is considered that these instructions, together with the other instructions and warnings) on the label, are adequate.

8.3 Baysol Snail & Slug Spray

In essence, the same instructions together with an illustration appear on labels for the home garden product Baysol. The cautionary statement "DO NOT allow chemical containers or product to get into drains, sewers, streams or ponds" is also featured. A side panel warns that: "Pets may find the bait attractive. If eaten, they will be poisoned which could lead to death". There is no reference to the toxicity of methiocarb to other organisms.

Based on the hazard assessment, which found toxicological hazards to birds and mammals that consume baits, it is considered that the label should be varied so that it includes the following instructions within the label's CAUTION section:

> Clean up spilled pellets so that they are not eaten by animals and birds.

9 RECOMMENDATIONS

9.1 Product registrations

Variations to the respective conditions of registration of each product are not recommended.

9.2 Label approvals

Variations to label warnings are recommended. In each case, changes are indicated by the use of italics. This formatting is not intended to follow through to the label.

9.2.1 Mesurol 750 Bird Repellent and Snail and Slug Spray

It is recommended that the current warning of toxicity to fish:

> "Dangerous to fish. Do not contaminate dams, rivers, ponds, waterways or drains with the chemical or used containers"

be varied to read:

> "Dangerous to fish *and aquatic invertebrates*. Do not contaminate dams, rivers, ponds, waterways or drains with the chemical or used containers".

9.2.2 Mesurol Snail and Slug Bait

No variations are recommended.

9.2.3 Baysol Snail & Slug Spray

It is recommended that the current CAUTION section:

> "Avoid application of pellets to foliage of edible crops. DO NOT allow chemical containers or product to get into drains, sewers, streams or ponds."

be varied to read:

> "Avoid application of pellets to foliage of edible crops. *Clean up spilled pellets, so that they are not eaten by animals and birds*. DO NOT allow chemical containers or product to get into drains, sewers, streams or ponds."

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