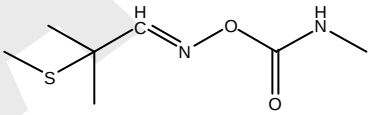
SECTION 7: ENVIRONMENTAL ASSESSMENT

1. Introduction

Aldicarb scored highly against selection criteria for the review program from an environmental perspective, particularly in light of overseas incidents and regulatory action (bird kills and groundwater contamination in the US).

Aldicarb has high water solubility and is formulated as granules for incorporation beneath the soil. It disperses through the soil with soil moisture on release from the granules, and is taken up by plant roots and translocated through the plant to provide systemic protection against chewing and sucking insect and nematode damage.

2. Chemical Identity

Name (CAS):	2-methyl-2-(methylthio)propanal *O*-methylcarbamoyloxime
Common name:	Aldicarb
CAS number:	116-06-3
Molecular formula:	$C_7H_{14}N_2O_2S$
Molecular weight:	190.25
Structural formula:	

3. Physico-Chemical Properties

Melting Point:	99-100^{o}C (decomposes above 100^{o}C)
Vapour Pressure:	13 mPa at 25^{o}C
Water Solubility:	6000 mg/L at 25^{o}C
Partition Coefficient:	P = 1.13; log P = 0.053 (*n*-octanol/water)
Dissociation constant:	no readily dissociable functionality

4. Formulation Of End-Use Products

Information on the website of Rhône-Poulenc Rural Australia Pty Ltd indicates that Temik is formulated by impregnating gypsum granules with a solution of aldicarb and a vinyl binding agent. After impregnation the granule is coated with a flow agent.

5. Overseas Regulatory Activity

Groundwater contamination and crop residue concerns have led to restrictions on the use of aldicarb in the USA, where the US EPA is addressing groundwater concerns through the special review process. The presence of aldicarb residues in groundwater raises particular sensitivities because of its very high mammalian toxicity. Aldicarb restrictions include voluntary cessation of use on potatoes in 1990 because of crop residue concerns. Similarly, restrictions were introduced in Florida citrus in 1991, and use on bananas was voluntarily cancelled in 1992. The US EPA has since (September 1995) approved reintroduction of the potato use in some geographic regions where the groundwater contamination risk is believed to be low, with more controlled application techniques to reduce crop residues. Aldicarb is listed as a restricted use pesticide in the USA because of acute oral toxicity and groundwater concerns, and remains under special review. A reregistration eligibility decision document is expected in 2001.

Currently registered US labels include an Environmental Precautions Booklet which aims to protect drinking water supplies. A general buffer of 50 feet (15 m) is prescribed around any drinking well. Application, washing, loading or emptying of application equipment must not occur within this area. Buffers must be increased to 300-500 feet (90-150 m) in some States where surface and/or subsoils are sandy and water tables are shallow (less than 8 m). Application is completely prohibited in some counties in northern California/southern Oregon and New York State. Users are advised that special care must be taken to avoid over-irrigation in soils with less than 15% moisture holding capacity. The booklet contains detailed listings by State of soil types considered vulnerable to leaching.

Use of aldicarb has also been restricted in Canada because of the above crop residue concerns. Aldicarb was voluntarily withdrawn from the potato market in 1990, and a registration submission for greenhouse ornamentals was also withdrawn.

6. Environmental Exposure

6.1 Environmental Release

6.1.1 Volume

Only limited information is publicly available on volumes of aldicarb used in Australia. Annual usage on Queensland sugar has been estimated at about 1.5 tonnes, occurring exclusively in the catchments around and to the south of Bundaberg (Hamilton and Haydon, 1996). Annual sales of Temik 100G, used in floriculture, were 300-500 kg (30-50 kg aldicarb) in Western Australia in 1986.

Information provided by registrants indicates that total use of aldicarb in Australia does not exceed 100 tonnes per annum. Only small amounts (less than 10 tonnes combined) are used in sugarcane, citrus (oranges and mandarins) and grapes. The main use is in cotton.

The California Department of Pesticide Regulation publishes information on its website on volumes of pesticides used in that State. Annual consumption of aldicarb has increased from 85 tonnes in 1991 to 239 tonnes in 1998. National use in 1992 was estimated at a little over 1900 tonnes.

6.1.2 Application and use patterns

Granules are incorporated into the soil, after furrow, band or broadcast application before planting, or side dressing in established crops. Aldicarb is too hazardous to be used in the home garden. Users are instructed to ensure that granules are incorporated and covered with soil. As noted below, irrigation is required after treating some crops and the label recommends waiting until rain is imminent if drip irrigation systems do not adequately wet the treated area. Aldicab should not be applied, nor should cleaning or loading of equipment occur, within 15 m of any drinking water well.

Sugarcane

Application to sugarcane (plant and ratoon) uses a microfeed applicator to apply granules across the width of the drill at 17 kg/ha (or 24 g/10 m row). Application is followed by light incorporation with rakes, discs or tynes, and by 12-25 mm irrigation within 24 hours. A single application per crop is allowed, up to the 3-5 leaf stage.

Sugarcane is grown in small areas of mainly alluvial soils along the Queensland coast, on river flats of the Clarence, Tweed and Richmond Rivers in northern NSW, and increasingly in the Ord River Irrigation Area in WA. In Queensland, some 264,000 ha of cane was harvested during 1994. Queensland cane growing areas occupy about 457,000 ha, or about 2% of their catchment areas (Hamilton and Haydon, 1996).

As noted above, only small volumes of aldicarb are used in sugar production. The 1996 estimate of 1.5 tonnes aldicarb (10 tonnes Temik 150G) would treat around 1000 ha of cane, but nematode damage is suspected to be occurring across a further 10,000-20,000 ha in the sandy soils of central and southern Queensland. Cane expansion into more marginal sandy areas may be expected to increase the area susceptible to nematode damage, and hence the market for Temik which is the nematicide of choice for most growers.

Nematode problems in Queensland sugarcane may be more widespread than generally recognised (Stirling, 1998). Nematode damage in sugarcane is largely diagnosed on the basis of root galling, which is symptomatic of parasitisation by root-knot nematodes. Root-knot nematodes occur mainly in sandy soils, and responses to nematicides such as aldicarb are more obvious in such soils as the toxicant disperses through the root zone more rapidly. Lesion nematodes occur in all Queensland

canefields, and stubby root nematodes in some 70% of fields tested. Aldicarb is nemastatic rather than nematicidal, and nematode activity usually resumes after 4-6 weeks. Lesion nematodes remain active for at least 9 months of the year, during which as many as 8 generations may be completed. Root damage from this species may be exacerbated by opportunistic fungal infection, and is likely to be diagnosed as such. Yield reductions are more pronounced in soils with lower fertility and water holding capacity, particularly in years of low or erratic rainfall.

Cotton

Application to cotton occurs in furrow at seeding, at rates of 3-7 kg/ha (450-1050 g/ha aldicarb). The preferred placement, just below the seed line, can be achieved by attaching the granule delivery chute so that granules are released just before the seed chute. Treatment should only occur where there is adequate soil moisture to allow uptake into the plant, and not under cloddy soil conditions. Aventis promotes aldicarb as part of integrated pest management in cotton, on the basis that its selectivity for sucking pests means that most predators and parasites will not be exposed to significant levels of aldicarb. However, it is acknowledged that predator and parasite populations may decrease following use of aldicarb due to the lack of a food source. Temik is promoted for use with Ingard cotton, where its early season control (up to 50 days) of sucking pests complements the activity of the Bt gene against *Helicoverpa* spp. Early season control of sucking pests and soil pests helps establish and maintain plant vigour, and also reduces the need for early season foliar sprays that can be wasteful because of the limited crop canopy. Aldicarb's ability to reduce spraying requirements could result in increased use in cotton, but the principal registrant considers that this is unlikely to occur because of stiff competition from alternative chemicals.

Cotton is grown over about 500,000 ha, mainly along the upper tributaries of the Darling and Fitzroy Rivers in NSW and Queensland. Planting occurs generally from late September to mid November (early April in the Ord River Irrigation Area). Much of the crop is irrigated, particularly in NSW. Irrigated cotton is typically grown on a 4-5 year rotation cycle, with 4 years of cotton followed by wheat or a legume (often the break crop is not irrigated, giving the soil an opportunity to dry out, assisting aeration, and ameliorating soil borne diseases). Rain-grown (dryland) cotton is an opportunity crop grown when conditions are suitable, including initial soil moisture status and expected net returns (ie price and yield), and the rotation of rain-grown crops depends on a range of factors, such as rainfall, farm cropping mix and soil type.

Cotton is grown on a range of soil types, mainly neutral to alkaline, grey and brown cracking clays in NSW and Qld. The grey and brown clays are moderate to very deep clay soils which crack deeply on drying and are often alkaline throughout the profile. Some are slightly acid at the surface and become alkaline at shallow depths, and sometimes they are strongly acidic in the deep subsoil below an alkaline or slightly acid topsoil.

As well as the established industry in NSW and Queensland, cotton is making a comeback to the Ord River Irrigation Area, after previous attempts to introduce cotton to the region were defeated by heavy pest pressure and the rapid development of resistance, with some growers requiring 50 sprays per season.

Citrus and grapes

Control of citrus leaf miner in non-bearing citrus uses an area rate of 7 g/m^2 (equivalent to 70 kg/ha product), with repeat applications if new leaf mines are found. Alternatively, banded treatment at 30 g/tree may be used, with granules applied in 20-50 mm wide bands extending 150-300 mm along the rows on each side of the tree, some 200 mm from the trunk. This equates to an area rate in the order of 9 kg/ha product for planting rates of 300 trees/ha. Banded treatments should be incorporated to a depth of 30-50 mm.

Oranges (non trifoliata rootstocks only) may also be treated once at 14-77 kg/ha product from August to November as a band near the drip line for control of citrus nematode, with immediate incorporation to a depth of 30-80 mm and minimum 10 mm irrigation or rain. Citrus should not be treated within 3 months of transplanting. Non-trifoliata rootstock is in decline in Australia.

In Australia, citrus fruits are grown commercially in all states except Tasmania. Around 88% of all Australian citrus is grown in the major irrigated horticultural regions of New South Wales, along the River Murray in Southern New South Wales and northern Victoria (Sunraysia and Mid-Murray) and the Riverland region of South Australia. The Central Burnett region of Queensland, and production in Western Australia accounts for the majority of the balance. Citrus may be grown on highly permeable sandy soils, particularly in the Riverland.

Aldicarb does not appear to be widely used in NSW citrus. The Orchard Plant Protection Guide for Inland New South Wales, published by NSW Agriculture, lists pests and diseases likely to occur and recommended treatment methods. Petroleum spray oil is recommended for control of citrus leafminer, which can severely affect tree growth when trees are small. Citrus nematodes are not identified as a significant problem in citrus growing areas of NSW. However, as noted in the agricultural assessment, SA agricultural authorities include aldicarb in recommended pest management schedules for nematode control in citrus.

Furrow irrigation is still used extensively in some areas, such as the Riverina, but overhead systems are losing favour, particularly where water is in short supply or has salinity problems. New plantings frequently use low-level microjets or drip systems, and many existing groves are also upgrading irrigation practices.

New South Wales grows approximately 35% of total Australian citrus output. South Australia follows with 33%, Victoria 20%, Queensland 10%, Western Australia 2% and a small but growing industry in the Northern Territory.

There are approximately 3,000 citrus growers, cultivating 32,000 ha of land in Australia. The largest numbers of growers are situated in the Riverland region of South Australia. Of the nearly 1,000 citrus holdings in South Australia, 83% are 10 ha or less in size. In Australia, most citrus farms are mixed fruit growing operations and are relatively small, with the average area being harvested around 18 ha.

Total Australian citrus production has been gradually increasing from 513,000 tonnes in 1988-89 to 720,000 tonnes in 1994-95. This can be attributed to increases in production

of navel and Valencia oranges and mandarins. Grapefruit, lemons and limes have seen a decrease in overall production.

As noted above, aldicarb is also used off-label in Victorian vineyards, for control of nematodes and phylloxera. Band application in the same way as for citrus is the usual treatment method, occurring in early spring just before bud swell. The formerly registered application rate was 15 kg/ha Temik 150G. Use of aldicarb in grapes is expected to decline with increased plantings of resistant rootstocks.

6.1.3 Environmental monitoring

Aldicarb is not included among the analytes monitored in broadscale Australian monitoring programs such as the Central and North West Regions Water Quality Program. Another oxime carbamate insecticide, thiodicarb, used for heliothis control in cotton, has been included in this program in some years, including the most recently reported (Muschal, 1998). No detections have been reported, with a general detection limit of 1 µg/L (0.1 µg/L in 1997/98).

Some pesticide monitoring data was also available from the irrigation areas of south western NSW (Bowmer *et al*, 1998) but aldicarb was not included. Citrus is grown in the area, but does not appear to be a significant user of aldicarb.

Limited Australian monitoring information is also available from a series of individual trials in citrus, cotton and grapes, as described in the field dissipation section of this report. Only computer simulations have been presented for Australian sugarcane. More general environmental monitoring data from likely high use areas, such as citrus in SA where aldicarb is included in recommended pest management schedules, do not appear to be available.

The ability of aldicarb to contaminate groundwater has been confirmed in the USA, with contamination above 10 µg/L detected in 13 States. Most of these occurrences reflected use on potatoes at planting, but there were also problems with autumn applications to lily bulbs in northern coastal California, citrus in central Florida and sugarbeet in north Central Wyoming. The incidence of contamination has been declining because of continued degradation and improved management, including local bans (Long Island and some coastal counties in northern California and southern Oregon) and some rate and timing restrictions (potatoes in Wisconsin and the north-east, citrus in Florida and most Californian uses). For example, delaying application to potatoes allows better uptake by growing plants and more rapid degradation in warmer soils, while avoiding heavy early spring rains. Application during cool or rainy seasons should be avoided. Aldicarb may not be used within 15 m of a well, and loading and washing activities are similarly restricted. Over-irrigation should be avoided, especially in sandy areas.

The US Geological Survey collects data on pesticide contamination of surface and groundwaters 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

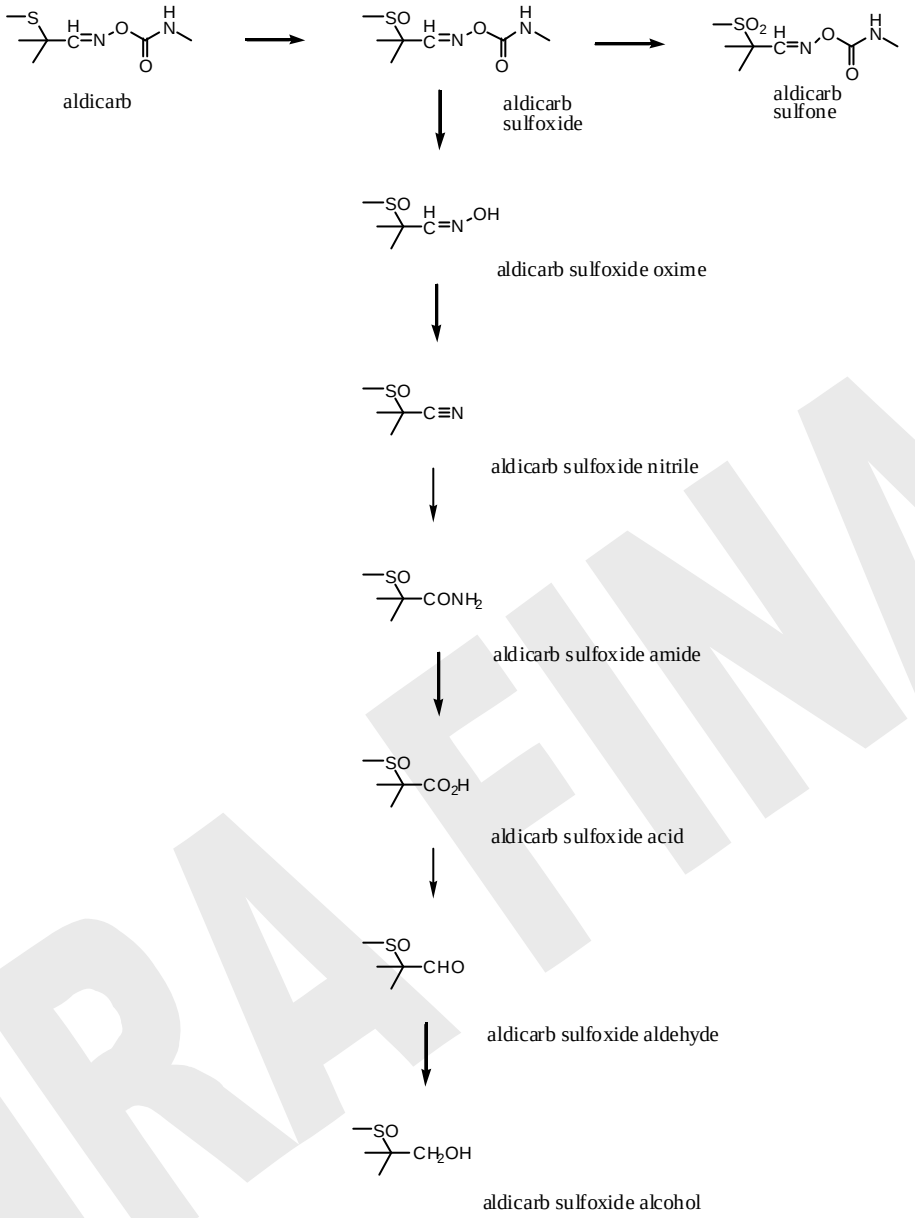
(NAWQA study units) across the US. The 76 herbicides, insecticides, and fungicides targeted in the study account for approximately 75 percent of agricultural pesticide use in the U.S. and a substantial portion of urban and suburban use.

In February 2000, results were available on the USGS website for 16 study units. Aldicarb residues (including sulfoxide and sulfone metabolites) were detected in surface or groundwater in 8 study units. All three analytes were detected in 3 study units. Contamination was most frequently detected in the Albemarle-Pamlico Drainage Basin, North Carolina and Virginia, with some 3% of groundwater samples testing positive for aldicarb sulfoxide in the 1992-95 period. On a national basis, this analyte reached levels in excess of 1 µg/L in groundwater and peaked at a little below 1 µg/L in surface water. Aldicarb itself remained at very low levels (<0.1 µg/L) when detected in groundwater and peaked at around 0.5 µg/L in surface water. The sulfone peaked at around 0.5 and 0.05 µg/L, respectively.

Information is also available on contamination of Canadian groundwater (CCREM, 1993). Monitoring was undertaken in Prince Edward Island, New Brunswick, Novia Scotia, Quebec and Ontario. Canadian potato growing regions in the maritime provinces were considered at risk of groundwater contamination following the discovery of high concentrations (up to 515 µg/L) in New York. Significant frequencies of detection, at levels up to 16.4 µg/L, occurred beneath potato growing areas of Prince Edward Island, New Brunswick and Quebec. Contamination of surface water was also reported in about 10% of samples taken from Prince Edward Island in 1983 and 1984. As noted in the introduction to this report, use of aldicarb on Canadian potatoes was subsequently withdrawn by the registrant on a voluntary basis.

6.2 Environmental Chemistry and Fate

Aldicarb is transformed in the environment through hydrolytic and oxidative reactions, each of which may predominate depending on the conditions. Hydrolytic pathways detoxify the molecule, while oxidative reactions transform aldicarb to its sulfoxide and sulfone, both of which retain biological activity. Microbial activity or chemical catalysis may intervene in both pathways, but catalytic hydrolysis tends to be the main degradation pathway for leached residues because of low microbial activity in deeper soils and subsoils. The rate of degradation is influenced by numerous factors, including temperature, pH, soil texture, redox potential, moisture, microbial activity and heterogeneous catalysis by unidentified substances. This is reflected in precautionary statements on US labels, which warn that combinations of permeable/sandy and acidic soil conditions, moderate to heavy irrigation and/or rainfall, high application rates (above about 20 kg/ha) and cool soil temperatures (below 10^{o}C) tend to reduce degradation and promote movement of residues to goundwater.



The pathway for degradation is represented above. Oxidative reactions transform aldicarb to its sulfoxide and sulfone, which can accumulate to significant levels in soils before detoxification occurs. Transformation of the carbamate linkage is illustrated for aldicarb sulfoxide but may also occur with aldicarb and aldicarb sulfone. The sequence in which the transformations occur may differ from that depicted.

A variety of detoxified products is formed by hydrolytic cleavage of the carbamate linkage and subsequent elimination, oxidation, reduction and hydrolysis reactions, as illustrated above. This detoxification pathway was found to predominate in a microbially viable aerobic aquatic system, with the formation of aldicarb acid as main degradation product after 30 days (some 80 half-lives) accompanied by carbon dioxide, aldicarb alcohol, aldicarb nitrile and traces of aldicarb amide. Similarly, detoxification of aldicarb was rapid in an anaerobic aquatic system, with aldicarb nitrile the main product after 10 days (5 half-lives) accompanied by aldicarb oxime,

aldicarb alcohol and aldicarb amide. Aldicarb sulfoxide was the only carbamate remaining, at very low levels.

Typical half-lives in surface soils for aldicarb residues (parent molecule, sulfoxide and sulfone) are in the range of 0.3 to 3.5 months. Residues continue to degrade in subsoils, apparently through heterogeneously catalysed hydrolysis by unidentified substances. This reaction can be rapid where the redox potential is low (anaerobic conditions) but is highly variable in rate, with half-lives from a month to three years inferred from field data.

Aldicarb and its toxic metabolites are highly mobile in soils and move with soil water. Residues that reach the saturated zone usually consist of the sulfoxide and sulfone. Groundwater contamination is likely in higher rainfall areas where water tables are shallow or where acidic sandy subsoils retard degradation.

Studies conducted to determine the environmental fate of aldicarb are described below. Most of these studies, particularly the unpublished ones, were provided by the principal registrant. Data gaps were filled with information from the published literature. 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, radiolabelled studies used S-methyl-^{14}C-aldicarb.

6.2.1 Hydrolysis

Studies submitted indicate that hydrolysis of aldicarb is slow under laboratory conditions. The toxic metabolites aldicarb sulfoxide and aldicarb sulfone also resist hydrolysis unless conditions are alkaline. Under environmental conditions, hydrolysis of the carbamate linkage occurs more readily (half-lives in the order of a week) because of catalysis by sediment.

Early studies (Lykins, 1971) examined the stability of aldicarb (0.5 mg/L) in distilled water (pH amended to 6.0, 7.0 and 8.0) and in samples of pH neutral surface water. It was not possible to determine a half-life as only limited degradation (10% in distilled water, 0-20% in pond/lake water) occurred over a 30 day period at 25^{o}C. However, inclusion of silt or mud in the surface water samples catalysed the degradation, such that aldicarb became undetectable (<2% remaining) within 25-30 days. The half-life was 5-6 days under these biologically activated conditions. The more rapid disappearance reflected degradation rather than sorption as only traces (<0.1 mg/kg total toxic aldicarb residues) were recovered from silt. Degradation products were not identified.

An unpublished review of aldicarb's environmental chemistry (Andrawes, 1981) reports that aldicarb was stable in sterile buffer solutions at acidic to neutral pH but degraded under basic conditions, mainly to oxime and nitrile derivatives. Respective half-lives of aldicarb and its sulfoxide and sulfone metabolites at pH 9 and 25^{o}C were 74.7, 2.3 and 0.9 days. The review notes that hydrolysis in pond or lake water was catalysed by bottom sediment, reducing half-lives to 7-10 days.

An international review (IPCS, 1991) reports variation of half-life with pH at 20°C as follows: pH 3.95, 131 days; 6.02, 559; 7.96, 324; 8.85, 55; and 9.85, 6. Note that the incubation period in these studies was less than 3 half-lives.

Details of a longer term hydrolysis study with the sulfoxide and sulfone metabolites of aldicarb are reported in a published paper (Lightfoot *et al*, 1987) that was included in the submission. Both were found to degrade according to pseudo first order kinetics, with a minimum hydrolysis rate around pH 5. Half-lives at 15°C were in the hundreds of days at pH 7, increasing to thousands of days at pH 5. The authors noted significant variability in their own experimental results and in previously published data. For example, half-lives obtained at pH 6.0 and 45°C for the sulfoxide varied between 8 and 60 days, and for the sulfone between 4 and 30 days. Underlying factors could not be identified, although possible catalysis by a wide range of metal ions was investigated. Ferrous ions at concentrations to 150 mg/L had no effect on reaction rates.

In contrast to the above, other workers (Bromilow *et al*, 1986) have found clear evidence that ferrous ions catalyse the breakdown of aldicarb (and the related carbamoyloximes oxamyl and methomyl). Half-lives in buffered solution (pH 6.7) at 30°C reduced from more than 2000 hours to 100 hours in the presence of 250 mg/L ferrous ions. Aldicarb nitrile was the only identifiable product. It is unclear why the outcomes from the two groups differed so markedly, although it is noted that solutions were deoxygenated before addition of the ferrous salt in this study. These authors have also found aldicarb degradation to be rapid in anaerobic suspensions of iron rich subsoils (see section 6.2.3.15).

6.2.2 Photolysis

The photostability of aldicarb in aqueous solution was determined from summary data contained in reviews. A report on soil surface photolysis was also submitted. Photolysis is unlikely to be a significant pathway for dissipation of aldicarb in the environment as it will be applied beneath the soil and appears resistant to photolysis in aqueous solution.

Water

An unpublished review of aldicarb's environmental chemistry (Andrawes, 1981) reports that aldicarb and aldicarb sulfone were decomposed in aqueous solution by UV light (290 nm) with respective half-lives of 8-12 and 36-38 days, but that aldicarb sulfoxide does not absorb at wavelengths above 290 nm and was stable. No details of the photodegradation were provided, other than that the presence of triplet photosensitisers had minimal effect.

The conclusion that aldicarb is photolabile in aqueous solution will be disregarded unless further evidence is presented. It appears questionable in light of other findings. For example, Lykins (1971) reported that exposure to a UV sunlamp did not significantly increase the rate of degradation of aldicarb in pond water. Howard (1991) found no data to indicate that aldicarb is photolysed at environmentally important wavelengths.

Soil

A review of aldicarb's environmental chemistry (Andrawes, 1981) notes that studies on soil photolysis are not applicable in the case of aldicarb because its use pattern normally entails incorporation into the soil where light does not penetrate.

Soil surface photolysis has been investigated on moist microbially active sandy loam soil, pH 6.2, spiked with radiolabelled aldicarb at 10.7 mg/kg and exposed for up to 5 days (12 hours/day) at 23-26^{o}C to artificial light from a xenon burner, with a 290 nm cutoff. The half-life was about 8 hours, extending to 14 hours in irradiated soil that had been sterilised by autoclaving, and to 46 hours in dark controls. Photodegradation in viable soil formed aldicarb sulfoxide, aldicarb sulfoxide amide, aldicarb sulfoxide nitrile and aldicarb sulfone, as determined by two dimensional thin layer chromatography and high performance liquid chromatography, as well as $^{14}CO_2$ (4.4% recovered from KOH traps after 24 hours). Aldicarb sulfoxide and aldicarb sulfoxide nitrile were the only products observed in sterile soil, while degradation in dark controls formed only aldicarb sulfoxide (Spare, 1994).

Air

A review of available fate and exposure data (Howard, 1991) notes that a half-life of 0.24 days has been estimated for hydrogen abstraction by photochemically produced hydroxyl radicals, but that the rate of such reactions will be reduced by partial adsorption of vapour phase aldicarb on to particulate matter.

6.2.3 Metabolism

Several aerobic metabolism studies conducted in a variety of soils were submitted, including detailed studies of the persistence of aldicarb and its toxic sulfoxide and sulfone metabolites in Dutch topsoils and subsoils. The focus of these studies was the persistence of toxic residues. Only limited investigations were conducted into the identities of detoxified metabolites. A single aerobic/anaerobic soil study was also submitted, together with aquatic metabolism studies under aerobic and anaerobic conditions, including simulated aquifer conditions. Many of the studies were conducted at lower temperatures than would prevail in Australian soils, making the results conservative predictors of persistence under Australian conditions.

Aldicarb is rapidly oxidised to aldicarb sulfoxide, thought to be the main active material in soil, and more slowly to aldicarb sulfone. These oxidative reactions occur concurrently with hydrolysis to oximes, which are further transformed to other compounds (amides, nitriles, alcohols and carboxylates). Only the sulfoxide and sulfone metabolites retain the high toxicity of aldicarb, which is lost upon hydrolysis of the carbamate linkage.

Detoxification half-lives in topsoils are typically a few months but exhibit considerable variability. The controlling factors are not well understood. The detoxification reaction can be very slow in some aerobic or partially aerobic subsoils. For example, aldicarb sulfone has been found to be essentially stable over periods of a year under such conditions, including in subsoils taken from three Dutch sites with

documented groundwater contamination. In contrast, detoxification can occur surprisingly rapidly (half-life a few days or weeks) in anaerobic soils.

The initial detoxification reaction (cleavage of the carbamate linkage) appears to be abiotic in nature. Oxidation of aldicarb may occur abiotically or with microbial involvement. Mineralisation of the detoxified metabolites appears to depend on microbial activity.

Detoxification reactions appear to proceed much more readily in aquatic systems, with half-lives of a few days in tests conducted under aerobic or anaerobic conditions. However, the occurrence of aldicarb residues in groundwater indicates that detoxification reactions do not occur readily in all aquatic environments, and persistence in samples of shallow groundwater has been confirmed in the laboratory under partially anaerobic conditions.

Early investigations in clay loam soil

Colorimetric procedures were used to follow the dissipation of aldicarb from Red River Valley clay loam soil, spiked at 0.05, 0.2 or 0.5 mg/kg and incubated at 23-32^{o}C for up to 13 weeks in flasks capped with cotton wool. Soil was taken from potato fields. Moisture lost through evaporation was replaced daily, except for the first 10 mL which was not replaced as this volume of water was used as vehicle to treat the soil with aldicarb. The analytical method did not distinguish between aldicarb and its toxic sulfoxide and sulfone metabolites. Toxic residues declined below 0.005 mg/kg after 5 weeks at the lowest concentration, increasing to 11 weeks at 0.2 mg/kg. At the highest concentration, residues declined to to 0.025 mg/kg (5% of applied) by 11 weeks, when the study was discontinued.

Stability in filtered water taken after rainfall from ditches near untreated fields was also investigated, at a concentration of 100 mg/L. Samples were exposed to sunlight during daylight hours. Toxic residues declined to 0.4 mg/L after 46 weeks (Quraishi, 1972).

Oxidation of aldicarb in sandy loam soil

Metabolism was studied on two sandy loams, one neutral in pH and with less than 1% organic carbon, and the other slightly acidic (pH 6.3) and containing 3.3% organic carbon after several years of peat amendment at 100 tonnes/ha. Air dried soil was moistened and held at 15^{o}C in the dark for a week before treatment with aldicarb or its sulfone metabolite, radiolabelled at the carbamate methyl position. Samples were incubated at 15^{o}C with moisture levels of 5, 10 or 15% by weight, or at 5 and 10^{o}C with 10% moisture, for 130 days. Metabolites were identified by liquid scintillation counting of acetone extracts.

Zero time samples contained around 20% aldicarb sulfoxide, but this oxidation may have occurred during extraction and separation rather than instantaneously on the soil. Half-lives for oxidation were very short, less than a day at higher temperatures and moisture levels, but hydrolysis proceeded much more slowly. The bulk (67-92%) of the applied aldicarb was transformed to the sulfoxide, particularly at higher moisture

levels. Oxidation to the sulfone was also a dominant reaction, accounting for 50-73% of applied aldicarb in these soils (Bromilow *et al*, 1980).

Metabolism in two clay soils with different pH

Metabolism was studied for up to 54 days at a concentration of 1 mg/g in two clay soils with similar texture, mineralogy and organic content but different pH (5.4 and 7.8). Soil samples were either maintained at 1/3 bar field moisture capacity or in an air-dry state during the incubation. Total toxic residues remaining in soil were determined by gas liquid chromatographic analysis of acetone/methanol extracts.

The half-life in the slightly alkaline soil was well above 54 days at 23°C, irrespective of soil moisture. Degradation was more rapid in the acidic soil, with half-lives of 28 days at field capacity and 15 days in air dry soil. The faster degradation in the acidic soil, particularly when dry, seems paradoxical given the relative ease of alkaline hydrolysis, but may reflect other differences between the soils. Batch adsorption studies (see section 6.2.4.1) revealed that aldicarb was excluded (negative adsorption) from the acidic soil but weakly sorbed to the alkaline soil, probably because of differences in the reactive sites contained in the soils' organic matter.

Volatilisation from 25 g samples under an air flow of 27 mL/min was also investigated. Only minor amounts (less than 0.1% of applied) were lost over an 18 day period, after initial equilibration for 24 hours. Volatilisation increased with decreasing soil moisture, thought to reflect movement of aldicarb to soil/air interfaces as water evaporated, but ceased in air dry soils (Supak *et al*, 1977).

Mechanistic investigations in soil from North Carolina

Aldicarb degraded rapidly following addition of sufficient aqueous stock solution to air-dried North Carolinan top soil to achieve a concentration of about 0.3 mg/kg and restore soil moisture to field capacity. The half-life at 25°C was 1.0 day, with formation of sulfoxide and sulfone metabolites as confirmed by HPLC analysis. Total carbamate residues dissipated with a half-life of 44 days. Prior sterilisation by autoclaving increased the half-life of aldicarb to 2.5 days, but persistence of total carbamate residues was reduced (half-life 10 days). This suggests that oxidation of aldicarb is biologically mediated but that cleavage of the carbamate linkage is favoured more by abiotic factors, probably surface catalysis, and that this is enhanced by autoclaving. Only limited oxidation occurred in sterile soil, with hydrolysis the main mechanism for decomposition. Even simple physical mixing of soil suspensions led to significant changes in degradation rates (Lightfoot *et al*, 1987).

Microbial oxidation in soil from North Carolina

This study followed the degradation of radiolabelled aldicarb (10.5 mg/kg) on sandy loam soil (pH 6.1, 0.6% organic carbon) from New Jersey for 60 days in the dark at 25°C and 75% field moisture capacity. Soil extracts were analysed by HPLC for metabolite quantification and identification. Recoveries remained quantitative, with a maximum 1.4% recovered from volatile traps. Aldicarb degraded rapidly (half-life 2.3 days) with the formation of aldicarb sulfoxide (86.1% after 14 days) and aldicarb sulfone (80.1% after 21 days). Results are somewhat erratic, with sulfone very much

predominant at 21 days but sulfoxide at 14 and 30 days, suggesting some irregularities with the analytical procedure (Das, 1990).

Metabolism of aldicarb sulfone in Dutch topsoils and subsoils

Aldicarb sulfone (4 mg/kg) was added as aqueous solution to the surface of various soils (see table) and well mixed before incubation at 15°C. Apart from the greenhouse soil, soils were taken from arable land, with the silty subsoil taken from beneath the clay loam, and the sandy subsoil from beneath the peaty sand. Residual sulfone was determined at intervals to 294 days by gas chromatography, after extraction of the soil with acetone, partitioning into chloroform, and chromatographic purification.

Soil	pH	% oc	Period	Half-life
Clay loam	7.2	2.5	1-56 days	24 days
			56-168 days	18 days
Sandy loam	7.4	0.6	1-112 days	39 days
Greenhouse soil	6.0	9.3	1-112 days	69 days
			112-294 days	36 days
Peaty sand	5.4	5.2	1-294 days	154 days
Silt layer (70-90 cm)	7.8	0.4	1-294 days	46 days
Sand layer (90-110 cm)	5.0	0.3	1-294 days	>> 294

A biphasic degradation was observed in some soils, with the rate of degradation increasing in the latter parts of the incubation period. Variable degradation rates are often seen in laboratory incubations, but tend to decline as microbial populations become depleted. Conversely, transformation may occur more rapidly in soils with prior exposure to a particular chemical or class, which allows microbial populations to become adapted. The authors of this study suggest that changes in the microbial population may account for the biphasic degradation.

Persistence in the topsoils increased with increasing soil acidity. Aldicarb sulfone was particularly persistent in the acidic sandy subsoil, probably due in large part to the limited microbial activity. There was no clear loss of aldicarb sulfone from this soil sample during 294 days of incubation (Smelt *et al*, 1978a).

Metabolism of aldicarb sulfoxide in Dutch topsoils and subsoils

Aldicarb sulfoxide (4 mg/kg) was incubated in the same manner as the sulfone (see above) with residues determined at intervals to 111 days. Degradation followed pseudo first order kinetics, with half-lives of 20, 30, 41, 46, 53 and >>111 days, respectively. Degradation in the deeper sand layer approximated 15%. The sulfoxide was oxidised relatively rapidly to the sulfone, which then decreased more slowly. Conversion factors in the four topsoils ranged from 52% to 76%, and maximum amounts from 19% to 32%.

Effects of temperature were investigated in the clay loam and the greenhouse soil. Rates of degradation increased by a factor of about 3.6 from 6°C to 15°C, and by a further 1.5-2.1 from 15°C to 25°C. A biphasic degradation was observed in the clay loam at 15°C and the greenhouse soil at 25°C, with faster degradation in the latter parts of the incubation (Smelt *et al*, 1978b).

Metabolism of aldicarb in Dutch topsoils

Metabolism of aldicarb was studied in the same four topsoils that were used for the sulfoxide and sulfone. Degradation followed pseudo first order kinetics. Half-lives in clay loam, sandy loam, greenhouse soil and peaty sand were 2.2, 3.0, 7.2 and 5.3 days, respectively. The sulfoxide reached 70-90% of applied between 7 and 28 days after treatment before declining. The sulfone metabolite increased steadily throughout the 58 day incubation, except in the clay loam where a plateau of about 15% was reached. Half-lives in the greenhouse soil and peaty sand varied between fresh and stored soils. In the greenhouse soil, the half-life decreased to 4.3 days, probably because the fresh samples had received steam treatment which would have disturbed microbial populations. The half-life in the peaty sand increased to 8.9 days. The authors have no explanation for this, but declining microbial populations in stored soils would appear a likely explanation (Smelt *et al*, 1978c).

Metabolism of aldicarb sulfoxide and sulfone in Dutch subsoils

Metabolism of sulfoxide and sulfone metabolites was investigated in subsoils from above and below the water table (0.8-1.0 m deep) at four Dutch sites. Three of the soils sampled had a pH of about 7.5, being a sand (0.3% organic carbon at 1.2-1.6 m), another sand (0.5% organic carbon at 0.4-0.6 m) grading to loamy fine sand (1.3% organic carbon at 1.1-1.5 m) and a loamy fine sand (0.7% organic carbon at 0.6-0.8 m and 0.6% at 1.3-1.7 m). The other soil, sampled at 0.6-0.9 m and 1.3-1.7 m, was an acidic fine sand (pH 4.5) with very little organic carbon. Soils were sampled with an auger and lightly dried before treatment and incubation in the dark at 10°C and 13-23% soil moisture content for up to 299 days. Anaerobic conditions were created in some subsamples by flooding with groundwater and purging with nitrogen. Some samples were also sterilised by autoclaving.

Degradation was monitored by HPLC and found to follow pseudo first order kinetics, with half-lives as tabulated below. Italicised entries were obtained with soils that had been stored in the laboratory for 2 months before treatment. Degradation in soil from below the groundwater table can be surprisingly fast, and much faster than degradation in the overlying aerobic soil layers. Aerobic metabolism of the sulfoxide led to the sulfone (maximum 16% of applied after 200 days in the sand) but no such oxidation occurred under anaerobic conditions.

Soil	Depth	Conditions	Sulfoxide	Sulfone
Sand	1.2-1.6 m	Anaerobic	*2-5* days	5.6 days
Sand	0.4-0.6 m	Aerobic	84 days	82 days
		Sterile aerobic		297 days
Loamy fine sand	1.1-1.5 m	Anaerobic	2.3 days	6.7 days
		Sterile anaerobic		~18 days
Loamy fine sand	0.6-0.8 m	Aerobic	*194* days	116 days
	1.3-1.7 m	Anaerobic	*2.6* days	5.1, *11* days
Fine sand	0.6-0.9 m	Aerobic	*410* days	1100 days
	1.3-1.7 m	Anaerobic	*27* days	131 days

The rate of degradation of aldicarb sulfone in the 0.4-0.6 m sand samples decreased with time, with a concomitant decrease in redox potential, when samples were maintained under anaerobic conditions. Conversely, when samples of this soil from below the water table were made aerobic, the half-life increased to 175 days. Sterilisation appeared to retard degradation, but the significance of microbial activity

can not be determined unequivocally because the physical and chemical properties of the soil were altered (Smelt *et al*, 1981).

Metabolism of aldicarb sulfoxide and sulfone in a Dutch subsoil

The saturated subsoil for this study, taken by auger from 2.5-3.5 m below the surface, was a blue-gray iron containing sand with low redox potential (-45 to -85 mV measured in the field). Incubation samples comprising 50 g soil and about 7 mL groundwater, which covered the soil to a depth of about 5 mm, were maintained under aerobic or anaerobic conditions at 10°C, but steadily increasing redox potentials illustrated the impossibility of maintaining anaerobic conditions for extended periods in the laboratory, even with occasional refreshment of the nitrogen atmosphere. Some samples were sterilised with gamma-irradiation. Each flask was treated with about 40-60 µg of radiolabelled test material, the transformation of which was studied using standard wet extraction and chromatographic techniques.

The two radiolabelled test substances were transformed most rapidly under anaerobic conditions, with half-lives of about a month for the sulfoxide and 2-3 months for the sulfone. Loss of parent material was accompanied by the formation of several polar metabolites, of which one became dominant. The dominant metabolites were thought to be nitriles. This transformation was not retarded in sterilised soils, indicating that the initial breakdown is probably abiotic in nature. The initial breakdown slowed considerably in aerobic soils but was not completely suppressed.

Significant quantities of $^{14}CO_2$ (27-58% for the sulfoxide and 20-74% for the sulfone) were evolved from the anaerobic samples after about 2 months incubation, but only under non-sterile conditions. This suggests that mineralisation of the initial detoxified breakdown products depends on microbial activity (Vonk, 1991).

Metabolism of aldicarb sulfoxide and sulfone in Dutch subsoils

The rates of transformation of aldicarb's toxic oxidation products were studied in four Dutch subsoils, including three low humic sandy soils from high risk areas with documented groundwater contamination. The fourth site had a loamy topsoil with sandy subsoil. Soils were sampled from the water saturated layer 2-5-3.5 m below the surface. All were slightly acidic (pH 5.6-6.8).

Incubation samples consisted of 205 g soil with 45 mL of the accompanying groundwater, and were equilibrated under nitrogen and 5 mm water at 10°C for 20-26 days in the laboratory. After equilibration in the laboratory, samples were spiked with radiolabelled material in low or high doses (equivalent to 0.14-0.17 or 8-13 mg/L in the water phase) and incubated under a nitrogen atmosphere for up to a year, during which time conditions gradually became more aerobic as evidenced by increases in the redox potential.

In general, no distinct decreases in concentrations were seen for the three subsoils with a record of contamination. In one soil, slow transformation of the sulfoxide, mainly to the sulfone, was observed. This soil was taken from the same location as in the above study. Unchanged sulfoxide after a year amounted to 68-74% at the high

dose and 41-44% at the low dose. Slow transformation of the sulfoxide (40-53% remaining after a year) was also seen in another soil, but only at low dose.

Transformation was very rapid in the other, more anaerobic subsoil. Only 2% of applied sulfoxide could be recovered after 3 months. The sulfone was initially transformed at a rapid rate (19-36% remaining after a month) but the rate slowed such that 7-15% remained unchanged at the end of the incubation. The slowing rate coincided with increases in the redox potential. Several transformation products were recovered from this soil, but not identified. Soil extracts contained declining amounts of radioactivity, which could be partially accounted for in that radioactivity was recovered from a KOH trap. The authors speculate that volatile transformation products may have been lost by diffusion through silicone rubber septa (Smelt *et al*, 1992).

Anaerobic soil metabolism

Anaerobic metabolism of radiolabelled aldicarb was studied in Muskingum silt loam soil (pH 5.4, 0.7% organic carbon) with metabolites identified by thin layer chromatography, autoradiography and scintillation counting. Soil was activated in the greenhouse by growing beans and ryegrass, and then transferred to the laboratory and air-dried for 48 hours. The test substance was added in aqueous solution, with mechanical rolling, to achieve a concentration of 2.7 mg/kg. Soils were incubated in pots at 75% field moisture capacity and 22°C for 30 days before transfer to glass columns. Anaerobic conditions were created by sealing in glass jars under nitrogen.

Total toxic residues were less than 5% of applied after the initial aerobic incubation. These residues declined further in soil columns to 2.9% after a further 60 days under constantly aerobic conditions, and to 0.1% of applied in the samples transferred to anaerobic conditions. Carbon dioxide was the main metabolite, with respective production of 31.9, 65.5 and 76.9% of applied (Sheets and Hirsh, 1976).

Aerobic aquatic metabolism

Radiolabelled aldicarb decomposed rapidly following addition at 10.4 mg/L to microbially viable pond water (pH 7.7) and sediment (20% dry weight). The half-life was 8.6 hours. Degradation followed a different pathway from that observed in soil, with the formation of aldicarb acid, aldicarb alcohol and aldicarb nitrile as identified by reverse phase high performance liquid chromatography of samples taken at intervals during 30 days of incubation at 25°C. The intermediate aldicarb amide was also identified, but oxime and aldehyde intermediates were not seen. Aldicarb acid was the main metabolite, reaching 48.6% of applied after 50 hours before declining to 25.6% after 30 days, by which time some 30% had been evolved as CO_2 and a further 31.3% had formed bound residues (Skinner, 1995a).

Anaerobic aquatic metabolism

Radiolabelled aldicarb (2 mg/L) was incubated under anaerobic conditions for 14 days in a 4:1 mixture of pond water and loamy sand sediment (pH 5.4, 2.3% organic carbon). Water and soil extracts were analysed by two dimensional thin layer chromatography for metabolite identification and quantification, and soil residues were determined by combustion.

Aldicarb degraded with a half-life of 1.9 days, forming aldicarb nitrile as major product (maximum 14.2% in the water phase after 10 days) accompanied by aldicarb oxime, aldicarb alcohol and aldicarb amide (each about 2% after 14 days). Only one carbamate metabolite, aldicarb sulfoxide, remained in the water phase at low levels (0.09%) at the end of the 14 day incubation.

Aldicarb nitrile (2.71% after 14 days) was also the main product recovered from the soil phase, with smaller amounts (each < 1%) of aldicarb sulfoxide, aldicarb sulfoxide oxime and aldicarb sulfone nitrile. Aldicarb sulfoxide was the only carbamate to persist throughout the incubation, remaining at 0.31% of applied after 14 days.

Accountability declined to 54.6%, but separate studies with constant nitrogen purging revealed volatilisation losses, including around 10% unchanged aldicarb. Small amounts of aldicarb sulfoxide, aldicarb alcohol, aldicarb nitrile and aldicarb sulfone nitrile were also recovered from moisture traps (-12^{o}C). The main volatile metabolite was aldicarb nitrile, recovered from a second cold trap (-12^{o}C) filled with butyl cellosolve, and reaching 65% of original label after 14 days in this separate study (Lee and Andrawes, 1986).

Ferrous ion catalysed anaerobic aquatic degradation

Metabolism flasks (500 mL) were purged with nitrogen and partially filled with greoundwater before addition of wet soil (80-200 g dry weight) and further nitrogen purging. Aldicarb (5 mg) was added in 5 mL nitrogen purged water to achieve a concentration of 40-50 mg/L. Flasks were maintained at 19-24^{o}C, and sampled periodically for HPLC analysis. Three Dutch subsoils (1.8-2.5 m) were investigated, with properties as tabulated below. Respective ferrous ion concentrations in soil solution were 41, 27 and 0.65 mg/L.

pH	Content (g/kg)				Redox potential
	Organic matter	Clay	Silt	Total iron	
7.7	22	43	301	13	-60 to 60 mV
4.6	1	32	47	2.6	50 to 130 mV
5.0	1	12	8	0.9	500 to 600 mV

Aldicarb degraded rapidly in the first two soils, with respective half-lives of 12 and 4 hours. Two products, aldicarb nitrile and aldicarb aldehyde were formed in 2:1 ratio in the first soil and roughly equal proportions in the second. In contrast, aldicarb showed little degradation over a 72 day period in the third soil. Similar trends were seen with aldicarb sulfoxide and aldicarb sulfone, although their degradation was less rapid than for the parent compound. Degradation in these soil-water systems was

more rapid than in solution alone, perhaps because the ferrous ions would be present in complexed forms with different redox potentials, or held in high concentrations on clay surfaces. The authors note that groundwater problems characteristically occur where sandy soils overlie acid subsoils with low iron content where reducing conditions generating ferrous ions would not be expected. (Bromilow *et al*, 1986).

Metabolism in groundwater

Aldicarb sulfoxide and aldicarb sulfone were added separately to incubations simulating aquifer conditions. Sediment and groundwater were taken from three depths (0.5, 5 and 10 m) below the water table under a sandy Wisconsin soil. The water table occurred at about 6 m and had ongoing problems with aldicarb contamination, notwithstanding a local phase out of the chemical. Samples were buffered to maintain pH (5.8, 6.5 and 7.2, respectively). The shallower samples were maintained aerobically (0.2 atm oxygen) and the deeper sample anaerobically (0.015 atm oxygen, or about 0.8 mg/L) at 10^{o}C in the dark for up to 356 days. Degradation was monitored by HPLC with a quantitation limit of 1 µg/L.

Half-lives were very variable (less than a month to years) with degradation favoured under higher pH and lower oxygen conditions such as found at depth. Half-lives exceeded 2 years in the more shallow and aerobic samples, but shortened to around 2-4 weeks in the 10 m samples. The sulfone degraded more rapidly than the sulfoxide, which resisted oxidation at all levels, and showed no evidence of any degradation in the 0.5 m simulation. Lengthy half-lives in local groundwaters have been attributed to the cold temperatures prevailing in the Wisconsin Central Sands. A similarly long half-life (2-3 years) in Long Island groundwater has been inferred from monitoring data. At warmer locations (Florida and California) laboratory simulations and monitoring data indicate half-lives of a few weeks to a few months (Kraft and Helmke, 1992).

6.2.4 Mobility

Several standard batch adsorption studies were conducted in a variety of soils in order to determine the partitioning behaviour of aldicarb and its toxic sulfoxide and sulfone metabolites. These studies were supported by standard column leaching studies, again with aldicarb and its toxic metabolites, and by a specialised leaching study designed to demonstrate upward movement under drying conditions. Movement of aldicarb through the soil profile was modelled at three canefield sites with sandy soils in the Bundaberg district.

Standard batch equilibrium studies indicate that aldicarb is only weakly adsorbed by soils, and its oxidation products even less so. Aldicarb and its toxic metabolites share significant water solubility and tend to move with soil moisture through the soil. Low adsorption coefficients indicate that mobility in soils is high, and this has been confirmed in leaching experiments with soil columns. Simple model calculations identify aldicarb as a probable leacher. More sophisticated computer models found relatively low mobility, with residues confined to the surface 200-400 cm, but assumed a relatively rapid degradation (15 day half-life) which is appropriate for the site studied (Bundaberg) but would not be representative of areas where groundwater contamination by the more persistent sulfoxide and sulfone metabolites has occurred.

Sorption to clays

Batch adsorption studies were conducted on bentonite, illite and kaolin clays from the USA. Bulk clay samples were dispersed in pH 9.5 sodium carbonate solution, and the clay fraction (2-0.2 µm) was isolated by centrifugation, saturated with aluminium or calcium by sequential washings with aqueous solutions of their chlorides, washed with distilled water and methanol, and freeze-dried. Studies were also conducted on one acid and two calcareous clay soils and on the organoclay complexes isolated therefrom. Duplicate samples of the adsorbents were equilibrated by shaking for 4 hours with aqueous solutions of radiolabelled aldicarb (2-62 mg/L) in 1:5 ratio (1:10 for the illite and kaolinite samples). Preliminary experiments established that the equilibration period was long enough to allow maximum adsorption with minimal degradation.

Aldicarb was not adsorbed to any great degree by any of the adsorbents studied. It underwent weak adsorption to the illite and kaolinite clays, but exhibited negative adsorption, or exclusion, with the montmorillonite. Concentrations of aldicarb in the aqueous phase showed an increase after equilibration with this expanding clay because of hydration of interlayer cations and clay surfaces. This effect was more pronounced with the calcium saturated clay. A similar phenomenon was seen with the acidic clay soil and the organoclay complex isolated from it, but not in the other two soils, despite their having similar mineralogy. Positive adsorption in the calcareous clay soils may reflect adsorption by calcium carbonate, or more likely different reactive sites in the organic matter contained in the acidic and basic soils (Supak *et al*, 1978).

Sorption to soils

The sorptive behaviour of radiolabelled aldicarb was investigated in four soils (see table for details) following prior sterilisation with sodium azide. Only limited adsorption (3.3-9.6%) occurred from 2 mg/L solution in a 24 h preliminary study at 1:5 soil:water ratio. Unchanged aldicarb was the dominant analyte (80.2-90.7%) in supernatants.

Soil type	pH	% oc	% sand/silt/clay	Koc
Sand	7.4	0.3	92/4/4	79
Sandy loam	6.5	0.4	54/36/10	44
Silt loam	7.1	1.3	14/68/18	25
Clay	6.7	1.3	8/34/58	50

The definitive study was conducted at 25^{o}C using a 3 h equilibration period and four concentrations of aldicarb. Correlation coefficients of 0.83-0.98 were obtained when results were fitted to the Freundlich equation. Soil organic carbon partition coefficients place aldicarb in the very high mobility class, based on the McCall scale (McCall *et al*, 1980). Freundlich coefficients were less than one. Desorption coefficients (2054, 7125, 87.4 and 110, respectively) place sorbed residues in the high to immobile mobility classes, but should be treated with caution because of inaccuracies associated with the very low levels retained by the soils during the adsorption step (Fennessey, 1988).

Adsorption of aldicarb sulfoxide

The sorptive behaviour of radiolabelled aldicarb sulfoxide was investigated in four soils and a sediment (see table for details). Aldicarb sulfoxide is much more soluble in water (the stated solubility is 330 g/L at 25°C) than aldicarb. Preliminary studies found a soil:water ratio of 1:5 to be optimal, and demonstrated that sorptive equilibrium required 20 h for adsorption and 4 h for desorption.

Soil type	pH	% oc	% sand/silt/clay	Koc
Silty clay loam	6.7	1.99	14.8/53.6/31.6	13.3
Sandy loam	5.3	0.84	73.2/13.6/13.2	20.6
Silt loam	6.7	1.42	17/62/21	18.2
Loamy sand	5.1	0.28	80.8/14/5.2	74.3
Sediment	8.1	0.76	59.2/13.6/27.2	47.9

The definitive batch adsorption study was conducted at 24-26°C with concentrations of 0.27, 0.99, 2.52, 5.01 and 10.01 mg/L and equilibration periods of 20 h for adsorption and 4 hours for desorption. Material balance remained good (96.3±2.5%). HPLC analysis of the lowest dose adsorption and desorption solutions identified at least 95% of radiolabel to be unchanged aldicarb sulfoxide. This was also the dominant analyte (at least 95%) in soil pellet extracts. Freundlich exponents (1/n) were greater than 1 (mean 1.30) indicating that adsorption is enhanced at higher concentrations. Such enhancement can occur when a solute sorbs more strongly to sorbed solute than to the unamended adsorbent. The low soil organic carbon adsorption coefficients indicate that aldicarb sulfoxide sorbs weakly to soils, and is in the very high mobility class (high in the loamy sand) according to the McCall scale (McCall *et al*, 1980). Desorption coefficients were significantly higher (158, 524, 108, 1050 and 286, respectively, placing sorbed residues in the high to low mobility classes. However, only a minor proportion of this water soluble material would enter the sorbed state (Skinner, 1995b).

Adsorption of aldicarb sulfone

The sorptive behaviour of radiolabelled aldicarb sulfone was investigated in the same four soils and a sediment as used for the sulfoxide study. Aldicarb sulfone is slightly more soluble in water (the stated solubility is 8000 mg/L at 25°C) than aldicarb. Preliminary studies found a soil:water ratio of 1:5 to be optimal, and demonstrated that sorptive equilibrium required 2 h for adsorption and 4 h for desorption.

The definitive batch adsorption study was conducted at 24-26°C with concentrations of 0.22, 0.98, 2.49, 4.98 and 9.99 mg/L and equilibration periods of 16 h for adsorption and 4 hours for desorption. Material balance remained good (98.4±0.9%). HPLC analysis of the lowest dose adsorption and desorption solutions identified at least 97.5% of radiolabel to be unchanged aldicarb sulfone. This was also the dominant analyte (at least 97%) in soil pellet extracts. Freundlich exponents (1/n) were greater than 1 (mean 1.11). The low soil organic carbon adsorption coefficients (11, 14, 13, 32 and 29, respectively) indicate that aldicarb sulfone sorbs weakly to soils, and is in the very high mobility class according to the McCall scale (McCall *et al*, 1980). Desorption coefficients were significantly higher (239, 201, 316, 614 and 286, respectively, placing sorbed residues in the medium mobility class. However,

only a minor proportion of this water soluble material would enter the sorbed state (Skinner, 1995c).

Column leaching of aldicarb

Temik 10G granules were incorporated in the surface 2.5 cm of a 17.5 cm column and leached with 2.5 cm water per week for several weeks. Only a very minor proportion of the applied dose could be recovered (0.24% from a sandy loam and 2.8% for a muck soil) with total toxic residues found in roughly equal amounts in soil and leachate. The balance was assumed to have been transformed to non-carbamate compounds. Levels in leachate from the sandy loam peaked in the second week before declining, while the peak was delayed to the seventh week for the muck soil, with no detections for the first 3 weeks. Soil concentrations were fairly uniform, apart from elevation below the incorporation layer in the muck soil (Romine *et al*, 1968).

Column leaching of aldicarb and metabolites

Aldicarb and its sulfoxide and sulfone were found to migrate at comparable rates in soils when studied on 15 cm columns (diameter 2.5 cm) of four soils. The initial 50% of the applied dose was found to move 2.2-2.5 units for each unit of water added to columns of fine sand, sandy loam or sandy clay loam soils at a flow rate of 15-20 drops/minute. Aldicarb moved only 0.3 units through a muck column for each unit of water added (Richey, 1972a).

Column leaching of aldicarb and metabolites

Leaching of aldicarb was studied on 12 cm diameter columns of four Dutch soils taken from the field. All had near neutral pH and moderate organic carbon content (around 2%). In one set of experiments, columns of a calcareous silt loam (28 cm, treated at 27.7 kg/ha) and humic sand (25 cm, treated at 15.9 kg/ha) were treated with 23 mm/day artificial rain in simulated showers every 36 minutes until 3 pore volumes had eluted. Two calcareous loamy soils were treated at a little over 5 kg/ha as 50 cm columns, with the surface 20 cm first screened and repacked to remove heterogeneity. A more moderate elution rate of 12.2-13 mm/day was used to collect 2.5 pore volumes of eluent. Aldicarb and its toxic metabolites were monitored in the eluent using gas-liquid chromatography.

Substantial amounts (72% of applied over 16 days) leached through the silt loam, with a peak after about 5 days corresponding closely to a single water-filled pore volume of eluent. The main component was aldicarb sulfoxide. Similarly, the humic sand column was poorly retentive, with some 20% of applied leaching through the column over 10 days, mainly as the sulfoxide. Aldicarb's toxic metabolites formed on the column and also leached readily through the two loamy soils, peaking in eluent soon after the passage of a single pore volume. The sulfoxide was again the main component, but accompanied by substantial amounts of sulfone with the slower elution rate. The amounts leached over a 7 week period were 65 and 47%.

The behaviour of aldicarb and its toxic metabolites was modelled for the two loamy columns. Sorption coefficients used for the models were very low. The models used a high conversion rate (0.25/day) for oxidation to the sulfoxide and a lower rate (0.03-

0.06/day) for oxidation to the sulfone. The rate of decomposition for the sulfone remained unclear (Leistra *et al*, 1976).

Upward movement

The high mobility of aldicarb suggests that it would be likely to move in an upward direction under drying conditions as evaporation draws moisture to the soil surface, and this has been confirmed experimentally. Radiolabelled aldicarb was added in acetone solution at 4.5 kg/ha to the surface of a water saturated 15 cm column of fine sandy soil, and then covered by a further 10 cm soil which was saturated with water. After equilibration for 16 hours, the surface of the column was heated to 38^{o}C under gentle air flow for 7 days, by which time moisture content had almost stabilised at 51% of capacity.

The distribution of aldicarb on the column was determined by radioassay of soil extracts. More than half the recovered radioactivity (47.6% from 93.1%) was found in the surface 2.5 cm, where concentrations were about four times higher than in the next most enriched (2.5-5 cm) fraction. Upward movement was much more pronounced than downward under these drying conditions. Small amounts in the 10-12.5 cm fraction were thought to reflect settling rather than leaching (Richey, 1972b).

Simple model predictions

The potential for pesticides to leach can be readily estimated from the nomogram of Gustafson (1989) provided that soil adsorption and persistence data from the field are available. Application of the above soil organic carbon partition coefficients (13-79) and a field half life of 2 months identifies aldicarb as a probable leacher with GUS values well above 3.

Modelling studies

Movement of aldicarb was modelled using PRZM2 at three canefield sites with sandy soils in the Bundaberg district. Three sequential annual applications at 17 kg/ha were assumed, with post-application irrigation of 3 or 7.5 cm, depending on the moisture capacity of the soil. Soils were characterised in 25 cm increments to 75 cm and assumed to remain unchanged in composition from 50 to 500 cm. A half-life of 15 days was selected, irrespective of depth, and a soil organic carbon partition coefficient of 20. The moderate half-life is probably appropriate for warm Bundaberg soils but would underestimate persistence at colder locations where carbamate residues leach to groundwater.

Recharge below the root zone ranged from 25 to 57 cm per year during the simulation, or 19-45% of the total precipitation (and irrigation) input into the model.

Computed residues at 2 weeks after application were slightly less than half of applied, and were mainly retained in the top 100 cm of soil. Residues dissipated below 0.1 kg/ha within 2-4 months. Residues predicted in the 100-200 cm increment exceeded 0.2 kg/ha on occasion at one site and 0.1 kg/ha at the other two. No residues were predicted to leach below 400 cm, or 200 cm at two of the sites (Boussemart and Jones, 1993).

6.2.5 Field dissipation

Reports of field investigations in the UK, US and Australia were submitted. Results confirm the laboratory predictions of high mobility for aldicarb, and highlight the importance of soil properties in determining the degree of off-target movement.

Soil residue studies on UK grassland found oxidation to be a significant metabolic pathway, together with hydrolytic degradation pathways that left only 2% toxic residues after 2 months.

Investigations of persistence and mobility beneath California vineyards illustrate the importance of meteorology to the dissipation and movement of aldicarb. Half-lives were much longer after winter treatment (3.5 months) than when aldicarb was applied in spring (2 months) because of colder soil temperature. Leaching to deeper groundwater (below 10 m) from winter treatments became noticeable when late winter and early spring rains carried aldicarb down through the soil profile. Contamination in the order of 10 µg/L was detected over the following two seasons, together with higher contamination (93 µg/L) remote from the treated area because of preferential lateral flow through a perched water table. Higher residues (a spring peak of 135 µg/L) were seen in shallow groundwater (< 2 m) and recurred over the following two seasons (77 and 113 µg/L, respectively).

Aldicarb dissipated more rapidly during the summer growing season in Georgia, with half-lives in the order of 2-3 weeks for total carbamate residues. Field dissipation rates were around three times faster than those observed in the laboratory. Leaching did not appear to be a problem with these more rapid degradation rates, notwithstanding application to well drained sandy soils. No residues were detected below 1.2 m during 4 consecutive years of study.

Studies in citrus groves on sandy soils in SA found residues in shallow tile drainage, at about 10 µg/L at one site and 50 µg/L at another, following application of aldicarb at about 10 kg/ha. Contamination of tile drainage proved persistent following these high rates of application to sandy soils, remaining at about 50 µg/L with little sign of dissipation after a year at one location. Aldicarb sulfoxide was the main contaminant.

Little off-site movement was apparent when aldicarb granules were used at lower rates (< 1 kg/ha) in Australian cotton planted on clay soils. The half-life appeared from limited data to be about a week near the soil surface. Analysis of surface and groundwater samples generally failed to detect aldicarb. The highest detections occurred in inter-row tailwater (116 µg/L) and tile drainage (37 µg/L) when samples were taken a day after treatments that coincided with significant rainfall.

Dissipation beneath UK grassland

Aldicarb was applied as aqueous solution at 16.8 kg/ha to grassland on sandy loam soil in late winter. Application was followed by 2.4 cm rainfall over the next 2 days. Analysis of soil samples at 11 days after treatment found only 1% of the applied dose as unchanged aldicarb, but accompanied by 30% as the sulfoxide and 4% as the sulfone. Residues were mainly (80%) retained in the surface 10 cm. Sulfoxide and

sulfone metabolites were present in equal amounts by 2 months after treatment, but 98% of toxic residues had dissipated. The sulfone was the only detectable analyte at 4 months after treatment. Negligible quantities of toxic residue were recovered from below 30 cm (Bromilow, 1973).

Residues in vegetation following soil treatment

Grass and weed samples were taken from in and around dryland and irrigated areas receiving aldicarb applications at 1.7 kg/ha (17 kg/ha 10G formulation). The highest residue in dryland areas was 42.8 ppm in a composite sample of nightshade, ironweed and careless weed collected from within the treated area 7 days after treatment. These residues declined to 0.96 ppm at 29 days after treatment. Residues remained generally below 10 ppm, but 19.6 ppm was detected in a sample of thistle collected some 4 m from treated areas at 43 days after treatment.

In irrigated areas, residues were found at 23.6 ppm in a composite sample of careless weed and Johnsongrass collected 51 days after treatment some 4 m from treated areas. All other residues were well below 10 ppm, but no samples were taken earlier than 23 days after treatment (Woodham *et al*, 1973).

Autumn application to California vineyards

Field studies were conducted on small vineyard plots (0.16 and 0.22 ha). Soils (fine sandy loam and loamy sand) were slightly acidic and contained little organic matter, particularly deeper in the profile. The smaller plot was underlain by intermittent hardpan layers and a perched water table on a layer of green gray silty clay between 9 and 12 m. The water table dropped from 12.6 m to below 16 m during the course of the study because of drought. The second site had a quite shallow water table, less than 2 m during the irrigated part of the growing season. Aldicarb was applied in December/January at 4.5 kg/ha with incorporation to 0.1 m. Monitoring wells were constructed to allow sampling of groundwater, and stratified core samples were taken from the soil profile at 1, 2, 4 and 6 months after treatment, with a further sample taken at 8 months from the smaller site. Total carbamate residues were determined by HPLC.

The half-life for total carbamate residues (aldicarb and its sulfoxide and sulfone) was 3.5 months at the smaller site, significantly longer than the 1.5-2 months established in earlier work following spring applications. Residues did not leach below 1 m until the late winter/early spring rains. Subsequent irrigation further accentuated downward movement, such that residues exceeded 5 µg/kg at a depth of 5.4 m at the 8 month sampling. Earlier studies had found no residues of this magnitude below 3 m after a spring application. Significant groundwater contamination (up to 93 µg/L) was detected in one well located roughly 15 m downgradient from the treated area, but had declined below 10 µg/L two years later. A potable well situated downgradient from the treated area remained clean, as did the well beneath the treatment area until a detection of 2 µg/L 20 months after treatment. Contamination at this well increased to 11 µg/L over the subsequent year before declining to undetectable levels over the next year. The anomalous contamination at the downgradient well was thought to reflect lateral movement in the perched water table to a more permeable zone near the well.

Residues began entering groundwater beneath the larger site after about 6 months because of the shallow water table. Residues were cyclic with a peak in spring. The highest recording was 135 µg/L a year after treatment, declining to 23 µg/L in the autumn. Residues were slightly lower (77 and 17 µg/L) in the following year, but rose again to reach a spring high of 113 µg/L three years after treatment. The persistence of residues indicates that half-lives are likely to be between 1 and 2 years in the saturated zone. Outside the treated area, no residues were found from 3 years after treatment and contamination did not exceed 10 µg/L at any time.

Results indicate that the likelihood of groundwater contamination is increased when application occurs under cool conditions, with subsequent rain. Off-site contamination can occur rapidly by preferential flow, for example through perched water tables (Jones, 1996).

California citrus

Aldicarb was applied in early spring in bands around orange trees with incorporation followed by irrigation. Application rates were 2.8, 5.6, 11.2 and 22.4 kg/ha. Soil samples (30 cm deep) were taken at intervals for 154 days and analysed for total toxic residues.

Residues remained relatively constant for the first three weekly samplings, at around 0.3, 0.6, 0.8 and 2.5 mg/kg, before degrading. Terminal residues were 0.01, 0.19, 0.16 and 0.09 mg/kg, respectively (Gunther *et al*, 1975).

Peanuts in Georgia

Detailed studies were conducted over a four year period at a 3.9 ha site in Georgia in order to evaluate transformation rates in the field and monitor vertical movement. Soils on the study site were a poorly drained fine sandy loam and well drained loamy sands, in roughly equal proportions. Four distinct soil horizons (0-30, 30-42, 42-65 and 65-95 cm) were present. The slope was 1%, and the water table varied seasonally between 3 and 10 m. Aldicarb was applied simultaneously with the planting of peanut at target rates of 2.24 kg/ha in the first year and 3.36 kg/ha in the following three years, banded along each seed row. In addition, the easternmost 36 rows received a heavier treatment (12.6 kg/ha) in the third season.

Soil samples were extracted with aqueous methanol and analysed by HPLC for carbamate residues. Overall depth integrated half-lives were 14.4, 19.3, 19.9 and 16.0 days, respectively, for the four years of study. No significant variation with application rate was evident in the third year. Transformation was more rapid than in the laboratory, where half-lives of 42 days had been determined in the surface 20 cm, increasing to 62 days at depth (94-107 cm). Further investigation in the final year of the field study estimated a half-life of 13.5 days in the surface 5 cm based on data collected between 3 and 10 days after application. Degradation appeared to be pseudo first order over this period. No significant losses occurred in the first two days, until 1.1 cm rain fell. A major rainfall event occurred at the end of this period.

There was no evidence of migration into the saturated zone in this study. Aldicarb residues degraded almost completely within 90 days and were not found below 1.2 m in the soil (Smith and Parrish, 1993).

Results from this study were used to investigate the predictive capacities of the pesticide root zone model and the aggregate model. Models were found to give relatively poor and variable predictions regarding the fate and movement of aldicarb (Parrish *et al*, 1992).

Lysimeter studies

Radiolabelled aldicarb was surface applied at 1.25 kg/ha to undisturbed cores (0.5 m^2 x 1 m) of loamy sand enclosed in fibreglass cylinders and placed in the ground. Sugar beet was sown at the time of treatment and harvested 6 months later. This was followed by a winter wheat crop, which was harvested 15 months after treatment. Lysimeters received 1300 mm of precipitation/irrigation over this period.

Similar volumes (127 and 129 L) of leachate were collected from each lysimeter, but containing different levels of radiolabel (0.4 and 1.7%). Carbamate residues were only found in the more radioactively enriched leachate, which contained 0.23 µg/L aldicarb sulfoxide and 1.50 µg/L aldicarb sulfone. Differences were thought to reflect soil heterogeneity (Adams and Parsons, 1994).

Residue trials in Australian cotton

Randomised split plot residue trials were conducted at four sites in the Narrabri-Collarenabri region in relatively flat country with a grey cracking clay soil type. Aldicarb was applied at seeding or as side dressing after crop emergence, at a rate of 450 g/ha. Sampling was limited, with soil samples collected from three depths on two occasions. Residues were extracted with aqueous acetone and quantified by gas chromatography after oxidation to the sulfone and purification on a florisil column.

The highest residues were detected near the surface (3-5 cm fraction), reaching 5-7 mg/kg at the first sampling 9 days after treatment. Residues at 10-12 cm were typically less than 1 mg/kg, and at 18-20 cm they were mostly undetectable. The half-life for carbamate residues in the 3-5 cm fraction appeared to be about a week, based on samples taken at 17 days (Keats, 1991a).

Drainage losses from citrus at Waikerie

This trial was conducted in late 1992 in the Waikerie irrigation area in the South Australian Murray Mallee District, on a property selected because of its sandy soils and shallow tile drains. The citrus orchard was located on a low sandhill with sandy soil (pH 8-9) underlain at 218 cm by loamy sand, containing moderate levels (3-6%) of lime below about 80 cm. Aldicarb was soil applied at 11.25 kg/ha (75 kg/ha Temik 150G) to a 0.82 ha area. Drainage at a depth of 1.75 m where tile drains entered three interconnected sumps was sampled at weekly intervals for the first month, and thereafter monthly. Samples were also taken from the inlet to a sump further downstream, outside the treated area and receiving drainage from other areas.

Samples were analysed for aldicarb and its sulfoxide and sulfone metabolites. Residues in the three sumps below the treated area showed a similar pattern, appearing first in the second month sampling and peaking at about 15 µg/L in the fourth month after treatment before declining to about 2 µg/L in three subsequent samplings. Aldicarb sulfoxide remained the main analyte. Residues appeared to have become diluted at the sump outside the treated area, reaching a peak of 10 µg/L (Keats, 1994a; Howie, 1994a).

Drainage losses from citrus at Loxton

This trial was conducted in the same county, on a sandhill area with coarse reddish sandy soil (pH 8.5) with moderate levels of lime below 380 cm. Aldicarb was soil applied once in October 1992 at 9.75 kg/ha (65 kg/ha Temik 150G). An underlying impermeable clay layer at 1.5 m to 2.0 m necessitates the creation of artificial drainage systems at this site. Water samples were taken on the same schedule as at Waikerie from the inlets to two sumps beneath the 2.6 ha treated area and from an outlet pipe 500 m downstream that also received drainage from other areas.

Samples were analysed for aldicarb and its sulfoxide and sulfone metabolites. Residue profiles differed between the two sumps beneath the treated area, which was not unexpected as they received drainage from opposite sides of the orchard. Residues at the eastern sump increased gradually to reach about 45 µg/L in the third month, and remained in the 35-45 µg/L range for the next seven samplings apart from a dip below 10 µg/L in the seventh month. A similar pattern occurred at the western sump, except that residues did not exceed 40 µg/L until the sixth month and peaked at 46 µg/L at the final sampling 50 weeks after treatment. Residues at the downstream site peaked at 48 µg/L in the sixth month but then declined sharply to remain about 10 µg/L for the remainder of the study. Aldicarb sulfoxide was the main analyte at all sampling points, except for the initial 2 months when unchanged aldicarb was present in greater concentrations (Keats, 1994b; Howie, 1994b).

Cotton in NSW

Exploratory monitoring at water supply points was conducted at three sites where aldicarb (as Temik 150G) was applied at 600 g/ha in early spring 1990. Bore water from an aquifer 29 m below the surface of a property near Moree was sampled at a depth of 11 m where the bores intruded through a red clay layer. Two bores were situated 10 m from the treated field, and the third some 300 m distant. North of Narromine, downstream river water from the Macquarie River, situated some 200 m from the treated field, was sampled. East of Mungindi, samples were taken from a small dam collecting runoff from adjacent cotton fields. Samples were taken at 1, 2, 4, 8, 12 and 16 weeks after treatment and analysed for toxic residues by HPLC, with a detection limit of 5 µg/L. All tested negative (Keats, 1991b).

Cotton in Queensland

These trials involved application at 750 g/ha with cotton seed at planting. Tailwater samples were taken from furrow, drain and holding dam at a gently sloping property situated on black cracking clay-loam soil near Emerald, and analysed by a gas chromatographic method with a limit of quantification of 10 µg/L. Two other sites

near Emerald were situated on relatively flat country over duplex soils. Tile drainage and stormwater were sampled at one property, and tailwater samples were collected from furrow and holding dam at the other. These samples were analysed using a carbamate analysis system with a limit of quantification of 5 µg/L.

Residues at the first property remained below the quantitation limit. The highest residue was estimated to be 4 µg/L, in inter-row tailwater sampled 17 days after application. It appears that this was the time of first sampling.

Tile drainage samples (0.5 m depth) at the second property contained the equivalent of 37 µg/L aldicarb one day after treatment, which coincided with 50 mm rain. Surface water samples taken from the stormwater drain 10 and 32 days after treatment remained negative.

For the remaining property, higher residues (116 µg/L) occurred in inter-furrow tailwater sampled from furrows on the day after treatment, after 25 mm rain. Residues had declined below the limit of quantification at 39 days after treatment, and were similarly undetectable in samples taken 15 days after treatment from the holding dam (Keats, 1991c).

Grapes in Victoria

A preliminary unreplicated trial was conducted near Mildura on an alkaline red loamy sand typical of the region, with tile drains at a depth of about 1.2 m beneath every fourth row. The report states that much of the water used for irrigation at this location exits through tile drains within 24 hours. Aldicarb was band applied in early spring, when soil temperatures at 10 cm were 14°C, with incorporation to a depth of 4-8 cm. The stated rate is 15 kg/ha Temik 15G, but there is some ambiguity with the analytical report stating that Temik 10G was used.

The treated area was furrow irrigated with about 100 mm on the night following application, but received little rainfall over the subsequent three weeks, during which samples were taken daily for a week and at 10, 14 and 21 days from a tail drain exiting the property. Analysis found no residues of aldicarb and associated toxic metabolites in any sample, but with an insensitive limit of detection (0.04 mg/L). The author acknowledged that further work would be needed to confirm that residues do not leave the site more than three weeks after treatment (Nash, 1990).

6.2.6 Bioaccumulation

As hydrophilic compounds, aldicarb and its toxic sulfoxide and sulfone metabolites would be expected to have a very low capacity for bioaccumulation, and this has been confirmed experimentally in bluegill sunfish.

Bluegill sunfish were tested through 8 weeks (4 weeks exposure followed by 4 weeks depuration) under static conditions, using equimolar amounts of aldicarb and its toxic sulfoxide and sulfone metabolites at total concentrations of 0.1 and 0.01 mg/L. Water analyses were conducted three times per week, with concentrations corrected as needed. Preliminary testing indicated that bluegills tolerated these concentrations but suffered heavy mortality (80% in 5 days) at 0.35 mg/L. There were no signs of

toxicity in the fish, which accumulated negligible quantities of the toxicants (bioconcentration factors of 3-5 in the definitive test and 2.4 in preliminary exposures). Residues declined by 90% during the first week of depuration (Copeland and Fink, 1973; Romine, 1973).

6.2.7 Summary of environmental fate

Testing has been conducted in the following areas to determine the environmental fate of aldicarb.

Hydrolysis

Studies submitted indicate that hydrolysis of aldicarb is slow under laboratory conditions. The toxic metabolites aldicarb sulfoxide and aldicarb sulfone also resist hydrolysis unless conditions are alkaline. Under environmental conditions, hydrolysis of the carbamate linkage occurs more readily (half-lives in the order of a week) because of catalysis by sediment.

Photolysis

The photostability of aldicarb in aqueous solution was determined from summary data contained in reviews. A report on soil surface photolysis was also submitted. Photolysis is unlikely to be a significant pathway for dissipation of aldicarb in the environment as it will be applied beneath the soil and appears resistant to photolysis in aqueous solution.

Metabolism

Several aerobic metabolism studies conducted in a variety of soils were submitted, including detailed studies of the persistence of aldicarb and its toxic sulfoxide and sulfone metabolites in Dutch topsoils and subsoils. The focus of these studies was the persistence of toxic residues. Only limited investigations werte conducted into the identities of detoxified metabolites. A single aerobic/anaerobic soil study was also submitted, together with aquatic metabolism studies under aerobic and anaerobic conditions, including simulated aquifer conditions. Many of the studies were conducted at lower temperatures than would prevail in Australian soils, making the results conservative predictors of persistence under Australian conditions.

Aldicarb is rapidly oxidised to aldicarb sulfoxide, thought to be the main active material in soil, and more slowly to aldicarb sulfone. These oxidative reactions occur concurrently with hydrolysis to oximes, which are further transformed to other compounds (amides, nitriles, alcohols and carboxylates). Only the sulfoxide and sulfone metabolites retain the high toxicity of aldicarb, which is lost upon hydrolysis of the carbamate linkage.

Detoxification half-lives in topsoils are typically a few months but exhibit considerable variability. The controlling factors are not well understood. The detoxification reaction can be very slow in some aerobic or partially aerobic subsoils. For example, aldicarb sulfone has been found to be essentially stable over periods of a year under such conditions, including in subsoils taken from three Dutch sites with

documented groundwater contamination. In contrast, detoxification can occur surprisingly rapidly (half-life a few days or weeks) in anaerobic soils.

The initial detoxification reaction (cleavage of the carbamate linkage) appears to be abiotic in nature. Oxidation of aldicarb may occur abiotically or with microbial involvement. Mineralisation of the detoxified metabolites appears to depend on microbial activity.

Detoxification reactions appear to proceed much more readily in aquatic systems, with half-lives of a few days in tests conducted under aerobic or anaerobic conditions. However, the occurrence of aldicarb residues in groundwater indicates that detoxification reactions do not occur readily in all aquatic environments, and persistence in samples of shallow groundwater has been confirmed in the laboratory under partially anaerobic conditions.

Mobility

Several standard batch adsorption studies were conducted in a variety of soils in order to determine the partitioning behaviour of aldicarb and its toxic sulfoxide and sulfone metabolites. These studies were supported by standard column leaching studies, again with aldicarb and its toxic metabolites, and by a specialised leaching study designed to demonstrate upward movement under drying conditions. Movement of aldicarb through the soil profile was modelled at three canefield sites with sandy soils in the Bundaberg district.

Standard batch equilibrium studies indicate that aldicarb is only weakly adsorbed by soils, and its oxidation products even less so. Aldicarb and its toxic metabolites share significant water solubility and tend to move with soil moisture through the soil. Low adsorption coefficients indicate that mobility in soils is high, and this has been confirmed in leaching experiments with soil columns. Simple model calculations identify aldicarb as a probable leacher. More sophisticated computer models found relatively low mobility, with residues confined to the surface 200-400 cm, but assumed a relatively rapid degradation (15 day half-life) which is appropriate for the site studied (Bundaberg) but would not be representative of areas where groundwater contamination by the more persistent sulfoxide and sulfone metabolites has occurred.

Field dissipation

Reports of field investigations in the UK, US and Australia were submitted. Results confirm the laboratory predictions of high mobility for aldicarb, and highlight the importance of soil properties in determining the degree of off-target movement.

Soil residue studies on UK grassland found oxidation to be a significant metabolic pathway, together with hydrolytic degradation pathways that left only 2% toxic residues after 2 months.

Investigations of persistence and mobility beneath California vineyards illustrate the importance of meteorology to the dissipation and movement of aldicarb. Half-lives were much longer after winter treatment (3.5 months) than when aldicarb was applied in spring (2 months) because of colder soil temperature. Leaching to deeper

groundwater (below 10 m) from winter treatments became noticeable when late winter and early spring rains carried aldicarb down through the soil profile. Contamination in the order of 10 µg/L was detected over the following two seasons, together with higher contamination (93 µg/L) remote from the treated area because of preferential lateral flow through a perched water table. Higher residues (a spring peak of 135 µg/L) were seen in shallow groundwater (< 2 m) and recurred over the following two seasons (77 and 113 µg/L, respectively).

Aldicarb dissipated more rapidly during the summer growing season in Georgia, with half-lives in the order of 2-3 weeks for total carbamate residues. Field dissipation rates were around three times faster than those observed in the laboratory. Leaching did not appear to be a problem with these more rapid degradation rates, notwithstanding application to well drained sandy soils. No residues were detected below 1.2 m during 4 consecutive years of study.

Studies in citrus groves on sandy soils in SA found residues in shallow tile drainage, at about 10 µg/L at one site and 50 µg/L at another, following application of aldicarb at about 10 kg/ha. Contamination of tile drainage proved persistent following these high rates of application to sandy soils, remaining at about 50 µg/L with little sign of dissipation after a year at one location. Aldicarb sulfoxide was the main contaminant.

Little off-site movement was apparent when aldicarb granules were used at lower rates (< 1 kg/ha) in Australian cotton planted on clay soils. The half-life appeared from limited data to be about a week near the soil surface. Analysis of surface and groundwater samples generally failed to detect aldicarb. The highest detections occurred in inter-row tailwater (116 µg/L) and tile drainage (37 µg/L) when samples were taken a day after treatments that coincided with significant rainfall.

Bioaccumulation

As hydrophilic compounds, aldicarb and its toxic sulfoxide and sulfone metabolites would be expected to have a very low capacity for bioaccumulation, and this has been confirmed experimentally in bluegill sunfish.

Synopsis

Aldicarb is transformed in the environment through hydrolytic and oxidative reactions, each of which may predominate. Hydrolytic pathways detoxify the molecule, while oxidative reactions transform aldicarb to its sulfoxide and sulfone, both of which retain biological activity. 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 aldicarb residues (parent molecule, sulfoxide and sulfone) are in the range of 0.3 to 3.5 months. Cold temperatures retard degradation. Residues continue to degrade in subsoils, apparently through soil catalysed hydrolysis. This reaction can be rapid where the redox potential is low (anaerobic conditions) but is highly variable in rate, with half-lives from a month to three years inferred from field data. Acidic subsoils tend to favour persistence.

Aldicarb and its toxic metabolites are highly mobile in soils and move with soil water. Residues that reach the saturated zone usually consist of the sulfoxide and sulfone. Aquifer contamination, particularly shallow groundwater, is most likely to occur when aldicarb is applied at high rates to acidic sandy soils when soil temperatures are low and heavy rain or irrigation occurs. Under Australian use patterns, this combination of circumstance is most likely to arise in citrus grown in southern States, where high rates of application may coincide with heavy spring rains.

The extent to which groundwater may become contaminated depends on the rate of degradation deeper in the soil profile. This can occur rapidly, apparently through heterogeneously catalysed hydrolysis, but causal factors are not well understood. At some overseas locations, half-lives in subsoils and aquifers of a few years have been estimated. It is not possible to predict where such aquifer contamination may occur, except that high rates of application to sandy soils during cool and rainy seasons significantly increase the risk. These occur in the citrus growing areas of SA.

7 Environmental Effects

Most of the studies reviewed below, particularly the unpublished ones, were provided by the principal registrant. Data gaps have been filled with information from the published literature or by reference to the US EPA's draft data base 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.

7.1.1 Avian Toxicity

Reports were submitted on acute oral testing in five species and acute dietary testing in one species. Palatability of aldicarb granules was studied in cage trials with five species under laboratory or field conditions. Reports of detailed wildlife monitoring studies were also submitted.

Aldicarb is highly to very highly toxic to birds on an acute basis, with most LD50s below 5 mg/kg. Cage studies with 6 species show that birds can consume lethal quantities of aldicarb granules, particularly when food is in short supply, but that at least some individuals seem to reject the granules completely. Surveillance in the field in both the UK and the US confirmed that a limited number of birds are likely to be killed by use of aldicarb, but without affecting populations. Carcases were recovered in low numbers (generally less than ten specimens) from individual field study sites. Residue analysis confirmed exposure to aldicarb in around half of the specimens examined. Granules left exposed on the surface appeared to be the main source of exposure, but other sources such as contaminated earthworms were also identified.

Acute oral

Aldicarb is highly to very highly toxic to birds under conditions of acute oral exposure as indicated by the results tabulated below, expressed in terms of active ingredient.

Test	Species	LD50 (95% CI) mg/kg	Reference
Acute oral	Bobwhite quail	2.71 (2.17-3.39)	Clarkson and Rowe, 1970a
		3.29 (2.61-4.14)	
Acute oral	Japanese quail	6.68 (4.66-9.56)	Ross *et al*, 1977a
		3.76 (2.27-6.23)	
		4.04 (2.84-5.76)	
Acute oral	Pheasant	15.2 (13.5-16.9)	Medd *et al*, 1972
Acute oral	Mallard duck	1 (1-2)	Beavers and Fink, 1979a
Acute oral	Mourning dove	1	Kendall, 1990

The tabulated results for bobwhite quail were obtained by force feeding capsules, respectively containing the technical active on wild bird chow or commercial granules (10%), into the crop. Symptoms of toxicity (respiratory distress, copious salivation, hyperactivity) usually progressed to death within 2-10 minutes of feeding. Sublethally affected birds exhibited lethargy, ruffling of feathers and gasping before recovering in 4-8 hours. The LD50 equates to 3-4 average sized granules of the formulation used. Similar results are reported in a published paper (Hill and Camardese, 1984). Aldicarb was the most toxic of 13 anticholinesterase compounds tested on bobwhites, with LD50s of 2.0 (1.4-2.9) mg/kg for technical active and 2.5 (1.6-4.0) mg/kg for granules. Ingestion of a single granule could be life threatening to small birds such as bobwhites.

Results for adult Japanese quail were obtained following capsule delivery into the crop of three commercial formulations, respectively carried on gypsum, corn cob and coal. Birds became lethargic and unsteady after dosing, with excessive salivation in some cases.

Adult male pheasants were dosed with a coal based granule suspended in corn oil. Profuse salivation generally began within 10 minutes of dosing, with the onset of convulsions within 10-20 minutes resulting in some loss of test material through regurgitation. Symptoms of intoxication progressed inevitably to death, usually within an hour of dosing. Residues were determined in liver and crop, confirming the losses through regurgitation at higher doses. Thus the highest residues found in the crop of survivors (sacrificed at 24 hours) and dead birds (341 and 1046 ppm, respectively) followed administration of 16.6 mg/kg aldicarb. Respective maximum residues in crop at higher doses were 35 and 104 ppm.

Laboratory reared mallards (18 weeks old) were intubated with technical aldicarb in aqueous solution. Mortality reached 10% at 1 mg/kg, 50% at 1.59 mg/kg and 100% within 5 hours at doses of 2.51 mg/kg and higher. A published paper (Hudson *et al*, 1972) reports declining sensitivity with age in young mallards, consistent with earlier findings that young rats were almost always more susceptible to anticholinesterase compounds than were older animals. Respective LD50s in 36 hour, 7 day, 30 day and

6 month old mallards were 1.92 (1.55-2.37), 3.60 (2.90-4.49), 6.73 (5.29-8.55) and 4.44 (3.49-5.65) mg/kg.

Mourning doves were tested because of occasional field reports that this species had been killed following application of aldicarb. Wild caught birds were fasted overnight before intubation with aldicarb (0.74-1.4 mg/kg) in corn oil. Toxic effects (ataxia followed by salivation and wing droop) were evident very soon after dosing, with mortality generally occurring within a few hours. The initially estimated LD50 of 0.8 mg/kg was revised upwards to just above 1 mg/kg based on the observation that collection of blood samples exerted additional stress on the birds that retarded recovery from acute intoxication. In a separate experiment, sublethally dosed birds were released and monitored by radiotelemetry. Significant mortality (4 from 8 birds, 3 within 15 minutes) only occurred at the highest dose tested (1.07 mg/kg). Doves initially remained close to the site of release, but without seeking cover. The onset of serious physiological impairment occurred within 5-15 minutes of dosing, with general immobility for 20-30 minutes before recovery of survivors 1-1.5 hours after dosing.

The above study, with additional observations on bobwhite quail, has been published (Hawkes *et al*, 1996). Quail exhibited similar behavioural responses as doves. It appears that the rapid onset of aldicarb intoxication does not allow a cover seeking response, although this conclusion is compromised by the 5-10 minute post-dose holding period The authors conclude that acute mortalities from aldicarb in quail and doves are likely to occur within the treated area.

Acute dietary

A dietary study (Beavers and Fink, 1979b) confirmed that aldicarb is highly toxic to birds, returning an LC50 of 71 (59-85) ppm in laboratory reared bobwhites (14 days old). Mortality only occurred at the two highest dietary concentrations, reaching 20% at 56.2 ppm and 90% at 100 ppm. All deaths occurred in the first four days. The single survivor at the highest dose was asymptomatic by day 7.

No other reports of dietary toxicity testing were submitted. Literature reports confirm the high toxicity, with LC50s of 387 (336-445) mg/kg in Japanese quail, 594 (507-695) mg/kg in 5 day old mallards, and >300 mg/kg in pheasants. (IPCS, 1991).

Palatability to pheasants and pigeons

Early studies investigated the avian palatability of aldicarb on corn grit or coal granules. Adult male pheasants and adult pigeons were housed indoors in groups of 12 and offered mixtures of feed and Temik granules, together with standard flint grit and water. One group exposed to the coal granules had the normal food restricted to about 50% of usual requirements. There were no obvious differences in palatability between the two formulations. Among the pheasants offered unrestricted feed, a single bird died in each group on day 4 and a second in the coal group on day 11. Daily consumption of Temik per group was 12 and 25 g, respectively. With restricted feed, individual mortalities occurred on days 1, 9, 10 and 11, although one of these was thought to reflect cannibalism rather than intoxication, and daily consumption of Temik consumption increased slightly to 31 g. Grit consumption increased markedly

when normal feed was restricted. Similar dietary trends occurred in pigeons, but only one bird died, on day 3 in the restricted feed group.

Pheasants were also tested in groups of twelve under outdoor field conditions. Choice tests with unrestricted feed were conducted with feed and granules in separate containers or scattered on the ground. Where feed was restricted, feed and granules were offered in separate containers. Granule consumption increased by a factor of 3-4 when feed was restricted, and grit consumption also increased. The coal granule appeared to be much less palatable than corn grit when offered in containers. Consumption of granules scattered on the ground could not be monitored, but appeared significant for the corn grit formulation as mortality reached 50% in this group. Heavy mortality was also seen in mallards that were introduced into the outdoor cages 14 days after termination of the pheasant study, but only where corn grit rather than coal had been scattered (Medd and Roberts, 1972).

Palatability to Japanese quail

Investigations were also conducted into the avian palatability of aldicarb on corn grit or gypsum carriers after reports of bird deaths in the field from consumption of the corn grit product. Japanese quail were offered mixtures of feed and granules, with or without prior overnight fasting, or the granules alone after fasting overnight. Deaths began to occur in the first few hours of exposure, remaining below 10% where non-fasted birds had free access to clean food but increasing to 20-40% in fasted birds and 55-60% where only granules were available for consumption. Reformulation to a gypsum granule did not appear to reduce palatability. Similar results were obtained with wild caught sparrows, although these birds seemed better able to recover from poisoning. Use of granular aldicarb products appears to represent a danger to birds, particularly if food is in short supply (Hilbig, 1979).

Palatability to zebra finch

Palatability of uncoloured corn cob grit and blue dyed gypsum formulations spread evenly in an open furrow was studied in zebra finch. Feed was reduced to 75% of the normal ration on days 5-7 and to 30% on days 8 and 9 of the 10 day exposure period. Granule consumption remained at unmeasurably low levels except for the first day of dietary restriction. Mortality reached 30% in birds exposed to corn cob and 10% for the gypsum groups. It was considered that these mortalities probably reflected Temik consumption as some birds were seen pecking at the granules. However, some birds appeared to avoid the granules completely, and all birds remained asymptomatic while alive. Both formulations were judged to be unpalatable to zebra finch (Ross *et al*, 1978a).

A second study examined the effects of granule size on palatability of a light brown gypsum formulation to zebra finch. Granules were scattered daily over the floor of the pens at the beginning of each treatment period, roughly 30 minutes after dispensing food in the same manner. In the first week, treatment occurred at 10% of the rate normally used for potatoes (30 kg/ha), increasing to 30% in the second week. Birds were then moved to new pens and placed on a restricted diet (75% of normal) for a week, with introduction of granules at 3 kg/ha. This was increased to 6 kg/ha in

the second week with further dietary restriction to 60% of normal intake, after again transferring birds to clean pens.

There was no clear effect of granule size on overall mortality, although there were some indications that mortalities occurred sooner with the larger, more toxic granules. Fewer mortalities occurred when sand was present on the cage floor, but the difference was not great (cumulative mortality 50-80%). Mortality was highest in the final week of dietary restriction. The authors note that much fewer than 10% of granules would be left exposed at the surface in commercial practice, and that boredom must be considered as a factor in granule consumption for laboratory finches (Ross *et al*, 1979).

Palatability to pheasants

The same protocol was used to study palatability of corn cob and gypsum formulations to pheasants. Consumption of food and granules was difficult to determine precisely because of spillage but did not appear to be affected. There was some indication of greater granule consumption when first introduced and when diets were first restricted. Three birds exhibited symptoms of intoxication, with one recovering. The dead birds had been offered the corn cob formulation. Acceptance was limited for both formulations, with some birds apparently avoiding the granules completely, but there were indications that consumption may increase when food is scarce (Ross *et al*, 1978b).

Comparative palatability to pheasants

Pheasants in this study were offered mixtures of test material (corn cob, red gypsum and blue gypsum formulations of aldicarb and commercial formulations of thiofanox, carbofuran and terbufos) and feed (75% of mean daily *ad libitum* consumption) in separate containers (interchanged daily) for 7 days, followed by a 7 day observation period. In a second part of the study, clean feed was offered *ad libitum* as a choice with feed containing 5% test material.

In the first part of the study, mortality reached 70, 10, 50, 0, 70 and 10%, respectively. Mortalities in the corn cob group occurred in the first two days. Only one mortality (blue gypsum group) occurred in the second part of the study. Consumption of the test materials remained very low, although some birds in all test groups were occasionally observed pecking at the test material (Ross *et al*, 1978c).

Field studies with caged bobwhite quail

Birds in this study were young adult bobwhite quail, housed in pairs in outdoor cages over areas where Temik 10G corn cob formulation (11.2 kg/ha) had been incorporated in-furrow at a depth of 1-2 cm when planting cotton seed, or incorporated as side dressing to 8-10 cm at 33.6 kg/ha when the cotton was 30-60 cm tall. Only two birds died from seventy two tested. Aldicarb poisoning was not confirmed in either case, but one bird may have consumed exposed granules and the other newly emerged foliage (Back, 1968).

The study was repeated, using application in-furrow (but without planting of cotton seed) and broadcast treatments at 22.4 kg/ha with incorporation to 10-15 cm or at 11.2 kg/ha without incorporation. Three different formulations, identified as 10GC, 10GV and 10CVB4 but not further described, were tested. Three cages, each containing a pair of birds, were used for each treatment, and moved to new locations each day for 7 days. The effects of sprinkler irrigation were investigated for each treatment.

No signs of illness were seen on the day of application, although the birds exposed granules when digging shallow holes in the dry soil. Irrigation markedly increased bird activity. When cages were moved the following morning, fourteen birds were found dead. All had been exposed to the 10GV formulation, rather than the 10GC formulation that was also tested, and most (10/14) were from non-irrigated plots. There was no indication of differences between broadcast or in-furrow treatments. A single bird died in each of the non-irrigated 10GV treatments the following day, and another over the remainder of the 7 day exposure period.

In-furrow and broadcast treatments were compared in a second series of tests using the same two formulations and a third known as 10GVB4. Mortality only occurred on non-irrigated plots, and mainly with the 10GV formulation. Three birds were recovered dead from the plots treated in-furrow, and six from the broadcast plots. Mortality on the 10GVB4 plots was about half this level.

Results from a subsequent choice test, in which quail were offered feed or granules in separate cups, suggest that the low acceptance of the 10GC formulation following appplication to soil reflects its soil blending colour. Only the 10GC formulation elicited mortality while clean feed was available in choice tests.

Wild birds also appeared susceptible, as seven starlings died in one test where Temik 10GV was applied in furrow (Clarkson and Rowe, 1970b).

Simulated spills

A group of ten pheasants was acclimatised for 50 days before exposure to simulated spills of Temik (corn cob grit) for 63 days and to Temik in feed hoppers for 15 days, initially mixed with feed and then with all feed removed.

Birds showed no interest in spilt Temik granules, and displayed no symptoms of intoxication. Females began to lay eggs shortly before introduction of the granules, and continued laying through the exposure period. The only mortality occurred 6 days after removal of feed from the hoppers. Remaining birds survived another 5 days under these conditions before release back to the wild. The author concluded that pheasants will not be readily attracted to this formulation of Temik, although spills may give rise to some mortality in marginal pheasant range when normal food is in short supply (Lund, 1970).

Field studies on English sugar beet fields

Effects on birds visiting sugar beet fields treated in the drill with 11.2 kg/ha Temik were evaluated by observation and carcase searching on two rectangular plots (8 and

18 ha) in Suffolk, the smaller of which was completely surrounded by woodland and wind breaks. A total of 57 species was observed over a 7 week period on, over or around the sugar beet planting, including birds thought to be more likely to be exposed to Temik because of their habits (red-legged partridge, pheasant, wood pigeon, skylark, songthrush, blackbird, robin, starling, chaffinch and house sparrow). There were no significant differences between pre-drilling and post-drilling observations. Observations were similar at the larger site.

Carcase searches recovered four pheasants from around the smaller field, one still alive but vomiting in the middle of the treated area on the day after treatment. Three dead birds were found over the subsequent three days, two in adjacent wooded areas. All contained aldicarb (2-5 ppm) in the crop and aldicarb sulfoxide (0.5-1 ppm) in organs such as lungs, liver or kidneys. At the larger site, four birds (a pheasant and three pigeons) were found on or around the treated field on the day after treatment, but all tested negative for aldicarb residues. A yellow hammer recovered dead from the middle of the treated area 4 days after treatment was found to contain 1 ppm of the sulfoxide metabolite. Four pigeons recovered from nearby wooded areas the following day contained 1-5 ppm aldicarb in crop and gizzard, and another pigeon found dead the following day near the smaller site was similarly contaminated.

A local gamekeeper with strong recollections of dieldrin impacts expressed a view that use of aldicarb had no effect on wildlife in the area, based on his observations. The author of the study notes that most of the casualties observed were thought to have been exposed to granules spilt at the ends of the field, and that a technical solution to such problems would appear feasible. There were also occasional granules exposed in the body of the field, a more difficult problem to overcome for shallow drilled seeds such as sugar beet (Anon, 1970).

An adjoining 12 ha loamy sand plot, completely surrounded by woodland or hedges and with an extensive forest area to the south, was studied in 1972. Temik (coal) was applied at 11.2 kg/ha over 8 ha using a granule applicator mounted on the seed drill.

Some 59 bird species were observed during 52 hours of searching by local ornithologists, including a number actually feeding on the field. There was little variation in the frequency with which these species were seen before and after treatment. Many birds were breeding and successfully rearing young.

Carcase searches conducted in and around the field, including in adjacent woodland, recovered a dead wood pigeon from a hedge some 100 m from the field on the day after treatment, heavily scavenged remains of a moorhen in grassy headland 12 days later, and two small songbirds on the field after crop emergence. Only one of these carcases (a linnet recovered when the crop was at the 2-4 leaf stage) contained significant levels (0.77 ppm, after removal of head and legs) of toxic residues. The wood pigeon was in good condition but with an empty crop, and contained less than 0.05 ppm in liver, and a dunnock recovered when the crop was at the cotyledon stage contained less than 0.08 ppm body residue.

The author concluded that reformulation of Temik as a coal granule as used in this study substantially reduced the hazard to English birds in the field (Tait, 1972).

English field observations

Surveillance activities were conducted at eight sites across the UK where potatoes or sugarbeet were treated under a provisional clearance with a 10% coal based formulation of aldicarb. Application rates were 5.6-11.2 and 22.4-33.6 kg/ha, respectively. There was considerable variation between sites in soil conditions, weather, timing and technique of application. Birds such as pied wagtails, skylarks, pigeons and game birds were seen feeding on treated areas.

A number of dead birds were recovered, but most appeared to be victims of disease or trauma. A pied wagtail and a skylark were probably poisoned by aldicarb as toxic residues (3.8 and 1.2 ppm, respectively) were found in their gizzards. Relatively large numbers of dead and dying earthworms were seen at the surface at two of the eight sites studied. A sample from one location contained 6.2 ppm aldicarb, and an earthworm pellet regurgitated by a bird contained 2.5 ppm (Brown *et al*, 1975).

Further insight into the earthworm observations is available from published sources (see section 7.1.3.2).

English wildlife surveys

Detailed and exhaustive searches of eight small plots in East Anglia planted to sugar beet or potatoes and treated with a 10% gypsum based formulation (5-11 and 20-34 kg/ha, respectively) found only one dead bird, a yellowhammer exhibiting symptoms of intoxication (erratic flying followed by convulsions) prior to death. Wildlife observations revealed no unusual behaviour suggestive of intoxication and no effects on abundance. Results indicate that the formulation used (blue gypsum) is of low hazard to local wildlife when used according to standard procedures to treat potatoes (with subsequent harrowing) or sugar beet (in the drill at planting) in this part of England (Ross *et al*, 1977b).

Wildlife surveys in US field studies

Field studies were conducted on 28 plots with a total area of 550 ha dispersed across 7 sites (citrus in Florida and Texas, cotton in Texas and Arizona, and potatoes in Delaware, Idaho and Michigan). Plots received a single application of Temik granules at the highest label rate, with no attempt to incorporate granules spilt in turnaround areas. Large numbers of birds followed the application equipment and fed actively in the freshly disturbed soil. Effects on wildlife were monitored using a range of techniques (carcase search efficiency determinations, carcase removal rates before and after baiting, avian census including observations of abnormal behaviour, searches for carcases and feather spots, and residue analysis).

Results from post-application carcase searches are tabulated below. Chemical analyses conducted on 38 of the 45 carcases recovered found detectable residues (above 0.1 ppm) in 22 specimens (11 birds, 9 mammals and 2 reptiles). The authors conclude, based on the low incidence of mortality, that use of Temik on citrus, cotton and potatoes is expected to exert minimal impact on non-target vertebrate populations (Fletcher, 1988).

Crop	State	Bird	Scavenged bird	Feather spot	Mammal	Reptile	Amphibian
Citrus	Florida	2		6	6	2	1
Citrus	Texas	4	4	6	2		
Cotton	Texas	4		8	3	1	
Cotton	Arizona	1		3			1
Potato	Delaware	4		1			
Potato	Idaho		2		9		
Potato	Michigan	3	1		2		

7.1.2 Aquatic Toxicity

A basic aquatic toxicity package for aldicarb was submitted, consisting of acute tests with rainbow trout and bluegill sunfish, chronic tests with rainbow trout, acute tests with daphnids and mysids, reproductive testing with daphnids, and algal growth inhibition tests with a green alga. Limited data for sulfoxide and sulfone metabolites were also submitted. Laboratory results were supplemented by limited field data.

Available test results indicate that aldicarb is highly toxic to most fish under conditions of acute exposure. Threshold concentrations for toxic effects are similar for acute and chronic exposures, and chronic toxicity to fish is slight according to Dutch criteria. Crustaceans share similar acute sensivity, but are affected by lower concentrations when chronically exposed. Maternal mortality rather than reproductive impairment is the main indicator of chronic effects in daphnids. Aldicarb is slightly to moderately toxic to a green alga. Laboratory effects on aquatic fauna have been confirmed in the field, with mortality of fish and frogs reported from exposures in the low mg/L range but few further details available.

Aldicarb sulfoxide and aldicarb sulfone share the high toxicity of aldicarb when tested with daphnids. The three toxicants also appear to share similar toxicity towards green algae. However, fish toxicity of metabolites is markedly reduced, being moderate for the sulfoxide and no more than slight for the sulfone.

Fish acute toxicity

Aldicarb was found to be highly toxic in static testing with rainbow trout and bluegill sunfish, as indicated by the results tabulated below. Results are generally expressed as nominal concentrations, which did not depart significantly from measured concentrations.

Test	Species	LC50 (95% CI)	Reference
96 hour static	Rainbow trout	0.88 (0.62-1.25) mg/L	Beliles *et al*, 1966
96 hour static	Rainbow trout	0.56 (0.47-0.68) mg/L	Schneider *et al*, 1979a
96 hour static	Rainbow trout	1.73 (1.46-2.35) mg/L	Thun, 1990a
96 hour static	Bluegill sunfish	0.15 (0.12-0.17) mg/L	Knott and Beliles, 1966
96 hour static	Bluegill sunfish	0.1 mg/L	Clarkson, 1968
96 hour static	Bluegill sunfish	0.063 (0.052-0.077) mg/L	Schneider *et al*, 1979b

The early rainbow trout test was conducted at 12^{o}C using a 10% granular formulation added directly to jars containing 15 L water and five fish (mean weight 1.5 g). A single mortality occurred at 0.32 mg/L, and all fish died within 48 hours at 1.8 mg/L.

Loss of equilibrium was noticed within 6 hours at nominal concentrations above 1 mg/L. A positive control (DDT) returned an LC50 of 1.5 µg/L.

A more recent rainbow trout test followed a similar protocol but introduced the toxicant in acetone solution. Mortality only occurred at the two highest test concentrations. The nominal no observed effect concentration was 0.18 mg/L; fish became irritated after 24 hours at 0.32 mg/L.

The most recent rainbow trout test used a 5% granular formulation to prepare a stock solution for dosing the aquaria. The test was conducted under static conditions, but analytical concentrations remained at least 80% of nominal between 0.1 and 10 mg/L.

Bluegills were tested at 22°C in the same laboratory as the early rainbow trout test and according to the same protocol. The dose-response was steep, with only a single mortality towards the end of the exposure period at 0.1 mg/L but complete mortality, preceded by loss of equilibrium, within 24 hours at 0.32 mg/L. At 0.18 mg/L, mortality increased through the exposure period to reach 70%. A positive control (DDT) returned an LC50 of 5.6 µg/L.

The second bluegill test used purified aldicarb dispensed as aqueous acetone solution into jars containing 2 L pond water and five fish (mean weight 5 g). Mortality increased sharply from 5% at 0.06 mg/L to 100% within 24 hours at 0.25 mg/L. Testing of aldicarb sulfoxide and sulfone found these metabolites to be less toxic than the parent (LC50s of 4 and > 64 mg/L, respectively).

A steep dose-response was also evident in the most recent bluegill test. Mortality reached 20% at 0.056 mg/L and 100% within 48 hours at 0.100 mg/L. The nominal no observed effect concentration was 0.032 mg/L.

The US EPA database provides insight into the disparate sensitivities of the two species for which test reports were provided. Fathead minnows share the relative insensitivity of rainbow trout, with a 96 hour LC50 of 1.37 mg/L. Marine species share the sensitivity of bluegill sunfish, as indicated by results for sheepshead minnow (41, 170 µg/L), pinfish (80 µg/L) and spot (200 µg/L).

Fish chronic toxicity

Chronic exposure of rainbow trout did not reveal any additional sensitivity compared with acute exposure.

Rainbow trout (mean weight 1.15 g) were exposed to aldicarb at nominal concentrations between 0.0056 and 0.56 mg/L for 21 days under flow-through conditions. Sub-lethal effects (swimming at the surface or on the bottom, increased pigmentation, loss of equilibrium) were only seen at the highest test concentration (nominally 0.56 mg/L, mean measured 0.65 mg/L) which was also the lethal threshold concentration. Mortality increased through the exposure period to reach 60% after 21 days (Handley *et al*, 1991a).

A similar test was conducted under static-renewal conditions with an aldicarb stock solution (10 mg/L) prepared from a 5% granular formulation. Mortality was only

observed at the highest test concentration (1.73 mg/L) and only in the initial 2 days of exposure, reaching 40%. Sub-lethal effects (abnormal curvature of the body) were seen at and above 0.175 mg/L (Thun, 1990b)

Aquatic invertebrate acute toxicity

Aldicarb is highly to very highly toxic to aquatic arthropods, particularly crustacea, as outlined below.

Test	Species	48 hour EC50 (95% CI)	Reference
Static	*Daphnia magna*	411 (338-499) µg/L	Vilkas, 1977
Static	*Daphnia magna*	1.45 (1.24-1.66) mg/L	Thun, 1990c
Static	*Daphnia magna*	75 (54-89) µg/L	Young Song *et al*, 1997
Static	*Artemia* sp	5.46 (0.86-10.20) mg/L	Young Song *et al*, 1997
Static	*Aedes aegypti*	0.29 (0.28-0.30) mg/L	Young Song *et al*, 1997
Static	*A taeniorhynchus*	0.15 (0.11-0.19) mg/L	Young Song *et al*, 1997
		96 hour EC50 (95% CI)	
Static	Mysid shrimp	13 (10-17) µg/L	Hollister, 1981
Static	Mysid shrimp	10.7 (8.2-13.9) µg/L	Schupner, 1980
		24 hour EC50 (95% CI)	
Static	Midge larvae	9.9 (9.1-10.3) µg/L	Fisher *et al*, 1993

Mortality of *Daphnia magna* exposed to technical aldicarb occurred at all five doses tested, increasing from 5% to 95% as concentrations increased from 0.1 to 1 mg/L. All mortalities except one occurred in the second 24 hour exposure period. The sulfoxide (Handley *et al*, 1995) and sulfone (Handley *et al*, 1994a) metabolites exhibited similar toxicity when tested in this way, respectively returning 48 hour EC50s of 0.80 (0.68-0.95) and 0.55 (0.47-0.64) mg/L.

Mortality was also observed across all concentrations tested (0.51-5.1 mg/L aldicarb) when daphnids were exposed to a 5% granular formulation, prepared into an aqueous stock solution before introduction to the test vessels.

The third, more sensitive EC50 for *Daphnia magna* in the above table was obtained at 27^{o}C in a static bioassay conducted according to US EPA protocols, except that test organisms were fed during the exposure period. Toxicity at 20^{o}C was around an order of magnitude lower, consistent with results obtained by other laboratories. Brine shrimp and two mosquito species were also tested at 27^{o}C using the same procedure in this published study.

Mysid shrimp were tested in natural seawater with analytical aldicarb as toxicant. Mortality was complete within 96 hours at concentrations of 25 µg/L and above. The earlier test used synthetic seawater and technical grade aldicarb. Mortality was complete within 48 hours at 32 µg/L. Other marine crustacea share similar sensitivity; for example, the US EPA database lists a 96 hour LC50 of 12 µg/L in pink shrimp.

The midge test involved exposure of 4th instar *Chironomus riparius* for 24 hours to aldicarb, introduced to the test medium as acetone solution. Some amelioration of toxicity was noted when the toxicant was first applied to sediment, with the nominal LC50 moving to 26.7 (23.3-30.6) µg/L. Exposure concentrations were not confirmed

analytically, and it is unclear whether the amelioration in toxicity reflects retention by the sediment or degradation.

Aquatic invertebrate reproduction

Maternal toxicity appeared to be the dominant response in reproductive testing with daphnids, and occurred at lower concentrations than from acute exposure.

The effects of exposure to aldicarb on reproductive capacity were studied in a 21 day semi-static test with *Daphnia magna*. Analyses of the test media found mean measured concentrations to be 106% of nominal concentrations, which were used to report results. The EC50 was 0.09 mg/L, and survivors at 0.18 mg/L were markedly smaller in size and paler in colour than controls. Toxicity to adults reduced the total number of young produced by this group to 13% of control levels, but did not significantly affect the number of young produced per female. The EC50 for reproduction could not be determined but must be less than 0.56 mg/L, a concentration that killed all the parent generation (Handley *et al*, 1991b).

A second semi-static test examined the effects of a 5G formulation, at concentrations from 0.018 to 1.45 mg/L aldicarb with a serial dilution factor of 2.4. Analytical concentrations remained at least 80% of nominal. All daphnids died within 4 days at the highest dose, but rates of immobilisation did not differ significantly between test and control organisms at lower concentrations. The number of offspring per surviving adult remained unaffected except for a reduction on day 9 at 0.6 mg/L. Dead offspring were a more sensitive indicator of effects, being significantly higher on day 21 at 0.25 mg/L and on days 11, 16, 18 and 21 at 0.6 mg/L. The data did not allow estimation of EC50 values for immobilisation or reproduction (Thun, 1991).

Toxicity to molluscs

Freshwater mussels and Asiatic clams survived 96 hours static exposure at 21^{o}C to aldicarb concentrations ranging up to 320 mg/L. However, cholinesterase activity in mussel adductor muscle was depressed at concentrations as low as 0.1 mg/L. Toxicity increased sharply with increasing temperature, with mussel mortality occurring at 5 mg/L at 30^{o}C (Moulton *et al*, 1996).

The low toxicity of aldicarb to molluscs is confirmed by the US EPA's database, which lists a 48 hour EC50 of 8.8 mg/L for Eastern oysters.

Algal toxicity

Testing in two different laboratories found aldicarb to be slightly to moderately toxic to the green alga *Scenedesmus subspicatus*. Toxicity of sulfoxide and sulfone metabolites fell within the same range.

Test	Species	EC50	Reference
Static	*Scenedesmus subspicatus*	1.4 mg/L (96 hours)	Handley *et al*, 1991c
Static	*Scenedesmus subspicatus*	42.4 mg/L (72 hours)	Hillman, 1990

The first of the two tabulated results was obtained using analytical grade aldicarb. Algae were cultured under continuous illumination on an orbital shaker at 24°C. Analytical concentrations remained at 93% of nominal. Clumping and deformation of cells was seen at 0.8 and 1.6 mg/L. The EC50s were the same with respect to growth rate (24-48 hours) and biomass.

Similar bioassays were conducted with sulfoxide and sulfone metabolites. The nominal 96 hour EC50 for aldicarb sulfoxide was 12 mg/L based on biomass and 22 mg/L with respect to growth rate (0-24 hours). No abnormalities were seen in control or test cultures, even at the highest dose of 50 mg/L. Concentrations declined during the exposure phase, such that EC50s based on final measured concentrations were about 70% of nominal. Losses were thought to reflect sorption to algal cells or to glassware, but this was not confirmed (Handley *et al*, 1994b). For the sulfone, nominal EC50s based on biomass and growth rate through the initial 24 hours were 4.1 and 3.9 mg/L, respectively. Suspected sorption losses reduced final analytical concentrations to 19-58% of nominal, with the greatest shortfalls at lower concentrations (Handley *et al*, 1994c).

The earlier study used Temik 5G as toxicant. Algae were cultured in Erlenmeyer flasks, with regular shaking to maintain cells in suspension. Results are expressed as active ingredient. No analytical confirmation of nominal test concentrations was reported. The EC50 based on growth rate was 153 mg/L.

Field studies

Aldicarb was applied at 1.12 kg/ha to the surface of artificial ponds (25-30 cm deep) containing caged mosquito fish (*Gambusia affinis*). The nominal exposure concentration was about 0.4 mg/L. Treatment was said to be relatively harmless to these organisms, and to tadpoles of *Bufo boreas*, tadpole shrimp and diving beetle larvae and adults (Mulla, 1966).

The first page only of another field study was provided. Fish and frogs were reportedly killed by exposure to an initial 3 mg/L aldicarb. Concentrations declined to 0.06 mg/L over the following 6 weeks, by which time the pond water was no longer toxic to bluegills (Clarkson *et al*, 1968).

7.1.3 Non-target Terrestrial Invertebrates

A limited package of data was submitted to address toxicity to these organisms. Reports of laboratory testing with bees were not provided, but high toxicity is documented in the literature. However, bees are unlikely to receive high exposure to this soil applied insecticide. Because of its systemic properties, limited exposure of bees to aldicarb may occur through consumption of nectar containing residues. A study was submitted confirming that bees in citrus groves can be killed through this exposure route, but in relatively low numbers and only for a limited period.

Earthworm toxicity studies were also not submitted. Published results indicate that aldicarb is moderately toxic to toxic to earthworms.

Carabid beetles also appeared susceptible to aldicarb, suffering complete mortality soon after exposure to heavily treated sand.

Field studies indicate no long term damage to non-target insect populations from use of aldicarb.

Laboratory tests with bacteria and fungi indicate that effects on microbial populations in the field are unlikely.

Bees

No reports of laboratory bioassays with bees were submitted, but a Union Carbide Product Bulletin included in the submission indicates that aldicarb is inherently very toxic to honeybees as a contact poison. This is confirmed by the LD50 of 0.285 µg/bee listed in the US EPA's database. However, no significant problems are said to arise in commercial use because of the low likelihood that bees will encounter surface residues following application of granules to soil. Limited mortality of honeybees foraging on nectar from treated citrus has been reported, as outlined in more detail below, but these minor mortalities were considered to be of no apicultural concern. The Product Bulletin (issued in 1986) emphasises that no significant bee poisonings have been reported from 15 years of commercial use on pollinator-dependent crops.

Temik 15G was applied just before bloom to navel and Valencia orange groves in order to determine whether toxic residues would occur in blossom or pollen. Valencias were treated with 22.4 kg/ha spread over 54% of the block. Single navel orange trees were treated with the equivalent of 22.4, 11.2, 5.6 and 2.8 kg/ha. Granules were incorporated to 5 cm and irrigated.

The highest treatment of navels led to 20% mortality of honey bees at 20 days post-treatment, increasing to 52% at 23 days before declining to nontoxic levels at 25 days. Lower doses also led to noticeable toxicity at 23 days. Low level toxicity was seen in Valencias, at 20 days post-treatment only (Atkins *et al*, 1975).

Earthworms

Standard earthworm toxicity tests were not submitted. A review of earthworm toxicity testing (Edwards and Coulson, 1992) cites the following LC50s (mg/kg dry weight soil) from exposure of various species to a range of concentrations of aldicarb for 14 days: *Eisenia fetida* 16, 3.3, 8; *Apporectodea calignosa* 4; *A chlorotica* 4; *Lumbricus rubellus* 4-8; *L terrestris* 26. These results indicate that aldicarb is moderately toxic to toxic to earthworms. High toxicity (LC50s of 3.1-50 ppm) was also apparent in a non-standard test involving brief immersion in aldicarb solution before placement on clean soil. Another paper (Edwards, 1992) in the same collection notes that aldicarb is taken up into earthworm tissue from waterlogged field soils only as the parent and not as the degradation product. IPCS (1991) citing the same source (but as an abstract from the original German) states that LC50s for *E fetida* and *L terrestris* are 65 (58-75) and 530 (490-565) mg/kg dry soil substrate.

A literature study on uptake from water was included in the submission. Macerated worms were shaken for 30 minutes in an aqueous solution of aldicarb, with uptake determined by analysing the supernatant. Equilibration required a few minutes. A similar exercise was conducted for desorption. Distribution coefficients for adsorption and desorption were 44 and 263, with the higher figure for desorption thought to reflect hysteresis or degradation. For aldicarb sulfoxide, a coefficient of 6 was obtained (Lord *et al*, 1980).

The above results confirm the field observations of earthworm residues (see section 7.1.1.11). Further detail on such field observations is available in a review of secondary hazards to vertebrates from consumption of earthworms (Cooke *et al*, 1992). Consumption of exposed granules or contaminated earthworms was suspected in a series of incidents that occurred in the UK in 1975 and 1976, involving kills of up to 100 birds including gulls, lapwings, moorhens and gamebirds. Intensive field investigations at a site where sugarbeet had been treated at planting with aldicarb granules found dead earthworms on the soil surface 6 days after drilling, but without detectable residues. However, moribund earthworms containing aldicarb residues were subsequently discovered on the soil surface at other sites in wet conditions. Modifications to application equipment that minimised granule exposure proved effective in reducing such incidents. Two incidents involving deaths of gulls and partridges were subsequently reported in association with poorly incorporated application. Earthworms were present in the gizzards of gulls examined, but the question of whether exposure to granules or earthworms (or both) was responsible for the kills observed was not resolved.

Carabid beetles

Temik 5G (equivalent to 100 kg/ha) was mixed into the surface 1-2 cm of sand and watered in before introduction of carabid beetles (*Poecilus cupreus*) to test vessels. The test was terminated early on the second day after application because all test beetles had died. Beetles were obviously lethargic 2 hours after introduction to the test chambers, and some were observed on their backs after 4 hours. Maintenance of control and reference beetles through 15 days confirmed the validity of the test (Pietrzik, 1992).

Insect populations in citrus

Insect populations were sampled from June to November 1983 in Florida citrus groves, using pitfall traps and insect flight traps. Plots were selected to represent different levels of aldicarb treatment over the previous four seasons. The report contains no details of aldicarb use during 1983.

The eight most abundant arthropods (earwigs, ants, caterpillars, larval and adult beetles, spiders, springtails and crickets) were enumerated from pitfall trap collections. Springtails were by far the most abundant arthropods collected, but no distinction could be made between treated and untreated groves. Ants were also quite numerous, and more so in untreated groves at one of the two locations studied. In contrast, earwigs were most numerous at treated sites at one of the two locations studied. No consistent relationship between population size and treatment history was

apparent for other organisms. High variability in trap counts was noted, even at the same site on the same day.

The most abundant insects collected in flight traps were moths, bees, wasps and flies. Five groups (ground beetles, long-legged flies, braconic and ichneumonid wasps and click beetles) were enumerated. No consistent relationships could be determined.

The authors conclude that insects remain abundant in aldicarb treated citrus groves, and report incidentally that birds, rabbits, snakes and lizards are also often present. Long term effects of aldicarb treatment on insect populations are not apparent, but any such effects would be difficult to determine in the face of tremendous variation both between and within groves (Haag and Habeck, 1984).

Insect populations in cotton

A performance review of the effect of Temik 10G on populations of beneficial organisms in US cotton was submitted, covering 31 studies from five cotton producing States. Decreases and increases in populations occurred with equal frequency. The average reduction in beneficial numbers was 53%, and effects were suspected to be transitory. Factors other than Temik exposure were thought to be responsible for most of the observed decreases as rate dependence could only be demonstrated in 26% of dosage range tests examined (Zigas, 1973).

As noted in the agricultural assessment, predators may be exposed to aldicarb as residues in their prey, or from limited feeding on plant material. Indirect effects (loss of a food source) may also intervene. However, most beneficial insects are able to sustain or increase populations in aldicarb treated areas.

Soil microrganisms

Agar incorporation and soil mycelial growth tests found little to no growth inhibition of microorganisms (bacteria and fungi, including saprophytes and parasites) exposed to aldicarb and a range of known and postulated metabolites. The agar incorporation tests used a concentration of 100 ppm, and soil tests were conducted with the equivalent of 56 kg/ha active ingredient. The only compound showing some activity was aldicarb nitrile, with a low level of activity to some bacteria in agar incorporation tests. The authors contrast the lack of activity in laboratory bioassays with earlier field observations that suggest suppression of microbes, for example control of powdery mildew on new growth of apples and roses, and delayed onset of *Verticillium* wilt in potaoes. Mildew control probably reflects increased plant vigour rather than fungal inhibition, while improved resistance to *Verticillium* may reflect control of nematodes which are known to be part of disease complexes with certain soil-borne fungal pathogens.

Further experiments investigated whether aldicarb would support the growth of various microorganisms. The fungus *Rhizoctonia solani* made very little growth when aldicarb was the only organic compound in the medium, but grew more than twice as fast in the presence of both mannitol and aldicarb as in the presence of mannitol alone. The growth medium was analysed by thin layer chromatography for residues after removal of the fungus. Only aldicarb was found, and only in the

organo-soluble fraction. Any metabolites that may have been formed were presumably retained within the fungus. Another fungus, *Aspergillus niger*, did not grow well on an aldicarb substrate, and may have been inhibited somewhat by aldicarb, albiet at high levels, in the presence of mannitol. *Alternaria solani* made slight growth on aldicarb alone but appeared unaffected by aldicarb in the presence of mannitol. The plant-pathogenic soil bacterium *Agrobacterium tumefaciens* made a small amount of growth on aldicarb alone, but growth rates in the presence of mannitol were halved by addition of aldicarb.

The authors conclude that growth of soil microrganisms should not be adversely affected by field use of aldicarb, and that the toxicant can be expected to be rapidly utilised by certain organisms (Spurr and Sousa, 1974).

7.1.4 Mammals

Aldicarb has one of the highest mammalian toxicities among currently used pesticides. The acute oral LD50 in rats is less than 1 mg/kg (Tomlin, 1997).

Field study on English sugar beet fields

Effects on small mammals living near a treated sugar beet field (8 ha) were evaluated by live trapping of representative species (wood mice and bank voles). Avian monitoring was also conducted at this and a nearby larger site (see section 7.1.1.10).

Preliminary trapping over three nights at the smaller field caught seven bank voles (three recaptures) and eleven wood mice (fifteen recaptures). Only the latter was trapped in the field to be treated. Pre-drilling monitoring used more traps and caught twelve bank voles and twenty-one wood mice (six and fourteen recaptures, respectively). Seventeen of the thirty-three animals captured were already marked from the preliminary monitoring. Post drilling, some fourteen bank voles and forty-eight wood mice were captured/recaptured, with only eleven not having been caught previously. Other mammals (hares, moles, roe deer, red squirrels and a fox) remained active in the area (Anon, 1970).

Consideration was given to repeating the study at an adjoining site in 1972, but advice from local small mammal ecologists led to the work being abandoned. It was considered that bank voles would not be at risk during the sowing period because they would not be likely to enter the fields until late summer. Wood mice could be at risk, but there was uncertainty as to whether any valid conclusions regarding the extent of this risk could be reached even if investigations were conducted over several seasons using hundreds of traps (Tait, 1972).

7.1.5 Phytotoxicity

Sweetclover and alfalfa were grown in plastic pouches containing 25 mL of Bryan's solution spiked with 5, 50 and 500 ppm aldicarb. Average dry weight was only suppressed at the highest exposure level (Lin *et al*, 1972).

Use of aldicarb increases yield in a broad range of crops by controlling insect and nematode damage. Phytotoxicity does not appear to be a problem in crops treated directly with aldicarb, including those treated at the time of seeding.

7.1.6 Summary of Environmental Toxicity

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

Birds

Reports were submitted on acute oral testing in five species and acute dietary testing in one species. Palatability of aldicarb granules was studied in cage trials with five species under laboratory or field conditions. Reports of detailed wildlife monitoring studies were also submitted.

Aldicarb is highly to very highly toxic to birds on an acute basis, with most LD50s below 5 mg/kg. Cage studies with 6 species show that birds can consume lethal quantities of aldicarb granules, particularly when food is in short supply, but that at least some individuals seem to reject the granules completely. Surveillance in the field in both the UK and the US confirmed that a limited number of birds are likely to be killed by use of aldicarb, but without affecting populations. Carcases were recovered in low numbers (generally less than ten specimens) from individual field study sites. Residue analysis confirmed exposure to aldicarb in around half of the specimens examined. Granules left exposed on the surface appeared to be the main source of exposure, but other sources such as contaminated earthworms were also identified.

Aquatic organisms

A basic aquatic toxicity package for aldicarb was submitted, consisting of acute tests with rainbow trout and bluegill sunfish, chronic tests with rainbow trout, acute tests with daphnids and mysids, reproductive testing with daphnids, and algal growth inhibition tests with a green alga. Limited data for sulfoxide and sulfone metabolites were also submitted. Laboratory results were supplemented by limited field data.

Available test results indicate that aldicarb is highly toxic to most fish under conditions of acute exposure. Threshold concentrations for toxic effects are similar for acute and chronic exposures, and chronic toxicity to fish is slight according to Dutch criteria. Crustaceans share similar acute sensivity, but are affected by lower concentrations when chronically exposed. Maternal mortality rather than reproductive impairment is the main indicator of chronic effects in daphnids. Aldicarb is slightly to moderately toxic to a green alga. Laboratory effects on aquatic fauna have been confirmed in the field, with mortality of fish and frogs reported from exposures in the low mg/L range but few further details available.

Aldicarb sulfoxide and aldicarb sulfone share the high toxicity of aldicarb when tested with daphnids. The three toxicants also appear to share similar toxicity towards green algae. However, fish toxicity of metabolites is markedly reduced, being moderate for the sulfoxide and no more than slight for the sulfone.

Non-target terrestrial invertebrates

A limited package of data was submitted to address toxicity to these organisms. Reports of laboratory testing with bees were not provided, but high toxicity is documented in the literature. However, bees are unlikely to receive high exposure to this soil applied insecticide. Because of its systemic properties, limited exposure of bees to aldicarb may occur through consumption of nectar containing residues. A study was submitted confirming that bees in citrus groves can be killed through this exposure route, but in relatively low numbers and only for a limited period.

Earthworm toxicity studies were also not submitted. Published results indicate that aldicarb is moderately toxic to toxic to earthworms.

Carabid beetles also appeared susceptible to aldicarb, suffering complete mortality soon after exposure to heavily treated sand.

Field studies indicate no long term damage to non-target insect populations from use of aldicarb.

Laboratory tests with bacteria and fungi indicate that effects on microbial populations in the field are unlikely.

Mammals

Rodent data indicate that mammals are likely to be at least as sensitive to aldicarb as are birds.

Plants

Aldicarb does not appear to affect the germination and growth of plants, apart from improvements to plant vigour as a result of insect and nematode control.

8. Prediction Of Environmental Hazard

Aldicarb is mobile in most soils to which it is applied, but particularly in sandy soils (sands, loamy sands and sandy loams) where any water input tends to recharge rapidly through the profile, carrying aldicarb with it. Aquifer contamination, particularly shallow groundwater, is most likely to occur when aldicarb is applied at high rates to acidic sandy soils when soil temperatures are low and heavy rain or irrigation occurs. Under Australian use patterns, this combination of circumstance is most likely to arise in citrus grown in southern States, where high rates of application coincide with spring rains.

Aldicarb has high to very high toxicity to birds, mammals, aquatic organisms and non-target invertebrates. These toxic properties indicate a potential hazard to birds, mammals and non-target invertebrates exposed to aldicarb at the site of application, and to aquatic fauna exposed to residues in water draining treated areas. Again, hazard is highest in citrus because of the high rates used.

The environmental hazard of aldicarb is assessed below. The approach used below 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. A potential acute risk is indicated where Q falls above this threshold but below 0.5, but may be mitigated by restricted use classification. Higher Q values indicate high acute risk and possible regulatory action. 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.

8.1.1 Terrestrial hazard

Birds and mammals may be exposed to aldicarb by direct consumption of granules, contaminated insects or plant material. Arthropods will be exposed to residues in soil solution or plant fluids. Risks from these exposures are discussed below.

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 LD50 per square foot (roughly equivalent to 10 LD50s/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.

Crop	Application rate	Exposure (LD50s/m^2)
Sugarcane	2550 g/ha	12750
Cotton	450-1050 g/ha	337-787
Citrus	2100-11550 g/ha	10500-57750

The above procedure greatly overestimates risk when applied to aldicarb as granules are incorporated beneath the soil. If 1% of granules remain exposed at the surface, exposure levels in cotton fall below the US EPA's level of concern, but remain significantly above 10 LD50s/m^2 for sugarcane and citrus. For these more heavily treated crops, granule incorporation levels need to be between 99.9 and 99.99% in order to reduce exposure of small birds below the US EPA's level of concern.

Avian exposure in treated areas will not be uniform as application in bands or in-furrow will leave most of the paddock untreated. Exposure within treated bands can be expected to be at least an order of magnitude than the above estimates based on treatment of the whole area. Birds may forage preferentially within treated areas where soil has been disturbed.

The submission contains a report of a granule incorporation study (Fish, 1988) that used inert gypsum granules coated with a fluorescent dye to qualitatively determine the efficiency of granule incorporation using photographic methods. Granules were applied to citrus at 37 kg/ha by soil injection and at 75 kg/ha as broadcast in-furrow treatment, and to cotton at 22.4 kg/ha as side dressing by soil injection and at 7.8 kg/ha in-furrow at planting. Incorporation using these methods, with care taken to disengage application equipment before row ends, was said to be excellent. Discing of row ends was effective in incorporating any granules spilt in these situations. Wildlife impact is predicted to be minimal where granules are incorporated beneath the soil as required.

Predictions of minimal wildlife impact need to be substantiated by surveillance activities when products enter the market. Such activities form an integral part of the product stewardship programs operated by most agricultural chemical registrants. Australian registrants will be asked to provide any information that they may be aware of regarding wildlife impacts from use of aldicarb in Australia, and to provide an undertaking that any such future incidents that they may become aware of either in Australia or overseas will be promptly brought to the attention of the National Registration Authority.

Mammals

A similar analysis can be carried out as for birds. Risks to mammals appear low provided that granules are efficiently incorporated beneath the soil. Few mammals other than pest rodents would be expected to be present in Australian cotton fields, canefields or citrus groves.

Invertebrates

Estimated concentrations of aldicarb assuming even dispersion through 30 cm soil (density 1.2) are tabulated below. In reality, concentrations will be uneven with the highest residues near the site of application.

Crop	Application rate	Exposure (mg/kg soil)
Sugarcane	2550 g/ha aldicarb	0.71
Cotton	450-1050 g/ha aldicarb	0.12-0.29
Citrus	2100-11550 g/ha aldicarb	0.58-3.2

The upper end of the predicted exposure range overlaps with the more sensitive results from earthworm toxicity testing, suggesting the likelihood of a hazard to earthworms in the field. This conclusion is supported by field observations of earthworm mortality in aldicarb treated areas, particularly when soils are wet.

The broad spectrum of insecticidal and nematocidal activity suggests that aldicarb will be hazardous to many soil dwelling arthropods in treated areas. This is illustrated by the early onset of toxicity in laboratory testing with carabid beetles.

Hazard to surface dwelling arthropods is likely to be relatively low for exposure reasons. Aldicarb is incorporated in soil and taken up into plants. Sucking and

chewing insects are likely to suffer adverse impacts if they feed on plants containing aldicarb residues. Field observations indicate that this hazard even extends to bees because of residues in nectar and/or pollen, but for a limited period only. Predatory insects may be exposed to aldicarb residues in prey or from limited feeding on plant material. As noted in the agricultural assessment, disruptions to integrated pest management programs in citrus have been experienced with use of aldicarb.

8.1.2 Aquatic hazard

Aquatic exposure to aldicarb and its toxic metabolites may arise when drainage water enters natural bodies of water. Contamination by aerial drift should not arise as aldicarb is applied to the soil in granular form and incorporated. Similarly, residues are unlikely to be washed off the soil surface by erosive rainfall in the sediment phase of runoff because they will remain for the most part below the soil surface. Rather, residues will mainly be confined to subsurface drainage. The persistence of aldicarb residues in soil means that drainage water is likely to remain contaminated for extended periods, particularly in acidic subsoils where degradation is slower. Residues may leach to groundwater or move laterally with tile drainage into irrigation drainage systems, and subsequently to natural surface water.

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 aldicarb in a 2 m pond, based on this model, are tabulated below.

Crop	Application rate	Predicted concentration
Sugarcane	2550 g/ha	19 µg/L
Cotton	450-1050 g/ha	3.4-8 µg/L
Citrus	2100-11550 g/ha	16-87 µg/L

Fish

The most sensitive acute LC50s for fish are 560 µg/L in cold water (rainbow trout) and 63 µg/L in warm water (bluegill sunfish). Predicted concentrations remain below 56 µg/L (10% of the LC50 for rainbow trout) except towards the upper end of the citrus range. However, these predictions would appear conservative in light of results from field studies in Australian citrus, which found that maximum residues in tile drainage did not exceed 50 µg/L. Given dilution in receiving waters, it appears unlikely that runoff from Australian citrus would give rise to concentrations in adjacent waterways that would be toxic to cold water fish such as rainbow trout.

Predicted concentrations exceed 6.3 µg/L (10% of the LC50 for bluegill sunfish) for sugarcane, citrus, and higher rate applications to cotton. This simple screening evaluation suggests that a hazard may exist for more sensitive fish such as bluegills, particularly in shallow water (note that the above predictions assume a water depth of 2 m which is likely to be deeper than commonly found in Australian cropping situations). Additional concerns are raised by the likely repetitive nature of the exposures. Local

field studies show that runoff from citrus can remain contaminated for up to a year with little evidence of declining concentrations.

Invertebrates

For invertebrates, the usual indicator organism is *Daphnia magna*. The most sensitive acute EC50 is 411 µg/L, disregarding the more sensitive result obtained under conditions of temperature stress. Predicted concentrations remain below 10% of this concentration, except at the upper end of the citrus range. The preceding comments regarding the conservative nature of these predictions, and the low likelihood that toxic concentrations would arise in practice, remain valid.

Other invertebrates such as chironomids and mysid shrimp exhibit greater sensitivity, with LC50s around 10 µg/L. Aldicarb contaminated runoff appears more likely to exert adverse impacts on sensitive invertebrate organisms such as these.

Environment Canada has established an interim water quality guideline for protection of freshwater aquatic life at 1 µg/L (sum of aldicarb, aldicarb sulfoxide and aldicarb sulfone). The guideline was derived by applying an assessment factor of 0.1 to the most sensitive lowest observed effect level (0.01 mg/L for *Daphnia laevis*) obtained in a chronic study. The corresponding interim marine guideline is 0.15 µg/L, derived from a lowest observed effect level of 1.5 µg/L in mysid shrimp (CCREM, 1993). No Australian and New Zealand Environment and Conservation Council guideline has been proposed for protection of aquatic life. The drinking water guideline of 1 µg/L is currently being reviewed by the National Health and Medical Research Council.

Groundwater

Simple calculations illustrate the capacity for aldicarb to contaminate groundwater (Harkin, 1981). These calculations are based on the estimated concentration in surface soil together with expert judgement as to how much leaches through the soil. The maximum application rate of 11.5 kg/ha aldicarb corresponds to a residue of 3.2 mg/kg in evenly distributed through 30 cm of topsoil with a density of 1.2. Most of this is likely to be retained within the surface soil fraction. However, if just 1% of the applied aldicarb leaches, residues of 32 µg/kg would occur in subsoil. Limited sorption would leave aldicarb mainly in the aqueous phase, at concentrations in the order of 300 µg/L assuming 10% soil moisture content. Groundwater contamination at the levels observed can occur when only very minor proportions of applied aldicarb leach to the water table. Label warnings are clearly warranted, as illustrated by the detailed Environmental Precautions Booklet appended to US labels.

The extent of any groundwater contamination in Australia from use of aldicarb remains unclear because few investigations have been undertaken. Contamination appears most likely in citrus grown in southern States, because of high application rates, sandy soils, cool temperatures at the time of application, and the likelihood of heavy spring rains. One option for minimising this risk would be to delay application, allowing soils to warm before aldicarb is applied.

9. Labelling

It is a condition of purchase of the product set by the registration of Temik 150G that certain requirements be met to ensure minimum risk to users, others and the environment. The label stipulates that all users attend a training program and be accredited prior to purchase and use of the product. Specilised application equipment for use in citrus must be approved by the registrant.

The well protection measures that exist on current labels fall short of those in the US, where additional buffers apply in vulnerable situations. It is therefore recommended that the following statement be added to product labels:

> "DO NOT allow aldicarb to enter groundwater supplies. Application washing or loading or emptying of application equipment must not occur within 15m of any drinking water well. This distance must be increase to 150m where soils are sandy and water tables are shallow.

The following aquatic warning it to be added:

> "Dangerous to fish and aquatic invertebrates".

10 Conclusions

Aldicarb is a moderately persistent and highly mobile, hydrophilic carbamate nematicide/insecticide which is mostly used in cotton but also has relatively small but important uses in sugarcane, citrus and grapes. It is applied to soil at relatively high rates in granular form and incorporated beneath the soil surface. Soil moisture liberates aldicarb from the granules and distributes it through the root zone, where it helps control damaging nematode populations. Uptake by plant roots offers systemic protection against sucking and chewing insect attack for several weeks.

A recent international evaluation of aldicarb (IPCS, 1991) concluded that it would not cause effects on organisms in the environment at the population level. Incidents of kills of individual birds and mammals will occur where granules are not fully incorporated into the soil. Aquatic organisms are not at risk from aldicarb. The report recommends that exposure of terrestrial vertebrates be minimised by fully incorporating aldicarb granules into soil to a depth of 5 cm, as recommended by the manufacturer.

Aldicarb granules represent a primary poisoning hazard to any mammals and birds that may eat them, particularly if they have relatively low body weight. Incorporation beneath the soil as required by the label minimises this hazard. It is important that label instructions are closely followed in this regard if wildlife impacts are to be avoided.

Risks to most terrestrial invertebrates are also relatively low because aldicarb remains below the soil surface. Short term impacts to earthworms have been recorded, and some transient effects on pollinators visiting citrus as well as disruption to integrated pest management programs in this crop.

The mobility and persistence of aldicarb and its toxic sulfoxide and sulfone metabolites raise concern for groundwater contamination. Overseas experience suggests that such problems are less likely in cotton and sugarcane because of the warm soils which facilitate breakdown. Contamination appears more likely in citrus grown in southern States, because of high application rates, sandy soils, cool temperatures at the time of application, and the likelihood of heavy spring rains. Persistence of aldicarb in groundwater is highly variable, but half-lives may extend to several years under cold and acidic conditions. US labels are more detailed with respect to well protection than the Australian labels.

High intensity of use is a key risk factor for groundwater contamination. The principal registrant has indicated that only small amounts of aldicarb are used in citrus, where risks could otherwise be significant because of high application rates, sandy soils, cool temperatures at the time of application, and the likelihood of heavy spring rains. Further monitoring of this use pattern may be warranted if use intensifies.

Contamination of surface water also merits consideration, given the mobility and toxicity of aldicarb. Simple screening methods indicate a potential hazard to more sensitive fish species. Hazard to more sensitive invertebrate species such as shrimps is also apparent. However, effects are likely to be transient as aldicarb does not persist in surface waters, and longer term invertebrate impacts would not be expected given the high reproductive capacity characteristic of such organisms. It is emphasised that these adverse effects are predicted using simple screening methods. A more refined analysis is likely to reach a less conservative outcome. However, data to refine the evaluation, such as actual monitoring data in Australian surface waters, are limited to a few individual experiments, with no information from recent seasons.

In summary, action appears warranted in the following areas:

- wildlife: an update of incident information from registrants, and a commitment to notify future incidents as soon as registrants become aware of them;

- groundwater: the need for further label amendments such as present on US labels, in light of the different use pattern and climatic conditions in Australia

11 References

Adams AM & Parsons RG (1994) Aldicarb Lysimeter Study (Interim Report). Document No 200773 dated 27 October 1994. Rhone-Poulenc Agriculture Ltd, Essex UK. Unpublished.

Andrawes NR (1981) Environmental Chemistry. Review dated 11 May 1981. Union Carbide Corporation, West Virginia. Unpublished.

Anon (1970) Wildlife Survey Temik 10G Aldicarb Pesticide on Sugar Beets; Suffolk, England, 1970. Unnumbered report, Union Carbide Corporation UK, 1970. Unpublished.

Anon (1992) East and West are Poles Apart? Citrograph, 77: 13-14 (April 1992).

Atkins EL, Kellum D, Neuman KJ, Macdonald RL & Ferguson DT (1975) Effect of Pesticides on Apiculture. Project No 1499, 1975 Annual Report. University of California at Riverside.

Back RC (1968) Temik 10G Granular Pesticide: Field Evaluation of Potential Hazard to Bobwhite Quail. Union Carbide Corporation report dated 25 October 1968. Unpublished.

Beavers JB & Fink R (1979a) Acute Oral LD50 – Mallard Duck, Technical Grade Aldicarb. Wildlife International Project No 142-119 dated 12 June 1979. Union Carbide Corporation, Florida. Unpublished.

Beavers JB & Fink R (1979b) Eight-Day Dietary LC50 – Bobwhite Quail, Technical Grade Aldicarb. Wildlife International Project No 142-118 dated 6 June 1979. Union Carbide Corporation, Florida. Unpublished.

Beliles RP, Knott W & Wright L (1966) UC-21149 Safety Evaluation on Fish and Wildlife (Bobwhite Quail and Rainbow Trout). Woodard Research Corporation Report dated 28 March 1966. Union Carbide Corporation, New York. Unpublished.

Boussemart MJ & Jones RL (1993) PRZM2 Modelling: Aldicarb on Sugar Cane in Australia. Internal correspondence dated 27 September 1993, reference ACD/MJB/4850. Rhone-Poulenc Agriculture. Unpublished.

Bowmer KH, Korth W, Scott A, McCorkelle G & Thomas M (1998) Pesticide Monitoring in the Irrigation Areas of South-western NSW, 1990-1995. CSIRO Land & Water Technical Report 17/98 dated April 1998.

Bromilow RH (1973) Breakdown and Fate of Oximecarbamate Nematicides in Crops and Soils. Annals of Applied Biology, 1973, 75: 473-479.

Bromilow RH, Baker RJ, Freeman MAH & Görög K (1980) The Degradation of Aldicarb and Oxamyl in Soil. Pestic Sci, 1980, 11, 371-378.

Bromilow RH, Briggs GG, Williams MR, Smelt JH, Tuinstra LGMTh & Traag WA (1986) The Role of Ferrous Ions in the Rapid Degradation of Oxamyl, Methomyl Aldicarb in Anaerobic Soils. Pestic Sci, 1986, 17, 535-547.

Brown PM, Bunyan PJ, Stanley PI & van den Heuvel MJ (1975) A Report on the Field Surveillance of the Possible Wildlife Hazards Associated with Use of the Nematicide Aldicarb During its Early Commercial Use in the Spring of 1975. Chemistry Department Report No 17 dated September 1975, Pest Infestation Control Laboratory, Ministry of Agriculture Fisheries and Food.

CCREM (1993) Canadian Water Quality Guidelines: Updates (April, 1993). Canadian Council of Resource and Environment Ministers.

Clarkson VA (1968) Toxicity of Temik, Temik Sulfoxide, and Temik Sulfone to Bluegill Sunfish. Project No 111B32 dated 15 November 1968. Union Carbide Corporation. Unpublished.

Clarkson VA, Rowe BK & Romine RR (1968) Field Evaluation of the Persistence of Temik and its Carbamate Metabolites in Pond Water and Their Effect on Pond Fauna. Project No 111B32 dated 11 November 1968. Union Carbide Corporation, North Carolina. Unpublished.

Clarkson VA & Rowe BK (1970a) LD50 Values for Technical Temik and Temik 10GV on Bobwhite Quail. Project No 111B32 dated 6 January 1970. Union Carbide Corporation, North Carolina. Unpublished.

Clarkson VA & Rowe BK (1970b) Field Evaluations of the Toxic Hazard of Temik Formulations 10G, 10GV, 10GC and 10GVB4 to Bobwhite Quail. Project No 111B32 dated 18 February 1970. Union Carbide Corporation, North Carolina. Unpublished.

Cooke AS, Greig-Smith PW & Jones SA (1992) Consequences for Vertebrate Wildlife of Toxic Residues in Earthworm Prey. In: Greig-Smith PW, Becker H, Edwards PJ & Heimbach F (1992) Ecotoxicology of Earthworms, Intercept Ltd UK.

Copeland GL & Fink R (1973) Acute and Chronic Exposure of Bluegill Sunfish to Aldicarb Carbamate Residues – Aldicarb, Aldicarb Sulfone and Aldicarb Sulfoxide. Hazleton Laboratories Project No 400-612. Report dated 11 May 1973 to Union Carbide Corporation, West Virginia. Unpublished.

Das YT (1990) Metabolism of [S-methyl-^{14}C]Aldicarb under Aerobic Soil Conditions. Project No 90020, Innovative Scientific Services Inc, New Jersey. Report dated 31 December 1990 to Rhone-Poulenc Ag Company, North Carolina. Unpublished.

Edwards CA (1992) Testing the Effects of Chemicals on Earthworms: The Advantages and Disadvantages of Field Tests. In: Greig-Smith PW, Becker H, Edwards PJ & Heimbach F (1992) Ecotoxicology of Earthworms, Intercept Ltd UK.

Edwards PJ & Coulson JM (1992) Choice of Earthworm Species for Laboratory Tests. In: Greig-Smith PW, Becker H, Edwards PJ & Heimbach F (1992) Ecotoxicology of Earthworms, Intercept Ltd UK.

Fennessey M (1988) Soil Adsorption/Desorption with ^{14}C-Aldicarb. ABC Preliminary Report #37352 dated 22 November 1988. Rhone-Poulenc Ag Company, North Carolina. Unpublished.

Fish JD (1986) Temik Brand 15G Aldicarb Pesticide Granule Incorporation Study, Rhône-Poulenc 1988.

Fisher SW, Lydy MJ, Barger J & Landry PF (1993) Quantitative Structure-Activity Relationships for Predicting the Toxicity of Pesticides in Aquatic Systems with Sediment. Environ Toxicol Chem, 12: 1307-1318.

Fletcher DW (1988) Application of Temik Brand 15G Aldicarb to Three Major Crops: A Terrestrial Vertebrate Field Study. Bio-Life Associates Limited Study No 87 FV 3 dated 8 April 1988. Rhone-Poulenc Ag Company, North Carolina. Unpublished.

Gunther FA, Carman GE, Baines RC & Westlake WE (1975) Aldicarb (Temik) Residues in Oranges, Orange Leaves and Soil after Soil Application in an Orange Grove. University of Riverside, California. Unpublished.

Gustafson DI (1989) Groundwater Ubiquity Score: A Simple Method for Assessing Pesticide Leachability. Environ Toxicol Chem, 8: 339-357.

Haag KH & Habeck DH (1984) The Effect of Aldicarb on Nontarget Organisms in Citrus Groves. Proc Fla State Hort Soc, 97: 62-66.

Hamilton D & Haydon G (1996) Pesticides and Fertilisers in the Queensland Sugar Industry - Estimates of Usage and Likely Environmental Fate. Project: ICM-R&D.94.01. Resource Management Institute, Department of Primary Industries, Indooroopilly, Queensland, January 1996.

Handley JW, Sewell IG & Bartlett AJ (1991a) The Prolonged Toxicity of Aldicarb to Rainbow Trout (*Oncorhynchus mykiss*). Safepharm Report Reference 282/120 issued 14 October 1991. Rhone-Poulenc Agrochimie. Unpublished.

Handley JW, Sewell IG & Bartlett AJ (1991b) An Assessment of the Effect of Aldicarb on the Reproduction of *Daphnia magna*. Safepharm Report Reference 282/112 issued 14 October 1991. Rhone-Poulenc Agrochimie. Unpublished.

Handley JW, Mead C & Bartlett AJ (1991c) Assessment of the Algistatic Effect of Aldicarb to *Scenedesmus subspicatus*. Safepharm Report Reference 282/111 issued 14 October 1991. Rhone-Poulenc Agrochimie. Unpublished.

Handley JW, Grant-Salmon D & Bartlett AJ (1994a) The Acute Toxicity of Aldicarb Sulfone to *Daphnia magna*. Safepharm Report Reference 282/444 issued 29 December 1994. Rhone-Poulenc Secteur Agro, Sophia Antipolis. Unpublished.

Handley JW, Mead C & Bartlett AJ (1994b) Aldicarb Sulfoxide: Algal Inhibition Test. Safepharm Report Reference 282/441 issued 29 December 1994. Rhone-Poulenc Agrochimie. Unpublished.

Handley JW, Mead C & Bartlett AJ (1994c) Aldicarb Sulfone: Algal Inhibition Test. Safepharm Report Reference 282/443 issued 29 December 1994. Rhone-Poulenc Agrochimie. Unpublished.

Handley JW, Grant-Salmon D & Bartlett AJ (1995) The Acute Toxicity of Aldicarb Sulfoxide to *Daphnia magna*. Safepharm Report Reference 282/442 issued 6 January 1995. Rhone-Poulenc Secteur Agro, Sophia Antipolis. Unpublished.

Harkin J (1981) Aldicarb. Report dated 9 November 1981. Union Carbide, West Virginia. Unpublished.

Hawkes AW, Brewer LW, Hobson JF, Hooper MJ & Kendall RJ (1996) Survival and Cover-Seeking Response of Northern Bobwhites and Mourning Doves Dosed with Aldicarb. Environ Toxicol Chem, 15: 1538-1543.

Hilbig V (1979) Report on Palatability Studies and Trials Regarding the Acute Toxicity of the Plant Protection Products Temik 10G and Temik 10GGF (gypsum) with Japanese Quails, Chickens and Sparrows.

Hill EF & Camardese MB (1984) Toxicity of Anticholinesterase Insecticides to Birds: Technical Grade versus Granular Formulations. Ecotoxicology and Environmental Safety, 8: 551-563.

Hillman E (1990) Algae Growth Inhibition Test, Test Article Temik 5G. International BioResearch Project No 95-92-0285-01-90 dated 27 June 1990. Rhone-Poulenc Agro GmbH, Cologne. Unpublished.

Hitch (1982a) EPA-540/9-82-021 Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate. US Environmental Protection Agency, Washington DC, Office of Pesticide Programs, 18 October 1982. See also the updated versions of these test guidelines, available through the Internet at http://www.epa.gov/OPPTS_Harmonized/

Hitch (1982b) EPA-540/9-82-024 Pesticide Assessment Guidelines, Subdivision E, Hazard Evaluation: Wildlife and Aquatic Organisms. US Environmental Protection Agency, Washington DC, Office of Pesticide Programs, 18 October 1982. See also the updated versions of these test guidelines, available through the Internet at http://www.epa.gov/OPPTS_Harmonized/

Hollister TA (1981) Acute Toxicity of Temik to Mysid Shrimp (*Mysidopsis bahia*). AG&G Bionomic Report No BP-81-6-89 dated June 1981. Union Carbide Corporation, Georgia. Unpublished.

Howard PH (1991) Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Volume III, Pesticides. Lewis Publishers, Michigan, pp 1-10.

Howie B (1994a) Analysis of Tile Drain Water for Presence of Aldicarb Following Application of Temik 150G to Citrus at Waikerie in Australia. Rhone-Poulenc Rural Australia Pty Ltd. Report dated 31 August 1994. Unpublished.

Howie B (1994b) Analysis of Tile Drain Water for Presence of Aldicarb Following Application of Temik 150G to Citrus at Loxton in Australia. Rhone-Poulenc Rural Australia Pty Ltd. Report dated 31 August 1994. Unpublished.

Hudson RH, Tiucker RK & Haegele MA (1972) Effect of Age on Sensitivity: Acute Oral Toxicity of 14 Pesticides to Mallard Ducks of Several Ages. Toxicology and Applied Pharmacology, 22: 556-561.

IPCS (1991) Environmental Health Criteria 121: Aldicarb. International Programme on Chemical Safety, World Health Organisation, Geneva, 1991.

Jones RL (1996) Measurement of Aldicarb Degradation and Movement for Winter Application to Grapes. File number 45049 dated 16 April 1996. Rhone-Poulenc Ag Company, North Carolina. Unpublished.

Keats A (1991a) Aldicarb Residue Study in Soil and Cotton, Australia 1991. Rhone-Poulenc Rural Australia Pty Ltd report no AK/TN/AK91009 dated August 1991. Unpublished.

Keats A (1991b) Aldicarb Residue Study in Well, River and Dam Waters, Australia 1991. Rhone-Poulenc Rural Australia Pty Ltd report no AK/JG/AK001 dated September 1991. Unpublished.

Keats A (1991c) Aldicarb Residue Study in Surface Waters, Australia 1991. Rhone-Poulenc Rural Australia Pty Ltd report no AK/TN/AK91011 dated September 1991. Unpublished.

Keats A (1994a) Residues of Aldicarb and its Associated Metabolites Aldicarb Sulphoxide and Aldicarb Sulphone in Citrus Grove Drainage Water – Waikerie South Australia 1992. Rhone-Poulenc Rural Australia Pty Ltd report no AK94-054 dated 6 October 1994. Unpublished.

Keats A (1994b) Residues of Aldicarb and its Associated Metabolites Aldicarb Sulphoxide and Aldicarb Sulphone in Citrus Grove Drainage Water – Loxton South Australia 1992. Rhone-Poulenc Rural Australia Pty Ltd report no AK94-053 dated 5 October 1994. Unpublished.

Kendall RJ (1990) Behaviour, Survivability and Biochemical response of Wild Mourning Doves (*Zenaida macroura*) Dosed with Temik. TIWET Study No 08035 dated 23 March 1990. Rhone-Poulenc Ag Company, North Carolina. Unpublished.

Knott W & Beliles RP (1966) UC-21149 Acute Toxicity in Sunfish. Woodard Research Corporation Report dated 19 January 1966. Union Carbide Corporation, New York. Unpublished.

Kraft GJ & Helmke PA (1992) Dependence of Aldicarb Residue Degradation Rates on Groundwater Chemistry in the Wisconsin Central Sands. J Environ Qual, 21: 368-372.

Lee RE & Andrawes NR (1986) Aldicarb Anaerobic Aquatic Degradation. Union Carbide Agricultural Products Company, North Carolina. Company File No 34578. Report dated 3 April 1986. Unpublished.

Leistra M, Smelt JH & Lexmond TM (1976) Conversion and Leaching of Aldicarb in Soil Columns. Pestic Sci, 1976, 7: 471-482.

Lightfoot EN, Thorne PS, Jones RJ, Hansen JL & Romine RR (1987) Laboratory Studies on Mechanisms for the Degradation of Aldicarb, Aldicarb Sulfoxide and Aldicarb Sulfone. Environ Toxicol Chem, 6: 377-394.

Lin S-C, Funke BR & Schulz JT (1972) Effects of Some Organophosphate and Carbamate Insecticides on Nitrification and Legume Growth. Plant and Soil, 37: 489-496.

Lord KA, Briggs GG, Neale MC & Manlove R (1980) Uptake of Pesticides from Water and Soil by Earthworms. Pestic Sci, 11: 401-408.

Lund RC (1970) Potential Hazard of Temik 10G Aldicarb Pesticide to Ring-Necked Pheasant (*Phasianus colchicus terquatus*) from Simulated Spills. Letter report dated 17 September 1970 from New Jersey Department of Conservation and Economic Development to RG Haines, Union Carbide Corporation, New York. Unpuiblished.

Lykins HF (1971) Stability of Aldicarb in Water. Project No 111A13, Report dated 9 August 1971, Union Carbide Corporation, West Virginia. Unpublished.

McCall PJ, Swann RL, Laskowski DA, Unger SM, Vrona SA & Dishburger HJ (1980) Estimation of Chemical Mobility in Soil from Liquid Chromatographic Retention Times. Bull Environ Contam Toxicol, 1980, 24: 190-195.

Medd RK & Roberts NL (1972) Palatability and Acceptability of Temik (Corn Cob and Coal Formulations) to the Pheasant and the Pigeon. Huntingdon Research Centre Report No 5419/72/815 dated 29 September 1972. Union Carbide Switzerland. Unpublished.

Medd RK, Burrows IE, Roberts NL & Way DR (1972) The Determination of the Single Dose Oral LD50 (24 hour value) and Residual Levels of Temik (Coal) in the Pheasant. Huntingdon Research Centre Report No 5535/72/751 dated 28 September 1972. Union Carbide Europe. Unpublished.

Mensink BJWG, Montforts M, Wijkhuizen-Maślankiewicz L, Tibosch H & Linders JBJH (1995) Manual for Summarising and Evaluating the Environmental Aspects of Pesticides. Report No 679101022, RIVM (National Institute of Public Health and Environment), Bilthoven, the Netherlands, July 1995.

Moulton CA, Fleming WJ & Purnell CE (1996) Effects of Two Cholinesterase-Inhibiting Pesticides on Freshwater Mussels. Environ Toxicol Chem, 15: 131-137.

Mulla MS (1966) Toxicity of New Organic Insecticides to Mosquito Fish and Some Other Aquatic Organisms. Mosquito News, 26: 87-91.

Nash J (1990) Aldicarb Residues Exiting from Tile Drains in a Temik Treated Vineyard. Rhone-Poulenc Rural Australia Pty Ltd, report dated 15 November 1990. Unpublished.

Parrish RS, Smith CN & Fong FK (1992) Tests of the Pesticide Root Zone Model and the Aggregate Model for Transport and Transformation of Aldicarb, Metolachlor, and Bromide. J Environ Qual, 21: 685-697.

Pietrzik J (1992) Assessment of Side-Effects of Temik 5G on the Ground Beetle *Poecilus cupreus* L in the Laboratory. GAB Biotechnologie GmbH Report No 283/01-Pc dated 25 February 1992. Rhone-Poulenc Agro GmbH, Cologne. Unpublished.

Quraishi MS (1972) Edaphic and Water Relationships of Aldicarb and its Metabolites. Canadian Entomologist, 104: 1191-1196.

Richey FA (1972a) Water Leaching of Aldicarb, Aldicarb Sulfoxide, Aldicarb Sulfone and Internal Standard Chloride Ion in Columns of Four Soil Types. Project No 111A12, Report dated 7 January 1972, Union Carbide Corporation, West Virginia. Unpublished.

Richey FA (1972b) Upward Movement of Aldicarb through Soil during Water Evaporation. Project No 111A12, Report dated 18 August 1972, Union Carbide Corporation, West Virginia. Unpublished.

Romine RR (1973) Accumulation of Aldicarb Residues in Fish Tissue from Chronic Exposure to Aldicarb, Aldicarb Sulfoxide and Aldicarb Sulfone in Aquaria Water. Project No 111A13, Report dated 10 December 1973, Union Carbide Corporation, West Virginia. Unpublished.

Romine RR, Halstead CB and Gibson CE (1968) Leaching Characteristics of Temik 10G in Soils. Union Carbide Corporation, West Virginia. Unpublished.

Ross DB, Roberts NL & Cameron DM (1977a) A Comparison of the Acute Oral Toxicity (LD50) of Three Formulations of Temik to the Japanese Quail. Huntingdon Research Centre Report No UNC 68 WL/771042 dated 29 December 1977. Union Carbide UK. Unpublished.

Ross DB, Roberts NL & Ceichler AJ (1977b) Temik 10G – Gypsum Formulation (Blue) Wildlife Surveys Following Application to Four Sugar Beet and Four Potato Fields. Huntingdon Research Centre Report No UNC 57/774581 dated 20 December 1977. Union Carbide UK. Unpublished.

Ross DB, Roberts NL & Cameron DM (1978a) A Comparison of the Palatability to the Zebra Finch of Two Formulations of Temik. Huntingdon Research Centre Report No UNC 69 G/78398 dated 20 April 1978. Union Carbide Switzerland. Unpublished.

Ross DB, Roberts NL & Cameron DM (1978b) A Comparison of the Palatability to the Ring-Necked Pheasant of Two Formulations of Temik. Huntingdon Research Centre Report No UNC 69 G/78399 dated 18 April 1978. Union Carbide Switzerland. Unpublished.

Ross DB, Roberts NL & Cameron DM (1978c) A Comparison of the Palatability to the Ring-Necked Pheasant of Three Formulations of Temik 10G with Other Granular Pesticides. Huntingdon Research Centre Report No UNC 69C/78938 dated 16 October 1978. Union Carbide Switzerland. Unpublished.

Ross DB, Roberts NL & Cameron DM (1979) The Effect of Granule Size on the Toxic Hazard to Passeriformes of Temik 10G. Huntingdon Research Centre Report No UNC 69B/78721 dated 1 May 1979. Union Carbide Switzerland. Unpublished.

Schneider C, Vilkas AG & Hutchinson C (1979a) The Acute Toxicity of Aldicarb Technical to the Rainbow Trout *Salmo gairdneri* Richardson. Union Carbide Environmental Services, New York. Project No 11504-14-03 dated 19 March 1979. Unpublished.

Schneider C, Vilkas AG & Hutchinson C (1979b) The Acute Toxicity of Aldicarb Technical to the Bluegill Sunfish *Lepomis macrochirus* Rafinesque. Union Carbide Environmental Services, New York. Project No 11504-14-03 dated 19 March 1979. Unpublished.

Schupner JK (1980) The Acute Toxicity of Technical Grade (95.6%) Temik to the Mysid Shrimp, *Mysidopsis bahia*. Union Carbide Environmental Services, New York. Project No 11504-14-01 dated 19 May 1980. Unpublished.

Sheets KP & Hirsh DH (1976) Metabolism of Aldicarb in Anaerobic Muskingum Silt Loam Soil. Project No 111A13, Report dated 23 June 1976, Union Carbide Corporation, West Virginia. Unpublished.

Skinner WS (1995a) Aerobic Aquatic Metabolism of [^{14}C]Aldicarb. PTRL Report No 467W-1 dated 19 September 1995. Rhone-Poulenc Ag Company, North Carolina. Unpublished.

Skinner WS (1995b) Soil Adsorption/Desorption of [^{14}C]Aldicarb Sulfoxide by the Batch Equilibrium Method. PTRL Report No 463W-1 dated 21 February 1995. Rhone-Poulenc Ag Company Study No EC-94-276. Unpublished.

Skinner WS (1995c) Soil Adsorption/Desorption of [^{14}C]Aldicarb Sulfone by the Batch Equilibrium Method. PTRL Report No 464W-1 dated 21 February 1995. Rhone-Poulenc Ag Company Study No EC-94-277. Unpublished.

Smelt JH, Leistra M, Houx NWH & Dekker A (1978a) Conversion Rates of Aldicarb and its Oxidation Products in Soils. I. Aldicarb Sulfone. Pestic Sci, 1978, 9: 279-285.

Smelt JH, Leistra M, Houx NWH & Dekker A (1978b) Conversion Rates of Aldicarb and its Oxidation Products in Soils. II. Aldicarb Sulfoxide. Pestic Sci, 1978, 9: 286-292.

Smelt JH, Leistra M, Houx NWH & Dekker A (1978c) Conversion Rates of Aldicarb and its Oxidation Products in Soils. III. Aldicarb. Pestic Sci, 1978, 9: 293-300.

Smelt JH, Dekker A, Leistra M & Houx NWH (1981) Conversion of Four Oxime Carbamates in Soil Samples from Above and Below the Water Table. Institute for Pesticide Research, The Netherlands.

Smelt JH, Groen AE & Leistra M (1992) Transformation of ^{14}C-Aldicarb Sulfoxide and ^{14}C-Aldicarb Sulfone in Four Water-Saturated Sandy Subsoils. Confidential report generated by Winard Staring Centre for Integrated Land, Soil and Water Research, Wageningen, the Netherlands. Unpublished.

Smith CN & Parrish RS (1993) A Field Study to Evaluate Leaching of Aldicarb, Metolachlor, and Bromide in a Sandy Loam Soil. J Environ Qual, 22: 562-577.

Spare WC (1994) Soil Photolysis of Aldicarb. Agrisearch Project No 1515. Report dated 20 January 1993, amended 2 February 1994. Rhone-Poulenc AG Company, North Carolina. Unpublished.

Spurr HW & Sousa AA (1974) Potential Interactions of Aldicarb and Its Metabolites on Nontarget Organisms in the Environment. J Environ Qual, 3: 130-133.

Stirling G (1998) Nematodes are Important on Sugarcane. Australasian Nematology Newsletter, July 1998.

Supak JR, Swoboda AR & Dixon JB (1977) Volatilisation and Degradation Losses of Aldicarb from Soils. J Environ Qual, 1977, 6: 413-417.

Supak JR, Swoboda AR & Dixon JB (1978) Adsorption of Aldicarb by Clays and Soil Organo-Clay Complexes. Soil Science Society of America Journal, 1978, 42: 244-247.

Tait F (1972) Aldicarb. Wildlife Survey 1972. Unnumbered report, Duphar-Midox Ltd, UK. Unpublished.

Thun S (1990a) Final Report on the Investigation of the Lethal Effects of "Temik 5G" to Rainbow Trout (*Salmo gairdneri*) According to OECD Guideline 203. International BioResearch Project No 80-91-0285-04-90 dated 15 June 1990. Rhone-Poulenc Agro GmbH, Cologne. Unpublished.

Thun S (1990b) Final Report Prolonged Fish Toxicity Test in Rainbow Trout (*Salmo gairdneri*) Test Article Temik 5G. International BioResearch Project No 80-91-0285-05-90 dated 15 June 1990. Rhone-Poulenc Agro GmbH, Cologne. Unpublished.

Thun S (1990c) Final Report on the Investigation of the Lethal Effects of "Temik 5G" to *Daphnia magna* According to OECD Guideline 202. International BioResearch Project No 80-91-0285-02-90 dated 15 June 1990. Rhone-Poulenc Agro GmbH, Cologne. Unpublished.

Thun S (1991) Final Report 21 d Reproduction Test in Daphnia Test Article: "Temik 5G". International BioResearch Project No 80-91-0285-03-90 dated 7 January 1991. Rhone-Poulenc Agro GmbH, Cologne. Unpublished.

Tomlin CDS (Ed) (1997) The Pesticide Manual, 11th Edition. British Crop Protection Council, 1997.

US EPA (1994) Pesticide Reregistration Rejection Rate Analysis - Ecological Effects. United States Environmental Protection Agency (Prevention, Pesticides and Toxic Substances). EPA 738-R-94-035, December 1994.

Urban DJ & Cook NJ (1986) Hazard Evaluation Division Standard Evaluation Procedure Ecological Risk Assessment. US EPA document no 540/9-85-001 dated June 1986.

Vilkas AG (1977) The Acute Toxicity of Aldicarb Technical to the Water Flea *Daphnia magna* Straus. Union Carbide Environmental Services, New York. Project No 11504-14-01 dated 15 November 1977. Unpublished.

Vonk JW (1991) The Transformation of the Oxidation Products of Aldicarb in an Anaerobic Saturated Subsoil. TNO Institute of Environmental Sciences Report No R90/454 dated 5 November 1991.

Woodham DW, Reeves RG & Edwards RR (1973) Total Toxic Aldicarb Residues in Weeds, Grasses, and Wildlife from the Texas High Plains Following a Soil Treatment with the Insecticide. J Agric Food Chem, 21: 604-607.

Young Song M, Stark JD & Brown JJ (1997) Comparative Toxicity of Four Insecticides, Including Imidacloprid and Tebufenozide, to Four Aquatic Arthropods. Environ Toxicol Chem, 16: 2492-2500.

Zigas P (1973) Effect of Temik 10G on Beneficial Organisms Associated with Cotton Grown in the USA. Unnumbered Report prepared 20 October 1973. Union Carbide Corporation, California. Unpublished.