Section 6

Environmental Assessment

TABLE OF CONTENTS

1 INTRODUCTION

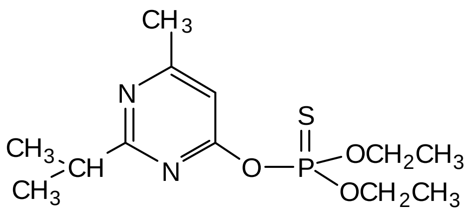
Diazinon is an organophosphorus insecticide with widespread uses. Its major use is for the control of lice, blowflies, ked, ticks in sheep, cattle, goats and dogs etc. Agricultural uses are for control of aphids, caterpillars, moths, butterflies, jassids, various worms, thrips, locusts, grasshoppers and scale in pastures, orchards, vegetables and field crops. There are other uses for commercial, industrial and domestic buildings, farm buildings and garbage containers for control of cockroaches, silverfish, carpet beetles and other household pests, maggots in garbage etc.

Diazinon has been reviewed by the Danish Environmental Protection Agency and their report was published in 15 December 1994. It has also been reviewed by the Dutch CTB in November 1992 and by the English MAFF in April 1991. There is also a 1993 report commissioned by Ciba-Geigy on the environmental impact of diazinon from use in sheep dips in the UK. These reports were available to Environment Australia.

In July 1990, the USEPA finalised the cancellation of registration for use of diazinon on golf courses and sod (turf) farms (but not domestic lawns) due to unreasonable risk to birds. The USEPA is currently reviewing diazinon as part of their re-registration progress for all organophosphate insecticides and a draft report has been published on the Internet (US EPA, 2000).

1.1 Chemical Identity

Chemical name:	O,O-Diethyl O-(2-isopropyl-6-methylpyrimidine-4-yl) phosphorothioate [CAS]
Common name:	Diazinon
Manufacturer's code:	GS 24480
CAS Registry number:	333-41-5
Molecular formula:	$C_{12}H_{21}N_2O_3PS$
Structural formula:	



Molecular weight:	304.3

1.2 Physico-Chemical Properties

The following physico-chemical properties are from the TGAC submission of Ciba-Geigy. They refer to the pure ingredient unless otherwise stated. The technical grade material is >90.2% pure.

Appearance:	Colourless liquid. The TGAC is a clear yellow to brown liquid.
Odour:	Not specific
Melting Point:	Not applicable
Boiling Point:	83-84 °C @ 0.002 mm Hg
Specific Gravity/Density	TGAC approximately 1.11 @ 20 °C
Vapour Pressure:	4.7 x 10^{-3} Pa @ 20 °C
Solubility in Water	40 mg/L @ 20 °C
Octanol-Water Coefficient.	Log P_{ow} = 3.95
Henry's Constant	3.53 x 10^{-7} atm.m^3/mol
Dissociation Constant:	Given as Ka = 230 ± 0.05.

1.2.1 Henry's Law Constant

The calculation of the Henry's Law constant for diazinon was conducted by Environment Australia and was based on the above data for vapour pressure and water solubility. The constant H, was determined to be 3.53 x 10^{-7} atm.m^3/mol and indicates that diazinon has low volatility from water.

1.2.2 Summary of Physico-Chemical data

From the physico-chemical properties, diazinon is moderately soluble in water and highly soluble in organic solvents. It has a strong partition coefficient and moderate binding to sediment/soil is expected. It is slightly volatile but has low volatility from water.

2 ENVIRONMENTAL EXPOSURE

2.1 Environmental Release

2.1.1 Volume

There are over 100 currently registered products in Australia and 31 registrants. These products are EC formulations, micro-encapsulated products, powders and solid formulations. The breakdown of the number of products used in various markets is given below in Table 1 for 1997. In 1996-7 there were approximately 163 tonnes of active used. Use of diazinon for ectoparasiticides control in sheep and in dog washes is decreasing, with use for fly control in cattle expected to increase. Overall use of diazinon is expected to remain stable or slowly decease, in particular dog washes and collars declining (See Agricultural Assessment).

Product type	Number of Products	Product type	Number of Products
Agricultural	4	Home and Garden	13
Ectoparasiticides	29	Dog washes	5
PCO	13	Flea collars	32
Turf use	3		

Table 1. Breakdown of products and their principal uses for 1997.

2.1.2 Application and Use Pattern.

2.1.2.1 Agricultural

Diazinon (as a 800 g/L EC formulation) is registered for use on field crops; pasture, lucerne, cereals (including maize and sorghum), oil seed crops (including cotton), sugar cane and rice and is for the control of cabbage moth, cabbage white butterfly, midge, locust, grasshoppers, webworm, armyworm, cutworm, bloodworm and hoppers. For plantation and orchard crops, diazinon is used to control scale, borers, thrips, citrus leaf miner, bugs and coccid, with use in grapes for mealy bugs. For vegetable crops it is used to control caterpillars, cabbage moth, potato moth, cabbage white butterfly, midge, locust, grasshoppers, webworm, armyworm, cutworm, bloodworm and loopers.

The maximum use rates stated on the label are: 1-1.4 L/ha (800-1120 g ai/ha) for grasshoppers in field and pasture crops; 3–5 L/ha for seed maggots in beans: 125 mL/100 L (100 g ai/100 L) for banana borer and macadamia felted coccid in bananas and macadamia nuts and 0.7-4 L/ha for caterpillars, cabbage moth, cabbage white butterfly and cutworms in vegetable crops. The label for agricultural uses is summarised in Table 2.

Rates on label,	Crops	Pests
800-1120 g ai/ha	Pasture, sorghum	Grasshoppers
280-560 g ai/ha	Sorghum	Sorghum midge
560-680 g ai/ha	Pastures, cereals, oil seed crops, sugar cane and soybeans	Spur throated, Plague and Migratory locusts
800 g ai/ha	Pasture and cereals	Armyworm, cutworm
60-280 g ai/ha	Rice	Brown plant hopper and bloodworm
52 g ai/100 L	Apples, pears, citrus, stone fruit, pineapples	Range of orchards pests, including scale, aphids
100 g ai/100 L	Macadamia nuts, bananas	Felted coccid, banana weevil borer
1200-2400 g ai/100 L	Pineapples	Mealy bug
24 g ai/100 L	grapes	Mealy bug
560-1120 g ai/ha	Brassicas, capsicum, eggplant, sundry vegetables	Caterpillars, cutworms, cabbage butterflies and moths
280 g ai/ha	Beans, cucurbits, tomatoes	Bean fly, thrips
800 g ai/ha	Potato	Potato moth
2400-4200 g ai/ha	Beans	Seed maggot

Table 2. Summary of label for currently registered agricultural uses.

Current usage is limited with the agricultural report identifying pineapple, mushrooms, macadamia nuts, ornamentals and some vegetables crops (onions, garlic, cucurbits, capsicum, carrot, celery, sweet corn, cauliflower, rhubarb, silverbeet, beetroots and beans) as principal current uses. The use in mushrooms is at spawning and after casting. When applied at spawning the rate is 110 g ai/10 L of water per tonne of moist composed and the rate after casting is 24 g ai/10 L per tonne of moist compost sprayed over the top of the casing soil.

It is normal practice in orchards situations to spray to runoff, normally requiring 1500 to 3000 L/ha of spray solution for pome and stone trees but this could be as high as 4000 L/ha for larger trees and in citrus 6000-10,000 L/ha. These figures correspond to application rates of between 780 g ai/ha and 1560 g ai/ha but could be as high as 2000 g ai/ha for 65 mL/100 L. For citrus the application rates correspond to 3.12-5.2 kg ai/ha again at 65 mL/100 L.

The use pattern, as stated on the label, is as necessary or when pests are present for most field crops and orchards. For vegetable crops the label states application when necessary or every 10-14 days.

The labels give directions for application to field and pasture crops by aircraft, boom sprayers and mister and for vegetables by boom sprayer and knapsack. Aerial application is normal for application to cotton (very little diazinon is used in cotton) and has been used on rape, turnips, tomatoes, bananas, capsicums, potatoes and forage brassica crops.

Product labels do not specify types of spray equipment or any information concerning the use of low volume application equipment. Information on minimising spray drift—size of spray droplets etc., is also not given on the label.

2.1.2.2 Veterinary Uses

Veterinary usage is the major use, with most use for control of lice, ked and blowfly on sheep by dipping or jetting, with other significant uses being as shower dip or hand spray for lice and buffalo fly on cattle, lice on goats, lice and mange on pigs. There are approximately 30 products registered for used as ectoparasiticides on a range of animals. The rates used are 50 or 100 mL/100 L for dips, 200 mL/100 L for jetting and 250 mL/100 L for hand spraying. Table 3 gives a more detailed listing for some of these products and the use pattern. Note that some products in Table 3 are in combination with other actives.

In addition to the above uses in dips etc, diazinon is used in backrubbers to control buffalo fly in cattle. The Coopers Di-jet directions for this use are 100 g ai/10 L of oil and soak the backrubber, with repeats as necessary. Diazinon is also used in insecticidal cattle ear tags to control buffalo flies.

There are diazinon product/formulations for use as wound dressing in sheep, cattle and horses. Superficial wounds are to be treated with the material applied undiluted directly to the wound. This is applied directly (puffers, powders, sprays etc) to the wound and is used after mulesing, shearing and de-horning.

For domestic animals, diazinon is used in dog washes at 0.5 g ai/L of the wash and in pet shampoos to control fleas, lice and ticks. It also used in some cat and dog collars to control fleas.

Product	Animal	Pests	Rates and Comments
Coopers 4-in-1 Dip	Sheep	Lice, ked itch mite and blowfly	Plunge and shower dip: 150 g ai/1000 L, Constant replenishment shower dip: 300 g ai/1000 L
Coopers Blaze Long Woolled Sheep Lice Treatment	Sheep	Lice	5 mg/sheep, wool 6 weeks to 4 months 10 mg/sheep, wool 5-9 months
David Grays Diazinon Sheep Dip Jetting Fluid and Blowfly Dressing	Sheep	Lice, and ked	Plunge, shower and constant replenishment shower dip: 100 g ai/1000 L.
		Blowfly	Plunge and shower dip: 200 g ai/1000 L; Constant replenishment shower dip: 400 g ai/1000 L; jetting: 400 g/1000 L
Coopers Di-Jet Sheep Dip/Jetting Fluid, Cattle and Pig Spray	Sheep	Lice and ked	Plunge, shower and constant replenishment shower dip: 100 g ai/1000 L.
		Blowfly	Plunge and shower dip: 200 g ai/1000 L; Constant replenishment shower dip: 400 g ai/1000 L; jetting: 400 g/1000 L
	Goats	Lice	Hand spray at 10 g ai/20 L. Second treatment may be required 16 days later
	Cattle	Lice	Hand spray at 50 g ai/100 L. Second spraying 16-17 days to break life cycle
	Pigs	Lice	Hand spray at 50 g ai/100 L. 3 applications at 10 days intervals

Table 3. A sample of some of the labels for diazinon used as ectoparasiticides. Products used for plunge and conventional shower dips have additional instructions for replenishment (topping up) and reinforcement (dipping out).

2.1.2.3 Other Uses

There are other uses for diazinon on registered labels. Use in homes, flats, hotels, commercial and industrial buildings (including kennels, stables and piggeries), ships, refuse areas and garbage containers for control of cockroaches, silverfish, carpet beetles and other household pests, maggots in garbage. It is also used for mosquito control in ponds and stagnant water as well as on hides and skins to control skin and hide beetles.

Domestic uses included use for control of ants (both as EC and powder formulations), use in home gardens for citrus leaf miner, cabbage white butterflies, caterpillars, aphids etc. and for lawn grubs and other pests. There is a surface spray product for crawling insects.

2.1.2.4 Micro-encapsulated Formulation (CS)

A micro-encapsulated formulated product, Knox-Out, is registered for use in homes, flats, hotels, commercial buildings, industrial buildings, and buildings (including kennels, stables and piggeries), ships, refuse areas and garbage containers for control of cockroaches, silverfish, carpet beetles and other household pests. The two rates on the labels are 50-100 g ai/10 L for cockroaches, silverfish and ants, and 100 g ai/10 L for fleas, ticks, flies and perimeter treatment. Application is as a fine spray to homes, flats, hotels, commercial buildings, etc or by paint brushes for cockroaches and silverfish. Pennside, another CS product by the same registrant, is used for turf use to control Argentine stem weevil (30-60 g ai/15 L per 100 m^2), African black beetles (30 g ai/15 L per 100 m^2), mole crickets (48 g ai/15 L per 100 m^2) and caterpillars (7.2 g ai/15 L per 100 m^2). Pennside is sprayed onto turf with directions to irrigate immediately after application with equivalent of 2 mm of water.

2.1.3 Environmental Occurrences

2.1.3.1 Australian reports

Diazinon has been detected (0.1 µg/L detection limit) in surface water drains from farms twice during 1991-1993 in the irrigation areas of NSW and once in 1994-1995 at 0.13 µg/L (Bowmer, Korth, Scott, McCorkelle and Thomas, 1998).

Diazinon has also been found in several sewage treatment plants (STP) effluent in Sydney at concentrations up to 1.81 µg/L, with median concentrations of between 0.14 and 0.39 µg/L for a number of STPs (Sydney Water Corporation, 1999). As this is from just 4 samples per STP taken after treatment (secondary and tertiary) of the sewage and as significant adsorption to the organic matter (sludge) is expected, the results are unexpected. These indicate that significant amounts of diazinon are entering the sewage system. While the report from the Sydney Water Corporation does not indicate the likely source of the diazinon, these residues are likely from domestic use for insect control, and disposal of used dog washes and shampoos. Note that domestic insect control is done by both householders and from professional pest control operators (the latter shouldn't dispose of waste diazinon to sewage). As well, the use of dog washes and shampoos containing diazinon to control ticks, fleas etc is carried out by the general public and professional operators (including companion animal groomers, kennels and mobile pet washers/groomers).

In a flow-up study, whole effluent toxicity testing using effluent from 18 sewage treatment plant (STP) and *Ceriodaphnia dubia* as the test organism showed that 15 of the effluents were toxic to *C. dubia* and most of the toxicity considered due to organophorphorus insecticides (Bailey, Krassoi, Elphick, Mulhall, Hunt, Tedmanson and Lovell, 2000). Diazinon was identified as the principal toxicant in 6 of these STP effluents with concentrations ranging from 0.34 µg/L to 1.81 µg/L.

Diazinon is a significant contaminant of Australian wool, with monitoring of the wool clips in 1997/98 finding a mean concentration of 5.4 mg ai/kg wool (Savage, 1998). When the wool is scoured, most of the pesticides are removed with the wool wax, with approximately

65% of the wax discharged in the scouring effluent, and could be a significant source of environmental contamination.

2.1.3.2 Overseas reports

Diazinon was the most commonly detected insecticide from streams in the urban areas of the USA, with 70% of streams tested having >0.01 μg/L and 30% >0.05 μg/L (Gilliom, Barbash, Kolpin and Larson, 1999). This report is from the US Geological Survey under the National Water Quality Assessment Program and covered approximately 40% if the conterminous US and 60-70% of water use in the US. Approximately 75% of streams in urban areas and 25% in the agricultural areas exceed the US aquatic life criteria for diazinon. There was only 10% of streams in the agricultural areas showing diazinon at >0.01 μg/L and <5% with levels of >0.05 μg/L. There were effectively no detections in groundwater of any note. A similar report has been published on the World Wide Web at http://water.usgs.gov/pubs/circ/circ1225.

Hoffman et al (2000) have published a more detailed analysis of the detection of pesticides in urban streams in the US. Diazinon and carbaryl were the insecticides most frequently detected (70 and 44% of samples, respectively), dominating the total insecticide concentration (>80% on 76% of the sampling dates) and exceeding the criteria for the protection of aquatic life in many of the urban streams in spring and summer. The highest detected level was 1.4 μg/L.

Farm ditches in the Lower Fraser River Valley in British Columbia, Canada were tested for pesticides during a 6 month period from July to December (Wan, Szeto and Price, 1994). These ditches drained farmland only used for production of market garden type crops. Diazinon was found in all 7 ditches during the period of testing, with the most contaminated ditch having maximum levels of 0.51 μg/L (9/14 samples had detectable residues, mean 0.12 μg/L).

In a review of the impact of golf courses on water quality in the US, a number of studies were summarised which showed that from 57 surface water samples 8 contained detectable residues of diazinon (Cohen, Svrjcek, Durborrow and Barnes, 1999). The highest detection was 1.4 μg/L. It is noted by the authors that diazinon use was banned earlier and that the diazinon detected is likely to have come from home lawn use. In the US golf courses are frequently part of housing developments.

In a report on the risks of pesticides to groundwater ecosystems in the Netherlands, diazinon was reported to have been found in groundwater in Europe (Health Council of the Netherlands, 1996). There are few details on the extent of the contamination or on the concentration at which it was found. Diazinon was been found in the Ebro (Spain) and Louros (Greece) Rivers at levels of 0.028 and 0.030 μg/L respectively in one sample each (the Ebro was sampled twice and the Loures 3 times) (Steen, Leonards, Brinkman, Barcelo, Tronczynski, Albanis and Cofino, 1999).

In a study of streams in two urban areas in Northern California during the precipitation season (October to May) over a 2 year period, the concentration of diazinon in 231 samples ranged from below detection (< 0.030 µg/L) to 1.50 µg/L, with a median of 0.210 µg/L (Bailey, Deanovic, Reyes, Kimball, Larson, Cortright, Connor and Hinton, 2000). Diazinon has been detected and found to be one of the primary toxicants in the Sacramento-San Joaquin river delta, with measured concentrations between 0.11 and 0.422 µg/L (Werner, Deanovic, Connor, De Vlaming, Bailey and Hinton, 2000). It should be noted that chlorpyrifos was mostly detected with diazinon but at lower concentrations.

Stuifzand et al (2000) report that high concentrations (up to 0.6 µg/L) of diazinon were detected twice in the River Meuse during 1996. During one of these incidental diazinon peaks, almost complete mortality (95-99%) of hydropschyhid caddis flies and chironomids was observed. Note that this level is lower than the daphnia end point used in the hazard assessment, though the impact of other toxicants in the river is unclear.

2.1.4 International Reviews And Data

As noted above the US EPA is conducting a review of diazinon under their Re-registration Eligibility Decision (RED) program and has published a preliminary risk assessment report (US EPA, 2000) seeking public comment on the use of diazinon in the US. The use pattern for diazinon in the US is that most uses are non-agricultural, some 75% of the total 2 600 tonnes used annually, with 39% used by homeowners. These uses are for structure and lawn pest control around building and the highest agricultural use is for almonds. In Australia the major use is for veterinary usage (see section 2.1.2.2 above).

In the US EPA review there is reference to incidents reports for both aquatic and birds. There were 58 bird kills reported to the US EPA in the last 5 years (more than for any other pesticide) and roughly 200 reported, the majority since 1987 with a number of these were associated with lawn and other turf uses. The report indicates that this represents a small number of the total bird kills due to this pesticide. These incidents have occurred with both liquid and granular formulations (unclear as to what are liquid formulations but assumed to be EC formulations). This is despite of a review in 1988 into bird kills associated with use of diazinon and the deletion of use for golf courses and sod farms, label changes and reduced rates. Diazinon has caused the second largest number of total known incidents of bird mortalities in the US, exceeded only by carbofuran.

Additional water monitoring studies are reported in the US EPA Review, again showing that diazinon is a wide spread contaminant in surface waters, especially in urban areas. Diazinon is reported in major USA rivers, including the Rio Grande, Mississippi and the Columbia. The finding of diazinon in these very large rivers is extremely significant given the size of the river flow, indicating the total mass of the pesticide in these rivers is high. Many wastewater treatment facilities have high diazinon residues in their effluent. The review states that diazinon is the most common organophosphate compound detected in air, rain and fog.

Following the public comment phase, the US EPA reached agreement with makers of diazinon to phase out both indoor and outdoor residential uses of the pesticide (Chemical Regulation Reporter 2000). There is to be a 50% phase-down in production of the pesticide by 2003, with the product not expected to be available for retail sale for the above uses after 2004. By contrast some agricultural uses such as almonds, prunes, plums, lettuce and nectarines, among other foods, will continue.

Concern has recently been expressed that diazinon use may pose a threat to salmon, considering that concentrations found in the US Geological Survey are above aquatic life trigger levels in West Coast States (Chemical Regulation Reporter 2001a). National Marine Fisheries Service studies are said to suggest that diazinon exposure can disrupt the salmon's sense of smell, making it difficult for them to find their way to their spawning grounds. This has caused the Californian water agencies to tell the US EPA that they are concerned that the agency's agreement with diazinon registrants is insufficient to protect the State's water quality. Other stakeholders are also seeking a more rapid phase-out (Chemical Regulation Reporter 2001b).

The US EPA has recently agreed to technical registrants' requests to terminate all indoor and some agricultural uses of diazinon registrations (Chemical Regulation Reporter 2002). The indoor uses include applications for pet collars, aircraft, food and feed handling establishments, greenhouses, schools, residences, commercial buildings, sports facilities stores, warehouses and hospitals. Among the 28 agricultural uses to be cancelled are applications to a variety of fruit, vegetable and cotton crops, along with uses for forestry, tobacco and pastures.

2.1.5 Formulation, handling and disposal

Diazinon as an emulsifiable concentrate is currently formulated and sold at between 800 to 60 g ai/L containing hydrocarbon solvents, surfactants and other additives. There are several other formulation types registered including powders (15 g/kg) and solutions (1 g/L) as wound dressings for sheep and cattle, backlines, micro-encapsulated (capsulated suspensions, CS) and as solid formulations for ear tags and flea collars. The micro-encapsulated formulation is prepared from the TGAC in water containing emulsifiers and a suspending agent. The EC formulation is sold in a range of containers from 200 mL bottles for domestic use to 200 L drums for farm use.

Formulating the EC from the imported TGAC is a straightforward process of mixing the chemical with the hydrocarbon solvent and other additives to make the emulsifiable concentrate. The EC formulation is then transferred into the relevant containers. During these processes the chances of a significant spill are minimal and any spills are expected to be treated according to the MSDS, and involve sweeping up spills by use of absorbent materials such as hydrated limes, saw dust, clay or fuller's earth etc (based on European MSDS). Likewise spills that occur during transport are also expected to be treated according to the MSDS.

Some of the labels from different companies do not appear to comply with current labelling practices with respect to rinsing and disposal of used containers. All currently registered labels and currently sold products should comply with the current labelling requirements with respect to rinsing and disposal of containers, ie

> Triple rinse or preferably pressure rinse empty containers before disposal. Add rinsings to the spray tank. Do not dispose of undiluted chemical on site. Return the empty container for recycling where this is an option or for disposal at a landfill authorised to accept that waste. If none of these options are available, bury the containers below 500 mm in a disposal pit specifically marked and set up for this purpose, clear of waterways, vegetation and roots. Empty containers and product should not be burnt.

3 ENVIRONMENTAL FATE

3.1 Chemical Degradation

All of the following reports for chemical fate and degradation were submitted by Novartis in response to the ECRP data call-in, unless otherwise stated. The studies presented here were performed according to Good Laboratory Practices and according to internationally acceptable guidelines.

Diazinon is known to form toxic metabolites on storage, in particular sulfotep (O,O,O,O-tetraethyldithiopyrophosphate,) and monotep (O,O,O,O-tetraethylmonothiopyrophosphate). These toxic metabolites were not detected in the hydrolysis, photolysis or metabolism studies, nor would such metabolites be expected. These metabolites and their formation have been discussed at some length in the Chemistry Section of this report.

3.1.1 Hydrolysis as a function of pH

3.1.1.1 Study No 1

The hydrolysis of radiolabelled diazinon (^{14}C in ring) was determined at pH 5, 7 and 9 at a concentration of approximate 10 mg/L in aqueous solutions (Matt, 1988). The study was conducted according to US EPA Guideline 161-1.

The sterile buffered solutions in duplicate were kept at 23-25 °C in the dark and sampled at days 0, 2, 5, 8, 11, 14 and 21 for pH 5 and days 0, 5, 11, 21, 29 and 32 for pH 7 and 9. The solutions were analysed by liquid scintillation counting (LSC) and HPLC. The samples for the last sample interval were also analysed by 2D TLC. Sterile handling techniques were used during sample preparations.

From the first order rate constant, the half lives were calculated to be 12 days (pH 5), 138 days (pH7) and 77 days (pH 9). The fit to first order kinetics equation was >0.954 in all cases, showing that hydrolysis could be adequately be described as first order.

The hydrolysis products were not identified but a reference was made to published report that showed that 6-hydroxy-2-isopropyl-4-methylpyrimidine was the major product.

3.1.1.2 Study No 2

The hydrolysis of diazinon (purity not given) was determined at pH 5, 7 and 9 at a concentration of 10 mg/L in aqueous solution (1% acetone) (Burkhard, 1979). The buffered solutions were kept at 30, 50 and 70 °C and sampled at various time intervals. The solutions were analysed by gas chromatography (GC). There was no indication given in the report that conditions were sterile.

From the first order rate constant and the Arrhenius equation, the half lives at 20 °C were calculated to be 3.8 days (pH 5), 78 days (pH 7) and 40 days (pH 9). The fit to first order kinetics equation was >0.98 in all cases, showing that hydrolysis could be adequately be described as first order.

There were two hydrolysis components noted in the HPLC, one of which was identified as 6-hydroxy-2-isopropyl-4-methylpyrimidine (oxypyrimidine or G 27550, see Attachment 1) by comparison with authentic samples. The other component in the HPLC analysis was not identified and not reported in the TLC analysis. It is unclear in the report as to whether this unidentified component is an artefact of the HPLC analysis or not.

It is noted by Environment Australia that the half lives in study No.1 (Matt, 1988) are longer than for study No. 2. A clear explanation is not readily identifiable from the two reports. However, the studies were not performed in identical conditions, the presence of acetone in study No.2 and the samples may not have been kept under subdued light together with the lack of sterile conditions may account for some of the apparent increase in the rate of hydrolysis in this study.

3.1.1.3 Literature

In an old report the kinetics of hydrolysis of diazinon and diazoxon have been reviewed and studied (Gomaa, Suffet and Faust, 1969). The study was performed similar to that described above but the water used was likely to be sterile (double distilled from alkaline permanganate). The half-life was determined to be 11.77 hours (pH 3.1), 30.9 days (pH 5.0), 184.8 days (pH 7.4), 134.8 days (pH 9.0) and 144.9 hours (pH 10.4).

The hydrolysis product was collected from the GC and identified (IR and UV) as 6-hydroxy-2-isopropyl-4-methylpyrimidine (oxypyrimidine) by comparison with an authentic sample. The yield of this product was demonstrated to be essentially quantitative.

The hydrolysis of diazoxon was performed as for diazinon and the half-lives calculated to be 22.8 minutes (pH 3.1), 30.7 hours (pH 5.0), 28.9 days (pH 7.4), 18.4 days (pH 9.0) and 10.1 hours (pH 10.4). The hydrolysis of diazoxon is quicker than diazinon.

3.1.1.4 Conclusion

From three experiments, it may be concluded hydrolysis of diazinon is relatively slow at pH 7 and 9 and is classified as slightly hydrolysing (Netherlands classification, see Mensink, Montforts, Wijkhuizen-Maślankiewicz, Tibosch and Linders, 1995). At pH 5 the hydrolysis is faster and diazinon is classified as fast to moderately hydrolysing. Hydrolysis could be a significant contributor to the overall degradation of diazinon in the environment under acidic conditions.

3.2 Photodegradation

3.2.1 Aqueous Photolysis

3.2.1.1 Aqueous Photolysis - US EPA Guidelines Artificial Light

The aqueous photolysis of ^{14}C-diazinon methyl (labelled at C2) was performed according to US EPA Guideline 161-2 (Spare, 1988).

The study was conducted at pH 7 in phosphate buffer at 25 °C and at a nominal concentration of 10 µg/mL for a period of 192 hours of continuous exposure under sterile conditions (in duplicate). A medium pressure mercury lamp with a filter (290 nm and lower cut off) was used as the light source. It was stated that the spectrum of the lamp approximated natural sunlight but the intensity was approximately twice that of natural sunlight at Maryland USA during a clear summer day (39.25° N latitude, midday).

The half-life was determined to be 121 and 122 hours of continuous exposure in replicate one and two respectively, based on TLC analysis of the parent compound (average from 2 solvent systems). The half-lives are based on the first 144 hours of irradiation due to build up of particulate matter in the external water jacket after 144 hours which reduced exposure. The dark control did not show any significant degradation, with 97% recovery of diazinon after 192 hours. There was some degradation due to abiotic hydrolysis with 2.5% of oxypyrimidine in the dark control at the end of the study.

There were three metabolites detected in the TLC analysis, one of which was major and identified as oxypyrimidine by TLC and 2D-TLC using reference compound. The other two metabolites did not exceed 10% of applied radioactivity and therefore were not identified.

Assuming 12 hour exposure days and that the lamp has twice the intensity of natural sunlight, the half lives correspond to approximately 20 days of natural sunlight.

3.2.1.2 Aqueous Photolysis - US EPA Guidelines Natural Light

The aqueous photolysis of ^{14}C-diazinon (labelled at C2) was performed according to US EPA Guideline 161-2 (Spare, 1988A).

The study was conducted at pH 7 in phosphate buffer at 25 °C and at nominal concentration of 10 µg/mL for a total period of 360 hours of continuous exposure under sterile conditions (in duplicate). The samples were exposed during reasonably clear days at 39° 25` latitude from 9 May to 11 June. When not exposed the samples were stored in a refrigerator at 4 °C in the dark.

Samples were taken at 0 and 5 hours, and 1, 2, 4, 6, 12, 20 and 30 days during the exposures, with one exposure day being equal to 12 hours of sunlight exposure. All samples were analysed by liquid scintillation counting (LSC) and TLC (2 solvent systems), with the day 30 samples being also analysed by 2D-TLC. The half-lives were determined by first order kinetics.

The half-lives were calculated as 559 or 620 hours of continuous exposure, depending on the solvent system used for the TLC analysis. The exposure data used was corrected for degradation observed in the dark controls. Using the assumption that there are 12 hours of sunlight per day, the half-lives are 46.6 and 51.7 days. The major metabolite was oxypyrimidine, which slowly increased to reach 37.5% of the applied dose at the end of the study period from one-dimensional TLC. In the 2D-TLC, the radioactive zones were scraped and analysed by LSC, which gave 17.1% of the AR as oxypyrimidine. Other metabolites were individually < 10% of the applied radioactivity and were not identified.

3.2.1.3 Phototransformation in water according to German Guidelines.

A study was undertaken to determine the phototransformation of diazinon in water in accordance with UBA Test Guideline "Phototransformation of Chemicals in water" (Klöpffer, 1991).

The method used is based upon the experimental determination of the quantum yield and subsequent calculation of the half-life in water under natural sunlight. The UV absorption showed little significant absorption above 307 nm and the photodegradation experiment was performed using monochromatic light at 304 nm for a total of 310 hours (experiment performed in a grating monochromatic apparatus). Analysis of the solution was performed by HPLC.

Analysis of the irradiated solutions showed no significant degradation over the period of irradiation. A limit of the quantum yield was determined as <0.3 (assuming maximum degradation = C_o – standard deviation.). This was then used to determine the minimum environmental half-life in central Europe during April as >0.2 x 10^4 days for distilled water, 1 cm deep. These results indicate that direct aqueous photodegradation of diazinon is unlikely under environmental conditions.

There is some discrepancy between these results and those of the previous study in natural sunlight done according to US EPA Guidelines. Given that the US EPA results used natural sunlight and are experimentally derived, these are considered by Environment Australia as being more relevant.

3.2.1.4 Earlier Study No. 1

The aqueous photolysis for a sample of ^{14}C-diazinon (position of label not given) was performed according to AG-208, 'Preparation of a Model System to Study Aqueous Solution Photolysis in a Laboratory Environment" (Frank, Balu and Hofberg, 1972). This protocol is not recognised as being internationally accepted and is likely to be an in-house method.

Aqueous solutions of ^{14}C-diazinon were prepared and exposed to artificial and natural sunlight. For each exposure there was a dark control. The sunlight exposure lasted for approximately 14 days at Ardsley, New York. There was no information on the type of artificial light source used or how this relates to environmental exposures. The aliquots taken during the exposures were extracted then analysed by GC and thin layer chromatography (TLC). Photolysis products were identified by mass spectroscopy.

The analysis of the artificial sunlight exposure samples showed that after 3, 20 and 97 hours of exposure there was 4.2%, 11.5% and 52.6% reduction in the diazinon concentration compared to controls. Analysis of the products showed that only one product was detected which was identified as oxypyrimidine. For the dark controls there was no detectable decrease in the concentration of diazinon. It is noted by Environment Australia that the half-life would be approximately 100 hours.

In contrast, analysis of the sunlight exposed and dark control samples after approximately 14 days showed no significant difference. There was 67.3% of the initial diazinon recovered in the exposed samples and 79.5% in the control sample. Since both samples showed 20-30% decomposition, it was concluded that the observed difference of 12.2% was not significant.

Environment Australia notes that this study was not performed to current international requirements and the description of the methodology used is brief and is missing critical information on exposure conditions. Therefore the results are of limited value.

3.2.1.5 Earlier Study No. 2

The photolysis of ^{14}C diazinon was studied using an artificial light source in buffered water solution (Martinson, 1985).

An aqueous solution of radiolabelled diazinon (concentration 8.39 mg/L, in deionised water buffered to pH 7.0) was irradiated for up to 362 hours using a mercury vapour lamp. A UV filter was used to cut out wavelength below 280 nm. The irradiated solutions were sampled (0, 18, 42, 69, 100, 150 and 362 hours), then directly spotted to TLC plates for analysis. The bands were detected using UV and autoradiography. The zones were scraped and then quantified by liquid scintillation counting (LSC).

After 6 days (150 hours) of exposure, significant degradation of diazinon (approximately 60%) had occurred and after 15 days only 3% of the applied diazinon was recovered. By contrast the dark controls had 85% of the original diazinon at the conclusion of the experiment. The half-lives were determined as 55.9 hours and 144 days for exposed and control respectively.

The only photodegradation product identified was oxypyrimidine, which reached approximately 35% of total activity after 6 days then decreased to 16% at the end of the exposure periods. In addition another 5 unidentified products accounted for up to 59% of AR. Two of the unknown products accounted for >10% of AR. Material at the origin of the TLC plate amounted to 15% of AR at the end of the exposure.

The limited analysis of photodegradation products is a significant deficiency in the study. There was no information on whether the solutions were sterile or if conditions used maintained sterility during the irradiation. However, the study does show that photodegradation in water is possible and that oxypyrimidine is likely the first product, which then under goes further degradation.

3.2.2 Photolysis Rate on Soil

3.2.2.1 US EPA Requirements - Artificial Light

The photolysis of ^{14}C-diazinon (labelled at C2) on soil was according to US EPA Guideline 161-3 (Spare, 1988B).

A layer of an air dried sandy loam soil (1.3% organic matter, 76.0% sand, 17.0% silt and 7.0% clay, pH 7.8, bulk density 1.51 g/mL) was dosed at approximately 10 µg/g (nominal) with ^{14}C-diazinon. The dosed soil was exposed to a medium pressure mercury arc lamp with a Pyrex filter (290 nm cutoff) for 120 hours of continuous exposure. The radiation level of the mercury light was given as 4-5 times that of natural sunlight at Maryland, USA, in August. (Note this lamp is the same as used for the aqueous photolysis study above.) The soil samples were exposed as layers 0.6-0.7 cm thick and were air dried. There were dark controls used.

Soils were sampled times at 0, 2, 4, 8, 28, 48, 72, 96 and 120 hours. The soil samples were extracted and then analysed by TLC. First order kinetics were used to determine the half-life.

The average half-life for replicates 1 and 2 was 54.9 hours of irradiation. However, there are problems with the analysis. There was no measure of applied radioactivity or a time 0 analysis and the results are given as percentage of average recovered radioactivity from all samples. Further, there was no analysis of non-extractable radioactivity in the soil samples. There was no indication in the report that the soil was sterilised, however, the intensity of the light used (4-5 times sunlight) would be expected to partially sterilise the soil and at the very least reduce microbial activity. The results do show that photodegradation could be a significant degradation pathway in soils. However, because of the analysis problem indicated above, the study is considered supportive only and not suitable for regulatory use.

3.2.2.2 US EPA Requirements - Sunlight

The photolysis of ^{14}C-diazinon (labelled at C2) on soil was according to US EPA Guideline 161-3 (Spare, 1988 C).

A layer of an air dried sandy loam soil was prepared as for the artificial exposure above and exposed to sunlight for 4 days (12 hours of sunlight per day) at a temperature range of 10-30 °C. The dosed soil samples were held at 90° to the sunlight. The samples were exposed during reasonably clear days at 39° 25` latitude from 9 to 14 May. When not exposed the samples were stored in a refrigerator at 4 °C in the dark. The study was done in duplicate with dark controls (exposed to the same environmental conditions but covered).

Sample times were at 0 and 6 hours and 1, 2, 3 and 4 days. The soil samples were extracted and then analysed by TLC. First order kinetics were used to determine the half-life.

The half-life was determined as 2.5 days (30 hours). There was only one photodegradate, oxypyrimidine, that accounted for > 10% of the AR and reached a maximum of 64% of the dose at the end of the study. As the soil was not sterilised and exposed to environmental conditions, the half-life is likely to include some metabolism. However, metabolic activity in dry soil is expected to be relatively low.

3.2.2.3 Earlier Study No. 1

The photolysis of ^{14}C-diazinon (labelled in the ring) in soil was determined under artificial light (Burkhard, 1978).

Oven dried (assumed to be 105 °C and therefore sterile) silty loam soil (3.6% organic matter, 38.4% sand, 49.4% silt and 12.2% clay, pH 6.1 and 38% water holding capacity) was dosed at approximately 10 µg/g (nominal) with a mixture of ^{14}C-diazinon and exposed to a xenon arc lamp for 24 hours continuous exposure at a temperature of 45 ± 5 °C. The spectral irradiance of the xenon lamp was comparable to normal sunlight. The radiation level of the xenon light was approximately twice that of natural sunlight at 380 metres in Switzerland. The soil samples were exposed as layers 0.6-0.7 cm thick and were either dry or moistened to 33% of holding capacity. There were dark controls for both the dry and moist soil samples.

After 24 hours the soil samples were extracted, then the extracts were analysed by GC individually. The metabolites were isolated and identified by TLC, GC and GC-MS and compared to authentic material.

When exposed to the xenon lamp for 24 hours the level of diazinon in the soil decreased to 28% in the moist soil and 23% in the dry soils. The dark control samples (kept under identical conditions but in the dark) had decreased to only 79% and 67% of initial dose for moist and dry samples respectively. As radioanalysis demonstrated no decrease during the photolysis experiment, it was concluded that there were no significant volatile products formed.

Only one extractable product was formed and identified as oxypyrimidine by TLC, GC and GC-MS. This represented 45% of the applied radioactivity (AR) in both the dry and moist soils from the acetone extract and was the only compound in the methanol extracts (which represented 17% and 11% of AR, dry and moist soils respectively). As there was only one sample taken, half-lives were not determined.

3.2.2.4 Earlier Study No. 2

The photolysis of ^{14}C-diazinon (ring labelled at C2) on a sandy loam soil was study using both natural and artificial sunlight (Martinson, 1985A). The study was not performed to current Guidelines or GLP.

The sandy loam soil (pH 5.4; 54.8% sand; 29.4% silt; 15.8% clay, organic matter 2.0%) was applied as a strip to a silica gel coated TLC plate, then the plate dried at 103°C overnight (therefore the soil was sterile at start) before the ^{14}C-diazinon (4.6 µg, area of soil 83.8 mm^2) was applied to the soil in solution. The plates were then exposed to natural sunlight (at latitude 39° N, 1-10 October, bright clear days only) by being placed out each morning then retrieved each evening for a total of 32 hours. The artificial sunlight exposure (Chroma 50 lamps, approximately 2.2 µwatts/cm^2) was continuous and lasted for a total of 10 days. No attempt was made to capture any volatile products following a preliminary study which showed <1% volatile products were formed.

The plates were sampled after 0, 1, 8, 21, 27.2 and 32.6 hours of exposure for the natural sunlight and after 0, 1, 8, hours, 1, 3, 7, 9 and 10 days of exposure for the artificial light. At each sampling the plates were developed, then the radioactive zones (detected using autoradiography) were scraped and counted for total radioactivity. The soils zones at the origin were combusted and the residues determined. Degradation products were identified by TLC only.

The half-lives were determined as 17.3 hours for sunlight, 5.5 days for artificial light and 14.7 days for dark exposures. As the soils started out sterile and the dry conditions of the exposure are not expected to allow for significant metabolic activity, the soils are considered sterile. The major metabolite was oxypyrimidine, which represented 23.7% of AR for sunlight (mean of 3 plates), 40.9% for artificial light and 16.4% for dark controls. A minor metabolite noted in the sunlight exposure was 6-hydroxy-2-(2-hydroxy-2-propyl)-4-methylpyrimidine (GS-31144, see Attachment 1) which reached a maximum of 2.4% of AR. The residues at the origin for the plates exposed to sunlight (30.1% of AR) were greater than for artificial light (10.5% of AR) or dark control (4.4%).

The mass balance as determined by recovery of ^{14}C was good for all samples.

3.2.2.5 Earlier Study No. 3

This study was performed as above (study 2) but under GLP and to fulfil the requirements of US EPA Section 161-3 (Blair, 1985). Total natural sunlight exposure was 58 hours and 210 hours for the artificial sunlight (Chroma 50). The artificial sunlight exposures were done in a chamber and volatile products were trapped.

The half-lives were determined as 37.4 hours for sunlight and 926 hours (38 days) for dark control by first order analysis. For the artificial light after 100 hours (approximately 50% degradation) photodegradation appeared to cease and therefore there was no half-life determined. TLC analysis of the natural sunlight after 37.4 hours showed only one major product (13.2% of AR), identified as oxypyrimidine by TLC co-chromatography, together with two minor products (5.3% and 2.9% of recovered radioactivity). The soil bound residues represented 34.3 and 25.8% of AR (2 replicates). Additional extraction of the soil from the 21 hour samples with methanol and water showed that oxypyrimidine (5.9% of AR) was the only identifiable product in the soil bound residues.

Analysis by TLC of the artificial sunlight exposure samples showed the same products were formed and in similar amounts as for the natural sunlight exposures. No volatile organics or evolved CO_2 were observed in the artificial sunlight samples.

Recoveries were acceptable, 87.7%, 91.5% and 96.0% of AR for natural sunlight, artificial sunlight and dark controls respectively.

3.2.3 Summary and conclusion of photodegradation

3.2.3.1 Aquatic

Based on 3 laboratory studies using artificial sunlight lamps photodegradation in water is possible and 6-hydroxy-2-isopropyl-4-methylpyrimidine is the major metabolite. The half-lives were determined for two of these studies only and ranged from 55.9 to 122 hours. From these laboratory studies, the half-life under environmental conditions was not determined.

Based on 2 studies, degradation in natural sunlight was slower. Only one study determined a half-life, that of 49 days (average of two replicates). A study on photodegradation, performed to German Guidelines and based on the experimental quantum yield of diazinon, showed that direct aquatic photodegradation of diazinon is unlikely under environmental conditions.

Environment Australia concludes that photodegradation in water is unlikely to be a significant route of degradation under environmental conditions.

3.2.3.2 Soil

Based on 3 soil photolysis studies using natural sunlight, the half-life of photodegradation of diazinon in air or oven dried soils was calculated to be 17.5, 30 and 37.4 hours. The major metabolite was identified as 6-hydroxy-2-isopropyl-4-methylpyrimidine, similar to the aquatic photolysis.

There were additional 3 studies that used artificial light. One study showed that after 24 hours exposure at 45 °C there was 28% of the applied diazinon remaining (half-life not determined) and in the other studies the half lives were determined as 4.3 and 5.5 days. These studies used different lamps and cannot be readily related to natural conditions.

It was concluded that photodegradation in soil could be a route of environmental degradation in Australia, given the high light levels during summer.

3.3 Degradation

3.3.1 Soil And Aquatic Metabolism

3.3.1.1 Aerobic Soil Metabolism

Study No 1

The degradation of ^{14}C-diazinon was studied in a sandy loam soil under aerobic conditions (Keller, 1981).

A sandy loam soil (sand 47.0%; silt 49.1%; clay 3.9%; oc 1.1%; pH 7.5) was dosed with ^{14}C-labelled diazinon (labelled at C2) at 10 mg/kg. The soil was moistened to 75% of field capacity then incubated in a stream of moist air for a total of 166 days. Volatile products were trapped in gas traps (ethylene glycol, H_2SO_4 and NaOH). The soil was sampled as indicated in Table 4.

The soil samples were analysed by extraction followed by combustion of the soil. The extracts were analysed by TLC, GC and GC-MS. The results are given in Table 4.

	Days After Treatment					
	0	14	28	56	84	166
Diazinon	101.6	12.3	5.3	3.2	2.0	0.3
G 27550	3.1	72.9	55.9	69.6	49.0	4.7
G 31144	nd	nd	nd	nd	nd	1.5
Unknown metabolite	nd	nd	nd	nd	0.5	4.8
CO_2	—	2.6	6.9	15.6	20.4	55.6
Non-Extractable	0.4	4.2	5.5	9.1	9.1	15.1

Table 4. ^{14}C residues of diazinon during an aerobic soil metabolism study. Results as percentage of initial applied dose, rounded to one decimal point. G 27550 = 6-hydroxy-2-isopropyl-4-methylpyrimidine (oxypyrimidine); G31144 = 2-(1'-hydroxy-1'-methylethyl)-6-hydroxy-4-methylpyrimidine

The principal metabolite, G 275550 (6-hydroxy-2-isopropyl-4-methylpyrimidine, see Attachment 1), amounted to 73% of applied radioactivity (AR) after 14 days and then declined to 4.7% at the end of the study. During the course of the study CO_2 was slowly evolved and reached 55.6% of AR by the end of the study period. There were no other significant metabolites detected. The overall half-life of diazinon was determined to be 11 days under aerobic soil metabolism conditions.

It was concluded by the authors that diazinon is degraded to the hydrolysis product oxypyrimidine, which is subsequently mineralised to CO_2.

While the study was not performed to current standards, the study is acceptable to Environment Australia.

Study No. 2

The degradation of diazinon in one soil under a range of aerobic conditions was studied to meet Danish requirements, Order No. 791 (Seyfried, 1994).

Radiolabelled diazinon (^{14}C, C4) was used to dose a Les Evouettes silt loam soil (pH 7.7, oc 1.39%, sand 31.9%, silt 61.1% and clay 7.0%) at 7.5 mg ai/kg of soil, corresponding to a field rate of 3.75 kg ai/ha for 5 cm deep. One sample was dosed at a tenth the rate, 0.75 g ai/kg. The soils were then moistened to the required field capacity (FC) and incubated in a stream of moist air for a total of 119 days. Any volatile products were trapped in gas traps (ethylene glycol, H_2SO_4 and NaOH).

Soil samples were taken at 0, 3, 7, 14, 21, 35, 65 and 119 DAT and analysed by extraction followed by combustion of the soil. The extracts were analysed by TLC and the radioactive zones scanned by an automatic linear analyser and significant radioactive zones counted and integrated for quantification of metabolites. From this data the half-lives of parent and the main metabolite were determined. These are given in Table 5.

Experimental conditions	Exper. No.	% CO_2 after 119 days incubation	Diazinon		G 27550	
T °C, FC%		% AR	DT50	DT90	DT50	DT90
20°, 60%	1	86%	5	22	13.6*	45*
20°, 30%	2	20%	8	44		
10°, 60%	3	9%	12	71		
20° 60%, tenth rate	4	73%	4.5	31	17.8*	59*
20°, 60%, sterile	5	0.1%	118	392		

Table 5. Summary of the degradation rates in days for a silt loam soil under a range of conditions. AR = applied radioactivity. * Calculated by Environment Australia

With increasing incubation, the amount of non-extractable radioactivity increased together with the main metabolite, G 27550 (oxyprymidine, 2-isopropyl-4-methyl-6-hydroxypryimidine). This metabolite reached between 75% and 82% of AR after 21 days and then declined in experiment 1 and 4 respectively, with the half-life calculated for these experiments as 13.6 and 17.8 days respectively and correlation coefficients (r^2) of 0.86 and 0.92. For the other two experiments, there was insufficient degradation of G 27550 after 120 days to calculate a half-life. It should be noted that concentration of the metabolite was the highest in these experiments, 79.3% and 82.4% after 65 days for experiment 2 and 3 respectively.

The evolution of CO_2 slowly increased and total CO_2 evolved was as indicated in the table. Again the drier conditions and lower temperature used in experiment 2 and 3 reduced the biologic activity significantly reducing the rate of mineralisation.

This is the most modern study presented, was performed well, and is considered highly reliable.

3.3.1.2 Degradation in soil at 10 °C

The degradation of diazinon was studied using radiolabelled (^{14}C) material in two soils at 10 °C and at an initial concentration of 10 mg/kg (Vonk and de Jong, 1987). The purity of the radiolabelled material was only 87.3%, with 12.7% of the radioactivity as the oxypyrimidine.

The two soils used, a loamy sand (om 4.5%, sand 84.4%, silt 7.9%, clay 3.1%; pH 5.4) and a loam (om 2.1%, sand 26.7%, silt 40.6%, clay 22.7%; pH 7.3) were incubated for 10 days (1/3 bar moisture) before being dosed with diazinon to a nominal dose of 10 mg/kg. The dosed soils were then incubated at 10 °C in the dark for 32 weeks. Samples were taken at 0, 4, 8, 16 and 32 weeks for both soils and on week 1 (for loam) and 2 (for loamy sand). Evolved CO_2 was analysed at each sampling. The soils were extracted and the extract analysed by TLC. The non-extractable residues were determined by soil combustion analysis. Results given in Table 6 are average of duplicates unless there is significant difference between duplicates.

	Weeks After Treatment					
	0	1	4	8	16	32
Loam soil						
Diazinon	54.0, 66.1	48.6, 68.5	26.2	43.8, 20.1	10.6	21.4, 9.3
oxypyrimidine	35.1, 26.3	43.3, 22.9	56.2	39.4, 57.0	71.5	48.7, 63.2
Others	5.7, 1.8	4.4, 2.1	8.6	1.5, 6.7	3.6	10.3, 0.5
Non-Extractable	1.2	3.2	5.4	7.8	9.8	15.3
Loamy sand soil		(2)				
Diazinon	81.5	73.7, 67.0	61.9	66.9, 54.2	33.5, 49.1	28.6
oxypyrimidine	15.3	18.1	25.5	18.4, 30.7	45.5, 29.7	41.9
Others	1.7	0.6	5.0	1.3	1.7	3.7
Non-Extractable	0.6	3.7	4.5	6.6	7.4	13.1

Table 6. ^{14}C residues of diazinon during aerobic soil metabolism study for two soils. Results as percentage of initial applied dose, averaged from duplicates unless duplicates are different, then both given. oxypyrimidine = 6-hydroxy-2-isopropyl-4-methylpyrimidine (G27550).

The half-lives for degradation of diazinon at 10 °C was calculated as approximately 16 weeks for the loam soil but the correlation coefficient is low (r^2 = 0.61). For the loamy sand, the half-life was calculated as 22 weeks by Environment Australia with r^2 = 0.968. The evolution of CO_2 was very low for both soils, <4% after 32 weeks. The low rates of degradation and mineralisation reflect the low temperature at which the study was performed, similar to that in the previous study but with significantly longer half-lives.

3.3.1.3 Mineralisation of a CS formulation

The mineralisation of a capsule suspension of diazinon was compared to that of the non-formulated active ingredient in a single soil (Keller, 1990). The soil used was a sandy loam soil (sand 58.0%; silt 31.4%; clay 10.6%; oc 1.8%, pH 5.4). The soil was dosed at approximately 10 ppm of active for both and incubated at 20 °C in the dark for 12 weeks. The evolved CO_2 was collected in gas traps. The soil was analysed after dosing and at the end of the incubation period only.

There were no half-lives available from the data (only two data points) and therefore the study is of limited value. There was little difference in the rate of mineralisation, 8.3% and 8.1% of the AR recovered as CO_2 for formulated and non-formulated. However, the rate of degradation for the CS formulation was significantly slower than for the non-formulated material, with 26.1% versus 1.0% of the applied diazinon recovered after incubation (determined by TLC analysis of extracts).

3.3.1.4 Degradation in acid soil

The degradation of diazinon in an acid soil was studied using two different formulations, a granule (5G) and an emulsion (25EC) (Keller, 1976).

Samples of the acid soil, a sandy loam (sand 77.1%; silt 12.4%; clay 10.5%; oc 1.1% pH 4.8), were dosed with the formulations to give an initial concentration of 10 ppm of active. The soils were then moistened (40% of holding capacity) and incubated at 22 °C in the dark for 56 days. Samples were taken 0, 7, 14, 21, 28, 42 and 56 DAT. The soil samples were extracted and analysed by GC.

The half-lives were given as approximately 40 days. Based on the data for the loss of diazinon presented, Environment Australia calculates the half-lives as 40.3 and 36.1 days with r^2 of 0.974 and 0.957 for 5G and 25EC respectively.

3.3.1.5 Published papers

The degradation of diazinon in two different soils was studied, a sandy loam (sand 72.1%; silt 16.6%; clay 8.6%; om 2.7% pH 6.3) and a sand soil (sand 92.0%; silt 3.4%; clay 2.6%; om 2.0%; pH 6.0) [US classifications] (Bro-Rasmussen, Nøddegaard and Voldum-Clausen, 1968). A range of conditions were used: two moisture levels (75% and 25% water capacity), two concentrations (equivalent to 1 and 10 kg ai/ha in 10 cm deep soil) and sterilised (steam treated to 100 °C) and non-sterile soils. The interactions of all 4 factors were examined in duplicate and the half-lives of degradation determined after incubation at between 20-23 °C. Table 7 gives results for the non-sterile soils only. The sterile results show the half-life is significantly longer, up to double for all conditions tested.

Soil type	Moisture	Concentration	Half life in days
Sandy loam	Moist, 75% FC	Low	21.6
Sandy loam	Moist, 75% FC	High	26.6
Sandy loam	dry, 25% FC	Low	42.3
Sandy loam	dry, 25% FC	High	48.5
Sand	Moist, 75% FC	Low	38.8
Sand	Moist, 75% FC	High	58.1
Sand	dry, 25% FC	Low	52.0
Sand	dry, 25% FC	High	59.9

Table 7. The degradation of diazinon in under a range of conditions for two soils. Low concentrations equivalent to 1 kg ai/ha and high is equivalent to 10 kg ai/ha in soil depth of 10 cm.

Table 7 clearly shows that in dry conditions the degradation of diazinon slows down and soils type influences the degradation rate. Presumably, these are because of the effects on microbial activity.

In a review of the residues in soils from use of diazinon, the time for 50% degradation of diazinon is stated to be approximately 2 and 4 weeks (Bartsch, 1974). This is dependent on temperature, moisture and pH value as expected. However, in a fen soil (17% om) the 50% degradation is given as 5 weeks and after 7 months there was 10% remaining.

3.3.2 Aerobic Aquatic Metabolism

The degradation of diazinon was studied in two different aquatic/sediment systems under aerobic conditions at an initial concentration of 1 mg/L (Keller, 1983). The studies were not performed to current standards.

The aquatic/sediment systems consisted of natural surfaces water from the Rhine River and 1% of soil (two soils used) or pond water and 1% sediment from the same location. The water and sediments were field collected in spring and again in summer and were not more than 1 week old before starting the experiments. Table 8 gives physical properties of the soil/sediments and water used.

Water Characteristics						
Rhine river water		pH range 7.8-8.2			ppm O_2 = 8-9 20 °C	
pond water		pH range 7.2-7.9			ppm O_2 = 8-9 20 °C	
Soils/Sediments Used						
Sediment/soil	pH	organic carbon	sand	silt	clay	USDA classification
Les Barges, May	7.7	1.7	9.4	86.4	4.2	Silt
Les Barges, August	7.6	1.7	62.0	24.9	13.1	Sandy loam
Pond, May	7.2	9.1	16.3	57.7	26.0	Silt loam
Pond, August	6.8	10.9	26.3	45.8	27.9	Loam

Table 8. Physical properties used in the degradation of diazinon in aquatic systems.

The sediment/soil (5 g dry weight) was mixed with water (500 mL), then 12 hours later ^{14}C-diazinon (in ethanol) was added to give a final concentration of 1 mg/L. Each trial was done in duplicate. The sediment/water systems were incubated at 25 °C in the dark and ventilated by a gentle stream of air, scrubbed of CO_2. The air stream passed through gas adsorption bottles to trap volatiles and CO_2. Samples of the aqueous phase were collected at 0, 2, 7, 14, 21 and 28 DAT and the soil/sediment sampled at the end of the experiment. Total radioactivity in the water and soil samples was determined then the samples extracted and the extracts analysed for diazinon and possible metabolites by HPLC. Non-extractable residues were not determined. Table 9 gives the amounts of diazinon in the aqueous phase as average of duplicates.

Time, days	Rhine river		Pond water	
	Spring (May)	Summer (August)	Spring (May)	Summer (August)
0	0.80	0.74	0.76	0.68
2	0.76	0.68	0.63	0.51
7	0.55	0.63	0.41	0.34
14	0.10, 0.36	0.62, <0.10	0.24	<0.10
21	<0.10, 0.18	<0.10, —	<0.10	—
28	—, 0.15	—	—	—
Half life, days (r^2)	9 (0.97), 14 (0.95)	15 (0.70), 8 (0.89)	9.5 (>0.96)	7 (>0.98)

Table 9. Residues of diazinon in water from the aerobic aquatic metabolism study. Results are average of duplicates unless results were not similar, then both given. Results are from HPLC and are expressed as mg/L (ppm). Half-lives calculated as first order.

The overall ^{14}C-mass accountability was moderate, with ≥ 78.9% of applied radioactivity recovered at the end of all experiments. The majority of this radioactivity was recovered as CO_2 (see Table 10). The non-CO_2 volatiles comprised up to 9.9% of the total applied radioactivity and these were identified as diazinon. The results for the mass balances are summarised in Table 10.

	Rhine river		Pond water	
	Spring (May)	Summer (August)	Spring (May)	Summer (August)
water phase	18.0	15.3	8.5	11.6
*CO_2	36.8	57.1	48.3	69.3
sediment	8.6	9.1	12.0	12.6
volatiles	9.9	4.6	6.6	4.2
Total	78.9	80.2	79.7	91.7

Table 10. Residues of ^{14}C from the aerobic aquatic metabolism study as percentage of applied radioactivity, 28 DAT. * Includes both CO_2 from gas traps and that dissolved in the aqueous phase. Total includes samples taken for analysis but not listed in Table.

There was only one metabolite identified, the hydrolysis product oxypyrimidine. Maximum amount was 0.10 to 0.14 mg/L in most of the trials at approximately 7 DAT. Thereafter the metabolite disappeared rapidly. The production of CO_2 commenced after a lag phase of 5-12 days.

The study shows that degradation of diazinon is fast, with half-life in water of between 7-15 days. While the study was not performed to current standards and the mass accountability was modest, the number of trials and their relatively consistency gives confidence to the overall conclusion and is therefore acceptable.

3.3.2.1 Second Study

In an older study, diazinon in distilled water (2.4 L at approximately 34 mg/L) was added to soil (266 g) collected from a pond and the system incubated for 9 days (Banzer, Frank and Hofberg, 1972). There was no analysis given of the pond soil. The water was sampled on 0, 7 and 9 DAT, and the soil sampled on 9 DAT only. All samples were extracted using standard procedures and the extracts analysed by GC for diazinon. Only the 9 DAT sample was analysed for oxypyrimidine.

The results show rapid reduction in the concentration of diazinon from the initial concentration of diazinon of 32.1 mg/L to 0.8 mg/L, 9 DAT. There were no significant changes in the concentration in the control (without soil), 34.7, 38.6 and 38 mg/L for 0, 7 and 9 DAT respectively. The amount of diazinon left in the aqueous phase was 1.9 mg and in soil was 3.9 mg, 9 DAT, which represents about 7% of the applied diazinon.

The concentration of oxypyrimidine found was 13.9 mg/L in the water and 3.6 mg/kg in soil 9 DAT. (Concentration in soil is given as 0.96 mg, corresponding to 3.6 mg/kg of soil for 266 g of dry soil.). No oxypyrimidine was detected in the controls.

This study was not performed to current standards nor would it meet the requirements for an aquatic metabolism study. There was insufficient data to determine a half-life of diazinon under the test conditions.

3.3.2.2 Published papers

The degradation of diazinon in three flooded soils was studied (Sethunathan and McaRae, 1969). The air dried soils (Maahas clay, pH 6.6; Luisina clay, pH 4.7 and Pila clay loam, pH 7.6) were flooded with water containing diazinon and then incubated at 30 °C in a greenhouse. The same soils were also sterilised and incubated. After 1, 15, 25, and 50 days of incubation, and in the case of Pila soils 70 days incubation, the soil/water systems were sampled in triplicate and extracted. The extracts were analysed by GC. A second part of the study involved using radiolabelled diazinon with air passing over the samples, then into gas traps to capture CO_2.

The results show that diazinon disappeared with half-lives of 8.8, 17.4 and 9.9 days for non-sterile systems for Maahas, Pila and Luisina soils respectively and 33.8, 43.8 and 0 (? typographical error) days in the sterile systems. The authors explain this by the instability of diazinon in acid solutions and that in the non-sterile system the pH decreased during the study period while in the sterile case the pH remained low at 4.7. These results may have been determined graphically.

The rate of mineralisation was low, with <0.7% of the applied radioactivity recovered as CO_2 after 50 days. Again this is an old study and of limited value.

3.3.3 Anaerobic Aquatic Metabolism

No studies presented.

3.3.4 Anaerobic Soil Metabolism

No studies presented. The US EPA report includes a summary for an anaerobic soil metabolism study and states a half-life of 34 days using a sandy loam soil.

3.3.5 Ready Biodegradation Test

The biodegradation of diazinon was studied in a modified Sturm test following OECD Guideline 301 B, 1981 (Bader, 1990).

The biodegradability of diazinon was measured by evolution of CO_2 in an incubation with bacteria (from a sewage treatment plant) compared to the theoretical CO_2. After 28 days of incubation there was 4% or less of theoretical CO_2 evolved. It is concluded that diazinon is not readily biodegradable in the test.

3.4 Conclusion-Soil And Aquatic Metabolism

Only one aerobic metabolism study was performed to current (Danish) Guidelines. No other metabolism studies were performed to current guidelines.

—Aerobic Soil Metabolism

The degradation of diazinon under aerobic conditions in soil is fast to moderate, with a half-life of 4.5 to 8 days at 20 °C in the most reliable study under a range of temperature and soil moisture conditions. In other studies the half-life ranged between 11 to 59 days in 4 different soils and under a range of conditions as above. The initial product is 6-hydroxy-2-isopropyl-4-methylpyrimidine, which is then slowly degraded and mineralised to carbon dioxide.

The mineralisation of diazinon TGAC was compared to a formulated product (microencapsulated, CS) in a sandy loam soil under aerobic conditions. The study showed little difference on the rate of mineralisation but the rate of degradation in the CS formulation was slower than for the non-formulated material, with 26.1% versus 1.0% of active remaining after 12 weeks.

In a review of literature studies on the degradation of diazinon in soil, the time for 50% degradation was stated to be between 2 and 4 weeks, depending on temperature, moisture and pH value. However, in a fen soil (17% om) the 50% degradation is given as 5 weeks and after 7 months there was 10% remaining.

—Aerobic Aquatic Metabolism

The degradation of diazinon in aerobic aqueous conditions is fast, with a half-life of between 7-15 days in natural river and pond water/soil systems. The initial product is 6-hydroxy-2-isopropyl-4-methylpyrimidine, which is then mineralised to carbon dioxide and other degradates. The degradation pathway appears to be hydrolysis followed by mineralisation of the hydrolysis product.

In another older study, the concentration of diazinon in water and pond sediment decreased from the initial 32 mg/L to 0.8 mg/L after 9 days. This represents 93% degradation of diazinon from the water/sediment system after 9 days.

In a published study, the degradation of diazinon in three flooded clay soils was studied using both non-sterile and sterile soil/water systems. The results show that diazinon disappeared with half-lives between 8.8-17.4 days for non-sterile systems and 33.8-43.8 days in the sterile systems.

—Anaerobic Aquatic Metabolism
No studies presented.

3.4.1 Conclusion

It is concluded that microbial degradation of diazinon in soil and aquatic conditions is fast to moderate under aerobic conditions. There was no information available on the degradation under anaerobic conditions. However, it is likely that hydrolysis and degradation will occur but it is unknown at what rate this will happen.

3.5 Mobility

3.5.1 Soil Adsorption/Desorption

A soil adsorption/desorption study was performed using the standard batch method (Guth, 1972). This was not performed or reported to current Guidelines. Six soils were used in the study, the characteristics of which are presented in Table 11.

Oven dried soil (5 to 50 g) was mixed with aqueous solution of radiolabelled diazinon (0.5 to 10 mg/L) then after 24 hours of shaking the liquid was separated by centrifuging and the liquid analysed by LSC. From the LSC data the concentration of diazinon in the aqueous phase was determined and used to determine the adsorption and desorption coefficients for all the soils used. The graphical data of the amount adsorbed against concentration for Uvrier I, Collombey, Les Evouettes and Vetroz show good linear fits and therefore use of the Freundlich equation is appropriate. These results are summarised in Table 12.

Origin	Soil Type	Organic Matter	pH	% Sand	% Silt	% Clay
Collombey	loamy sand	2.2	7.8	87.0	10.2	2.8
Illarsaz	peat	22.9	7.5	*	*	*
Les Evouettes	loam	3.6	6.1	38.4	49.4	12.2
Urier I	sand	1.0	7.4	91.6	5.0	3.4
Uvrier II	loamy sand	1.6	8.1	82.1	13.8	4.1
Vetroz	sand clay loam	5.6	6.7	57.8	19.6	22.6

Table 11. Characteristics of test soils. * Mechanical analysis could not be performed due to high organic matter

		Adsorption		
Origin	Soil Type	K_d, µg/g soil	K_{oc}	1/n
Collombey	loamy sand	5.6	255	0.63
Illarsaz	peat	113.5	496	0.70
Les Evouettes	loam	11.7	325	0.77
Urier I	sand	3.7	370	0.60
Uvrier II	loamy sand	4.5	281	0.55
Vetroz	sand clay loam	23.4	418	0.93

Table 12. The adsorption coefficients.

The results of the adsorption/desorption experiment for diazinon show that it is moderately absorbed to the six soils tested and shows that sorption is strongly dependent on the organic content of the soil. A graph of the Freundlich adsorption constant versus % organic matter shows a good linear relationship. Diazinon can be rated as having medium mobility in soil and binds to the organic fraction of the soil.

There was no desorption phase in the study.

3.5.1.1 Literature

The mobility of diazinon in 25 different soils with a range of mechanical properties was studied (Arieno, Crisanto, Sánchez-Martín and Sánchez-Camazano, 1994). The log Kom ranged from 2.08 to 3.39, average of 2.46, corresponding to Kocs between 207 and 4222 with average of 496. The K values for all soils were found to be correlated with organic matter of the soils (r = 0.84, K) and a stronger correlation for soils with high OM >2% (r = 0.94). The K values for soils with low organic matter <2% were correlated with silt and clay (r = 0.68) but not for clay alone (r = 0.34) and there was a negative correlation for soils with high OM (r = -0.69). These observations were explained by the authors as showing that organic matter of the soil was the most significant determinant of binding, with clay and silt being secondary and only being apparent in soils with low organic content.

3.5.2 **Mobility Using Soil Columns**

3.5.2.1 Study No.1

Diazinon (630 µg), equivalent to 5 kg ai/ha, was added to the top of packed soil columns (height of 30 cm), then water (equivalent to 200 mm of rainfall) was washed through the columns over a 48 hours period (Guth, 1978). The columns were sectioned into 2-cm segments and analysed for diazinon together with the percolates. Characteristics of the soils used are given in Table 13 and Table 14 gives the results.

Soil	USDA Classification	pH	Organic Matter	Sand	Silt	Clay
Collombey	loamy sand	7.8	2.2	87.0	10.2	2.8
Lakeland	sand	6.3	1.2	95.2	2.1	1.5
Les Evouettes	loam	6.1	3.6	38.4	49.4	12.2
Vetroz	sand clay loam	6.7	5.6	57.8	19.6	22.6

Table 13. Soil characteristics for soils used in column leach study.

	Depth of Soil, cm								
Soil	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-16	16-30*
Collombey	32.0	24.6	28.5	11.9	<0.5	<0.5	<0.5	<0.5	<0.5
Lakeland	27.0	18.2	17.4	15.0	9.5	2.3	2.5	1.1	<0.5
Evouettes	69.8	38.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Vetroz	81.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

Table 14. Vertical distribution of diazinon in various soils in 2 cm sections as percentage of applied. *All the 2 cm sections from 16 to 30 cm gave <0.5%.

There was no detection (<0.5% of applied) of diazinon in any of the leachates. The most movement occurred in Lakeland sand (see Table 14), followed by Collombey, Evouettes and Vetroz, where there was no movement of diazinon. The order of the depth of leaching into the columns correlates strongly with the amount of organic matter in each soil.

The study shows that in sandy soil with low organic content there is a possibility of limited vertical movement through the soil.

Study No 2

The leaching characteristics of diazinon was determined in four soils according to US EPA Guidelines 163-1 (Spare, 1987). The soils were not sterilised prior to use.

Samples of the four soils were dosed with ^{14}C-diazinon (labelled at C2), then samples of the soils were added to triplicate soil columns (30 cm long) of the corresponding soil. The columns were then leached with 50.7 cm of simulated rainfall at a rate not exceeding 2.54 cm per hour. After the leaching, the soil columns were separated into 2.54 cm sections and the total radioactivity in the leachate and each section determined. The leachate from each soil column was pooled and analysed by TLC for degradates.

The characteristics of the soils used are given in Table 15 and Table 16 gives the recovered radioactivity after leaching for each soil type, average of three replicates.

Soil	USDA Classification	pH	Organic Matter	Sand	Silt	Clay
Maryland	Sand	6.5	0.9%	95.6%	2.2%	2.2%
California	Sandy loam	6.5	0.5%	74.0%	19.6%	6.4%
Maryland	Clay	5.9	4.8%	25.2%	32.8%	42.0%
Mississippi	Silt loam	7.5	1.0%	39.5%	54.2%	6.3%

Table 15. Soil characteristics for soils used in column leaching study.

Column Section cm	Maryland sand	California sandy loam	Maryland clay	Mississippi silt loam
2.54	0.62	7.87	58.86	58.43
5.0	0.20	8.45	5.44	7.65
7.5	0.22	9.14	2.94	4.55
10	0.23	11.78	1.91	3.41
12.5	0.39	11.50	1.92	3.18
15	0.60	11.15	1.95	3.22
17.5	0.84	6.84	1.86	2.84
20	1.14	4.42	1.57	3.02
22.5	2.04	2.29	1.24	2.33
25	1.98	0.97	1.14	2.39
27.5	2.38	0.45	1.36	1.99
30 (bottom)	3.45	0.61	1.983	1.93
Total column	14.09	75.75	82.01	94.94
Leachate	81.25	17.55	16.00	6.04
Total recovered	95.34	93.30	98.01	100.98

Table 16. Average profile of diazinon leaching in four soils as percentage of applied radioactivity.

The TLC analysis of the leachates showed <2% AR was recovered as parent. The only metabolite identified in the leachates was G 27550 (2-isopropyl-4-methyl 6-hydroxypyrimidine: oxypyrimidine), 69%, 15%, 15% and 5% of AR in the sand, sandy loam, clay and silt loam respectively.

From these results, it is concluded that while diazinon is unlikely to leach, due to rapid degradation, the principle metabolite G 27550 could, especially in soils prone to leaching. These results show that for the Maryland sand G27550 is rapidly formed.

3.5.2.2 Aged leaching in four soil types

An aged soil leaching study of diazinon in four soils was conducted according to US EPA Guidelines (Shepler, 1993). The characteristics of the soils used are given in Table 17.

Radiolabelled diazinon (^{14}C at C2 in ring) was used to dose the sandy loam in Table 17 at approximately 10 ppm. After aging for 30 days under aerobic conditions at 75% of field moisture capacity in the dark, the soil was added to the top of untreated soil columns of loamy sand, sand, loam and silty clay loam. To minimise channelling, the soil columns were packed dry and saturated from the bottom up then allowed to drain before the aged soil was added. The columns were then leached with 50.7 cm of 0.01 M $CaCl_2$. Any volatile products and CO_2 evolved from the columns were trapped at both the top and bottom in a series of gas traps. The leaching was performed in duplicate for each soil column.

After leaching, the soil columns were segmented into 6 cm sections and the soil extracted. All extracts were analysed for radioactivity and extracts from 0-6, 12-18 and 24-30 cm from all soil columns were analysed by HPLC and TLC for metabolites. The residual radioactivity in the soils was determined by combustion. The leachates were analysed by LSC and HPLC. Results are given in Table 18.

USDA Classification	pH	Organic carbon	Sand	Silt	Clay
loamy sand	6.7	0.32	73	22	5
sand	6.5	0.42	90	6	4
loam	6.7	1.11	38	43	19
silt clay loam	5.7	0.99	16	55	29

Table 17. Soil characteristics for soils used in aged soil column leaching study.

The average recovered radioactivity from the soils columns was 100.6, 95.1, 95.0 and 94.9 for the sand, sandy loam, loam and silty clay soils respectively. Apart from parent compound and oxypyrimidine, three other metabolites were detected in the soil columns, none of which where >1.6% of AR. One of these minor metabolites was identified as GS 31144 (2-(1'-hydroxy-1'-methylethyl)-6-hydroxy-4-methylpyrimidine, see Attachment 1 for structure).

The study shows that while diazinon is only slightly mobile, the metabolites from soil degradation are more mobile and could leach in most of the soils tested.

Soil Type	Leachate	Total soil	Column sections				
			0-6	6-12	12-18	18-24	24-30
Sand TR	47.4	53.1	28.9	6.5	7.4	6.6	3.6
Diazinon	1.2		15.9	—	4.5	—	0.8
G 27550	44.3		2.2	—	1.2	—	2.3
Sandy loam TR	55.7	39.1	17.0	5.0	8.4	7.6	1.2
Diazinon	2.2		5.8	—	5.6	—	0.7
G 27550	51.1		1.2	—	0.8	—	0.4
Loam TR	45.23	49.5	28.8	14.7	2.5	1.5	1.9
Diazinon	<0.1%		13.1	—	0.2	—	<0.1
G 27550	42.5		6.1	—	1.5	—	1.4
Silty Clay loam	44.6	50.1	34.1	11.2	1.8	1.5	1.5
Diazinon	<0.1%		15.6	—	0.1	—	<0.1
G 27550	41.6		4.5	—	1.0	—	1.1

Table 18. The results of the analysis of leachates and soils from column sections as percentage of applied dose. Average of duplicate soil columns. TR = total radioactivity. The 6-12 and 18-24 cm soil sections were not extracted.

3.5.2.3 Older studies of leaching characteristics of aged diazinon residues in two soils

Study No. 1

An aged soil leaching study was performed using two soils, Collombey sandy loam and a Les Evouettes loam (Burkhard, 1980). The characteristics of the two soils have been given previously (Table 11).

Air dried samples of the soils were dosed with ^{14}C-diazinon (labelled in the ring), equivalent to 4.5 kg ai/ha in the top 2 cm of soil, then moistened to 50% of their water holding capacity before aging for 30 days under aerobic conditions. The aged soils were then applied to the top of untreated soil columns containing the same soils. The soil columns were leached for 45 days with simulated rainfall corresponding to 12.7 mm per day. The leachate was collected daily and analysed by liquid scintillation counting. After the leaching, the soils were separated in layers (2 cm high) then the extractable and non-extractable radioactivity determined.

After the aging process, a total 97.1% applied radioactivity (AR) was recovered from the sandy loam and 93.1% from the loam soil. The majority of the radioactivity was extractable from the soils, 85.8% of from sandy loam and 81.2% from the loam soils.

After leaching there was 32.5% and 51.2% of AR was recovered from soil columns for Collombey and Les Evouettes respectively. 14.1% and 21.5% of AR was extractable and 18.4% and 26.9% non-extractable, respectively.

In the leachates there was 32.7% and 25.3% of AR from the sandy loam and loam soils respectively. The elution pattern showed that the first significant radioactivity appeared after 9 and 12 days, with the peak levels of 5.1% of AR and 3.2% on days 12 and 17 respectively. Extraction of leachates followed by methylation of the extracts and TLC and GC of the methylated products showed that there was only two products, G 27550 (2-isopropyl-4-methyl 6-hydroxypyrimidine) and a new product, compound II, tentatively identified as 2-ethyl-4-methyl 6-hydroxypyrimidine. There was 9.8% and 7.8 % of AR as G 27550 and 15.2% and 13.4% of compound II in Collombey and Les Evouettes eluates respectively.

It was concluded that metabolites from soil metabolism could leach.

Study No. 2

An aged soil leaching study, similar to that directly above, was performed using the same soils except that there was no analysis of the soil residues and therefore no mass balance (Burkhard, 1979A). The leachates were collected and analysed as above.

There was 21.3% and 4.05% of the applied radioactivity was found in the Collombey and Les Evouettes column eluates respectively. Analysis of the leachates, showed the same two compounds present G 27550 and compound II. This represented 6.9% and 10.2% of AR in the Collombey for G 27550 and compound II respectively and 1.3% and 1.5% in the Les Evouettes leachates.

Again, the report indicates that the metabolites could leach.

3.5.3 **Volatilisation**

3.5.3.1 The Volatilisation of Diazinon from Two Soils

The volatility of diazinon from two soils under laboratory conditions was determined (Burkhard, 1977). The soils used were Collombey and Les Evouettes, the details of which have been given previously (Table 11).

The soils were placed into chambers (44 g of dry soil, surface area 48 cm^2) over which moist air could be passed at constant temperature. The dried soils were treated with 1, 2, 3 or 4 mg of diazinon, then water added to the soil (12% by weight, corresponding to 55% and 32% of FC for Collombey and Les Evouettes respectively). Moistened air was then passed over the samples and through a gas trap containing ethylene glycol to capture the volatilised diazinon. Analysis of the ethylene glycol involved extraction of the solutions followed by GLC. The material balance was randomly tested with ^{14}C-diazinon by combustion of the soils and by determination of the volatilised diazinon by LSC. In all cases, 95% of the applied radioactivity could be recovered.

The study was performed at 35, 45 and 55 °C, in the dark and with airflows of 15, 30 or 60 L/h (30 L/h corresponds to 100 changes of air over the soil per hour). The results are given in Table 19**.**

Soil	Temperature, °C	Initial soil Con. # µg/g	Volatilisation[1], µg/cm^2	Volatilisation rate, ng/cm^2/h ^{14}C	GLC
Collombey	35	20	1.82	97	76
	35	40	4.34	185	181
	35	60	6.41	245	267
	35	80	8.16	340	340
	45	60	22.56	-	940
	55	60	49.68	-	2070
	35	60	3.65	-	152 *
	35	60	8.02	-	334 **
Les Evouettes	35	20	0.48	-	20
	35	40	1.13	-	47
	35	60	1.82	68	76
	35	80	2.74	-	114

Table 19. Soil volatility study after 24 hours. Air flow at 30 L/h unless other wise indicated. * Air flow is 15 L/h, ** air flow 60 L/h. #On a wet soil-weight basis. [1]Results from GLC analysis only.

The analysis of the data showed that the volatilisation of diazinon increased with increasing concentration in a linear relationship. This rate was markedly influenced by the soil type used in the tests due to the adsorptive capacities of the two soils. It was shown that the Freundlish adsorption equation was valid. The adsorption isotherms were obtained by plotting the amount of diazinon in the soil against the concentration in the vapour phase. The volatilisation for Collombey soil was linear against the reciprocal of temperature for 35, 45 and 55 °C at constant soil concentration (60 µg/g) and extrapolation to 20 °C gave a rate of volatilisation of 48 $ng/cm^2/h$. It was concluded that the volatility from soil is low.

3.5.3.2 Volatility from plants and soil

The volatility of diazinon from maize seedlings was studied according to BBA Guidelines (Sandmeier, 1992).

Eight days old maize plants (2-3 leaf stage) in pots were sprayed with ^{14}C-diazinon, formulated as a WP 40, at a rate of 1146 g ai/ha. After spraying the pots were placed into a growth chamber at 20-21 °C with RH of 33-37% and an airflow of 220 air changes per hour.

Plant and soil samples were taken just after application (15 minutes) and then 1, 3, 6 and 24 hours later. The plants were analysed for surface residues and for the remaining radioactivity by combustion. The soil samples were extracted and the non-extractable residues determined by combustion. At each sample the plant washings and soil extracts were analysed by TLC. The plants from the final sample were extracted and analysis as for other samples. Radioactive zones on the TLC plate were scraped and quantified by LSC. Table 20 summarises the results.

Time	Plant, total %AR	Plant surface, total % AR	as parent on plant surface	Soil
0 (15 min)	21.5	19.8	19.3	78.5
1 hour	19.3	12.4	11.6	71.0
3 hours	15.9	6.7	6.3	71.2
6 hours	13.2	3.2	2.8	69.0
24 hours	12.7	1.5	0.7	63.7

Table 20. Residues on plants and soil as percentage of initial applied (from time 0 sample).

There was an overall loss of 23.6% of the AR over the 24 hours, with 40.9% loss of total plant residues. There was rapid loss of AR from the plant surfaces from 19.8% to 1.5% of AR, some of which was due to penetration into the plant. The penetration of diazinon into the leaves occurred with rapid metabolism and after 24 hours, only 17.2% of the extractable radioactivity from the penetrated radioactivity consisted of parent compound. There was essentially no degradation noted in the soil; 86% of the radioactivity in the soil was extractable, of which 97% was parent. It is noted that while there were some losses of radioactivity from the soil samples over time, this was not consistent with the steady loss that is reflected in the plant losses and therefore some of the observed loss could be due to variability in application.

3.5.4 Conclusions From Mobility Studies

Soil adsorption/desorption

The soil adsorption/desorption of diazinon was determined in six soils. The Kocs ranged from 255 to 496 and show that diazinon is moderately absorbed to the six soils tested. The sorption was strongly dependent on the organic content of the soil. Diazinon can be rated as having medium mobility in soil. There was no desorption done in the study.

In a published report on the mobility of diazinon in 25 different soils, the Kocs ranged from 207 to 4222 with an average of 496. The Koc was found to be highly correlated with organic matter of the soils with significant correlations with silt and clay for soils with organic matter <2%.

Leaching

In 2 soil column leaching studies using eight different soils, there was no leaching of diazinon but the metabolites were detected in the leachate. In 3 aged soil leaching studies using a total of 6 soils, it was shown that the metabolites from soil degradation are more mobile than diazinon itself, in particular the hydrolysis product, and these could leach from soil. It is concluded that the ready degradation together with the moderate adsorption of diazinon indicates that leaching of diazinon is unlikely but that the metabolites could leach.

Volatility

A study on the volatilisation of diazinon from two loam soil has been conducted but not to current guidelines. It was concluded that the level of volatilisation recorded (48 ng/cm^2/hr) indicates volatility from soil is low for the recommended rates of application.

The volatility from plant and soils was studied according to German Guidelines. The lost radioactivity from plants over 24 hours was 9% of the applied, with most of this loss assumed to be diazinon from the plant surfaces.

Volatilisation of diazinon from soils is not expected to be a significant route for the dissipation from soil. However, based on the vapour pressure of diazinon (rated as slightly volatile), volatilisation from other non-adsorbing surfaces and plant foliage could be possible.

3.6 Field Studies

There were extensive numbers of field studies presented, including several using Germany and USEPA Guidelines for both bare soil and crop dissipation studies. In addition, there are pond monitoring studies from the US and German lysimeters degradation and leaching studies. These have been summarised below.

3.6.1.1 Terrestrial Field Dissipation - According to BBA Guidelines

The following four studies on the dissipation of diazinon on bare soils were performed according to BBA Guidelines in Germany (Offizorz, 1990, 1990A, 1992, 1992A).

The four soils were treated with Basudin (diazinon, WP 40) at 1.8 kg/ha, corresponding to 0.72 kg ai/ha. The soils were sampled before, then immediately after application. Subsequent sampling was dependent on the individual studies but in general, these were approximately 7, 14, 28, 50, 90, 110 and 150 DAT. In the second set of studies, completed in 1992, the last two samples were not taken, which given the DT90, is acceptable.

The soil samples were segmented in 10 cm sections and analysed by extraction and partitioning followed by GC for diazinon and the metabolite G 27550. There was no analysis for this metabolite in the first 1990 study. Table 21 gives the soils texture and Table 22 the degradation rates. The data was analysed by Timme-Fisher analysis and used for the DT50 and DT90.

Location	Study date	pH	% oc	% sand	% silt	% clay	Texture
Lower Rhine	1990	6.2	2.1	15.3	70.1	14.6	Silt loam
Lower Saxony	1990A	6.2	1.3	36.2	53.1	10.7	Silt loam
Baden	1992	5.7	1.0	31.6	58.9	9.5	Silt loam
Bayern	1992A	6.9	1.4	7.8	79.8	12.4	Silt loam

Table 21. Soil characteristics for a range of German soils used in bare soil dissipation studies.

Location	DT50, Days	DT90, Days	Kinetic eq^{n}	R^2
Lower Rhine	27	89	1st order	0.95
Lower Saxony	4	44	Square root 1st order	0.99
Baden	9	47	1.5th order	0.96
Bayern	16	55	1st order	0.71

Table 22. Degradation rate in bare soil field dissipation studies from a range of German soils and equation used from Timme-Fisher analysis.

The studies dated 1990 were performed satisfactorily. However, the studies dated 1992 had problems with the recoveries in the analysis, in that the recoveries averaged 160% and 120% for study 1992 and 1992A respectively. Further, there was wide variation in the level of the recoveries, ranging from 109% to 200% (8 samples, average 160%) for one study and 97%-135% (4 samples, average 120% for other study. The results were corrected for recoveries. Provided the recoveries are consistent, it is unlikely to affect the degradation rate determined. However, as it indicates a potential weakness in the analyses, there is some concern.

The analysis of the metabolite G27550 was undertaken in the Baden and Bayern studies only and showed that the concentration peaked 7-28 days after treatment (0.12 and 0.18 mg/kg soil for the 0-10 cm section) and then degraded. There was a trace found in the lower 10-20 cm level.

3.6.1.2 Terrestrial Field Dissipation - Bare soil according to US EPA Guidelines

The following six studies on the dissipation of diazinon on bare soils were performed according to US EPA Guidelines in the following agricultural locations across the USA: Madera, California (Jacobson and Gresham, 1989), Phelps, New York (Bird, 1990), Gladstone, Illinios (Rice, Jacobsen and Gresham, 1990), Tulare, California (Walker, 1990), Windermere, Florida (Guy, 1990) and Reedley, California (Kimmel, Ruzo and Johnson, 1989).

The soils were treated with diazinon, at 11.2 kg ai/ha (5 mg/kg for 15 cm depth), as either a granular formulation (14G, 14% diazinon), emulsifiable formulation (AG500, 480 kg ai/L) or as a wettable powder (50W, 50% a.i). For each location there were triplicate plots treated together with controls. Details of the soils used are given in Table 23. The soils were sampled before, then immediately (1 hour) after application. Subsequent sampling was, in general, 1, 7, 14, 28, 60, 90, 120, 180, 270, 365, 454 and 540 DAT. At each sampling 5 cores were taken from each plot and sectioned into 15 cm sections which were pooled before analysis.

The pooled samples were analysed by extraction and partitioning followed by GC or HPLC. GC was used for diazinon and the oxygen analogue, diazoxon (G 24576), and HPLC for G 27550, demethylated G27550 and GS 31144 (see Attachment 1 for structures). There was recovery data and freezer stability data for all these metabolites. The limit of determination for diazinon was 0.01 or 0.02 mg/kg, depending on the study and for the metabolites 0.01 mg/kg. The stability data showed that diazinon is stabile under the storage conditions used in these studies for 6 months but G 24576 was less stable. The other metabolites were stable under the storage conditions.

Location	pH	% organic matter	% Sand	% Silt	% Clay	Texture
Madera, Cal.	6.3	0.1	85	9	6	Loamy sand
Phelps, NY	6.4	2.4	81	13	6	Sandy loam
Gladstone, Illinios.	6.6	1.6	93	3	4	Sand
Tulare, Cal.	8.1	0.9	-	-	-	Sandy loam
Windermere, Fl	6.0	2.1	94	0	6	Sand
Reedley, Cal	7.7	0.1	85	15	0.2	Loamy sand

Table 23. Soil analysis for the soils used in field studies for US EPA Guidelines

From the analytical data, the half-lives of diazinon and G 27550 was determined using first order analysis. The half-lives for the sites used is given in Table 24.

The application of diazinon did not reach the targeted concentrations of 5 mg/kg for any site except Phelps and was outside the range 80-120% of target for all sites. This is not significant for the determination of the half-lives but could affect the detection and movement of metabolites. This is, however, of concern for Tulare and Windermere due to the low initial concentrations in the soil.

Location	Conc. Diazinon at time 0, mg/kg	Diazinon*, DT50, r^2	G 27550*, DT50, r^2 (0-15 cm)	G 25770 DT50, r^2(at depth indicated)
Madera, Cal.	3.0	7 days, 0.92	16, 0.97	47, 0.8 (0-60 cm)
Phelps, NY	6.36	5.3 days , 0.99 (0-28 days);130 days, 0.83 (28-364 days)	7.2 days*, 0.91	56 days*, 0.36 (0-120 cm)
Gladstone, Illinios.	2.6	6 days, 0.98	20 days, 0.93	21 days, 0.96 (0-60cm); 77 days, 0.58 (0-180 cm)
Tulare, Cal.	2.3	6 days, 0.72 (0-28 days)	24 days, 0.41 (0-90 days); 17.5* days, 0.67 (3-90 days)	n.d.
Windermere, Fl	1.3	8 days, 0.86	12 days* , 0.88 (3-55 days)	n.d.
Reedley, Cal	3.3	13 days, 0.90	n.d.	n.d.

Table 24. The half-life of diazinon and the major metabolite G 27550 from USA studies. * Indicates that the half-life was calculated by Environment Australia. N.d. = not determined

For diazinon there was limited movement from the upper 15 cm of soil in all the studies. There were few detections in soils below 15 cm, most of these were <0.02 mg/kg. The highest occurred at Windermere, detected at 0.065 mg/kg for 1 and 7 DAT for 15-30 cm and 0.014 mg/kg for the 30-45 cm section. However, at this site there was excessive leaching, with 18.5 cm (7.3 inches) of rain falling within 2 weeks of application. These studies indicate that there is unlikely to be significant leaching of diazinon.

For the major metabolite G27550, the half-lives in the upper 15 cm at each site were significantly less than that in the total soil profile, which indicates that leaching is a significant dissipation pathway in the upper soil level. This metabolite was detected in all studies in the 45-60 cm soil section and for Windermere this metabolite was detected in the 90-120 cm section (0.012 mg/kg) at 14 DAT. The concentration of the metabolite was <10% of applied diazinon equivalent for all sites below 15 cm of depth. Other metabolites did not show significant leaching and at Windermere did not pass the 30-45 cm soil section.

The results clearly show the even under conditions conducive to leaching, the movement of diazinon was minimal. The major metabolite did show some leaching but only under conditions conducive to leaching.

3.6.1.3 Terrestrial Field Dissipation - Crop application according to US EPA Guidelines

The following six studies on the dissipation of diazinon on crops were performed according to US EPA Guidelines: Madera, California (Jacobson and Gresham, 1989A), Phelps, New York (Bird, 1990A), Gladstone, Illinois (Rice, Jacobsen and Gresham, 1990A), Reedley, California (Kimmel, Ruzo and Johnson, 1989A), Windermere, Florida (Guy, 1989) and Poplar, California (Guy, 1990A). Table 25 gives the location and soil types for each location in the 0-30 cm level.

Location	pH	% organic matter	% Sand	% Silt	% Clay	Texture
Madera, Cal.	5.6	0.2	71	21	8	Sandy loam
Windermere, Fl	5.4	1.4	94	2	4	Sand
Phelps, NY	6.4	2.4	81	13	6	Sandy loam
Gladstone, Illinios	6.6	1.6	93	3	4	Sand
Poplar, Cal.	7.4	0.92	70	18	12	Sandy loam
Reedley, Cal	7.7	0.1	85	15	0	Loamy sand

Table 25. Soil analysis for the soils used in crop field studies for US EPA Guidelines

The fields were treated with diazinon as either a granular formulation (14G, 14% diazinon), emulsifiable formulation (AG500, 480 g ai/L) or as a wettable powder (50W, 50% ai). For each location there were triplicate plots treated together with controls. Details of the application rates and number of applications together the crops used are given in Table 26. (Note that these rates used are close to, if not, the maximum rates used in Australia.) The soils were sampled before, then after each application. Subsequent sampling was, in general, 1, 7, 14, 28, 60, 90, 120, 180, 270, 365, 454 and 540 DAT. At each sampling 5 cores were taken from each plot and sectioned into 15 cm segments for 0-60 cm deep and then into 30 cm sections for 60-120 cm. The sections from each plot were pooled before analysis.

The pooled samples were analysed as above for the bare soil studies. Table 27 gives a summary of the results.

Location	Crop	Formulation type	Applications (target rate given)
Madera, Cal.	Corn, 1st application at 6 weeks after planting	Granular 14 G (14% ai)	4 weekly applications at 2.46 kg ai/ha
Windermere, Fl	35 year old orange trees,	Wettable powder, 50W, 50% ai	5 weekly applications, first 2 at 3.7 kg ai/ha, the rest at 6.2 kg ai/ha. Applied between tree rows
Phelps, NY	Newly planted (1 month) apple trees	Emulsifiable concentrate, Ag500, 480 g ai/L	7 applications at 3.7 kg ai/ha, 21 days between 1st and second, then fortnightly. Applied between tree rows (?)
Gladstone, Illinios	Corn, 1st application at approx. 7 weeks after planting	Granular 14G	4 weekly applications at 2.46 kg ai/ha
Poplar, Cal.	Newly planted (approx. 1 month) apple trees	Wettable powder, 50WP	7 applications at 3.7 kg ai/ha, applied fortnightly. Applied between tree rows
Reedley, Cal	12 year old orange trees,	Emulsifiable concentrate, Ag500	5 weekly applications, first 2 at 3.7 kg ai/ha, the rest at 6.2 kg ai/ha. Applied between tree rows

Table 26. Details of applications to field crop studies.

Location	Conc. Diazinon after last application, mg/kg	Diazinon*, DT50, r^2 (0-15 cm)	G 27550*, DT50, r^2 (0-15 cm)	G 25770 DT50, r^2 (at depth indicated)
Madera, Cal.	3.1	9 days (0-28 days), 0.74	21 days, 0.77	nd
Windermere, Fl	1.02	5.5 days (0-28 days) , 0.65	7.6 days*, 0.51	nd
Phelps, NY	0.68	2.8 days (0-14 days), 0.88 254 (14-364 days), 0.52	nd	nd
Gladstone, Illinios	2.1	5 days (0-28 days), 0.96	18 days, 0.89 (0-90 days);	25 days, 0.98 (0-60 cm); 75 days, 0.92 (0-180 cm)
Poplar, Cal.	1.25	9.9 days (0-60 days), 0.95	24 day,* 0.55 (0-90 days)	nd
Reedley, Cal	3.3	13 days (0-61 days), 0.90	nd	nd

Table 27. The half-life of diazinon and the major metabolite G 27550 from USA studies. * Indicates that the half-life was calculated by Environment Australia. nd = not determined

There was limited movement of diazinon from the upper 15 cm of soil in three studies, Madera, Phelps and Gladstone with very few detections in soils below the 15 cm, most of these were <0.02 mg/kg. The other study sites had occasional occurrences of diazinon in the 15-30 cm sections, maximum of 0.27 mg/kg at 0 DAT5 (days after treatment 5) for Windermere; 0.32 mg/kg at 0 DAT2 for Poplar and 0.07 mg/kg, 3 DAT5 at Reedley. However, there were no indications of excessive rain falling at the Polar and Reedley sites, with only normal irrigation occurring. There were few if any detections below 30 cm except for Windermere, where diazinon was detected at 0.035 mg/kg on 0 DAT5 in the 45-60 cm soils section. These residues apparently dissipated rapidly, within 7 days there were no further detections at these soil depths. As for the bare soils above, at Windermere there was excessive rainfall during the applications that could explain the greater leaching of diazinon noted at this site.

For the major metabolite G27550, the half lives in the upper 15 cm were significantly less than that in the total soil profile at Gladstone, which indicates that leaching is a significant dissipation pathway in the upper soil level. This metabolite was detected in the 45-60 cm soil section at all sites except for Madera and Phelps, where it was detected only down to 15-30 cm depth. For Windermere this metabolite was detected in the 90-120 cm section (0.014 mg/kg) at 0 DAT5. The concentration of the metabolite was <10% of applied diazinon equivalents for all sites below 15 cm of depth. Other metabolites did not show significant leaching and at Windermere none passed the 15-30 cm soil section.

The results clearly show the even under conditions conducive to leaching, leaching of diazinon was minimal. The major metabolite did show leaching potential at 3 sites, one of which was under conditions conducive to leaching.

3.6.1.4 Degradation and leaching of diazinon in two lysimeters.

A three year study was undertaken to investigate the leaching behaviour of ^{14}C-diazinon according to BBA Guidelines IV, 4-3 (Kubiak, 1995).

The two lysimeters of undisturbed loamy sand soil (130 cm deep) were placed outside in a field with their surfaces at the same level as the ground. Details of the soil used are given in Table 28. The lysimeters allowed collection of leachate. The lysimeters were cultivated during the three year study with sugar beets followed by winter wheat in the first and second years and in the third year rape was sown as a manure/intermediate crop followed by winter barley. Supplemental irrigation of the crops occurred after natural rainfall to ensure that >800 mm of precipitation occurred every 6 months.

Depth of soil	0-30 cm	30-60 cm	60-120 cm
Clay %	3.6	4.6	5.6
Silt %	5.6	15.6	12.5
Sand %	80.8	79.8	81.9
Organic Carbon %	1.0	0.2	0.1
US Classification	Loamy sand	Loamy sand	Loamy sand

Table 28. Soil used in the lysimeters.

Both lysimeters, designated as L5 and L6, were treated four times with diazinon at 240 g ai/ha monthly (approximately half the typical field crops and pasture rate for Australia) from May to August in the first year. In the second year only L5 was treated, again with four treatment at 240 g ai/ha as before. In the third year both L5 and L6 were left untreated with diazinon. Other chemical treatments were used as per standard agricultural practice for the crops.

The leachate was collected fortnightly during wetter winter months (November through to April) then monthly during summer months (May to October). The leachate was analysed for total radioactivity, $^{14}CO_2$ and extracted for TLC and HPLC analyses of metabolites. Results are in Tables 29 and 30.

Soil samples were taken in autumn and spring of every year to a depth of 30 cm and were sectioned into three 10 cm segments for analysis. At the end of the study the soil was sampled to 120 cm deep and sectioned into 10 cm sections for analysis. The soil samples were analysed for total radioactivity and then extracted and the extracts analysed by TLC.

Year	1st year		2nd year		3rd year	
Lysimeters	L5	L6	L5	L6	L5	L6
Leachate	0.5	1.1	0.3	0.3	0.1	0.1
Soil	7.0	9.1	6.8	9.3	4.0	7.8

Table 29. Average distribution of radioactivity in leachate and soil as percentage of applied. Note that in the second year lysimeter L6 did not receive any additional diazinon.

	1st year		2nd year		3rd year	
Lysimeters	L5	L6	L5	L6	L5	L6
diazinon	-	-	0.01 *	-	-	-
$^{14}CO_2$	0.05	0.05	0.02	0.01	0.02	0.02
G27550	0.10	0.38	0.02	0.11	-	-
GS 31144	0.06	0.10	0.04	0.03	0.02	0.01
not identified	0.01	0.01	-	-	-	-
Not extracted	0.28	0.53	0.15	0.17	0.02	0.05

Table 30. Metabolites in leachate as percentage of applied radioactivity, averaged over each year. Note that in the second year lysimeters L6 did not receive any additional diazinon. * One sample of leachate contained diazinon at 0.23%. G 27550 = oxypyrimidine, GS31144 = 2-(1'-hydroxy-1'-methylethyl)-6-hydroxy-4-methylpyrimidine

Diazinon was detected only once in a leachate sample, at 0.23% of AR in L5 after the second application in the second year. As this was an isolated result with no other sample showing any detectable diazinon, the authors suggested that this was perhaps attributable to a preferential flow channel in the lysimeter.

In the leachate the major metabolite detected was G 27550, oxyprimidine, which was reached a maximum in the second year in L6 (July), 0.9% of AR, approximately 11 months after the last application. The highest concentration of this metabolite in L5 was 0.42% of AR, 6 months after the first 4 applications.

From the soil analysis the majority of the radioactivity was detected in the upper 10 cm of the lysimeters. Greater than 68% of this radioactivity was non-extractable in either dichloromethane, methanol or water. Diazinon was not detected in any soil samples. The concentrations of individual metabolites in the extracts were below the detection limit of 10 μg/kg.

Overall, the result would seem to confirm the results in the column leaching studies that while diazinon is unlikely to leach, the metabolites could at low concentrations.

3.6.1.5 Agricultural runoff and pond monitoring studies

Three agricultural runoff and pond monitoring studies were performed as special studies (Biever, 1989, 1989A and B). The studies were undertaken in three different apple orchards in Pennsylvania, USA, identified as Ronald Rice (Biever, 1990), Jack Ely (Biever, 1990A) and P. R. Showers (Biever, 1990B). At each site there was a pond beside the orchards. Table 31 gives a brief description of the sites and the soil characteristics.

Each orchard received 6 sprays of diazinon at 3.36 kg ai/ha, the first two were pre-blooms (1.3 cm green leaves) and the remaining 4 after petal drop, approximately 30 days after the last of the pre-bloom sprays. The sprays were applied 14 days apart. Applications were done by the orchardists under normal commercial conditions using their own orchard sprayers. To measure the actual rate applied there were spray cards placed into the orchard canopy. In addition, cards (3) were placed round the ponds to measure spray drift and estimate its contribution to the concentration in the pond. There was no indication of wind direction during spray application.

The rainfall data presented was from the Jack Ely site and is presented in Table 32 for the significant rainfall only (>7.5 mm). No irrigation was used at any site. The rainfall was higher than the 10 year average for May, June and July and slightly below the 10 year average for April and August. Given that all sites were in the same area of Pennsylvania and relatively close to one another, having the rainfall data from only one site is acceptable.

Orchard	Soil (major type in water shed)	Site description	Pond
Ronald Rice	Gravelly loam (37% sand, 47% silt, 16% clay, 1.4% om). Deep to moderately deep well drained soil.	13.65 ha watershed with 5.7 (42%) as orchard and rest as woodland. The orchard was divided in two blocks, one 4.17 ha some 200 metres from pond, and the other 1.54 ha beside the pond	Area 0.28 ha, average depth of 140 cm, volume of 4000 m^3. Approximately 20% of pond borders the orchard.
Jack Ely	Fine granular silt loam (39% sand, 56% silt, 5% clay, 1.6% om). Deep to moderately deep well drained soil.	4.13 ha watershed, orchard made up the entire watershed.	Area 0.69 ha, average depth 148 cm, volume 10200 m^3. Approximately 70% of pond borders orchard
P. R. Showers	Granular silt loam (39% sand, 56% silt, 5% clay, 1.6% om).	28.1 ha watershed with 9.8 ha (35%) as orchard.	Area 1.95 ha, average depth 1.36 m, volume 26500 m^3. Approximately 25% of the orchard borders the pond

Table 31. Soil and site descriptions for the runoff and pond monitoring studies.

April		May		June		July		August	
Date	mm	Date	mm	Date	mm	Date	mm	Date	mm
15	10.6	1	34.8	3	12.7	4	52.3	6	22.4
19	7.9	5	57.4	6	7.6	5	24.4	19	21.8
		6	11.7	9	18.0	13	37.1		
		11	37.4	15	44.7	16	17.0		
		14	14.2	20	12.7	20	22.1		
		15	31.7	21	22.4	30	12.7		
		16	20.3	22	41.1	31	16.3		
		23	10.2	27	7.9				
		25	8.6						

Table 32. Rain fall at Jack Ely site, used for all sites. Rainfall for events of >7.5 mm for 1989, the date for the trials.

Each pond was divided into approximately 3 equal zones. Four integrated depth samples, 2 in deep water and 2 from shallow areas were taken from each zone and pooled to give the composite sample for the zone. A composite sediment sample was also taken from each zone from 4 core samples, again 2 from deep and shallow areas of the zone. There were daily samples for several days after significant rain events (2.5 cm or greater), as well as sampling on each application and the day after. At other times during the study period, samples were taken approximately weekly. In total each pond was sampled 48 times from 7 April to 31 October.

All samples were analysed by extraction of the matrix and GLC of the extracts. For all matrixes, including cards, pond water and sediment, field quality control samples as well as spiked laboratory samples were used to determine recoveries. Overall, the recoveries were acceptable, except for field fortified cards, where the recoveries ranged from 46% to 102%. However, 14 of the 18 samples were within 70 to 105% of nominal. Table 33 gives summaries of the pond water analysis at each application.

	Ronald Rice			Jack Ely			P. R. Showers		
Application	Date	Conc. µg/L,	Drift %	Date	Conc. µg/L,	Drift %	Date	Conc. µg/L,	Drift %
1	5/4	12.5	<1*	7/4	34.4	35	6/4	1.0	<1
2	18/4	53.4	<1*	20/4	44.1	8	19/4	0.8	<1
3	22/5	0.9	56	23/5	10.4	1	22/5	9.2	90
4	5/6	7.2	14	6/6	25.5	45	6/6	5.8	2
5	19/6	1.2	117	20/6	9.8	3	21/6	5.6	34
6	3/7	0.8	13	4/7	14.9	47	6/7	7.5	17

Table 33. Details of each application, the mean measured concentration in the pond after the application and the % due to drift as determined by 3 spray drift cards placed around pond. * drift cards affected by rain.

Results for pond waters

-Ronald Rice

At the Ronald Rice orchard the two highest mean concentrations in the pond water were measured after applications 1 and 2, 12.5 and 53.4 µg/L respectively, see Table 33. However, as it rained before the drift cards were collected and the rain may have washed the active off, the results form these cards may not be reliable. The third highest concentration occurred after the fourth application, 7.2 µg/L. The highest mean concentration in the pond that was clearly due to runoff (eg associated with rainfall and not on day of application) was measured on 5 July at 7.9 µg/L with the next highest of 5.5 µg/L occurred earlier on 2 May. By 17th August one zone in the pond had a concentration of diazinon below the detection limit (0.5 µg/L) but it wasn't until the last sample, taken on 31 October, that all 3 zones were below the detection limit.

The half life for diazinon in the pond was calculated for five intervals: 18 April to 9 May (9 points), 18 April to 16 May (11 points), 6 to 9 May (4 points), 21 to 29 June (7 points) and 4 to 25 July (11 points). Environment Australia considers that using over lapping periods is not valid and therefore used 18 April to 16 May, 21 to 29 June and 4 to 25 July. The half-lives for diazinon in the pond water ranged from 4.7 to 6.2 days and a mean of 5.6 days. The correlation coefficients were between 0.88 and 0.90 for all three periods.

-Jack Ely

At the Jack Ely orchard the four highest concentrations in the pond water occurred after application 1, 2, 4 and 6, with concentrations of 34.4, 44.1, 9.8 and 14.9 µg/L respectively. The highest concentration in the water that was clearly due to runoff occurred on 2 May, 13.6 µg/L. The last application was associated with significant rain of 52 mm but did not result in the highest concentration in the pond. The mean concentration on 13 September was 0.7 µg/L and by 31st October only one of the three zones in the pond had measurable concentrations of diazinon.

The half life in the pond was calculated for six intervals: 20 April to 16 May (11 points), 2 to 5 May (4 points), 6 to 9 May (4 points), 20 to 24 June (5 points), 4 to 25 July (11 points) and 4 July to 23 August (15 points). Again using only those periods without overlap, 20 April to 16 May, 4 to 25 July and 4 July to 23 August, the half-lives ranged from 5.1 days to 9.7 days with a mean half-life of 7.7 days. Environment Australia notes that July 25 to

August 23 is the second part of a biphasic distribution and calculated a half-life of 16.4 days and r^2 of 0.92 for this period.

-P. R. Showers

At the P. R. Showers orchard, the three highest concentrations were measured after applications 3, 4 and 6 with 9.2, 5.8 and 7.5 µg/L respectively. The highest mean measured concentration associated with runoff was 5.7 µg/L on June 22. It should be noted that on the proceeding day, the fourth application resulted in concentration in the water of 5.8 µg/L. Residues of diazinon were above the detection limit for all zones in the last 3 samples, taken on September 7th, 13th and 31st October, with mean concentrations of 2.9, 2.2 and 0.5 µg/L respectively.

The half-lives was determined for 3-5 May (3 points), 6-9 May (4 points) 16-20 June (4 points) 6-25 July (14 points) and 6 July to 23 August. The half-lives ranged from 4.4 days to 19.7 days with mean of 9.9 days and correlation coefficients (r^2) of 0.73 to 0.99. As for the Jack Ely data, using only the half-lives from a significant number of data points and good correlations, the mean half-life is 12.3 days.

Sediment

There were few if any detections of diazinon in the sediment that were above the limit of quantification for the method. This reflects the method used, which had relatively poor sensitivity. The limit of quantification used appears to be 50 µg/kg, based on the lowest concentration used for fortified samples. At the Ronald Rice site there were no quantifiable amounts of diazinon in any sediment samples from 5 April through to 13 September, although detections during this period ranged from 13.9 to 49.3 µg/kg. At the Jack Ely site there was only one sample that gave residues that were quantified, 144.5 µg/kg on 20 April after the second application, and only in one zone of the pond. There were no other quantifiable amounts of diazinon in any other samples and detections ranged from 11.2 to 24.9 µg/kg. For the Showers sites the sediment analyses were below the limit of quantification and ranged from 12.5 to 22.3 µg/kg.

Conclusion

The field runoff data from the 3 orchards sites showed that runoff from treated areas could cause relatively high concentration in ponds. However, the highest levels in the ponds occurred immediately after application. While the sampling cards used to monitor the spray drift showed that spray drift was a significant contributor to residues in the pond, this route did not appear account for all the residues found. The maximum concentration in ponds due to runoff only was 5.6 µg/L, which occurred some 14 days after the last application and followed heavy rain. The half-lives determined in these ponds under environmental conditions mainly in summer in the USA ranged from 2.2 days to 19.7 days and corresponds closely with that in the aquatic metabolism study of 7 to 15 days. The levels in sediment were low throughout the study period.

3.6.2 Field studies-Conclusions

Bare Soil
Ten bare soil studies were present, 4 performed according to German Guidelines and 6 to US EPA Guidelines. The German soils were classified as silt loams and the US soils as loamy sands or sandy soils. All the studies involved a single treatment followed by soil sampling and analysis. The sampling depth was 20 cm for German studies and 120 cm of the US studies.

The results of all these studies clearly showed the even under conditions conducive to leaching, the movement of diazinon was minimal. The major metabolite did show some leaching but the low concentration in the lower soils layers indicates that significant contamination of ground water would not be expected. The half-life of diazinon ranged from 4-16 days, with one at 27 days, and for the principal metabolite between 7-24 days in the upper 15 cm of the soil of 5 soils.

Field Crops
Six field crop studies were performed according to US EPA Guidelines. The study sites were largely the same as those used for the bare soil studies. There were 2 corn fields, 2 orange groves and 2 newly planted apple orchards. These studies were performed as for the bare soil studies, except that between 4-7 multiple applications were made. The results were similar and the conclusions were the same. The first half-life of diazinon was between 2.8 to 13 days and for the principal metabolite between 8 to 24 days in the top 15 cm of 4 soils.

Lysimeter Study
A three year lysimeter study was performed according to German Guidelines to investigate the leaching behaviour of diazinon. Crops were grown in the lysimeters which were treated as per normal agricultural practice. The leachate and soil from the lysimeters was analysed over the three year period at regular intervals. The results confirmed the column leaching studies in that they showed that diazinon did not leach and the major metabolite did leach but at low concentrations.

Runoff monitoring studies
Three agricultural runoff and pond monitoring studies were performed as special studies. The studies were undertaken in three different apple orchards in Pennsylvania, USA. The orchards were treated 6 times with diazinon under normal commercial practice. At each site there was a pond beside the orchards that received runoff from the orchards. In total each pond was sampled 48 times over a 6 month period. The sediment was also sampled each time the pond water was sampled.

The field runoff data from the 3 orchards sites showed that runoff from treated areas could cause relatively high concentration in ponds. The highest levels in the ponds occurred immediately after application. While the sampling cards used to monitor the spray drift showed that spray drift was a significant contributor to residues in the pond, this route of exposure did not appear account for all the residues found. The maximum concentration in ponds due to runoff only was 5.6 µg/L, which occurred some 14 days after the last application and followed heavy rain. The half-lives determined in these ponds under environmental conditions mainly in summer in the USA ranged from 2.2 days to 19.7 days and corresponds closely with that in the aquatic metabolism study of 7 to 15 days. Levels in sediment were low.

3.7 Bioaccumulation

3.7.1 Bioaccumulation and Elimination

The bioaccumulation of diazinon was studied in bluegill sunfish (*Lepomis macrochirus*) according to US EPA data requirements (Fackler, 1988).

The fish were exposed to water containing ^{14}C-diazinon at a concentration of 2.0 µg/L (nominal) under-flow through conditions. The water was sampled before the study and during the bioaccumulation phase. The concentration of diazinon remained relatively constant before commencement and throughout the study with a mean (±S.D) of 2.3 ± 0.53 µg/L (range 1.8 to 3.9 µg/L), as determined by radiometric analysis. The stability of the stock solution was not determined.

The accumulation phase lasted for 28 days and the depuration for 14 days. The fish were sampled at 0, 1, 3, 4, 7, 10, 11, 14, 21 and 28 days during the uptake phase and on days 1, 3, 7, 10, 11 and 14 for the depuration phase. Whole fish, edible and non-edible tissues were analysed by radiometric analysis. The steady state concentration in these tissues was 1.1 and 1.2 mg/kg (total radioactivity as ^{14}C-diazinon) for the edible and non-edible tissues respectively, which was reached by the seventh day. The depuration was fast, with 99% reduction in the concentration of diazinon in both the edible and non-edible tissues by the end of the depuration phase. The nature of the ^{14}C residues in the tissues was not determined.

The steady state bioaccumulation factors were determined to be 470X, 540X and 500X for the edible, non-edible and whole fish tissues respectively. Elimination of diazinon from these tissues was rapid, with half-life of between 1 and 3 days, indicative of rapid depuration.

3.7.2 Conclusion

The steady state bioaccumulation factors are low, with the highest being 540X for non-edible tissues. Elimination of diazinon from these tissues was rapid, with a half-life of between 1 and 3 days, indicative of rapid depuration. Bioaccumulation in the aquatic environment is not expected.

3.7.3 Residue Accumulation Study

A bio-concentration study using aged soil metabolites was performed according to older US EPA Guidelines (McAllister, 1979 [report amended in 1988]).

A sandy loam soil (65 kg) was dosed with ^{14}C-diazinon and then aged aerobically for 14 days. The level of dosing was determined to be 3.31 mg/kg from combustion analysis (corresponds to 2.25 kg ai/ha for 5 cm deep soil). Volatile products were not trapped during the aging process. The aged soil was then covered with water (30 cm, 1000 L) and the system equilibrated for 3 days before channel catfish were introduced into the system. The bioaccumulation phase lasted for 28 days before the fish were placed into clean flowing water for 14 days.

The samples of the soil were taken throughout the aging and the exposure phases and analysed for total radioactivity by combustion analysis. Metabolite analysis was also performed. The water was sampled through the bioaccumulation phase and analysed for total radioactivity and metabolites. The fish were also sampled during the bioaccumulation and depuration phase and analysed as whole fish, edible (fillet) and non-edible proportions for total radioactivity and metabolites. All the metabolite analysis involved extraction and TLC analysis of the extracts with quantification of radioactivity by scraping of spots and radioanalysis.

The soil analysis showed that the initial radioactivity declined from 3.31 to 2.55 µg/g at the end of the aging period. During the bioaccumulation phase the levels continued to decline from 1.97 µg/g on day 1 to 1.24 µg/g on day 28. The amount of diazinon in the soil decreased over the study period from 92% to 55% of AR after aging and decreased further to 17.4% of AR in the soil (sediment) at the end of the exposure period. There were corresponding increases in non-extractable bound residues and the metabolite G-27550.

In the water phase the total radioactivity (as diazinon) increased over the accumulation phase from 0.019 µg/mL to 0.073 µg/mL but the percentage due to diazinon decreased from 25% to 14% (from organic extractables only) and G-27550 increased, 19% to 26% (again organic extractables). There were increased amounts of radioactivity in the aqueous residues from 37% to 62% over the accumulation phase, which were not analysed for metabolites. The aqueous residues could include additional amounts of G-27550.

Total radioactive residues in the fish remained relatively steady from days 1 to days 28 of the accumulation phase, approximately equal to 1.4 µg/g for both edible and non-edible proportions. The metabolite analysis showed that the majority of these residues were diazinon, 80% and 54% on days 7 and 28 of accumulation respective. There was a small amount as G-27550, 14% on day 7 and 12% on day 28. During the depuration phase the radioactive residues decreased by 99% and were 0.02 and 0.014 µg/g for edible and non-edible respectively at the end. There was no metabolite analysis on the fish samples during the depuration phase.

Environment Australia concludes that the study shows that there is unlikely to be bioaccumulation of diazinon or its metabolites.

3.7.4 Conclusion-Bioaccumulation

The steady state bioaccumulation factors were determined to be moderate from a fish bioaccumulation study, with the highest being 540X for non-edible tissues. Elimination of diazinon from these tissues was rapid, with a half-life of between 1 and 3 days, indicative of rapid depuration. Bioaccumulation in the aquatic environment is not expected.

A bio-concentration study using aged soil metabolites was performed according to older US EPA Guidelines. A sandy loam soil was dosed with diazinon and then aerobically aged for 14 days. The aged soil was then covered with water (30 cm) and the system equilibrated for 3 days before channel catfish were introduced into the system. The bioaccumulation phase lasted for 28 days before the fish were placed into clean flowing water for 14 days. The study showed that there is unlikely to be bioaccumulation of diazinon or the metabolites.

3.8 Summary Of Environmental Fate And Degradation

3.8.1 Hydrolysis

From three experiments, it may be concluded hydrolysis of diazinon is relatively slow at pH 7 and 9 and is classified as slightly hydrolysing (Netherlands classification). At pH 5 the hydrolysis is faster and diazinon is classified as fast to moderately hydrolysing. Hydrolysis could be a significant contributor to the overall degradation of diazinon in the environment under acidic conditions.

3.8.2 Photolysis

3.8.2.1 Aquatic

Based on 3 laboratory studies using artificial sunlight lamps photodegradation in water is possible and 6-hydroxy-2-isopropyl-4-methylpyrimidine is the major metabolite. The half-lives were determined for two studies only and ranged from 55.9 to 122 hours. From these laboratory studies, the half-life under environmental conditions was not determined.

Based on 2 studies, degradation in natural sunlight was slower. Only one study determined a half-life, that of 49 days (average of two replicates). A study on photodegradation, performed to German Guidelines and based on the experimental quantum yield of diazinon, showed that direct aquatic photodegradation of diazinon is unlikely under environmental conditions.

Environment Australia concludes that photodegradation in water is unlikely to be a significant route of degradation under environmental conditions.

3.8.2.1 Soil

Based on 3 soil photolysis studies using natural sunlight, the half-life of photodegradation of diazinon in air or oven dried soils was calculated to be 17.5, 30 and 37.4 hours. The major metabolite was identified as 6-hydroxy-2-isopropyl-4-methylpyrimidine, similar to the aquatic photolysis.

There were an additional 3 studies that used artificial light. One study showed that after 24 hours exposure at 45 °C there was 28% of the applied diazinon remaining (half life not determined) and in the other studies the half lives were determined as 55 hours and 5.5 days. These studies used different lamps and cannot be readily related to natural conditions.

The photodegradation in soil could be a route of environmental degradation in Australia, given the high light levels during summer.

3.8.3 Metabolism

Only one metabolism aerobic metabolism study was performed to current (Danish) Guidelines. No other metabolism studies were performed to current guidelines.

3.8.3.1 Aerobic Soil Metabolism

The degradation of diazinon under aerobic conditions in soil is fast to moderate, with half-life of 4.5 to 8 days at 20 °C in the most reliable study under a range of temperature and spoil moisture conditions. In other studies the half-life ranged between 11 to 59 days in 4 different soils and under a range of conditions as above. The initial product is 6-hydroxy-2-isopropyl-4-methylpyrimidine, which is then slowly degraded and mineralised to carbon dioxide.

The mineralisation of diazinon TGAC was compared to a formulated product (microencapsulated, CS) in a sandy loam soil under aerobic conditions. The study showed little difference on the rate of mineralisation but the rate of degradation in the CS formulation was slower than for the non-formulated material, with 26.1% versus 1.0% of active remaining after 12 weeks.

A review of published studies on the degradation of diazinon in soil, the time for 50% degradation is stated to be between 2 and 4 weeks. This is dependent on temperature, moisture and pH value as expected. However, in a fen soil (17% om) the 50% degradation is given as 5 weeks and after 7 months there was 10% remaining.

3.8.3.1 Aerobic Aquatic Metabolism

The degradation of diazinon in aerobic aqueous conditions is very fast, with a half-life of between 7-15 days in natural river and pond water/soil systems. The initial product is 6-hydroxy-2-isopropyl-4-methylpyrimidine, which is then mineralised to carbon dioxide and other degradates. The degradation pathway appears to be hydrolysis followed by mineralisation of the hydrolysis product.

In another older study, the concentration of diazinon in water and pond sediment decreased from the initial 32 mg/L to 0.8 mg/L after 9 days. This represents 93% degradation of diazinon from the water/sediment system after 9 days.

In a published study, the degradation of diazinon in three flooded clay soils was studied using both non-sterile and sterile soil/water systems. The results show that diazinon disappeared with half-lives between 8.8-17.4 days for non-sterile systems and 33.8-43.8 days in the sterile systems.

3.8.3.2 Anaerobic Aquatic Metabolism

No studies presented.

Conclusion

It is concluded that microbial degradation of diazinon in soil and aquatic conditions is fast to moderate under aerobic conditions. There was no information available on the degradation under anaerobic conditions. However, it is likely that hydrolysis and degradation will occur but it is unknown at what rate this will happen.

3.8.4 Mobility

3.8.4.1 Soil adsorption/desorption

The soil adsorption/desorption of diazinon was determined in six soils. The Kocs ranged from 255 to 496 and show that diazinon is moderately absorbed to the six soils tested. The sorption was strongly dependent on the organic content of the soil. Diazinon can be rated as having medium mobility in soil. There was no desorption done in the study.

In a published report on the mobility of diazinon in 25 different soils, the Kocs ranged from 207 to 4222 with an average of 496. The Koc was found to be highly correlated with organic matter of the soils with significant correlations with silt and clay for soils with organic matter <2%.

3.8.4.1 Leaching

In 2 soil column leaching studies using eight different soils, there was no leaching of diazinon but the metabolites were detected in the leachate. In 3 aged soil leaching studies using a total of 6 soils, it was shown that the metabolites from soil degradation are more mobile than diazinon itself, in particular the hydrolysis product, and these could leach from soil. It is concluded that the ready degradation together with the moderate adsorption of diazinon indicates that leaching of diazinon is unlikely but that the metabolites could leach.

3.8.4.2 Volatility

A study on the volatilisation of diazinon from two loam soil has been conducted but no to current guidelines. It was concluded that the level of volatilisation recorded (48 ng/cm^2/hr) indicates volatility from soil is low for the recommended rates of application.

The volatility from plant and soils was studied according to German Guidelines. The lost radioactivity from plants over 24 hours was 9% of the applied, with most of this loss assumed to be diazinon from the plant surfaces.

Volatilisation of diazinon from soils is not expected to be a significant route for the dissipation from soil. However, based on the vapour pressure of diazinon (rated as slightly volatile), volatilisation from other non-adsorbing surfaces and plant foliage could be possible.

3.8.5 Field Dissipation Studies

3.8.5.1 Bare Soil

Ten bare soil studies were present, 4 performed according to German Guidelines and 6 to US EPA Guidelines. The German soils were classified as silt loams and the US soils as loamy sands or sandy soils. All the studies involved a single treatment followed by soil sampling and analysis. The sampling depth was 20 cm for German studies and 120 cm of the US studies.

The results of all these studies clearly showed the even under conditions conducive to leaching, the movement of diazinon was minimal. The major metabolite did show some leaching but the low concentration in the lower soils layers indicates that significant contamination of ground water would not be expected. The half-life of diazinon ranged from 4-16 days, with one at 27 days, and for the principal metabolite between 7-24 days in the upper 15 cm of the soil of 5 soils.

3.8.5.2 Field Crops

Six field crop studies were performed according to US EPA Guidelines. The study sites were largely the same as those used for the bare soil studies. There were 2 corn fields, 2 orange groves and 2 newly planted apple orchards. These studies were performed as for the bare soil studies, except that between 4-7 multiple applications were made. The results were similar and the conclusions were the same. The first half-life of diazinon was between 2.8 to 13 days and for the principal metabolite between 8 to 24 days in the top 15 cm of 4 soils.

3.8.5.3 Lysimeter Study

A three year lysimeters study was performed according to German Guidelines to investigate the leaching behaviour of diazinon. Crops were grown in the lysimeters which were treated as per normal agricultural practice. The leachate and soil from the lysimeters was analysed over the three year period at regular intervals. The results confirmed the column leaching studies in the they showed that diazinon did not leach and the major metabolite did leach but at low concentrations

3.8.5.4 Runoff monitoring studies

Three agricultural runoff and pond monitoring studies were performed as special studies. The studies were undertaken in three different apple orchards in Pennsylvania, USA. The orchards were treated 6 times with diazinon under normal commercial practise. At each site there was a pond beside the orchards that received runoff from the orchards. In total each pond was sampled 48 times over a 6 month period. The sediment was also sampled each time the pond water was sampled.

The field runoff data from the 3 orchards sites showed that runoff from treated areas could cause relatively high concentration in ponds. The highest levels in the ponds occurred immediately after application. While the sampling cards used to monitor the spray drift showed that spray drift was a significant contributor to residues in the pond, this route of exposure did not appear account for all the residues found. The maximum concentration in ponds due to runoff only was 5.6 µg/L, which occurred some 14 days after the last application and followed heavy rain. The half-lives determined in these ponds under environmental conditions mainly in summer in the USA ranged from 2.2 days to 19.7 days and corresponds closely with that in the aquatic metabolism study of 7 to 15 days. Levels in sediment were low.

3.8.6 Bioaccumulation

The steady state bioaccumulation factors were determined to be low from a fish bioaccumulation study, with the highest being 540X for non-edible tissues. Elimination of diazinon from these tissues was rapid, with a half-life of between 1 and 3 days, indicative of rapid depuration. Bioaccumulation in the aquatic environment is not expected.

A bio-concentration study using aged soil metabolites was performed according to older US EPA Guidelines. A sandy loam soil was dosed with diazinon and then aerobically aged for 14 days. The aged soil was then covered with water (30 cm) and the system equilibrated for 3 days before channel catfish were introduced into the system. The bioaccumulation phase lasted for 28 days before the fish were placed into clean flowing water for 14 days. The study showed that there is unlikely to be bioaccumulation of diazinon or the metabolites.

3.8.7 Conclusion

Diazinon is readily degradable aquatic environments and moderately to readily degradable in soils. Bioaccumulation is not expected. Due to the moderate binding in soil and rapid degradation, leaching is not expected. However, as the principal metabolite is more stable and mobile in soils, it could leach in soils that are prone to leaching.

While diazinon is not volatile from soil, it is slightly volatile from leaves and other surfaces. No information was presented on the photolysis in the vapour phase, but based on the readily degradation of other organophosphates in the atmosphere, diazinon vapours are not expected to persist in the air.

4

ENVIRONMENTAL EFFECTS

Most of the following reports were submitted by Novartis in response to the ECRP data call-in. Several of these studies are old and do not meet current requirements.

The regulatory studies are rated by Environment Australia as being reliable, acceptable or for information only. The ratings can be described as:

- Reliable: There is a high level of confidence in the results. The study has been performed satisfactorily and while there are only minor problems, they do not affect the results.
- Acceptable: The results of the study are scientifically sound but there is a lower level of confidence in the results due to a significant problem or lack of critical information. Often the results are nominal only.
- For information: There are sufficient problems in the test that the results are not suitable for regulatory use.

4.1 Avian Toxicity

4.1.1 Acute

The available results for avian toxicity of Diazinon are summarised in Table 34.

Study Type	Study Guideline	Species	Age	Results, LD50 or LC50 as ai	Rating	Reference
Acute, single dose	US EPA	Brown Headed Cowbird	-	85 (CI 35-209)mg/kg	R	Fletcher and Pedersen, 1988
		Peking duck	Adult	2.7 (CI 1.8-4.1) mg/kg	I	Sachsse and Ullmann, 1976
	US EPA	Mallard	19 weeks	1.63 (CI 0.8-2.5) mg/kg	R	Fletcher and Pedersen, 1988A
		Japanese quail	5 days	1.1 (CI 0.8-1-5.) mg/kg	A	Sachsse and Ullmann, 1975
		Japanese quail	50-60 days	3.8* (CI 2.8-5.0) mg/kg	A	Sachsse, 1973
		Japanese quail	54 days	9.4 (CI 7.9-11.3) mg/kg	I	Hayashi, Kurata and Ogura, 1977
		Bobwhite quail	-	2.1-10* mg/kg	I	Sachsse and Ullmann, 1975A
		Bobwhite quail	14 days	5.4 (CI 4.0-7.5) mg/kg	R	Fink, 1976
		Chicken	5 days	14 (CI 10.7-18.3) mg/kg	A	Sachsse and Ullmann, 1975B
Acute dietary	US Dept[1]	Mallard	5 days	202 (CI 149-273) ppm	I	Sachsse, 1973
	US EPA	Mallard	9 days	32 (CI 27-38) ppm	A	Fletcher and Pedersen, 1988B
	US Dept[1]	Japanese quail	50-60 days	1450* (CI 970-2570) ppm	I	Sachsse, 1972
	US EPA	Brown Headed Cowbird	-	38 (CI 26-57) ppm		Fletcher and Pedersen, 1988C
Chronic	US EPA	Mallard	Adults	NOEC 8.2 ppm (reproduction)	R	Marselas, 1989
	US EPA	Bobwhite quail	Adults	NOEC 32 ppm (reproduction)	R	Marselas, 1989A
		Bobwhite quail	-	NOEC 20 ppm (reproduction)	A	Shellenberger, 1970

Table 34. Toxicity of diazinon (technical or active ingredient) to avian species. [1]US Department of the Interior Wildlife Service "Procedure for Evaluation of Acute Toxicity of Pesticides to Fish and Wildlife". * Results recalculated by Environment Australia. Ratings used: R = result considered reliable, A = result considered acceptable, I = result for information only.

Comments on Table 34-Acute

Of the single dose acute tests in the Table, only three are considered reliable, the two performed to US EPA requirements and the test by Fink. The older test by Fink was not performed to current requirements but the method and results presented indicate that the test would meet these requirements, ie US EPA. The results using the brown-headed cowbird (order Passeriformes, family Icteridae) for acute and dietary toxicity tests used field collected birds, an unusual species for this type of testing. This species appears to be relatively insensitive with the highest LD50 of all bird species in Table 34. It is unclear why this species was chosen.

Although there was no control used in the studies of Sachsse (1973), Hayashi *et al* (1977) Sachsse and Ullmann (1975 and 1975B), the results are considered acceptable as doses used included a 0 response and 100% response. For the remaining test results, these are considered additional information only. There are a range of significant problems with the other studies including lack of controls, small size of test groups and limited number of test doses used.

The US EPA review (US EPA 2000) has 15 additional studies using the TGAC listed that were not presented to Environment Australia, with the most sensitive LD50 of 1.44 mg ai/ka for mallard duck. In addition, there are 8 studies listed using a range of end use formulations (EUP), with the most toxic LD50s for emulsifiable concentrate (EC), granular (G) and micro-encapsulated (CS) formulations being 1.18 (mallard), 1.8 (red-winged blackbird), and 108 mg ai/ka (Bobwhite quail) respectively. From the information in the US EPA report there would appear to be significant mitigation in the toxicity for the CS formulation.

4.1.1.1 Acute Dietary

Two of the acute dietary tests were performed to meet US EPA requirements. The birds were fed treated feed for five days, then observed for 3 days and the total number of mortalities recorded. These results would meet the requirements of the protocol that was followed. Chemical analyses of the treated feed were done for the lowest and highest test groups only and were within 80% of nominal. As not all dosed feed was analysed, the results are nominal. These studies are considered acceptable.

There was severe food avoidance noted in the 64 ppm treatment groups for both the cowbirds and mallard ducklings during the testing period. However, at day 8 of the study, the body weights of the cowbirds were comparable to controls. All the mallards from this treatment group (64 ppm) died.

The other two acute dietary results were based on older protocols from the US Department of the Interior. As there were only 3 treatment groups in each test the results are not considered to be reliable and are for information only. It is noted that in these studies diazinon appears to be less toxic than in the other two studies.

The US EPA review (US EPA 2000) has 8 additional studies acute dietary using the TGAC listed that were not presented to Environment Australia, with the most sensitive with LD50 of 32 ppm for mallard duck, the same study as in Table 34. In addition, there are 11 studies listed using a range of end use formulations (EUP), with the most toxic LD50s being 38 (mallard), 149 (mallard), and 140 (Bobwhite quail) ppm (ai) for EC, CS and wettable powder (WP) formulations respectively.

4.1.1.2 Conclusion—Acute

The above results for acute toxicity shows that diazinon can be rated (according to US EPA) as very highly toxic to most birds, highly toxic to chickens and moderately toxic to cowbirds by the acute oral route. The dietary route of exposure for birds is rated as moderately to highly toxic, based on reviewed studies but from the US EPA review of diazinon it is rated as very highly to slightly toxic.

4.1.1.3 Avian toxicity data for the micro-encapsulated product

The following bird toxicity studies on Knox Out 2 FM (identical to Pennside) have been provided for the micro-encapsulated product (see Table 35).

Study Type	Study Guideline	Species	Age	Results, LD50 or LC50 as product	Rating	Reference
Acute, single dose	Not stated	Bobwhite quail	20 weeks	472 (CI 380-587) mg/kg (= 108 mg ai/kg)	R	Beavers and Fink, 1978a
Acute dietary	Not stated	Mallard duck	14 days	649 (CI 464-908) ppm (149 ppm ai)	R	Beavers and Fink, 1978b
	Not stated	Bobwhite quail	14 days	1515 (CI 1147-2002) ppm (= 348 ppm ai)	R	Beavers and Fink, 1978c

Table 35. Toxicity of micro-encapsulated product to avian species.

- Comments on the acute single dose study

Test birds were acclimatised in pens (10 per pen) for two weeks prior to being given single doses of 0 (control), 251, 398, 631, 1000 and 1590 mg product/kg bodyweight in corn oil and intubated directly into the crop via a stainless steel catheter. Body weights and food consumption were measured regularly, and symptoms of toxicity and mortality recorded daily over the 14 day test period.

No mortalities occurred in the control group, and all birds were normal in both appearance and behaviour throughout. By contrast there was a 10% mortality at the lowest dose, 40% at 398 mg/kg, 60% at 631 mg/kg and 100% mortality at the two highest doses, with probit analysis used to estimate the LD50 tabled above. At the lowest dose lethargy, reduced reaction to external stimuli (sound and movement), loss of co-ordination and limb weakness were recorded, which had abated by day 3. At 398 mg/kg similar symptoms of loss of co-ordination and ataxia were noted after dosing and up to day 4, as well symptoms of depression, wing droop and prostrate posture were noted on day 1. Surviving birds at these levels showed a body weight loss for the first 3 days, but this was comparable with controls at the end of the study. Similar, but more severe symptoms were recorded at the higher levels prior to death of the birds.

Based on the above the study may be rated as reliable, though the US EPA review (US EPA 2000) rates it only as supplemental.

- Comments on acute dietary studies

Both species of birds (10 per pen) were exposed to product dissolved in corn oil added (in a 2:98 ratio) with standard game bird starter ration at a dietary concentration of 0 (control), 100, 178, 316, 562, 1000, 3160 and 5620 ppm for five days. Bodyweights and food consumption were measured, and symptoms of toxicity recorded daily throughout the 8 day study. A laboratory standard (dieldrin) was also tested.

There were no mortalities in the control mallard duck group, with only one control bobwhite quail dead, which was attributed to toe picking. All other control birds were normal in appearance and behaviour with no overt lesions noted upon gross necroscopy at the end of the study (though excessive food wastage resulted in abnormally high food consumption for one bobwhite quail).

With the mallards there was no mortality at 100 ppm, a 20% mortality at both the 178 and 316 ppm dose levels, 30% at 562 ppm, 60% at 1000 ppm, 90% at 1780 ppm and 100% at the two highest dose levels. Symptoms of toxicity noted prior to death included lethargy followed by depression, reduced reaction to external stimuli (sound and movement), wing droop, a ruffled appearance, loss of co-ordination and ataxia, prostrate posture, loss of righting reflex and lower limb rigidity. There was a dose related reduction in weight gain among surviving birds, and a marked dose related reduction in feed consumption.

By contrast no mortalities or abnormal appearances occurred at the 100 and 316 ppm dose levels with the bobwhite quail. At 178 ppm there were two mortalities attributed to nostril picking, with at the 562 ppm dose level only one bird exhibiting symptoms of toxicity similar to the above. Four mortalities occurred at the 1000 ppm dose level, with 60% dead at 1780 ppm, 80% at 3160 ppm and 100% dead at the highest dose level. Again symptoms of toxicity prior to death were similar to those above, with several birds in a comatose state immediately prior to death. From the 1000 ppm level there was a dose related reduction in feed consumption and body weight gain in surviving birds.

Probit analysis was used to calculate the LC50s tabled above. The reports note that in both instances the toxicity may have been accentuated by the inclusion of corn oil in the diet, which lead to leaching out of the active from the microcapsules. This was supported by differences in recovery at 0 and 8 days (63 vs 580 ppm respectively).

Based on the above analysis the studies may be rated as reliable, noting the US EPA review (US EPA 2000) rated them as core studies.

- Conclusion re micro-encapsulated toxicity

The above results indicate that the Knox Out 2 FM (= Pennside) product is acutely less toxic than the active ingredient itself, with the exception of the Brown-headed cowbird single dose and the first Mallard duck and Japanese quail acute dietary results in Table 34. However, based on US EPA classifications the active ingredient for the micro-encapsulated product is still moderately toxic to the bobwhite quail following a single dose, but highly toxic to both it and the mallard duck following acute dietary exposure.

4.1.2 Chronic Testing

One generation reproduction studies with the mallard duck and bobwhite quail were submitted by Novartis and performed according to US EPA Guideline 71-4 (Marselas, 1989 and 1988 A for the mallard and Bobwhite quail respectively).

Diazinon was administered via the diet to young birds approaching their first breeding season. The birds were fed with dosed feed for a total of 20 weeks with dosages of 5, 10 and 20 ppm for mallards and 10, 20 and 40 ppm for quail. After 7 and 8 weeks (for quail and mallard respectively) on the treated feed, the birds were induced to egg laying and the eggs collected daily. Effects upon shell thickness, egg production, quality of eggs, hatching health and survivability were examined as well as cholinesterase inhibition in both blood plasma and brain cholinesterase at study termination. Blood was collected at 7 days after commencement, at the start of egg laying, at 4 weeks after egg production and at study termination for plasma cholinesterase.

Analysis of the feed showed that the mean concentrations in the feeds over the 20 weeks of the study were used in determining the toxicological endpoints. In the quail study the actual concentrations were determined to be 8.3, 16.3 and 32.0 ppm for nominal concentration of 10. 20, and 40 ppm. In the mallard study results were 4.05, 8.30 and 16.33 ppm for nominal concentrations of 5, 10 and 20 ppm.

There were no treatment related mortalities, overt signs of toxicity, effects upon adult body weights, feed consumption or reproduction parameters studied at any dose during the quail study when compared to controls. The cholinesterase results showed that for all treatments there were statistically significant reductions in plasma cholinesterase. There was no effect on brain cholinesterase in the cock birds. For the hens the cholinesterase was significantly depressed but this did not show a dose response. The NOEC for reproduction was 32.0 ppm (corrected), the high dose tested, and <10 ppm for cholinesterase inhibition.

For the mallard study there were no treatment related mortalities, overt signs of toxicity or effects upon adult body weights when compared to controls at any treatment. In the highest treatment group there appeared to be a slight reduction in feed consumption for the first 2 weeks of the study. There were no apparent treatment related effects upon reproductive parameters tested in the 5 and 10 ppm treatment groups. In the 20 ppm treatment group there was a treatment related increase in the number of hens that continued to lay but did no start to incubate and reduction in the number of hatchlings and 14 days old survivors. The mean 14 days hatchlings body weight for the 20 ppm group was also significantly reduced. The NOEC for reproduction was determined to be 8.3 ppm, based on measured concentrations.

Serum cholinesterase was inhibited at all treatment levels and was dose responsive. The brain cholinesterase activity was also inhibited at all treatment levels but there was not a clear dose-response relationship in the cock birds. The NOEC for cholinesterase inhibition was <5 ppm.

The results for the chronic reproduction studies for Mallards and bobwhite quail are considered reliable.

In the older study in Table 34, the reproductive capacity of bobwhite quail was determined at nominal concentration of 7, 20 and 60 ppm of diazinon in the diet. The study used a 5-

week pre-treatment period, 5 weeks treatment and 4 weeks recovery. During the study, egg production, hatchability, and fertility were the reproductive parameters tested. In addition the adults bird body weight, feed consumption and cholinesterase was monitored.

Results for this study showed that egg production, hatchability, fertility, body weight and feed consumption the 7 and 20 ppm treatment groups were similar to controls throughout the 14 week study period. In the 60 ppm group, egg production, hatchability, fertility and feed consumption were slightly reduced during the treatment period. These parameters recovered during the 4 week recovery period. There were no apparent effects on body weight during the study in any group. Whole blood cholinesterase was markedly decreased in the 20 and 60 ppm groups at the end of the treatment period and was only partially recovered in the males after the recovery period but full recovered in the hen birds. Brain cholinesterase was not inhibited in any group during the study.

The study is considered as acceptable.

Again the US EPA review has additional studies for chronic toxic for EUPs. The NOECs are 35 ppm (ai) using an EC and 1.05-2.1 mg ai/day using treated seeds based on weight loss and reduced egg production. There were no additional studies using the TGAC.

4.1.2.1 Other avian studies

In a study on the effects of use of diazinon on ducks and geese, measurements of brain cholinesterase in duck and geese during treatment with diazinon was undertaken (Honeycutt, 1983). A semi-field study was also performed to assess the risk to ducks and geese.

For the cholinesterase sections, groups of ten-month old mallard ducks were treated with a single dose of diazinon technical (88% ai) at 0, 6, 8, 10 or 12 mg/kg, then brain cholinesterase was measured at 1, 2, 3, 8, 24, 48 and 96 hours after dosing. There were 10 birds (5 male, 5 female) used for each brain cholinesterase sample and the results were given as the average. All birds that died in the 6 and 10 mg/kg groups were analysed for brain cholinesterase immediately after death. Table 36 summarises these results.

Time of sample	6 mg/kg Males Females		8 mg/kg Males Females		10 mg/kg Males Females		12 mg/kg Males Females	
1 Hour	76	67	66	70	30	26	22	22
3 Hour	87	58	77	65	62	27	26	41
8 Hour	86	49	58	62	46	39	40	47
24 Hour	77	45	79	83	42	39	58	58
48 Hour	72	65	74	62	59	47	71	49
96 Hour	71	84	79	60	78	63	64	64
Dead/30 dosed	0	2	2	2	9	10	14	16
mean at death (No. of birds)	40* (1) 20 (1)				15 (8) 13 (6) 13 (3) 18 (1) 32**(1)		14 (5), 12 (5)	

Table 36. Brain cholinesterase levels as percentage of controls after mallard ducks received a single dose of diazinon. *Bird died 49 hours after dosing and may not be diazinon related. **Died 24 hours after dosing and may not be dose related.

The results in Table 36 indicate that there is a dose response relationship on brain cholinesterase activity and 10 mg/kg appears to cause mortality in approximately one third of the birds treated. When the two birds that died 24 and 49 hours after dosing are excluded, mortality occurred when the mean cholinesterase activity was between 12-18% of control values (mean 15± 2.8%).

Canadian geese were also dosed with diazinon at 6 (4 geese), 10 (4 geese), 18 (1 goose) and 24 (1 goose) mg/kg, then the brain cholinesterase levels measured at 1 and 3 hours after dosing. The level of inhibition in the geese was less than that for the ducks. After 3 hours the geese dosed at 18 and 24 mg/kg had cholinesterase levels of 72% and 61% of control values respectively.

In the semi-field study, 6 plots of turf were treated with diazinon as granular (14 G, 14% ai) or EC (AG-500, 48% ai) at 6.72 kg ai/ha (highest rate in Australia is 6 kg ai/ha for a CS formulation). Two of the plots were then irrigated (6.3 mm), one each for granular and EC. Fifty mallard duck were then introduced to each plot, both granular and EC, irrigated and non-irrigated. Geese (15 birds per plot) were introduced to two plots, a granular and EC, both non-irrigated. All birds were fasted for 24 before introduced to the plots and then only allowed to feed on naturally occurring feed in the plots for the first 3 days. Brain cholinesterase levels were measured on days 1, 3, 5, 7, 9, 14 and 21 days for the mallards (5 males and 5 females) and days 1, 3 and 7 for geese (five birds each time). In addition, a field dissipation study in turf, thatch and soils (0-7.5 cm) was undertaken and samples were taken on days 1, 3, 7, 9, 14, 21 and 70 for residues analysis. Residue results are in Table 37.

			DAT					
Formulation	Irrigation	Sample	0	1	3	7	14	21
14G	0	Grass Thatch	19 31	18 30	17 35	12 41	4.2 30	4.6 30
14G	6.3 mm	Grass Thatch	26 23	63 80	6.6 19	13 40	<1 8.8	1.9 16
EC	0	Grass Thatch	144 247	122 295	108 157	39 152	8 46	6.5 50
EC	6.3 mm	Grass Thatch	60 80	67 81	61 119	14 41	42 8.1	5.2 40

Table 37. Results of residues study from turf application. Results given ppm (µg/g).

There were no overt effects from treatment using the granular formulation on the mallard ducks in either irrigated or non-irrigated plots. Slight depression of cholinesterase levels (means 84-88% of control, 1 to 5 DAT {exposure}) was noted, which from the earlier study on cholinesterase and mortality would not be expected to cause any mortalities. Likewise, there were no overt symptoms from the EC formulation in either non-irrigated or irrigated plots. However, there was significant depression of average cholinesterase levels in the EC plots compared to control with means of 40-62% for non-irrigated and 61-70% for irrigated over the first 5 DAT.

There were no overt effects from treatment using the granular formulation on the Canadian geese but there were in the EC plots. In the EC plots symptoms on the first day included limb rigidity, wing droop, salivation and tremors. One 1 goose died in the first day. After 6 hours, all remaining geese stopped grazing and after 10 hours, the geese had recovered. On day 2 the geese resumed grazing but showed loss of coordination and were sluggish compared to those on control and granular plots. By day 4, when non-contaminated feed became available, all geese appeared normal. The mean brain cholinesterase levels in the granular plots were 94-98% of control (1-7 DAT) and 50-74% in the EC plots.

It was concluded by the authors that treatment of turf with the granular formulation at 6.7 kg ai/ha is unlikely to affect ducks and geese and that increasing the rate would be unlikely to affect waterbirds. However, as puddling of irrigation water could increase the hazard to waterfowl, excessive irrigation should be avoided. EC formulations are unlikely to affect ducks overly at the rates used in the study but higher rates could cause mortalities. This hazard to ducks could be reduced by watering in the EC applications thereby reducing the concentration on grass with the note that excessive watering that leads to puddling should be avoided. For Canadian geese, EC formulations to turf at 6.7 kg ai/ha could cause significant effects on brain cholinesterase and overt symptoms, typical of OP poisoning. As irrigation after application would be expected to reduce the concentration on grass, this could be used to mitigate the hazard to Canadian geese, with the note to avoid excess watering and puddling.

4.1.3 Published Reports

Using acute oral single dose tests (based on published methods), the toxicity of diazinon to starling and red-winged black birds nestlings and adults was determined (Wolfe and Kendall, 1998). There were 3 (red-winged) or 5 (starling) dose levels used together with controls and a minimum of 24 hours observation period to determine the LD50s. Technical grade active was dissolved in corn oil and given to the birds by oral gavage. The concentration of active in the oil was determined by GC. The age of nestlings used and the LD50s are given in Table 38.

Red-winged blackbird			Starling		
Age days	LD50 (CI)	Age ratio*	Age days	LD50 (CI)	Age ratio*
0-3	2.4 (1.3-6.1)	1.0	2	12.7 (10.9-15.1)	1.0
4-7	3.4 (1.3-9.0)	1.4	5	35.6 (23.1-69.3)	2.8
8-11	8.3 (6.6-10)	3.4	9	93.2 (72-126)	7.3
			15	102 (80.9-145)	8.0
			19	145 (na)	11
Adults	9.1 (3.88-15.9)	3.8	Adults	602 (398-893)	47

Table 38. Estimated LD50 and 95% confidence intervals, age and toxicity ratios of diazinon to Red-winged blackbirds and starlings. *Age ratio LD50/LD50 of youngest.

The results in Table 38 clearly indicate that nestlings are more sensitive to the effects of diazinon than adults and by a factor of approximately 50 in the case of starlings. It is noted that for Red-winged blackbirds the difference in sensitivity between the nestlings and adults is significantly less. During these studies the authors noted that some female blackbirds threw out of the nest any chicks that showed aberrant behaviour such as failure to beg or vocalise or in response to parental stimulation. These observations clearly indicate that sublethal exposures could cause significant effects on nestling mortalities.

The levels of brain and plasma cholinesterase were determined. For starlings and red-wings there was a dose dependent relationship as expected, which was strongest for survivors than for non-survivors. There was significant recovery in both brain and plasma cholinesterase after 48 hours in survivors.

In another published paper, the acute toxicity of diazinon to eight different stocks of bobwhite quail (from 8 different game farms) were compared (Hill, Camardese, Heinz, Spann and DeBevec, 1984). To eliminate the differences in husbandry, the birds were incubated from eggs and raised in the same facility. The results from acute single oral dose tests on each stock gave a range of LD50s from 13 (CI 8-21) to 17 (CI 11-25) mg/kg. The average LD50 was 14.9 mg/kg and the pooled LD50 was 14.7 (CI 13.1-16.5) mg/kg. These results are higher than those in Table 34 but not outside of what is considered the typical inter-laboratory variation in this type of test.

This is a large study with 14 birds used for each dose, 5 doses for each stock and pooled control of 40 birds, 5 from each stock and the results are considered reliable.

Cobb *et al* (2000) made comprehensive residue determinations in biota inhabiting orchards in Washington and Pennsylvania. Six applications of diazinon 50W were made to each orchard over 3 months (spring/summer 1989) in Pennsylvania and 5 in Washington; with a mean application rate each time of between 3.0-3.1 kg ai/ha, as determined by spray rates and treated acreage.

Dissipation from vegetation was found to be rapid, with best fit modelling of the samples analysed indicating that residual diazinon present on apple leaves and understory vegetation at day 14 should be 6 and 2 % respectively of levels immediately after application. In Pennsylvania 28 earthworms were analysed, with the mean diazinon concentration being 10.5 µg/g (at 18.1 µg/g this was considerably higher in the 4 dead worms collected). By contrast only eight earthworms were able to be collected in Washington, with half of them showing no residues and a mean of 0.39 µg/g.

Diazinon levels were determined in carcasses from birds found within the orchards, except for European starlings where nestlings were taken from boxes placed on the orchard perimeters to attract this species. One hundred and fifty one carcasses were found (80 in Pennsylvania), and twenty three of the 25 avian species collected contained diazinon in their gastro-intestinal (GI) tracts, with quantifiable residues in 17 species. By far the highest mean residues were 2.17 and 1.82 µg/g found in 12 Canada geese and in 4 killdeer nestlings, respectively, in separate Washington orchards. This was followed by 1.56 µg/g from 5 American robins in one Pennsylvanian orchard, with the next highest 0.31 µg/g for 3 specimens of the same bird in a Washington orchard, 0.25 µg/g for 4 Western meadowlark specimens in a Washington orchard and 0.21 µg/g for 3 European starling nestlings found in a Pennsylvanian orchard.

The authors note that Canada geese would not normally be associated with apple orchards (the affected orchard was on the banks of the Columbia River) though mortality may occur from consumption of diazinon residues on grass. However, the killdeer is a soil prober that feeds heavily on soil invertebrates, and its exposure potential would appear to be similar to the American robin. Hazard calculations indicated that 4 of the species noted above potentially received lethal doses, and that there was a risk of passerine poisoning during the first 4 days following application during which 78-84% of residues dissipated from the vegetation.

The above information is relevant to the assessment of hazard from use in the orchard situation (Section 5.2.1.2 of this report). However, as noted this does not appear to be a current use, except for occasionally in macadamias where the high rate (up to 4 kg ai/ha) would be of concern to birds. It is unclear whether this use will continue. Note also that spraying in pome fruit orchards, should this be continued, is at 1.56 kg ai/ha, half the rate used in Cobb *et al* (2000), and further that vegetables are generally sprayed at an even lower rate (0.56 kg ai/ha).

Wang *et al* (2001) tested whether northern bobwhite quail and gray-tailed voles would respond differently to equivalent concentrations of diazinon applied in granular or flowable formulations. The exact nature of the latter is not disclosed, but from common usage of the nomenclature it would appear to be the micro-encapsulated rather than the EC version. These were applied separately at one and two times the maximum allowable rate of 1.1 kg ai/ha (for pastures) to enclosures containing the test animals. Diazinon was applied by a hand broadcast spreader and tractor driven boom respectively, and was not watered in.

Trapping of the voles revealed that treatment appeared to have no effect on vole survival compared with controls. On the other hand it was clear that the diazinon granular treatment had more of an effect on bobwhite quail. Six dead birds were recovered (with granules in their crops) from a bare ground strip close to the enclosure fence during the first census 10 hours after application of the double rate treatment. Abnormal behaviour (lethargy, wing drop, ataxia, and hyporeactivity) was also observed. By contrast no dead birds or abnormal behaviour were observed in the control or liquid treatment enclosures.

While this study lends support to the hypothesis that liquid are less toxic than granular treatments, the results are confounded by the fact that analysis of the former indicated the actual dose rate was 75% of nominal at the higher treatment rate (and 50% at the lower). Since the actual application rate of the granular treatments was not determined, and most of the effects were noted at the highest rate for this treatment, any conclusions must be treated with caution. Further, grasses, as opposed to seeds, do not form a significant component of quail diets, so any attempt to extrapolate to the hazard of grass eating birds such as the Australian wood duck should be treated with extreme caution.

4.1.4 Report of Australian Incidents

Diazinon was involved in a bird poisoning incident in Australia when it was used to treat the lawns at Parliament House (Hansard, 1991). Two chemicals were used, malathion and diazinon (a micro-encapsulated formulation), to treat lawns for Argentine stem weevil with the chemicals watered into the lawn. In this incident there were 12 magpies found dead at Parliament House but anecdotal reports indicated that a larger number may have been affected.

There has been a recent incident at Gosford, NSW, where a school oval was sprayed with the micro-encapsulated product Pennside but at about 10 times the label rate a misuse situation and 46 ducks died as a result (Registration Liaison Committee, Meeting No. 18). Newspapers reports of the incident state that the oval was sprayed at 26 times the label rate and a teacher and student also became ill (Daily Telegraph, 28/6/2000, page 11).

4.1.5 US EPA Regulatory Action

In 1988 the US EPA banned the use of diazinon for golf courses and sod farms following a special review, which was started following "..the disturbing history of reported bird kills associated with diazinon use on golf courses and other large grassy areas" (Chemicals Regulation Reporter, 1988). The review determined that use of diazinon for golf courses and sod farms posed an unreasonable risk to birds in the US. Despite this restriction on use for golf courses etc, there are still 58 bird kills document in the US EPA review (US EPA, 2000) for the period 1994-1998 where diazinon is the primary toxicant but the specific source is not known and roughly 200 since 1987. While as noted above (Section 2.1.4) a number of agricultural uses will be cancelled in the US, the fate of any remaining turf uses is unclear.

4.1.6 Conclusion—Avian Toxicity

The avian single dose toxicity of diazinon is rated as very highly to moderately toxic with LD50s ranging from 1.1 to 85 mg/kg for all studies (6 species). The two modern and reliable studies give LD50 of 85 mg/kg for brown headed cowbird and 1.63 mg/kg for mallard. The 3 less reliable but acceptable results gave LD50s of 1.1, 3.8 mg/kg for Japanese quail and 14 mg/kg for domestic chicken. For the acute dietary toxicity, diazinon is rated as very highly to slightly toxic, with LC50 from 32 to 1450 ppm in the diet. The two reliable modern studies gave LC50 of 32 ppm for mallard and 38 ppm for brown headed cowbird. The US EPA review of diazinon rates it similarly.

The Pennside micro-encapsulated product is acutely less toxic than the active ingredient itself, with the exception of the Brown-headed cowbird single dose and the first Mallard duck and Japanese quail acute dietary results. However, based on US EPA classifications the active ingredient for the micro-encapsulated product is still moderately toxic to the bobwhite quail following a single dose, but highly toxic to both it and the mallard duck following acute dietary exposure

In the chronic reproduction studies over 20 weeks, the NOEC levels were 8.3 ppm for mallard and 32 ppm for bobwhite quail. For the bobwhite, the NOEC is the highest concentration tested, while for the mallard the MATC was 8.3 ppm to 16.3 and the LOEC of 16.3 ppm was based on reduced number of hatchlings and survivors in the 14 day old ducklings at this dosage.

A semi-field study showed that there were no overt effects to mallard ducks when exposed to diazinon on turf at 6.7 kg/ha as either EC or granular formulations. However, Canadian geese were overtly affected (limb rigidity, wing droop, salivation and tremors with one goose dying) at the same rate (6.7 g ai/ha) when the EC formulation was used but not with the granular formulation.

In recent study, the sensitivity of nestlings (red-winged black birds and starlings) was compared to adult birds in acute oral tests and it was shown that nestlings were more sensitive. Red-winged nestlings were 3.8 times more sensitive than adults (LD50 2.4 to 9.1 mg/kg) and starling nestlings 47 times more sensitive (LD50 12.7 to 602 mg/kg) than the adults.

Over 150 bird carcasses were found in a study of Washington and Pennsylvania orchards following 6 spray applications over 3 months with a mean application rate each time of between 3.0-3.1 kg ai/ha. Canada geese had the highest residues followed by killdeer and American robins, both of which feed on soil invertebrates. Hazard calculations indicated that 4 species potentially received lethal doses and there was a risk of passerine poisoning during the first four days following application, during which 78-84% of residues dissipated from the vegetation.

There are reported incidences of bird kills in Australia with the best documented being in 1991 involving use of diazinon to kill Argentine weevils in the lawns at Parliament House. Another incident that was well reported occurred in the city of Gosford, NSW, where a school oval was sprayed at 10 times the recommended rate and 46 ducks died.

4.2 Aquatic Toxicity

4.2.1 Regulatory Studies for Fish

The following aquatic toxicity results for the TGAC and emulsifiable concentrate were presented by Novartis.

Test	Test method	Species	Results LC50, mg ai/L	References
96 hour acute static	US Dept.[1]	Rainbow trout	2.6[**] (1.7-4.0)[##]	Sachsse, 1972A
		Crucian carp	7.6[**] (5.4-10.7)[##]	
		Channel catfish	2.7[**] (1.7-4.25)[##]	
		Bluegill	16[**] (10-25.5)[##]	
		Guppy	4[**] (2.5-6.45)[##]	
96 hour acute static	US Dept.[1]	Rainbow trout	3.2[**] (2.4-4.2)[##]	Sachsse and Ullmann, 1975C
		Crucian carp	23.4 (18.7-29.2)[##]	
96 hour acute static	Japanese MAF	Rainbow trout	1.4[** A]	Kurata and Kurosawa, 1991
96 hour acute static		Common carp	2.16[**] (1.21-2.63)*[##]	Koesoemadinata 1983
		Java carp (*Puntius gonionotus*)	3.96[**] (3.44-4.55)*[##]	
48 hour acute static	Japanese	Common carp	5.46[**] (4.9-6.1)*[##]	Yoshida, 1974
96 hour acute static	Japanese MAF	Common carp	6.28[**] (5.5-67.2)*[##]	Kurata and Kurosawa, 1990
96 hour acute static	—	*Tilapea mozambica*	2.91[**] (1.75-24.07)	Rao 1981
96 hour acute static	MAF (Japan)	Black carp (*Cyprinus carpio*)	5.35[**] (5.02-5.70)[A ##]	Dohke and Hatanaka 1977
96 hour acute flow-through	US EPA and OECD	Rainbow trout	NOEC >24 (for CS 300)[#]	Bettencourt, 1994
Early life stage, embryos and larvae, 34 days	US EPA 72-4	Fathead minnow	MATC 0.092-0.17 Geo. Mean 0.13[#]	Surprenant, (1988)

Table 39. Toxicity of diazinon technical to fish. [1]US Department of the Interior Wildlife Service "Procedure for Evaluation of Acute Toxicity of Pesticides to Fish and Wildlife". [**] Results are nominal. *Results were converted from EUP to active, see text. [A] Results recalculated by Environment Australia. [#] Result considered reliable, [##] result considered acceptable.

4.2.1.1 Comments on tests in Table 39.

The acute toxicity studies by Sachsse (1972) for a number of fish species are considered acceptable with the proviso that the results are based on nominal concentrations only. The LC50s were calculated by an older method but these have been recalculated using current probit methods and were not significantly different for rainbow and carp and therefore the original endpoints were used in Table 39. The results from Yoshida (1974) and Sachsse and Ullmann (1975C) are similarly acceptable, noting that the results again are nominal.

The results for common and java carp (Koesoemadinata, 1983) were based on an EC formulation of 600 g/L and have been converted to an active constituent basis. The results were based on graphic probit analysis and the raw data was not given. The method used did not follow acceptable testing guidelines and were based on older procedures. The description given indicates that although the report is lacking some details on the raw data, the LC50s given are considered acceptable.

The results for *T. mozambica* (Rao 1981) are not considered acceptable as there was no control in the test and only 3 concentrations were tested.

The results for the black carp (Dohke and Hatanaka, 1977) are from a test that followed procedures from MAF 1965 Guidelines. It is assumed that it is the Japanese Ministry of Agricultural and Fishery Guidelines but this is not clear in the report. As the results are nominal and there was no control used, there is some question as to the confidence in the results. However, as there were 6 doses used with one giving a zero response and 2 giving partial responses, the LC50 calculated was recalculated by Environment Australia and the results are considered acceptable.

The study for common carp (Yoshida, 1975) was performed according to the Standard method of the Evaluation of Acute Fish Toxicity of Agricultural Chemicals of the Japanese Government but it is unclear if these are related to the Japanese MAF above. The results are nominal but acceptable. Similarly, the studies by Kurata and Kurosawa (1990) were performed according to Japanese Ministry of Agriculture, Forestry and Fisheries Guidelines and are considered as acceptable. The study using rainbow trout (Kurata and Kurosawa, 1991) showed significant discontinuity in the dose response curve and confidence intervals were not obtainable. Despite this the study appears to be acceptable, noting that the results are nominal.

The flow-through test using rainbow trout was performed used a micro-encapsulated formulation (CS) formulated at 300 g ai/L. The protocol used followed US and OECD Guidelines and the results are considered reliable. Analysis of the test solution showed that the test concentrations were 88-110% of nominal. Undissolved material was noted at all test concentrations (2.9-22 mg ai/L nominal), which could be the micro-capsules in the formulation. No mortalities were noted at any concentration tested and the NOEC is 24 mg ai/L, based on measured concentrations.

The undissolved material and the lack of any toxicity could indicate that the micro-capsulates are not breaking down and therefore the active constituent is not bioavailable.

4.2.1.1 Fathead Minnow

As a substitute for a full life-cycle toxicity test, the toxicity of diazinon to the embryos and larvae of Sheepshead minnows was determined under flow-through conditions (Surprenant, 1988). The rationale, as stated by the authors of this study, is based on the observation that these embryo/larvae studies are reasonably accurate short-term predictors of the chronic life cycle studies. The criteria used to determine the maximum acceptable toxicant concentration (MATC) were based on larval growth (length and weight) at the termination of the test. Analysis of the test solution showed that the average test concentrations were 89 to 107% of nominal over the test period. The study was well performed and it meets the current Guidelines. The results are considered reliable and would suggest a high chronic to acute ratio.

4.2.2 Regulatory Studies for Invertebrates and Algae

The following studies on the toxicity of diazinon to aquatic invertebrates were presented by the registrants and have been summarised in Table 40.

Test	Test method	Species	Results EC50, µg ai/L	References
24 hr immobilisation	AFNOR	*Daphnia magna*	950 (680-1200)[**][A] (outlier?)	Hitz, 1982
48 hr mortality	US EPA 1975	*Daphnia magna*	LC50 0.96 (0.83-1.1)[**][##]	Vilkas, 1976
96 hr mortality, flow through	US EPA 1985	Mysid shrimp	LC50 4.2 (3.7-4.8)[##]	Surprenant, 1988A
48 hr immobilised	US EPA 1985	Ceriodaphnia	0.36-0.6[**][##]	LeLievre, 1991
3 hr mortality		*Daphnia carinata*	11.54[*] (8.07-16.25)[**]	Dohke and Hatanaka, 1977A
3 hr mortality		*Monia macrocopa*	4.0 (3.6-4.4)[**] mg/L	Kurata and Kurosawa, 1990A
Oysters, 96 hr shell growth	US EPA 1985	*Crassostrea virginica*	880 (630-1100)[#]	Surprenant, 1988B
21 day chronic	US EPA 1985	*Daphnia magna*	MATC 0.17 to 0.32[#]	Surprenant, 1988C
Growth Inhibition	AFNOR	*Scenedesmus subspicatus*	IC50 17.3 (16.4-18.1)[**][##] mg/L	Hitz, 1982A
Growth Inhibition	OECD 201	*Scenedesmus subspicatus*	8.54 (7.2-10)[**][##] mg/L	Oldersma, Hanstveit and Pullens, 1984
Growth Inhibition	US EPA 1985	*Scenedesmus capricornutum*	IC50 6.4 mg/L[##]	Hughes, 1988

Table 40. Toxicity of diazinon to aquatic invertebrates and algae. [1]US Department of the Interior Wildlife Service "Procedure for Evaluation of Acute Toxicity of Pesticides to Fish and Wildlife". [**]Results are nominal. [*]Results were converted from EUP to active, see text. [A] Results recalculated by Environment Australia. [#] Result considered reliable, [##] result considered acceptable. AFNOR = French "Norme Expérimentale" methods.

Comments on Table 40

4.2.2.1 Daphnia Magna

The acute 24 hours daphnia test (Hitz, 1982) was conducted according to the French "Norme Expérimentale" method AFNOR T 90-301. The result in the report was analysed graphically and has been re-analysed using current US EPA methods to give the EC50 (24 hour) and confidence limits. It is noted that the results are significantly higher (by 3 orders of magnitude) than for other tests. This may be due to a dilution factor but it is not possible to say definitely that this is the case based on the report presented. While the results are based on partially measured concentrations (5 for the 9 test concentrations) and there is no evidence in the report not consider the results as acceptable, they are clearly an outlier.

The 48 mortality test (Vilkas, 1976) was based on US EPA methods (US EPA, 1975) and used nominal concentrations. The result is considered acceptable. It should be noted the US EPA reviewed this study in 1987 and rated it as a core study.

A 21 day reproduction study was performed according to US EPA Guideline 72- using ^{14}C diazinon (Surprenent, 1988 C). The mean measured concentrations were between 43% and 83% of nominal concentration over the testing period of 21 days. The difference between the nominal and measured is high but as the measured concentrations were consistent over the study period, this is acceptable. As there was 100% mortality in the highest concentrations (0.83 and 0.32 µg/L after days 2 and 11 days respectively), the results from these concentrations were not used in the statistical analysis for reproduction. There was no effect on reproduction or growth (body length) at the lower concentrations tested. The MATC of 0.17-0.32 µg/L represents the NOEC and 100% mortality and dramatically illustrates how steep the toxicity curve is for daphnia. The result is considered reliable.

4.2.2.2 Mysid shrimp

The mysid shrimp study was performed according to US EPA Guidelines (Surprenant, 1988 A). There was no deviation from these guidelines and the results of analysis were satisfactory. However, for the 6.3 µg/L nominal, the analysis showed the concentrations to be significantly lower than nominal, 4.3 and 1.7 µg/L at time 0 (replicates A and B). At the end of the testing period, these had recovered to 6.7 and 6.9 µg/L and the average concentration over the entire test is 4.9 µg/L. Environment Australia has recalculated the LC50 without this point and it did not significantly affect the calculated LC50. The toxicity curve was noted to be steep (slope = 6; LC10 = 2.57 µg/L). The results are considered reliable.

4.2.2.3 Ceriodaphnia

While this study was performed according to US EPA Guidelines, there were several problems with the test (LeLeieve, 1991). There was no analysis of the test solutions, only an analysis of the stock solution, which was below nominal of 10.0 µg/L at 8.39 µg/L and there is some concern with the actual concentrations of the test solutions. In addition, there was only one test concentration that gave a partial response (0.36 µg/L, 27% response), therefore the LC50 is between 0.36 and 0.6 µg/L. The authors give an LC50 of 0.41 µg/L (0.36-0.6) using non-linear interpolation but this is not considered statistically acceptable. The test is considered as acceptable with LC50 of 0.36-0.6 µg/L and NOEC 0.08 µg/L.

4.2.2.4 Daphnia carinata

This study followed an older method (Method for Establishing Tentative Value using Water fleas) with *Daphnia carinata* used instead of *Daphnia magna*. This is the only test where formulated diazinon was used in the test but does not meet current requirements as the test was for only 3 hours. The results are nominal and appear to be for the formulation Basudin 60 EC. The results were recalculated using modern probit methods and corrected to active ingredient based on the stated strength of the formulated product. The short duration of the test means it is not suitable for regulatory use.

4.2.2.5 Monia macrocopa

As for the D. carinata above, this test is another old test (Method to Establish Tentative value) and has similar limitations and is not suitable for regulatory use due to the short duration of the test.

4.2.2.5 Oysters

The analysis of the test solutions showed that all were below nominal and significantly so for the highest concentration 2.5 mg/L, with the time 0 results of 0.76 and 1.4 mg/L for both replicates. The mean measured concentrations for the highest test concentration was 1.3 mg/L. The NOEC was 0.21 mg/L. The study is reliable.

4.2.2.6 Algae

The algae test of Hitz (1982A) is from French protocols Norme Expérimentale AFNOR T 90-304. Analysis of the test solution at time 0 showed that concentrations varied from 96 to 104% of nominal but on termination of the tests the samples varied between 48 and 75% of nominal. The IC50 was based on nominal concentrations and are consider acceptable.

The algae test of Oldersma *et al* (1984) was performed according to the OECD Guidelines and meets the Guideline. The test is considered acceptable and the results are nominal.

The algae test of Hughes (1988) was performed to meet US EPA Guidelines. However, in order to determine the NOEC a supplemental test was undertaken at nominal concentrations between 0.125 and 2 mg/L. The measured concentrations in the main test at time 0 were 48% to 79% of nominal and 34% to 97% on day 7. For the supplemental test the measured concentrations were again below nominal, 56% to 68% for time 0 and 32% to 83% of nominal on day 7. There was difficulty in dissolving the test material in the stock solutions, which was given as the explanation for the low recoveries of test solutions (the concentration of the stock solution was below the solubility limit). The endpoints were based on mean measured concentrations. The IC50 was determined as 6.4 mg/L and the 7 day NOEC was <0.41 mg/L in the first test and <0.06 mg/L in the second test. The IC50 from the main test is considered acceptable.

The author comments that in the supplemental test the NOEC was based on 10% inhibition, which while statistically significant, may not be biologically significant. Both the first and second test indicates that the NOEC for days 2, 3 and 4 is approximately 1 mg/L.

4.2.3 Other Aquatic End-points

A database from the Ecological Fate and Effects Division of the Office of Pesticide Programs, US EPA, to which Environment Australia has access, contains the presently known ecotoxicity endpoints for registered pesticides used in the US. The toxicity data put into the database is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable used in this report). It should be noted, however, that these studies use nominal results and some care is needed in using these for the risk assessment. The results from this database for fish are in Table 41 and those for aquatic invertebrates are given in Table 42.

Species	Study date	US EPA Test Guideline & category	Test Type, test material,	EC or LC 50, µg/L
Bluegill sunfish (*Lepomis macrochirus*)	1964	72-1 C	Static, 96 hr 91% ai	136
	1977	72-1 C	Flow-through 96 hr 92.5% ai	460
	1987	72-1 C	Static, 96 hr 48% ai	220
	1978	72-1 C	Static?, 96 hr 23% ai ME	500
	1980	72-1 C	Static, 96 hr 92% ai	168
Rainbow trout (*Onocorhynchus mykis*)	1980	72-1 C	Flow-through 96 hr 92% ai	90
	1978	72-1 C	Static, 96 hr 23% ai (23% ME*)	635
	1965	72-1 S	Static, 96 hr 91% ai	400
	1987	72-1 C	Static, 96 hr 48% ai	1800
	1977	72-1 C	Static, 96 hr 48% ai	1650
Cutthroat trout (*Onocorhynchus clarki*)	1980	72-1 C	Static, 96 hr 92% ai	1700
Lake trout (*Salvelinus namaycush*)	1980	72-1 C	Static, 96 hr 92% ai	600
Fathead minnow (*P. promelas*)	1977	72-1 C	Flow-through 96 hr 92% ai	7800
Brook trout (*Salvelinus variegatus*)	1977	72-1 C	Flow-through 96 hr 92% ai	770
Sheepshead minnow (*Cyprinidon variegatus*)	1979	72-3a C	Flow-through 96 hr 89% ai	1470
	1986	72-3	Flow-through 96 hr 95.1% ai	150
Stripped mullet (*Mugil cephalus*)	1986	72-3 S	Flow-through 48 hr 95.5% ai	150
Flagfish (*Jordanella floridae*)	1977	72-1 C	Flow-through 96 hr 92.4% ai	1600
Guppy (*Poecilla reticulata*)	1968	72-1 S	Static, 24 hr NR	1100
Fathead minnow (*P. promelas*)	1977	72-4a S	Flow-through 25 d >92.5% ai	LOEC 3.2
	1988	72-4a S	Flow-through 34 d >87.7% ai	MATC 0.092
Brook trout (*Salvelinus variegatus*)	1977	72-4a S	Flow-through 8 m >92.5% ai	LOEC 0.55
Sheepshead minnow (*Cyprinidon variegatus*)	1979	72-4a C	Flow-through 28 d >89% ai	MATC 0.47

Table 41. Summary of fish studies reviewed by the US EPA and found acceptable by them.
* Assumed to be the micro-encapsulated formulation.

Species	Study date	US EPA Test Guideline & category	Test Type, test material,	EC or LC 50, µg/L
Water flea, (*Daphnia magna*)	1987	72-2a C	Static, 48 hr Tech.	0.96
	1980	72-2a C	Static, 48 hr 89%	0.8
	1987	72-2b C	Static, 48 hr 48%.	1.1
	1977	72-2 C	Static, 48 hr, 23% ai (23% ME*)	0.5
Daphnid (*Simocephalus sp)*	1980	72-2a C	Static, 48 hr, 89% ai	1.4
Scud (*Gammarus fasciatus*)	1980	72-2a C	Static, 96 hr, 89% ai	0.2
Stonefly (*Pteronarcys sp*)	1980	72-2a C	Static, 96 hr 89% ai	25
Grass shrimp (*Palaemonetes pugio*)	1986	72-3c S	Flow through, 96 hr, 95.1% ai	28
Brown shrimp (*Penaeus azteecus*)	1986	72-3c S	Flow through, 96 hr, 95.1% ai	28
Water flea, (*D. magna*)	1988	72-4b	Static, 21 day, 87.7% ai	0.32 LOEC

Table 42. Summary of aquatic invertebrate studies reviewed by the US EPA and found acceptable by them. * Assumed to be the micro-encapsulated formulation.

It is clear from Tables 41 and 42 that together with Table 40, for which Environment Australia has reviewed the full reports, daphnia is one of the sensitive aquatic organisms with an acute EC50 of around 1 µg/L. The most sensitive organism is scud with LC50 of 0.2 µg/L. The results for fish range from an LC50 of 90 µg/L (static, 89% ai, 96 hr) for rainbow trout to a LC50 of 7.8 mg/L (flow-through, 92% ai, 96 hr) for fathead minnow. The early life stage studies on fish clearly show that the early life stages are very sensitive and there is a very large acute to chronic ratio for the effects of diazinon on fish, eg for sheepshead minnow the ratio is approximately 300.

It is noted that the micro-encapsulated formulation results in Tables 41 and 42 show similar toxicity to the other tests, an indication that there is little advantage in terms of the environmental toxicity to aquatic systems of this type of formulation.

4.2.3.1 ASTER data

The results from the US EPA ASTER database are summarised in Figure 1, which does not include the data from Tables 40, 41 and 42. This database is based on the scientific literature and other studies. These studies have not been assessed and the results given as are stated in the original database. It should be noted that the large range for some groups is due to insensitive species. In addition, the maturity of the test species is relevant, with early life stages in general being more sensitive. Based on the ASTER database, the toxicity to midge, the most sensitive group of organisms, is 0.03 (96 h LC50).

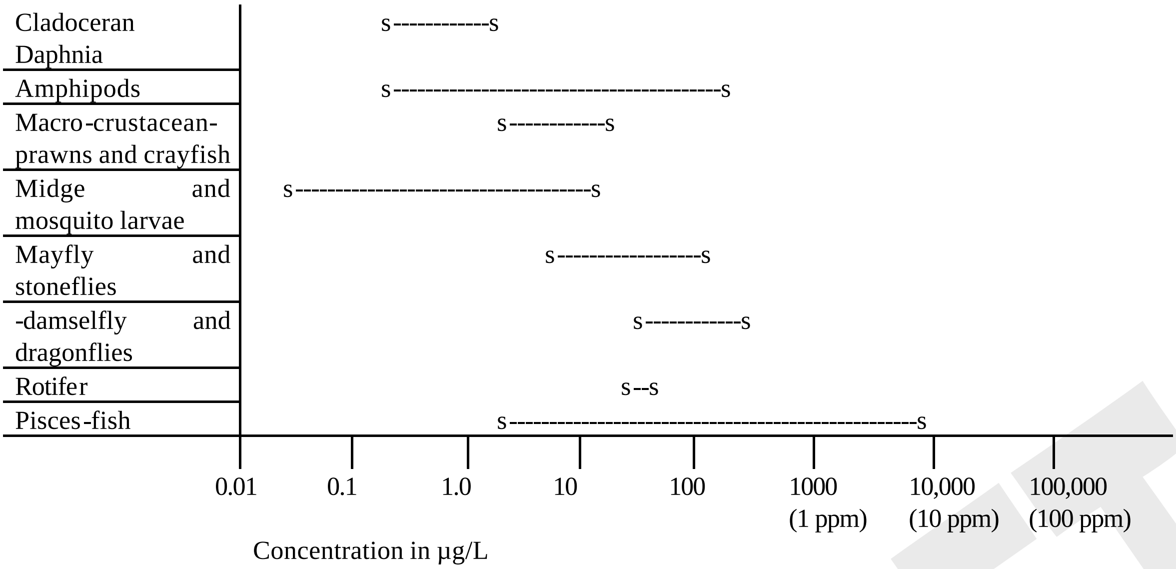


Figure 1. Graph of the toxicity of diazinon to aquatic organisms from the US EPA ASTER database. s-acute values (LD or EC50s). Positions are approximate only.

4.2.3.2 Published reports

The toxicity of diazinon to *Ceriodaphnia dubia* was determined as ranging from 0.26 µg/L to 0.58 µg/L in four tests conducted according to USEPA Guidelines (Bailey, Miller, Miller, Wiborg, Deanovic and Shed, 1997). The 96 hour toxicity was determined as 0.32 and 0.35 µg/L in two tests. However, in those tests the 48 hour results were 0.48 and 0.58 µg/L. These results are comparable to that for the same species in Table 39 and add support to the evidence that this is a sensitive species.

The effect of diazinon on several generations of *Daphnia magna* was studied using chronic 21-day exposures (Sánchez, Ferrando, Sancho and Andreu, 2000). The concentrations tested were 0.05, 0.1, 0.5, 0.75 and 1.0 ng/L, which were renewed daily. The test were initiated with exposure of 24 hr neonates (F_0 generation) to diazinon for 21 days and then taking the F_1 (first brood) and F_1 (third brood) and exposing these generations to the same levels of diazinon as the F_0 generation for 21 days. The number of young per female was significantly effected for all generations at 0.05 ng/L but the effect was pronounced in the F_1 generations. There was 100% mortality after 8 days at 1.0 ng/L in F_0, 2.5 days at 0.75 ng/L for F_1 (first brood) and 0.5 ng/L for F_1 (third brood). It was concluded that the daphnias from the first and third broods seem not to be adapted to the pesticide and they demonstrated high sensitivity than the parents. Environment Australia notes that these results are significantly lower than those of Surprenent, (1988 C) and all other results. Further, there are no analytical results and little detail available of the methods used or any of the raw data. These results are therefore not considered suitable for regulatory use.

A paper on the toxicity and sublethal effects of a number of pesticides associated with apple orchards on the northern leopard frog (*Rana pipiens*) and green frog (*Rana clamitans*), includes laboratory tests of toxicity of diazinon to Green frog eggs and larvae (Harris, Bishop, Struger, Ripley and Bogart, 1998). The tests using diazinon were discontinuous and consisted of 4 days exposure to embryos at stage 8, then uncontaminated pond water for 7.5 days and then a second 4 days exposure to pesticide to tadpoles. The frequency and characterisation of deformities were calculated on the 8th day of the test (4 days after the first exposure, at hatching) with hatching success and growth at the end of the second exposure. The 4 day LC50 was >25 and >50 µg ai/L for formulated (Basudin 500 EC) and technical active diazinon respectively. For the overall test, after the second exposure, the 16 day LC50 was 2.8 and 5.0 µg ai/L respectively. The EC50 based on deformities was 5.9 and 14 µg ai/L, with the deformities characterised as abdominal and head edemas and blistering, stunting of the tail, ventral and lateral flexure of the tail and underdevelopment of the gills.

There were no confidence limits given and the endpoints were calculated by trimmed Spearman-Karber, not Environment Australia's preferred method, ie probit analysis. Nevertheless, the results show that diazinon is highly toxic to the larval stages of frogs and likely to be toxic to other amphibians.

Stuifzand *et al* (2000) studied the effects of diazinon on two insects that commonly occur in rivers, young larval forms of the Caddis fly *Hydropsyche angustipennis* and the midge *Chironomus riparius*. These were studied in the laboratory for different exposure times (48 and 96 h), using mortality, activity and growth as end points. The test vessel was usually a glass container with water, except for the fourth midge instars where clean sediment was also present.

The earlier instars were clearly more sensitive than the older ones, with toxicity also increasing with exposure time. For example the 96 h LC50 for the caddis fly first instar was 1.3 µg/L (2.9 µg/L at 48 h), while that for the fifth instar was 29.4 µg/L (242.8 µg/L at 48 h). Chironomid larvae were clearly less sensitive under the conditions tested [96 h LC50 = 22.8 µg/L (first instar) and 167 µg/L (fourth instar) respectively].

While the paper notes that the caddis fly result is the second most sensitive recorded (and the chironomid the least), as noted above (Section 2.1.3.2) almost complete mortality (95-99%) of hydropschyhid caddis flies and chironomids at a concentration up to 0.6 µg/L occurred in the River Meuse during 1996. This represents about 50% of the caddis fly 96 h LC50, and is also lower than the daphnia EC50 used in our hazard calculations, though the effect from other toxicants in the river is unclear.

Sparling *et al* (2001) raise the possibility of the decline in frogs in California being related to diazinon (and chlorpyrifos) levels, as concentrations are highest (66-104 ng/L) at elevations where native anurans are showing the greatest decline. It is claimed these pesticides are reducing cholinesterase levels, which is associated with reduced activity, unco-ordinated swimming, increased vulnerability to predators, depressed growth rates and mortality in tadpoles. The quoted LC50 range of 2.8-5.0 µg/L for *Rana clamitans* tadpoles is from the above Harris *et al* (1998) paper, which indicates tadpoles are much more sensitive than fish, and approaching the level of the more sensitive aquatic invertebrates.

4.2.4 Mesocosm Studies

The mesocosm study was performed according to US EPA Guidelines (Giddings, 1992). Each mesocosm was 20 X 20 m by approximately 2.2 metres deep and contained sediment from a local farm pond. There were 4 replicates (ponds) used for control and treatment level 1 and 2, with 3 replicates for treatment levels 3, 4 and 5. The ponds were filled with water for at least 1 year before fish were introduced, 15 males and 15 females per pond.

There were 6 applications per mesocosm, the first, third and fifth as simulated spray drift and the alternate applications as runoff. The simulated spray drift was done by direct overspray at a low application rate and the runoff by using a recirculation system (water was pumped from mesocosm, dosed then returned over a 4 hour period). For each application, the doses used for spray drift were 0.37, 0.75, 1.5, 3.0 and 6.0 g ai/L and for the runoff the dosing was 1.53, 3.05, 6.13, 12.26 and 24.5 g ai/L, both for levels 1 through to 5. The first dose was applied on 6th May as spray drift, followed by runoff 1 week later. After 3 weeks the remaining 4 applications were done, again 1 week apart alternating spray drift/runoff, commencing with spray drift. The sixth and last application occurred on 24 June. All dates given in Table 42.

4.2.4.1 Sampling

The water was sampled in each mesocosm on day –1 (before 1st application), Day 0 (after 1st application) on Days 1, 4, 7 (2nd application), 8, 11, 14, 18, 21, 28 (3rd application), 32, 35 (4th application), 39, 42 (5th application), 46, 49 (6th application), 53, 56, 63, 77, 105 and 147. On the day of application, the water sample was taken after the application was complete. All samples were depth integrated samples from 4 locations in each pond and composited for analysis. Sediment samples were taken on the same dates excepted that for the 3rd to the 6th application, no sediment samples was taken on the day of application. There were 4 sediment samples taken per pond, which were sectioned into 3 sections, 0-2.5, 2.5-5 and 5-7.5 cm (measured from the water/sediment interface).

The biota in each mesocosm was sampled during the study and analysis for total biomass, number of taxa and total number of organisms in each taxa. Phytoplankton were measured in a sub-sample of the water samples and Periphyton sampled every 2 weeks. These organisms were analysed for total chlorophyll-a and phaeophytin as measures of total biomass. Zooplankton and macro-invertebrates (exuviae and emergent insects) were sampled weekly and the benthic organisms sampled fortnightly but statistical analysis was only done fortnightly. These taxa were enumerated and identified to the most practical taxa or to species levels. Minnow traps were used weekly to monitor the abundance and size of juvenile bluegill when bluegill larvae were first observed. When fish began to be trapped consistently, the sampling was increased to 3 times per week.

4.2.4.2 Measured concentrations

Concentrations of diazinon in water after the first application averaged 102% of expected and after the second application 103% of expected assuming a 7 day half life. Half-lives in water was calculated following the first, second and sixth application. The average half-lives

in water following the first application were 14.6, 9.8, 23.1, 26.0, and 18.2 days for level 1 to 5 respectively. However, the correlation coefficient was low ($r^2 < 0.8$) for levels 1, 3, 4 and 5. The average half-lives following the second application were 12.8, 10.7, 18.6, 16.5 and 15.5 days with good correlation coefficients, r^2 of 0.87 to 0.98 for levels 1 to 5 respectively. Following the sixth application, the half-lives decreased to 8.6, 7.2, 6.3, 5.4 and 6.8 days, levels 1 to 5 respectively with good correlation coefficients (ranged from 0.97 to 0.99).
The average concentrations in the water and sediment at time of each application are given in Table 43.

Concentration	Application No											
Level	1, 6/5		2, 13/5		3, 3/6		4, 10/6		5, 17/6		6, 24/6	
	W	S.	W	S.	W	S.	W	S.	W	S.	W	S.
1	0.40	*bdl*	1.99	*bdl*	0.84	*bdl*	1.95	0.85	1.73	1.33	2.30	1.01
2	0.96	*bdl*	3.51	0.59	1.95	1.75	3.73	2.93	3.38	1.81	4.30	4.23
3	1.37	*bdl*	5.95	1.27	3.60	4.43	7.03	4.73	6.73	4.6	9.20	3.85
4	2.73	*bdl*	13.4	2.10	8.18	5.13	15.7	16.2	10.9	7.50	12.5	10.0
5	5.40	*bdl*	26.7	4.48	16.7	21.0	27.0	22.8	24.3	19.7	29.7	19.9

Table 43. Average concentration of diazinon in water and sediment of mesocosms. W = water, S = sediment. Concentration in water is for time immediately after application. Concentration in sediment (0-2.5 cm) is immediately after application for applications 1 and 2 and for 4 days after application for others. *Bdl* = below limit of detection (1.0 µg/kg for sediment).

The temperature of the water varied significantly over the application period, ranging from 15.1 °C (first application, deep zone) to 27.6 °C (sixth application, shallow zone and 27.1 °C in deep zone). This temperature range could account for a significant part of the observed increase in the degradation rate noted above.

It is noted that the concentrations of diazinon between replicates showed high variation at times, ie for level 4, 4 days after the fourth treatment, 20.0, 26.0, 2.5 µg/L with average of 16.2 µg/L and for the sixth treatment, 15.0, 12.0 and 3.0 µg/L, again 4 days after treatment. A similar situation occurred for treatment level 5. This high variability in the concentrations that organisms were exposed to between replicates increased the coefficient of variation for toxic effects and therefore reduced the sensitivity of the statistical analysis.

The average concentration of diazinon decreased to 0.1 µg/L 56 days after the last application for all treatment levels. However, in the previous sample, 28 days after the sixth application, the residues levels were low and ranged from 0.27 to 1.7 µg/L for levels 1 to 5.

In the sediment, the concentrations of diazinon were irregular and but in general they were similar to those in the water (see Table 42). There was little evidence of vertical movement, with most remaining in the upper 0-2.5 cm layer. Maximum concentrations in the 2.5-5 cm layers were <0.5, 1.33, 1.88, 3.1 and 5.4 µg/kg for treatment levels 1 to 5 respectively. Due to the irregular concentrations in sediment, the half-lives in sediment were only calculated for levels 4 and 5 after the last application. The average half-lives in sediment was 8.1 and 14.2 days for levels 4 and 5 respectively.

4.2.4.3 Aquatic flora

There were no significant treatment related effects on phytoplankton chlorophyll concentrations and there were no significant treatment related effects on populations of phytoplankton. However, there was large variability between replicate mesocosms and the large variance could have masked more subtle effects. Diatoms (Bacillariophyceae) were significantly affected in one sample at the highest level. Taxonomic richness was significantly affected in the highest treatment level over the entire post treatment period.

Periphton chlorophyll was not significantly affected during the study, but as for phytoplankton, these were highly variable among mesocosms and within mesocoms across time. There were treatment related decreases in total periphyton densities over the treatment period at the highest level with the classes Bacillariophyceae and Chlorophyceae the most affected. The density of Bacillariophyceae was also significantly lower for a few samples in treatment 4. The taxonomic richness was reduced in levels 4 and 5 for one sample and in level 5 in the following sample event. However, it is noted that these samples were taken 6-8 weeks after the last application and therefore may not be treatment related.

For Macrophytes, there were no treatment related effects evident.

4.2.4.4 Aquatic fauna

For zooplankton, which was dominated by rotifers, there were major effects on cladocerans, which was significant at all treatments during the study. While these effects occurred in both the shallow and deep zones of the mesocosms, they were more statistically consistent in the shallow zones due to the higher populations. Levels 2-5 were statistically affected on the first biota sample after treatment (sample 5, 6 days after treatment 2) and level 1 was affected by next sample (sample 6, 13 days after treatment 2) but before the third diazinon treatment. However, in sample 5, cladocerans were reduced to <10% of their pre-treatment levels in Level 1 (average of 87.7 and 7.3 organisms for sample events 4 and 5 respectively) but controls also showed a sharp drop over the same period (125.3 to 17.8 organisms). In all treatments levels, on some sample events during treatment, the sampling showed there were no cladocerans in any of the replicates. These organisms slowly recovered to be statistically similar to control, with level 1 recovering first in the 12th biota sample event, 62 days after the last treatment, and remaining levels in the subsequent sample, 76 days after the last treatment. There was some recruitment for all levels in the sample previously to when the recovery became statistically significant and for levels 1 this was 48 days after the last treatment and 62 days after the last treatment for the other levels. This is presumably due to repopulation from other areas and coincided with increasing populations in controls.

For rotifers, there were effects for the order Ploima, the most common zooplankton, with effects occurring in treatment levels 3 to 5 for one sample only. The least sensitive zooplankton were the crustacean, orders Copepoda and Ostracoda, and rotifiers, order Flosculariaceae, with only one sample showing statistically significant effects in the level 5. Arthropods were less sensitive than rotifers. Total zooplankton density was reduced at the highest treatment level but recovered to control levels by the end of the study. Taxonomic richness was reduced in treatment levels 3 to 5 for 3 samples, taken during treatments 3 to 6.

Using artificial benthic substrates as samplers, Diptera of the order Trichoptera was the most sensitive taxon, which was significantly affected at all treatment levels during the treatment period. The Trichoptera recovered by the end of the study. The next most sensitive taxon was the tribe Pentaneurini, with significant reductions in treatments levels 3-5 in several samples, mainly during treatment period and for all treatment levels immediately after the last treatment. Densities of Diptera, Ephemeroptera and Odonata were significantly reduced at the highest treatment level using the artificial benthic substrates. The densities of several subclassifications in these orders were effected at lower treatment levels (levels 3-5). These were subfamilies Tanypodinae (order Ephemeroptera) and chironominea and the tribes Tanyarsini, chironomini and Pentaneurini. There were no effects on the class Gastropoda.

4.2.4.5 Benthic organisms

Using benthic cores, there were significant effects on several benthic classifications during the treatment period in the highest treatment level, specifically families Ceratopogonidae and Chaoboridae, subfamily Tanyodina and Tribe Pentaneurini. There were significant treatment related effects in levels 3 and 4 for Ceratopogonidae, Chaoboridae and Pentaneurini, which extend to beyond the last treatment for Ceratopogonidae and Pentaneurini. Odonates were the only other insect order significantly lower in number in the highest treatment during the treatment period. Crustacea were also significantly reduced but only for one sample in the highest treatment and at the end of the treatment period. Taxonomic richness was significantly affected for one sample in the highest treatment. All groups recovered by the end of the study.

From emergent insect traps, there were significant effects on the subfamily Tanypodina at all treatment levels and the main tribe affected was Pentaneurini for treatment levels 2 to 5. The emerging insects from the family Ceratopogonidae were significantly affected from the deep zones in the mesocosms at level 2 to 5 but only at level 5 in the shallow zones. The family of insects Ephemeroptera were affected at the highest treatment rate and only for two samples during the period of treatment. The order Odonata, the prevalent insect in the exuvia samples (on wire screens at the edge of ponds), was significantly affected by diazinon in level 5 for 4 samples, during and immediately after treatments, and level 4 only immediately after treatments. The taxonomic richness was significantly affected down to level 3 compared to control during treatment and in levels 4 and 5 immediately after treatments.

4.2.4.6 Fish

For the bluegills, there were no treatment related mortalities or effects on reproduction or number of juveniles. There was a dose-related increase in fish biomass and an increase in the length of both adult and juvenile fish in all treatment groups, which was significant in the treatment levels 4 and 5. There were no other effects observed that were considered treatment related.

4.2.4.7 Conclusion-mesocosm

The half-life of diazinon decreased with increasing number of applications and ranged from 10-26 days after the first application to 5.5 to 8.5 days after the sixth application. Maximum average concentrations of diazinon, which mainly occurred immediately after the sixth application were 2.3 µg/L for level 1, 4.3 µg/L for level 2, 9.2 µg/L for level 3, 15.7 µg/L for level 4 and 29.7 µg/L for level 5. It should be noted that in treatment levels 4 and 5, one pond (replicate) showed consistently lower concentrations and more rapid degradation than the other two ponds.

There were no detrimental effects on fish or plants at any treatment except for diatoms and green algae. Diatoms were significantly affected at the highest treatment with occasional reductions at lower levels and green algae affected occasionally.

Invertebrates were significantly affected by diazinon. For zooplanton, Cladoceran were the most sensitive taxon (significant reduction at all levels), followed by rotifers at levels 4 and 5 (one tribe affected at level 3) and Copepods once at the highest treatment level. For higher macroinvertebrates, Trichoptera were the most sensitive order (affected (reduced) at all treatments), with Diptera and Ephemeroptera intermediate (affected at treatment levels 3-5) and gastropods essentially unaffected. For the order Diptera, the family Chironomidae was the most significantly affected, with the tribe Pentaneurini (dominant tribe in subfamily Tanypondinae) affected at all levels and the tribes Tanytarsini and Chironomini (subfamily Chironominae) from levels 3 through to 5. Two other diptera families, Chaoboridae and Ceratopogonidae were effect at levels 2 and higher. The greatest effect on Chaoboridae occurred 2 months after the last treatment and may not be treatment related. All organisms recovered by the end of the study period, with Cladocerans taking the longest, up to 11 weeks.

It is concluded that while diazinon can significantly affect aquatic organisms at relatively low concentrations, especially invertebrates, these affected organisms are likely to recover. There is unlikely to be significant long term effects on populations, provided organisms are given adequate time to recover.

4.2.4.8 Conclusion—Aquatic Toxicity

The toxicity to aquatic organisms, especially invertebrates, is very high. The acute toxicity to fish from submitted studies (9 species) ranges from LD50 of 2.16 mg/L for common carp to 23.4 mg/L for crucian carp. Life cycle studies have not been performed but the embryonic and larvae life stages of fathead minnow have been tested and the maximum acceptable tolerated dose was determined to be between 0.092 and 0.17 mg/L. The early life stages are considered to be normally the most sensitive. In a database of regulatory-type studies that have been reviewed by USEPA, the toxicity to fish of diazinon ranges from LC50 of 0.09 mg/L for rainbow trout to LC50 of 7.8 mg/L for fathead minnow.

Diazinon is extremely toxic to invertebrates, which is typical for an organophosphate, with acute toxicity figures for *Ceriodaphnia* (EC50) of between 0.36-0.6 µg/L and for mysid shrimp EC50 = 4.2 µg/L. (Note that mysid is normally a very sensitive test species.) The chronic toxicity to daphnia has been determined and the MATC found to be between 0.17 and 0.32 μg/L. The USEPA database on reviewed regulatory studies gives the most sensitive species as scud, EC50 = 0.2 μg/L, and least sensitive invertebrate as grass shrimp EC50 = 28 μg/L. The acute EC50 for *Daphnia magna* (three studies) in this database ranged from 0.96 to 1.1 μg/L. From literature reports tadpoles and caddis fly larvae also seem very sensitive.

Diazinon is moderately toxic to green algae, with EC50s of 8.5 and 6.4 mg/L for two species of *Scenedesmus*.

In a detailed long term study, diazinon was applied to several mesocosms at several treatment rates. The maximum average concentrations of diazinon, which mainly occurred immediately after the sixth (last) application, were 2.3 μg/L for level 1, 4.3 μg/L for level 2, 9.2 μg/L for level 3, 15.7 μg/L for level 4 and 29.7 μg/L for level 5. It should be noted that in treatment levels 4 and 5, one pond (replicate) showed consistently lower concentration and more rapid degradation than the other two ponds. Also, the half-life of diazinon decreased with increasing number of applications, and ranged from 10-26 after the first application to 5.5 to 8.5 days after the sixth application.

There were no detrimental effects on fish or plants at any treatment except for diatoms and green algae. Diatoms were significantly affected at the highest treatment with occasional reductions at lower levels and green algae affected occasionally.

Invertebrates were significantly affected by diazinon. For zooplanton, Cladoceran were the most sensitive taxon (significant reduction at all levels), followed by rotifers at levels 4 and 5 (one tribe affected at level 3) and Copepods once at the highest treatment level. For higher macroinvertebrates, Trichoptera were the most sensitive order (affected (reduced) at all treatments), with Diptera and Ephemeroptera intermediate (affected at treatment levels 3-5) and gastropods essentially unaffected. For the order Diptera, the family Chironomidae was the most significantly affected, with the tribe Pentaneurini (dominant tribe in subfamily Tanypondinae) effected at all levels and the tribes Tanytarsini and Chironomini (subfamily Chironominae) from levels 3 through to 5. Two other diptera families, Chaoboridae and Ceratopogonidae were effect at levels 2 and higher. The greatest effect on Chaoboridae occurred 2 months after the last treatment and may not be treatment related. All organisms recovered by the end of the study period, with Cladocerans taking the longest, up to 11 weeks.

It is concluded that while diazinon can significantly affect aquatic organisms at relatively low concentrations, especially invertebrates, these affected organisms are likely to recover and there is unlikely to be significant long term effects on populations, provided organisms are given adequate time to recover.

The revised ANZECC environmental water quality guidelines volume 2, p256 (ANZECC & ARMCANZ 2000) contain a medium level freshwater trigger value of 0.01 μg/L using the statistical distribution method with 95% protection and an ACR (acute/chronic ratio) of 17.5.

4.3 Non-target Invertebrates

4.3.1 Toxicity to Bees

There were no regulatory studies on the toxicity of diazinon to bees presented by any registrants.

4.3.1.1 Published reports

The contact and oral toxicity of 60 pesticides under standard conditions to worker honey bees has reported (Stevenson, 1978). This report is a summary of results attained from 1964 to 1977 and includes diazinon. The contact LD50 = 0.22 µg/bee and oral LD50 = 0.20 µg /bee.

In another report, the toxicity of 31 pesticides to bee larvae was compared to the toxicity to adults (Atkins and Kellum, 1986). The toxicity to bee larvae was determined by direct injection of doses of pesticide to larvae in brood chambers and determining the surviving larvae one day before emergence. The LD50 of diazinon to bee larvae was determined as 1.21 X 10^{-4} µg/larvae and the contact LD50 to adults was stated as 0.372 µg/bee. As there was a limited number of test concentrations used for diazinon (3), the results are considered indicative only.

4.3.1.2 US EPA Database

Table 44 gives the values for the toxic of diazinon to bees from the Effects Division of the Office of Pesticide Programs, US EPA database (see above for further information on the database).

USEPA Guideline	Test substance	Study date	Endpoint	Category
141-1, Contact	Tech.	1975	0.37 µg/bee	Supplemental
141-2, Foliage	35% active	1967	0.86 kg/ha (0.77 lb/A)	Supplemental
141-1, Contact	Tech.	1968	0.2 µg/bee	Supplemental
141-1 Contact	NR	1964	0.22 µg/bee	Core
141-2, Foliage	40% WP	1967	0.28 kg/ha (0.25 lb/A)	Core

Table 44. The toxicity of diazinon to bees. NR = not recorded

Environment Australia has not reviewed the above studies, but the OPP in the US EPA considered that they demonstrate that diazinon is highly toxic to bees.

4.3.2 Other Invertebrates

There were no regulatory studies presented for the affects of diazinon on non-target terrestrial invertebrates. However, there were two literature reviews on the toxicity of diazinon to insects, mainly non-target insects.

In the first of these review, 56 field and laboratory reports were summarised (Sechser, 1991). A very condensed summary of the field data (24 out of the 56 reports) is presented in Appendix 2. From Appendix 2 it is clear that diazinon affects the predatory complex, including hymenopterous parasitoids, Chrysopa ssp, and predatory mites. Using the IOBC ratings, the field results show that diazinon is rated from 3 (moderately harmful) to 4 (harmful). It should be noted that the report includes information that resistance to diazinon occurs in wild population of predatory mites, which have been be used in IPM. The selectivity of diazinon can be increased by the correct timing of sprays to avoid beneficial insects (ie dormant spraying in deciduous fruit, timely spaced applications in greenhouses).

The second review (Sechser, 1994) used the same published reports as in the first review but presented the information in a different format. The conclusions are the same as above.

4.3.2.1 Published reports

Diazinon was included in a program to test the side effects of a range of agricultural chemicals on beneficial insects (Hassan, S.A., Bigler, F., Bogenschütz, H., Boller, E., *et al* 1988). These studies were conducted by the International Organisation for Biological Control (IOBC). There were five different tests used, details given in Appendix 3.

The results, which are presented in Appendix 3, show that diazinon is harmful to parasitic wasps, predatory mites and spiders tested in laboratory exposed conditions and less toxic in the laboratory "protected" tests. The semi-field tests showed that fresh residues of diazinon were harmful to the test organisms and the toxicity of diazinon was rated as ranging from slightly persistent to persistent (5 days to >30 days). The field tests showed that diazinon was harmful (>99% mortality) to the predatory mite tested.

Several of the genera of the species tested are found in Australia and are used as part of IPM programs. The wasp genera *Trichogramma, Encarsia* and *Aphidius* are present in Australia and are used as part of IPM. Most of the mite genera tested are also present in Australia and are used in IPM programs, together with the predatory beetle genera *Chrysopa, Syrphus, Bembidion* and *Pterostichus*. It is clear that diazinon is likely to significantly affect important beneficial insects in Australia.

4.3.3 Earthworms

The toxicity of diazinon to earthworms (*Eisenia foetida*) was tested according to OECD Guideline 207 using artificial soil (Vial, 1990). The pH of the soil was higher than that given in the Test Guideline, pH of 6.5-7.0 rather than 5.5-6.5. This minor change is considered unlikely to effect the results and there were no mortalities in the controls. Nominal concentrations of diazinon in the soil were used but apart from this, the test appears acceptable. The LD50 was calculated as 130 (CI 110-160) mg/kg of soil.

The toxicity of diazinon to earthworms has been tested under semi-field conditions at two concentrations (Schäpfer, 1977). This study did not follow any current Guideline. The soil was collected from a meadow (soil not characterised) with earthworms (*Lumbricus* *terrestris*) collected from the same meadow. The soil was mixed with diazinon at 4 and 20 mg/kg, corresponding to 4 and 20 kg ai/ha for soil 7.5 cm deep. After the worms were introduced to the soil, the container was covered with turf and left for 27 days before assessment. In the first trial, there were 0 and 20% mortalities for 4 and 20 mg/kg respectively and in the second trial there were 20% and 0% mortalities respectively. Controls showed 0 and 5% mortalities for trial 1 and 2 respectively. The results indicate that there are unlikely to be significant mortalities of earthworms at 20 mg/kg.

4.3.3.1 Published reports

Diazinon (10% granular) was lightly incorporated into a field at rates of 0.56, 1.12, 2.24 and 4.48 kg/ha (Kring, 1968). There were 4 rows treated per concentration with each row treated as a replicate. Tobacco was then planted into the treated rows and 6 days later, 7 days after treatment, the number of dead worms on the surface were counted. There was only one dead worm counted in the diazinon treatments (1.12 kg/ha), the same as in controls, and was not considered treatment related. Carbofuran was also used in the test and could be considered as a positive control for the method, with 62 dead worms counted in the carbofuran treated rows.

4.3.4 Conclusion—Non-Target Invertebrates

Diazinon is extremely toxic to bees by all routes of exposure. There were no regulatory studies presented but an old published report gives LD50s of 0.22 µg/bee (contact) and 0.20 µg/bee (oral). In addition, more recent published reports show that the toxicity to bee larvae is extremely high, with an LD50 of 0.000121 µg/bee. The USEPA database of studies that have been reviewed by them shows contact toxicity as 0.2 µg/bee and foliage contact LC50 as 0.28 kg/ha.

In reviews of the effects of diazinon on non-target insects, 56 reports were summarised. This summary showed that diazinon affects the predatory complex, including hymenopterous parasitoids, *Chrysopa* ssp, and predatory mites. From the field results summarised, diazinon can be rated, according to IOBC, from 3 (moderately harmful) to 4 (harmful). It should be noted that the report includes information that resistance to diazinon occurs in wild population of predatory mites, which have been be used in IPM.

In studies conducted by the International Organisation for Biological Control (IOBC), it was shown that diazinon is harmful to parasitic wasps, predatory mites and spiders tested in laboratory exposed conditions and less harmful in the laboratory "protected" tests. The semi field tests showed that fresh residues of diazinon were harmful to the test organisms and the toxicity was rated as slightly persistent to persistent (5 days to >30 days). The field tests showed that diazinon was harmful (>99% mortality) to the predatory mite tested.

Several of the genera of the species tested are found in Australia and are used as part of IPM programs. Most of the mite genera tested are also present in Australia and are used in IPM programs, together with predatory beetles.

It is clear that diazinon is likely to significantly affect important beneficial insects in Australia.

The toxicity of diazinon to earthworms was tested according to OECD Guidelines. The LD50 was calculated as 130 (CI 110-160) mg/kg of soil. The toxicity of diazinon to earthworms has been tested under semi-field conditions at 4 and 20 mg/kg, corresponding to 4 and 20 kg ai/ha for soil 7.5 cm deep. There was a maximum of 20% mortalities at the highest level. The results indicate that there is unlikely to be significant mortalities of earthworms at <20 mg/kg.

In a published report, rows of tobacco were treated with diazinon, then the number of dead worms on the surface was counted after 7 days. There was no difference compared to blank controls at the highest rated used (4.48 kg/ha).

4.3.5 Micro-organisms

4.3.5.1 Soil Micro-organisms

The effect of diazinon on soil microbes was determined using soil respiration, ammonification and nitrification (Guth, 1983). Two soils were used, a sandy soil (Collombey) and a silty loam (Strassenacker), the details of these soils are given in Table 45. The soil samples were freshly collected from the field less than one week before the studies started.

Soil	USDA Classification	pH	Organic Matter	Sand	Silt	Clay
Collombey Respiration	loamy sand	7.7	2.34	86.4	9.4	4.2
Nitrification	sand	7.4	1.43	91.1	6.2	2.7
Strassenacker Respiration	silt	7.9	1.89	11.7	80.8	7.5
Nitrification	silt	7.6	2.16	9.7	82.8	7.5

Table 45. Characteristics for soils used in soil micro-organisms study.

For the respiration study, samples of the soils were incubated under aerobic conditions and the amount of CO_2 liberated after 1, 3, 7, 14, 21 and 28 days determined. Diazinon was applied to the soils at 16 and 80 mg/kg soil, corresponding to 12 and 60 kg ai/ha for 5 cm deep (assumes a soil density of 1.5 g/cm^2). The soils used were either unamended or amended with chopped lucerne (0.5% by wt). For the nitrification studies the soils were unamended, amended with lucerne or amended with ammonium sulphate (100 mg N kg soil). All nitrification studies were aged for 28 days, with those amended with ammonium sulphate sampled as for the respiration study and the others only sampled at the end of the incubation period. The analysis for the nitrification studies was for ammonium, nitrite and nitrate.

Soil respiration was not significantly different to controls in the diazinon treatments at anytime. For the nitrification studies, there was a slight inhibition of nitrification during the first 7 days at the highest treatment, which was not considered a negative effect by the author. There was no significant difference in the concentration of nitrite or nitrate conversions at anytime. It was concluded that that diazinon has no adverse effect on soil processes.

4.3.5.2 Inhibition of aerobic bacteria.

The inhibition of aerobic bacteria was tested according to OECD Guideline 209 (Bader, 1990A).

Using activated sludge from a sewage treatment plant, the respiration of the bacteria was only slightly affected at 100 mg/L of diazinon, the highest concentration tested. The EC50 was determined as >100 mg/L.

4.3.5.3 Published reports

The toxicity of diazinon and its hydrolysis product to the bacteria *Photobacterium phosphorem* has been tested using the Microtox system (Somasundaram, Coats, Racke and Stahr, 1990). The EC50 for diazinon was 10.3 mg/L and for the hydroxypyrimidine (G 27550) 118 mg/L.

The rate of degradation in rice paddy water has been noted to increase following several applications of diazinon (Sethunathan and Pathak, 1970). There was rapid degradation in water from previously treated paddy, from 24 mg/L at day 0 to below detection after 5 days. In water taken from a rice paddy that was untreated, the degradation over the same period was not significant.

4.3.5.4 Conclusion

Diazinon has limited effects on micro-organisms. In tests using two different soil types, there was minimal effect on soil respiration and nitrification at 16 and 80 mg/kg soil, corresponding to 12 and 60 kg ai/ha. There were only limited effects on respiration of sewage micro-organisms at 100 mg/L.

Literature reports give the EC50 as 10.3 mg/L bacteria using the Microtox system. The rate of degradation in rice paddy water has been noted to increase following several applications of diazinon. There was rapid degradation in water from previously treated paddy, but in water taken from a rice paddy that was untreated, the degradation over the same period was not significant.

4.3.6 Mammals

Diazinon is moderately toxic to mammals by the oral route, with LC50s for rats between 66-635 mg/kg (females) and 96-967 mg/kg male and is classified by the US EPA in Toxicity Category II (US EPA Fact Sheet No: 96). In Australia it is scheduled as S6 for the EC and S5 for formulations with <2% active.

A more detailed study of the effects of diazinon treatment on mammals than that of Wang *et al* (2001) (see Section 4.1.3) was conducted by Sheffield *et al* (2001). Diazinon 4E (a liquid emulsifiable formulation) was applied by a CO_2 powered backpack, at two different rates, 0.56 and 4.5 kg ai/ha respectively, to small (0.1 ha) tall grass prairie ecosystem enclosures containing a variety of small mammals typically occurring within this ecosystem. Treatments were applied on two different occasions during the peak breeding season and enclosures were sampled on days 2, 16 and 30 after treatment. Diazinon seemed to persist in the enclosures during this period, with soil samples ranging between 5.3-7.7 ppm on day 2, 2.8-4.2 ppm on day 16 and 0.6-2.3 ppm on day 30 (note the depth sampled is not indicated).

While fewer animals were recovered from the treated plots, there was no evidence of any acute mortality at either treated rate. However, analysis of trapped animals revealed a number of sub-lethal effects had occurred, with effects generally greater though not restricted to the highest rate. Plasma and brain cholinesterase activities were significantly inhibited in all small mammal species, though they tended to recover by day 30. Voles seemed to survive better than hispid cotton rats, with which they normally compete strongly, in diazinon treated plots. Reproductive condition was significantly reduced in both diazinon-exposed male and female mammals (20-80 and 33-100% respectively). As a result reproductive productivity was also significantly affected, with the percentage of pregnant females ranging from 13.6-43.5% in diazinon-exposed animals compared with 40-80% for controls. The percentage of females giving birth was also significantly lower, ranging from 0-17% compared with 22-50% for controls.

The authors conclude that the oral routes of exposure, in particular consumption of dead and dying arthropods (said to be routinely seen in treated enclosures), as well as grooming, may be important. Overall ecological relationships in the enclosures were disrupted by diazinon treatment, probably through a combination of sublethal, particularly reproductive effects, impacting individuals and their populations.

These are important conclusions considering that apart from the simpler study of Wang *et al* (2001), this is the first available study examining impacts on wild mammals. It supports the tentative conclusion (Section 5.2.1.1 of this report) that the risk to mammals dying is fairly low, particularly considering the restricted current uses, though it does raise the possibility of sub lethal effects occurring, particularly at high dose rates.

4.4 Phytotoxicity

4.4.1 Vegetative vigour

A study on the effect of diazinon on the vegetative vigour of seedlings was tested according to USEPA Guidelines (Canez, 1988). A number of dicotyledon and monocotyledon seedling at the 2-3 true leaf stage were sprayed with diazinon at 11.2 kg/ha and then the seedlings grown for 22 days before harvesting. The seedlings were examined for visual effects on 7, 14 and 20 DAT and rated on a scale from 0 (no effect) to 4 (death). On harvest, the plant height and plant dry weight were also determined. Results are given in Table 46.

Seedling	7 DAT	14 DAT	20 DAT	Height, % difference	Dry Wt, % difference
Soybean	2.0	1.6	0.9	4	-14
Lettuce	0.0	0.4	0.8	-19	33
Carrot	0.0	0.1	0.1	-6	-26
Tomato	2.4	2.0	1.4	-29	-22
Cucumber	2.4	1.8	1.6	-29*	-53*
Cabbage	1.4	1.3	0.7	0	21
Oat	0.4	0.7	0.0	-7*	9
Ryegrass	0.0	0.0	0.0	-8	19
Corn	1.9	1.2	0.1	-6	-16
Onion	0.0	0.0	0.1	27	13

Table 46. Summary of phytotoxic effects of diazinon on seedlings. Percentage differences to controls are normalised to allow for difference between controls and treatment groups before treatment. * Indicates that results are significantly different at p=0.05 according to Duncan's Multiple Range Test

After treatment soybean, tomato, cabbage, cucumber and corn seedling tissue appeared water soaked. This tissue was desiccated by day 7 (see Table 46), with declines in toxic effects due to defoliation of affected tissue and continued growth of the plant. Some of the seedlings died due to the treatment. There was a decrease in the height of tomato, cucumber and lettuce plants, with other seedlings less affected. Dry plant weights decreased for carrots and cucumbers but increased for lettuce.

It is concluded that there is greater than 25% effect on tomato, cucumber, onion, lettuce and carrots seedlings, which is the US EPA criteria for additional Tier II testing.

4.4.2 Seedling germination and emergence

A study on the effect of diazinon on seedling germination and emergence was carried out according to USEPA Guidelines (Canez and Jones, 1988).

In the germination test, seeds were germinated in filter paper that had been moistened with a solution of diazinon (30 ppm). After the seeds were incubated for 5 days, the radicle length was measured. The seeds used are given in Table 45 together with results as percentage of control. In the emergence part of the study, the seeds were sown before the soil was oversprayed with diazinon at 11.2 kg/ha. The seeds were allowed to germinate and grown for 22 days before harvesting. The seedlings were examined for phytotoxicity, number of emerged seedlings and their height on 7, 14 and 20 DAT. On harvest, the plant height and dry weight were also reported. Results are in Table 47.

There was no significant effect on percentage of seed that germinated but the length of the radicle was affected (see Table 47). Carrot, tomato and oats were the most affected with corn and onions also showing significant effects. In the emergence tests there were no significant effects on phytotoxicity or seedling emergence. The effect on seedling height ranged from 6% increase for oats to 18% decrease for onions, with significant effects occurring during the 20 day observation period on lettuce, tomatoes, cucumbers, cabbage, ryegrass and onions. The dry weight of the seedlings ranged from 7% increase for oats to

23% decrease in ryegrass compared to controls, with reduced weights being significant for soybeans and ryegrass only.

Seedling	Germination test		Emergence test			
	Radicle length, %	Germination	Seedling height % of control 7 DAT	14 DAT	20 DAT	Dry Wt
Soybean	-16	10	-1	-7	-14	-11*
Lettuce	9	2	-18	-15*	0	6
Carrot	-43*	-17	-3	-4	2	-1
Tomato	-27*	7	-19*	-14*	-11	-16
Cucumber	-18	0	-16*	-10	-7	-2
Cabbage	-17	2	-10	-11*	-9*	-9
Oat	-26*	-12	-11	-4	6	7
Ryegrass	3	9	-41*	-29*	-16*	-23*
Corn	-13*	-6	-7	-2	-5	-6
Onion	-16*	-2	-33*	-20*	-18*	-1

Table 47. Summary of effects of diazinon on seed germination and seedling emergence. Results as percentage difference to controls. * Indicates that results are significantly different at p=0.05 according to Duncan's Multiple Range Test

It is concluded that while there are some relatively minor effects at the high rates tested (maximum US rates), at the rate used under Australian conditions effects on non-target plants are expected to be minimal.

4.4.3 Conclusion

There was greater than 25% effect on tomato, cucumber, onion, lettuce and carrots seedlings vegetative growth when the seedlings were oversprayed at 11.2 kg/ha. There are some relatively minor effects on seedling germination and emergence when tested according to USEPA Guidelines at the highest rate (11.2 kg/ha) used in the US. At rates likely to be used under in Australia, effects on non-target plants are expected to be minimal.

4.5 Summary of Ecotoxicity

Diazinon is a highly toxic organophosphate insecticide. It is toxic to most organisms and in particular aquatic invertebrates.

4.5.1 Avian

The avian single dose toxicity of diazinon is rated as very highly toxic to moderately toxic with LD50s ranging from 1.1 to 85 mg/kg for all studies (6 species). The two modern and reliable studies gave an LD50 of 85 mg/kg for brown headed cowbird and 1.63 mg/kg for mallard. The 3 less reliable but acceptable results gave LD50s of 1.1, 3.8 mg/kg for Japanese quail and 14 mg/kg for domestic chicken. For the acute dietary toxicity, diazinon is rated as very highly to slightly toxic, with LC50 from 32 to 1450 ppm in the diet. The two reliable modern studies gave LC50 of 32 ppm for mallard and 38 ppm for brown headed cowbird.

The Pennside micro-encapsulated product is acutely less toxic than the active ingredient itself, with the exception of the Brown-headed cowbird single dose and the first Mallard duck and Japanese quail acute dietary results. However, based on US EPA classifications the active ingredient for the micro-encapsulated product is still moderately toxic to the bobwhite quail following a single dose, but highly toxic to both it and the mallard duck following acute dietary exposure

In the chronic reproduction studies over 20 weeks, the NOEC levels were 8.3 ppm for mallard and 32 ppm for bobwhite quail. For the bobwhite, the NOEC is the highest concentration tested, while for the mallard the MATC was 8.3 ppm to 16.3 and the LOEC of 16.3 ppm was based on reduced number of hatchlings and survivors in the 14 day old ducklings at this dosage.

A semi-field study showed that there were no overt effects to mallard ducks when exposed to diazinon on turf at 6.7 kg/ha as either EC or granular formulations. However, Canadian geese were overtly affected (limb rigidity, wing droop, salivation and tremors with one goose dying) at the same rate (6.7 g ai/ha) when the EC formulation was used but not with the granular formulation.

In a recent study, the sensitivity of nestlings (red-winged blackbirds and starlings) were compared to adult birds in acute oral tests and it was shown that nestlings were more sensitive. Red-winged nestlings were 3.8 times more sensitive than adults (LD50 2.4 to 9.1mg/kg) and starling nestlings 47 time more sensitive (LD50 12.7 to 602 mg/kg) than the adults.

Over 150 bird carcasses were found in a study of Washington and Pennsylvania orchards following 6 spray applications over 3 months with a mean application rate each time of between 3.0-3.1 kg ai/ha. Canada geese had the highest residues followed by killdeer and American robins, both of which feed on soil invertebrates. Hazard calculations indicated that 4 species potentially received lethal doses and there was a risk of passerine poisoning during the first four days following application, during which 78-84% of residues dissipated from the vegetation.

4.5.2 Aquatic

The toxicity to aquatic organisms, especially invertebrates, is very high. The acute toxicity to fish from submitted studies (9 species) ranges from LD50 of 2.16 mg/L for common carp to 23.4 mg/L for crucian carp. Life cycle studies have not been performed but the embryonic and larvae life stages of fathead minnow have been tested and the maximum acceptable tolerated dose was determined to be between 0.092 and 0.17 mg/L. The early life stages are considered to be normally the most sensitive. In a database of regulatory-type studies that have been reviewed by USEPA, the toxicity to fish of diazinon ranges from LC50 of 0.09 mg/L for rainbow trout to LC50 of 7.8 mg/L for fathead minnow.

Diazinon is extremely toxic to invertebrates, which is typical for an organophosphate, with acute toxicity figures for *Ceriodaphnia* (EC50) of between 0.36-0.6 µg/L and for mysid shrimp EC50 = 4.2 µg/L. (Note that mysid is normally a very sensitive test species.) The chronic toxicity to daphnia has been determined and the MATC found to be between 0.17 and 0.32 µg/L. The USEPA database on reviewed regulatory studies gives the most sensitive species as scud, EC50 = 0.2 µg/L, and least sensitive invertebrate as grass shrimp EC50 = 28 µg/L. The acute EC50 for *Daphnia magna* (three studies) in this database ranged from 0.96 to 1.1 µg/L. From literature reports tadpoles and caddis fly larvae also seem very sensitive.

Diazinon is moderately toxic to green algae, with EC50s of 8.5 and 6.4 mg/L for two species of *Scenedesmus*.

In a detailed long term study, diazinon was applied to several mesocosms at several treatment rates. The maximum average concentrations of diazinon, which mainly occurred immediately after the sixth (last) application, were 2.3 µg/L for level 1, 4.3 µg/L for level 2, 9.2 µg/L for level 3, 15.7 µg/L for level 4 and 29.7 µg/L for level 5. It should be noted that in treatment levels 4 and 5, one pond (replicate) showed consistently lower concentration and more rapid degradation than the other two ponds. Also, the half-life of diazinon decreased with increasing number of applications, and ranged from 10-26 after the first application to 5.5 to 8.5 days after the sixth application.

There were no detrimental effects on fish or plants at any treatment except for diatoms and green algae. Diatoms were significantly affected at the highest treatment with occasional reductions at lower levels and green algae affected occasionally.

Invertebrates were significantly affected by diazinon. For zooplanton, Cladoceran were the most sensitive taxon (significant reduction at all levels), followed by rotifers at levels 4 and 5 (one tribe affected at level 3) and Copepods once at the highest treatment level. For higher macroinvertebrates, Trichoptera were the most sensitive order (affected (reduced) at all treatments), with Diptera and Ephemeroptera intermediate (affected at treatment levels 3-5) and gastropods essentially unaffected. For the order Diptera, the family Chironomidae was the most significantly affected, with the tribe Pentaneurini (dominant tribe in subfamily Tanypondinae) effected at all levels and the tribes Tanytarsini and Chironomini (subfamily Chironominae) from levels 3 through to 5. Two other diptera families, Chaoboridae and Ceratopogonidae were effect at levels 2 and higher. The greatest effect on Chaoboridae occurred 2 months after the last treatment and may not be treatment related. All organisms recovered by the end of the study period, with Cladocerans taking the longest, up to 4 months.

It is concluded that while diazinon can significantly affect aquatic organisms at relatively low concentrations, especially invertebrates, these affected organisms are likely to recover and there is unlikely to be significant long term effects on populations, provided organisms are given adequate time to recover.

4.5.3 Non-Target Invertebrates

Diazinon is extremely toxic to bees by all routes of exposure. There were no regulatory studies presented but an old literature report gives LD50s of 0.22 µg/bee (contact) and 0.20 µg/bee (oral). In addition, more recent published reports show that the toxicity to bee larvae is extremely high, with an LD50 of 0.000121 µg/bee. The USEPA database of studies that have been reviewed by them shows contact toxicity as 0.2 µg/bee and foliage contact LC50 as 0.28 kg/ha.

In reviews of the effects of diazinon on non-target insects, 56 reports were summarised. This summary showed that diazinon affects the predatory complex, including hymenopterous parasitoids, *Chrysopa* ssp, and predatory mites. From the field results summarised, diazinon can be rated, according to IOBC, from 3 (moderately harmful) to 4 (harmful). It should be noted that the report includes information that resistance to diazinon occurs in wild population of predatory mites, which have been be used in IPM.

In studies conducted by the International Organisation for Biological Control (IOBC), it was shown that diazinon is harmful to parasitic wasps, predatory mites and spiders tested in laboratory exposed conditions and less harmful in the laboratory "protected" tests. The semi field tests showed that fresh residues of diazinon were harmful to the test organisms and the toxicity was rated as slightly persistent to persistent (5 days to >30 days). The field tests showed that diazinon was harmful (>99% mortality) to the predatory mite tested.

Several of the genera of the species tested are found in Australia and are used as part of IPM programs. Most of the mite genera tested are also present in Australia and are used in IPM programs, together with predatory beetles.

It is clear that diazinon is likely to significantly affect important beneficial insects in Australia.

The toxicity of diazinon to earthworms was tested according to OECD Guidelines. The LD50 was calculated as 130 (CI 110-160) mg/kg of soil. The toxicity of diazinon to earthworms has been tested under semi-field conditions at 4 and 20 mg/kg, corresponding to 4 and 20 kg ai/ha for soil 7.5 cm deep. There was a maximum of 20% mortalities at the highest level. The results indicate that there is unlikely to be significant mortalities of earthworms at <20 mg/kg.

In a published report, rows of tobacco were treated with diazinon, then the number of dead worms on the surface was counted after 7 days. There was no difference compared to blank controls at the highest rated used (4.48 kg/ha).

4.5.4 Micro-organisms

Diazinon has limited effects on micro-organisms. In tests using two different soil types, there was minimal effect on soil respiration and nitrification at 16 and 80 mg/kg soil, corresponding to 12 and 60 kg ai/ha. There were only limited effects on respiration of sewage micro-organisms at 100 mg/L.

Literature reports give the EC50 as 10.3 mg/L to a bacteria using the Microtox system. The rate of degradation in rice paddy water has been noted to increase following several applications of diazinon. There was rapid degradation in water from previously treated paddy, but in water taken from a rice paddy that was untreated, the degradation over the same period was not significant.

4.5.5 Phytotoxicity

It is concluded that there is greater than 25% effect on tomato, cucumber, onion, lettuce and carrot seedlings vegetative growth when the seedling were oversprayed at 11.2 kg/ha. There are some relatively minor effects on seedling germination and emergence when tested according to USEPA Guidelines at the highest rate used in the US. At rates likely to be used under in Australia, effects on non-target plants are expected to be minimal.

5 PREDICTED ENVIRONMENTAL HAZARD

Environmental exposure to diazinon is expected to be highest in the vicinity where it will be applied. Agricultural uses are expected to give the highest environmental exposures, with veterinary and domestic uses lower exposures. Surface water, uncultivated land and nearby non-target plants (eg trees and grasses) may be contaminated through overspray, spray drift and/or run-off from agricultural applications. Veterinary uses for sheep, cattle and other animals are applied as plunge and shower dips, pour-ons, sprays or wound dressings and may cause environmental exposure from treatment solutions dripping from freshly treated animals and in the excrement from treated animals. The exposure may also be high to organisms exposed to wool scouring effluents which may contain residues washed from treated fleece. Other uses, including domestic and uses around buildings, could cause exposure to the urban environment and associated areas through release to sewers or entry to stormwater drains.

Hazards arising from registered use patterns are discussed below.

5.1 Summary of Use Patterns

5.1.1 Agricultural

Diazinon as an 800 g/L EC formulation is registered for use on field crops; pasture, lucerne, cereals (including maize and sorghum), oil seed crops (including cotton), sugar cane and rice and is for the control of cabbage moth, cabbage white butterfly, midge, locust, grasshoppers, webworm, armyworm, cutworm, bloodworm and hoppers. For plantation and orchard crops diazinon is used to control scale, borers, thrips, citrus leaf miner, bugs and coccid. For vegetable crops it is used to control caterpillars, cabbage moth, potato moth, cabbage white butterfly, webworm, armyworm, cutworm, bloodworm and loopers.

The maximum use rates stated on the label are: 1-1.4 L/ha (800-1120 g ai/ha) for grasshoppers in field and pasture crops; 3–5 L/ha for seed maggots in beans and onion maggots in onion and garlic; 125 mL/100 L (100 g ai/100 L) for banana borer and macadamia felted coccid in bananas and macadamia nuts; and 0.7-1.4 L/ha for caterpillars, cabbage moth, cabbage white butterfly and cutworms in a range of vegetables crops.

Current usage does not reflect all the uses on the label, with the agricultural report identifying pineapple, grapes, mushrooms, macadamia nuts, ornamentals and a number of vegetables (onions, garlic, cucurbits, capsicum, carrot, celery, sweet corn, cauliflower, rhubarb, silverbeet, beetroots and beans) as current uses. The use rates for these crops are given in Table 48 and are for the pests identified in the agricultural assessment as current uses. There was a range of vegetables identified where diazinon is currently used, these are: onion, garlic and cauliflower for onion maggots and cucurbits, capsicum, carrots, celery, sweet corn, silver beet, beetroots for cutworms, webworms and caterpillars. The labels for current agricultural uses are summarised in Table 48.

Crop	**Pest**	**Application**	**Rates**
Pineapple	Mealy bug	Max. 5 per year, 2 months between	1.2-2.4 kg ai/ha
Grapes	Mealy bug	One application late Nov., with follow up if required	24 g ai/100 L
Mushrooms	Phorids, cecids	Mixed into casting	-
Macadamia nuts	Feltid coccid	Occasional use	100 g ai/100 L
Bananas	Rust thrips	As required. Spraying of bananas bunches	40 g ai/100 L
Ornamentals	Gnats, staphlinid beetle	-	-
Onions, garlic and cauliflower	onion maggot	On seedlings	2.4-4.0 kg ai/ha
Cabbage, cauliflowers, broccoli, Brussels sprouts, kale and kohlrabi	Cabbage white butterfly, caterpillars, aphids, looper	10-14 days intervals	560-1120 g ai/ha or 112 g ai/100 L
Cucurbits, capsicum, carrot, celery, sweet corn, rhubarb, silverbeet, beetroots and beans	Cutworms, webworms and caterpillars,		560 g ai/ha

Table 48. Currently used crops and corresponds rates for targeted insect as identified in the agricultural assessment.

It is normal practice in orchards situations to spray to runoff, normally requiring 1500 to 3000 L/ha of spray solution but could be a high as 10 000 L/ha for citrus trees. Large mature Macadamia nut trees require approximately 4000 L/ha of spray (Neil Treverrow, NSW Agriculture, personal communication) and at 100 g ai/100 L these figures correspond to application rates of 4.0 kg ai/ha. For other orchard crops on the label the rates are 52 g ai/100 L, corresponding to 780-1560 g ai/ha (1500 to 3000 L/ha) but could be as high as 5.2 kg ai/ha for citrus at 52 g ai/ha.

For most field and orchard crops the use, as stated on the label, is as necessary or when pest are present, with some uses have re-treatments 10 days apart. For vegetable crops the label states application when necessary or every 10-14 days.

The labels give directions for application to field and pasture crops by aircraft, boom sprayers and misters and for vegetables by boom sprayer and knapsack. Aerial application is not normally used for most vegetable crops, but is used on processing tomatoes and sometimes on rape, turnips, tomatoes, capsicums, potatoes and forage brassica crops.

Applications to vegetable crops is normally by low boom spray but taller crops, such as tomatoes and corn are sometimes sprayed using high boom or vertical boom sprayers. Other sprayers are likely to be used in vegetable crops, particularly hand held types for smaller growers or for small plots.

Application to orchards has traditionally been by orchard air blasters using high volume equipment. In addition, many orchardists are now using low volume, and in some cases electrostatic ultra low volume equipment, although the latter are expenseive and not very common. As there are no directions on the label for such equipment for orchard crops, growers convert the high volume spraying rate to a low volume rate by multiplying the ratio of high to low volume, ie high volume L/ha divided by low volume L/ha, and apply that rate using the LV and ULV equipment. Thus, the amount of active per hectare remains the same as for high volume spraying. There is no information on types of spray equipment used or any information concerning the use of low volume application equipment. Information on minimising spray drift—size of spray droplets etc., is also not given on the labels.

In bananas diazinon is used as a bunch or basal spray to control rust thrips and is spot sprayed into banana bunches at early development.

According to the labels the use in mushrooms is at spawning and after casing. When applied at spawning the rate is 110 g ai/10 L of water per tonne of moist compost and the rate after casting is 24 g ai/10 L per tonne of moist compost sprayed over the top of the casting soil. The efficacy report indicates the current use is to mix diazinon into the casing during preparation. The casting is then spread over the compost in an even layer 4-5 cm deep. The report does not give any rate for this use pattern.

5.1.2 Veterinary Uses

Veterinary usage is the major use, with most use for control of lice, ked and blowfly on sheep by dipping or jetting, with other significant uses being as shower dip or hand spray for lice and buffalo fly on cattle, lice on goats, lice and mange on pigs. There are approximately 30 products registered for used as ectoparasiticides on a range of animals. The rates used are 50 or 100 mL/100 L for dips, 200 mL/100 L for jetting and 250 mL/100 L for hand spraying.

In addition to the above uses in dips etc, diazinon is used in backrubbers to control buffalo fly in cattle. Directions for use (from the Di-Jet label) are: 100 g ai/10 L of oil and soak the backrubber, with repeats as necessary. Diazinon is also used in insecticidal cattle ear tags to control buffalo flies.

There are diazinon product used as wound dressings in sheep, cattle and horses. Superficial wounds are treated by the products (powders, sprays) being applied directly to the wound and are used after mulesing, shearing and de-horning.

For domestic animals, diazinon is used in dog washes at 0.5 g ai/L of the wash and in pet shampoos to control fleas, lice and ticks. It also used in some cat and dog collars to control fleas.

5.1.3 Other Uses

There are other uses for diazinon on registered labels. Use in homes, flats, hotels, commercial buildings, industrial buildings, and buildings (including kennels, stables and piggeries), ships, skins and hides, refuse areas and garbage containers for control of cockroaches, silverfish, carpet beetles, maggots and other household pests at 5 g/L for sprayers. It is also used for mosquito control in ponds and stagnant water as well as on hides and skins to control skin and hide beetles. There is a micro-encapsulated formulation registered for similar uses at rates of 50-100 g ai/10 L for cockroaches, silverfish and ants, and 100 g ai/10 L for fleas, ticks, flies and for perimeter treatments.

Domestic uses include use for control of ants (both as EC and powder formulations), use in home gardens for citrus leaf miner, cabbage white butterflies, caterpillars, aphids etc. and for lawn grubs and other pests. The EC formulations are used at 5 g ai/L. The micro-encapsulated formulation Pennside is also used for turf use to control Argentine stem weevil, African black beetles and mole crickets at 30-60 g ai/15 L per 100 m^2, with caterpillars at a lower rate of 7.2 g ai/15 L per 100 m^2. There are surface sprays products for crawling insects.

5.2 Hazard Evaluation

The following hazard evaluation follows the US EPA approach (Urban and Cook 1986) to establish a Q-value from the ratio of the Estimated Environmental Concentration (EEC) and lowest effects concentration, such as an LC_{50}. While Environment Australia has no formal framework for assigning levels of hazard for a given Q, it considers that the following would be an appropriate guide in this assessment:

For the establishment of hazard from acute toxicological end points under the various scenarios (ie direct overspray and 10% spray-drift), if:

- Q>0.5 then hazard is unacceptable,
- 0.1≤Q≤0.5 hazard may be able to be mitigated by some form of risk management, such as label restraints for a specific use, and
- Q<0.1, hazard is considered low (and may or may not require some form of risk management, such as general label restraints).

For the establishment of hazard for chronic exposure under the various scenarios,

- if using chronic data, Q>1 is unacceptable, and

—if using acute data, Q>0.1 is unacceptable.

5.2.1 Terrestrial organisms

5.2.1.1 Mammals

Terrestrial animals could be at risk from diazinon when applications of the chemical are made or afterwards by contact with sprayed surfaces. Aerial applications could overspray larger non-target organisms, such as marsupials but this is not considered a common occurrence due to the low height of the spray aircraft at application, ie close to crop height, and it is expected that these animals will move some distance from the area where spray operations are occurring, while smaller mammals will be undercover. Similarly, overspray by tractor powered equipment is considered unlikely as animals will move some distance from the area where spray operations are occurring or be undercover. Most mammals are not expected to be oversprayed directly.

It is difficult to assess the risk to larger terrestrial organisms that enter sprayed areas and are dermally exposed to residues. Animals that enter recently sprayed areas are at some risk of exposure but as there are few, if any, reports of dead or dying animals, it is considered likely that the risk is relatively low. This is further reduced when the restricted scope of current uses is taken into account.

The literature paper by Sheffield et al (2001) appears to be the first available study examining impacts on wild mammals. It supports the conclusion that the risk to mammals is fairly low, particularly considering the restricted current uses, though it does raise the possibility of sub lethal effects occurring, especially at high dose rates (4.5 kg ai/ha), which are well above the usual in Australia.

The dipping and/or spraying of sheep, cattle and other animals as well as other uses are unlikely to affect other mammals.

5.2.1.2 Birds

Diazinon is highly toxic to birds, which could be exposed when used in orchards, vegetables, pastures, turf and to a lesser extent, veterinary uses. These are addressed in turn below.

Orchards and vegetables

Birds feeding on sprayed crops could be exposed to residues of diazinon. There are a number of bird species that are pests in orchards, grapevines etc. These species include silvereyes, parrots, lorikeets, rosellas, cockatoos, starlings, currawongs etc. Birds are not normally a pest in vegetable crops but ducks can occasionally be pests in lettuce crops (Leigh James, District Horticulturist NSW Agriculture, personal communication).

As the current labels include fruit, these will be examined. However, as this is not a current use, this examination will be brief. For fruit sprayed at 65 mL/100 L and using 3000 L/ha, the highest rate likely to be used in pome or stone fruit (birds don't eat citrus fruit) when trees have fruit, which corresponds to 1.56 kg/ha, the concentration of diazinon on the fruit is calculated as 21 mg/kg wet weight (160 mg ai/kg dry weight) from the modified Kenaga nomogram (Fletcher, Nellessen and Pfleeger, 1994). Using the mallard dietary LC50 = 32 ppm (mg/kg) in diet and assuming that these species ingest approximately 50% of their dietary intake as fruit, then Q = 0.33. Similarly, the concentration on lettuce leaves is calculated as 188 mg/kg (wet weight), and for a duck with the above assumptions, the quotient is 2.9 using the EC50 of 32 ppm. These indicate that there is some risk to birds from use of diazinon, especially for green leaf crops.

However, as the dietary EC50 is based on 5 days of exposure, birds are unlikely to continue feeding for five days on contaminated feed provided that the initial exposure does not cause mortality and there is uncontaminated food available, the hazard is expected to be lower than that calculated in the quotient. Also, the Kenaga nomogram is for the maximum residues on crops and therefore the results should be considered to be worst case rather than typical.

Diazinon is used in macadamia orchards at a high rate. While birds are not known to actively feed on macadamia nuts, they could generally use the orchards and therefore be exposed to diazinon residues on insects and foliage. While the hazard for this type of exposure is somewhat difficult to estimate, it would be expected to be less than that for birds that directly feed on sprayed fruit.

The literature study by Cobb et al (2000, see Section 4.1.3) supports that birds can be affected in orchard situations as over 150 bird carcasses were found following 6 spray applications over a 3 month period with a relatively high mean application rate of between 3.0-3.1 kg ai/ha each time. Canada geese, which would have consumed diazinon residues while eating grass, had the highest residues, followed by killdeer and American robins, both of which feed on soil invertebrates. Note that the authors estimated a risk of passerine poisoning during the first four days following application, during which 78-84% of residues dissipated from the vegetation.

Pastures

Application of diazinon to agricultural pastures is at 700 mL/ha (from the label for EC 800) and using the Kenaga nomogram maximum residues expected are 120 mg/kg for short grass and 55 mg/kg for long grass respectively. Using the LC50 for mallards of 32 mg/kg, Q = 1.9 and 0.86 for short and long grass, indicating a possible hazard to ducks. Note that while the semi-field study (Honeycutt, 1983) showed that there were few effects on mallards at 6.7 kg ai/ha, there were significant effects on Canadian geese. In addition, the US incident reports would indicate there is a potential hazard, although at higher rates than used for pasture in Australia.

Secondary effects on birds are possible from birds eating insects that are dead or dying from use of diazinon. Using the label rate for locust control (560 g ai/ha) with diazinon and the EPA food chain (Kenaga) nomogram, the concentration of residues on large insects is 7.0 mg ai/kg (wet weight, Fletcher, Nellessen and Pfleeger, 1994). A mallard consuming 70% of its diet as large insects and 30% as forage crops and all food is contaminated (worst case), Q = 0.66 for the worst case but assuming that 50% of the food is untreated, Q = 0.33, and the hazard is expected to be moderate from dietary intake of residues on insects. However, insectivores are attracted to locusts plagues and can they encounter high levels of exposure, especially as they tend to gorge themselves. This has been noted for fenitrothion, another organophosphate used for locust control by the APLC (application rate is 270 to 380 g ai/ha, almost half that of diazinon), where the APLC has reported contamination of black kites of up to 90 ppm in the stomach contents (Bunn, Best, Chapman, and New 1993).

Further adding to the possible hazard is that insects contact diazinon through a variety of routes such as inhalation, contact and ingestion and as insects move through areas of high and low exposure. As some locusts are likely to receive higher doses than others, it may be that these insects are eaten preferentially by scavenging birds. However, it should be noted that diazinon is not currently used for locust control in Australia by either authorities or landholders. Due to the potential for high avian hazard, Environmental Australia recommends that use for locust control be removed from the label.

Birds remaining in a sprayed area or entering an area that has been recently sprayed could be exposed either dermally or orally from preening contaminated feathers (Driver, Ligotke, Voris, McVeety, Greenspan and Drown, 1991). The literature does report that there are possible effects from such an exposure. This is difficult to estimate and given the hazard as indicated above, the increment due to dermal and oral exposure from preening is not expected to cause a significant increase in the overall hazard.

Turf

For uses in turf, the rate on one label is 3 kg ai/ha (200 g ai/L used at 150 mL per 100 m^2) but this appears to be for domestic use (200 mL container). However, this needs to be confirmed as it is based on the supposition that the small containers would limit its use to small areas. The high rate used in domestic lawns indicates that there is a potential for high avian hazard. While there is little use of most common diazinon formulations on lawns in Australia, unlike the situation in the US, the draft report indicated that Pennside was known to be used large lawn areas such as golf courses and sports grounds. One registrant indicated that there is significant use of this product on golf courses and bowling greens in NSW around the Sydney and Newcastle areas where the mole cricket is a particular pest. The registrant has also indicated that they had isolated reports of EC formulations being used off label instead of Pennside due to cost differences.

As a result the draft report sought:

- An indication of the size of grassed area treated with the micro-encapsulated product, Pennside, and a broad indication of location where it is used, frequency of use and rates at which it is used.

- Clarification of the extent of incidents in the US/overseas with the micro-encapsulated formulation and provision of the acute and dietary avian toxicity studies identified in the US EPA report to allow their use in hazard calculations.

In response the company has clarified that Campbell Pennside Flowable Microencapsulated Insecticide is predominantly used in golf and bowling greens in Australia, mainly between November and March. Modern application is based on insect pressure rather than on a regular basis, with no more than 3 applications made within the season. Rates are 125 mL (low infestation) to 250 mL (high infestation – rarely used) of product per 100 m^2 for the argentine stem weevil, 125 mL per 100 m^2 for the African black beetle, 200 mL per 100 m^2 for the mole cricket and 30 mL per 100 m^2 for grass eating caterpillars (armyworms, cutworms and webworms). Since the product contains 240 g diazinon per L, this equates to an application rate of between 0.72-6.0 kg ai/ha, but with most applied at 4.8 kg/ha or below.

According to the label the product is diluted with 15 L water and applied by boom spray. The company has clarified that the most commonly used spray equipment is:
a) electrically operated mini-spray booms (mostly on bowling greens), where approximately 1500 L water/ha is typically used;
b) tractor operated boom sprays, approximately 400 L water/ha is used and
c) Vertispray or high volume spray application where very high water volumes are used.
Droplet sizes are expected to be reasonably coarse which would limit spray drift potential.

The turf should be mowed to ensure no flowers are present and immediately after application the treated area should be irrigated with the equivalent of 2 mm water with the exception of "grass-eating caterpillars" such as armyworms etc where the treatment is generally left on the leaves. The company has noted that the environment of the bowling and golf green is peculiar in that both situations are watered regularly (hence leading to further watering in) and are mown daily (claimed to lead to removal of excess Pennside left on the leaf after a maximum exposure of less than 24 hours). Golf greens (the major use) can be watered up to four times a day in the hotter weather during which this product is used.

Based on the number of golf and bowling clubs and the area of their greens, it is estimated by the company that around 1 tonne of active is applied per annum, enough to cover about 350 ha of greens in total, covering about 20% of the total turf market.

The draft report (Section 5.2.1.2) noted that the US EPA review contained numerous reports of ducks and other waterfowl dying from feeding on turf/lawns that had been treated with diazinon as liquid and granular formulations, but that it was unclear whether this included the micro-encapsulated formulations. There was only one clear reference in the US EPA review to birds dying with the micro-encapsulated formulation - it was used at a concession stand and inadvertently swept outside. The manufacturer has responded that they are not aware of any incidents of environmental damage related to their product, noting that reports of bird kills on golf courses have been due to emulsifiable concentrate and granule formulations rather than the micro-encapsulated product.

However, as noted in Section 4.1.4, Pennside has been involved in bird poisoning incidents when used to treat lawns in Australia, one at Parliament House (together with malathion) and the other at Gosford, NSW. At Parliament House the products were watered into the lawns 15 minutes after application and the dead birds, that fed on dead or dying insects that had risen to the surface, were found the next day, while that at Gosford was an accidental misuse situation where it was used at over 10 times the label rate. In Australia, the wood duck, which gathers and feeds in golf courses and greens, is particularly vulnerable. Indeed there are anecdotal but poorly documented reports of this species dying from diazinon use on lawns, including on Chapman oval, ACT in 1984.

Table 49 below lists the Q values based on the modified Kenaga nomogram (Pfleeger *et al*, 1996) for the mallard duck and bobwhite quail using typical diets for these species and the acute dietary LC50s of 149 and 348 ppm (ai) respectively from the micro-encapsulated product data (see Section 4.1.1.3) for all the label rates and pests listed. The table also lists the modified Kenaga nomogram maximum residues expected for short grass and the resulting Q values for the Australian wood duck, based on its diet of short grass and herbage.

Pest	Label rate (kg ai/ha)	Q value (Mallard duck, Bobwhite quail respectively)*	Kenaga predicted residues (short grass); mg/kg	Q value (Australian Wood duck)**
Argentine stem weevil	3.0 (low infestation) 6.0 (high infestation)	0.78; 0.90 1.56; 1.81	643 1286	4.3 8.6
African black beetle	3.0	0.78; 0.90	643	4.3
Mole cricket	4.8	1.25; 1.44	1029	6.9
Grass eating caterpillars	0.72	0.19; 0.22	154	1.0

Table 49. Hazard from use of micro-encapsulated formulation on turf

* Quail value based on diet of 30% small insects, 70% grain and mallard duck value based on 30% grain, 70% large insects.

** Based on short grass as 100% of the diet and using the mallard duck LC50

The calculations suggest that a potential hazard exists in all situations except to Bobwhite quail/mallard duck at the low grass eating caterpillars' rate. The hazard for these species mainly comes from the consumption of dead or dying insects that rise to the surface. However, the hazard is particularly high to the grass and herbage eating wood duck, even at this low rate.

The label directions include irrigating the treated area following application with the equivalent of 2 mm water, which would be expected to reduce the hazard. However, the US review (US EPA 2000) states that "Incidents (of bird mortalities) have occurred despite watering-in (irrigation) on turf, possibly due to residues still on the turf blades or in the thatch...". Adding to the hazard from lawn uses is that heavy rainfall or over irrigation can lead to puddling, where birds can receive additional doses of diazinon via the dermal and contact routes through bathing in shallow pools caused by collection of surface water in depressions. The concentration of diazinon in these shallow puddles can be high (note comments on golf/bowling green irrigation practices above).

In conclusion assessment of the hazard to birds of use of the micro-encapsulated formulation on turf and other grassed areas based on the information provided in response to the draft report indicates that this is high, in particular to the grass and herbage eating Australian wood duck. This appears to contrast with the US experience that this formulation poses much less of a risk than granulated or emulsified concentrate forms of diazinon when used in this situation (though it is noted the US label bans golf or sod farm use, but allows use on home lawns). However, it is noted there have been at least two well publicised local bird kill incidents from use in these situations. It is therefore recommended that a watching brief be maintained, and appropriate be action taken if new information such as further bird poisoning incidents comes to hand through the use of the micro-encapsulated diazinon formulation, Pennside.

Hazard from oxon

In the above hazard analysis no consideration is made as to possible toxic metabolites, in particular the diazoxon metabolite. However, Environment Australia notes that diazoxon was not a significant metabolite in any of the fate studies and was more rapidly hydrolysed. This does not rule out formation on the surface on leaves and other avian food items.

Veterinary uses

For the treatment of cattle, sheep and other animals, contamination of the soil in areas where treatment will occur is unlikely to result in significant exposure to birds. It is possible, however, that some birds which have been observed to associate with cattle could be adversely affected. Such a situation has been reported in the US where another organophosphate insecticide, famphur pour-on treatment (application rate unspecified), killed magpies consuming cattle hair and hawks preying upon the magpies for up to 82 DAT (Haley, Matheson and Erikson, 1993). In Australia several native species, including the willie wagtail (*Rhipidura leucophrys*) live in close association with cattle (eg. perching on their backs, Macdonald 1973). The Cattle egret (*Ardea ibis*) also uses cattle as a vantage point and may feed on their ectoparasites (Marchant and Higgins 1990). Therefore, these birds may be exposed to diazinon. As the willie wagtail is a small bird with a relatively high metabolism and food consumption rate, the hazard is also expected to be higher with a given dose. Although treated animals are not expected to harbour large populations of ectoparasites, eg ticks, in sufficient numbers to impart an appreciable dose to feeding birds, Environment Australia is unable to assess this hazard without further data.

Other uses

There are a number of other uses on the labels, most of which are unlikely to result in significant avian exposure, with the possible exception of mosquito use. For mosquitoes the labels direction are for uses by sprayer, misters and foggers with direction for use in mosquito breeding areas. This could lead to contamination of streamside vegetation and other avian food items. The rates are 100 g ai/100 L for sprayers, 1.6 g per 100 m^2 (1600 g ai/ha) in diesel/kerosene for mister and 144 g ai/ha in fogging oil or distillate. The avian hazards from the rates used for both misters and foggers have been addressed above as have the terrestrial hazard. The aquatic hazards will be examined latter. It should be noted that the agricultural assessment did not indicate that use for mosquitoes was a significant current use. There are no currently registered granular formulations of diazinon.

Conclusion - Birds

In conclusion, the overall hazard to birds appears low for veterinary uses, moderate for agricultural uses and higher for lawn and turf uses. There are number of reports from overseas and in Australia of adverse effects, most of which relate to turf usage and grassed areas, ie golf courses. In the USA uses in golf courses and on sod farms has been banned due to the avian hazard, but there are continued reports of bird kills from other lawn uses. There is a potential hazard to birds from domestic uses on lawns but due to small size of areas treated, these are not likely to present a significant problem. No granular formulations are registered and therefore should not be available. These present a potentially higher hazard through direct ingestion when mistaken as grit for use in the bird's crop.

The micro-encapsulated product (Pennside) is used mainly on golf and bowling greens in Austalia. Assessment of the hazard to birds from this use indicates that this is high, in particular to the grass and herbage eating Australian wood duck. This appears to contrast with the US experience that this formulation poses much less of a risk than granulated or emulsified concentrate forms of diazinon when used in this situation. However, it is noted there have been at least two well publicised local bird kill incidents from use in these situations. It is therefore recommended that a watching brief be maintained, and appropriate be action taken if new information such as further bird poisoning incidents comes to hand through the use of the micro-encapsulated diazinon formulation.

5.2.1.3 Bees

Bees are at risk if spraying occurs when they are present in the crop. Using the typical application rate in orchards (65 mL/100 L, 1.5 kg ai/ha for 3000 L) and the Kenega monogram, the estimated dose is 20 µg ai per bee, and from the EC50 of 0.22 µg ai per bee, the Q = 100 and the hazard high. While the current use usage does not include orchards crops, macadamia nuts flowers are attractive to pollinators and the rates for macadamia nuts are higher that for other orchards (125 mL/100 L). In order to limit the exposure of bees to the pesticide, the crop should not be sprayed when there are bees present. This is the current label warning and is acceptable.

It should be noted that spray drift is expected to be extremely toxic to bees. Using the US EPA AgDRIFT model of spray drift in orchards (dense and tall trees) and the rate used in macadamia nuts (125 mL/100 L @ 4000 L/ha), at 100 metres the spray drift is 0.14% of application rate (5.6 g ai/ha). Assuming a bee is 1 cm^2 in contact area for the spray, then the dose per bee is 0.056 g/bee and Q = 0.25. While there is some hazard, this is considered moderate. However, the hazard to bee larvae would remain high (LD50 to larvae is 1.2 X 10^{-4} µg/larvae).

Other non-target terrestrial invertebrates and beneficial insects are at risk from the use of diazinon (see discussion above). Unless_resistant strains of predator insects are used, diazinon is not suitable for IPM use.

5.2.1.4 Soil Invertebrates

Earthworms and other soil dwelling invertebrates could be exposed to the pesticide, and at an application rate of 1.0 kg ai/ha, the top 5 cm of soil would contain diazinon EC residues at 1.5 mg/kg of soil (assumes no crop cover, density of soil 1300 kg/m^3). As this concentration is significantly below the EC50 of 130 mg/kg, significant effects on earthworms are not expected. Even at the high rates used for lawn usage of up to 6 kg ai/ha, the concentration in the top 5 cm is 9 mg ai/kg and significant effects are not expected. In addition, the semi-field study (Schäpfer, 1977) showed that at 20 kg ai/ha there were unlikely to be significant effects on earthworms.

Other soil invertebrates may be significantly affected unless they can move away from the sprayed areas or have become resistant in the past. There are no toxicity data available for these organisms and the hazard cannot be determined.

5.2.2 Conclusion

The overall hazard to birds appears low for veterinary uses, moderate for agricultural uses and higher for lawn and turf uses. Given there is a risk to birds when diazinon is used to control locust and grasshoppers and these are not current uses, they should be removed from the label. There are number of reports from overseas and in Australian of adverse effects, most of which relate to turf usage and grassed areas, ie golf courses. In the USA uses in golf courses and on sod farms has been banned due to the avian hazard, but there are continued reports of bird kills from other lawn uses. There is a potential hazard to birds from domestic uses on lawns but due to small size of areas treated, these are not likely to present a significant problem.

The micro-encapsulated product (Pennside) is used mainly on golf and bowling greens in Austalia. Assessment of the hazard to birds from this use indicates that this is high, in particular to the grass and herbage eating Australian wood duck. This appears to contrast with the US experience that this formulation poses much less of a risk than granulated or emulsified concentrate forms of diazinon when used in this situation. Noting there have been at least two well publicised local bird kill incidents from use in these situations, it is recommended that a watching brief be maintained, and appropriate be action taken if new information such as further bird poisoning incidents comes to hand through the use of the micro-encapsulated diazinon formulation.

The hazard to bees is high, particularly from direct application, and there is a possible hazard to soil invertebrates but there are no toxicity data for these organisms. Terrestrial mammals are not expected to show significant effects when diazinon is used according to current label directions. The micro-encapsulated formulation is expected to have a similar hazard to other terrestrial organisms as the EC formulation.

To strengthen the current warning label with regard to bees, the label for all formulations should be modified to read:

Do not spray any plants in flower, including ground covers and adjacent foliage, or while bees are present.

5.3 Aquatic Organisms - Agricultural Uses

5.3.1 First Tier — Direct over spray

Aquatic organisms are the most sensitive to the toxic effects of diazinon, based on the ecotoxicity data reviewed. Direct application to a body of water 15 cm deep at the rate of 1.0 kg ai/ha (highest rate expected for vegetables) is calculated to give a concentration in the water of 0.67 mg/L. Even at the lower rate, 560 g ai/ha currently used in vegetables, the concentration in water is 0.37 mg/L and the hazard to most aquatic organisms is high.

While higher rates than above are possible in some uses, application by boomspray and orchard air blasters is unlikely to result in direct overspray. However, aerial application could lead to such direct overspray and is of concern. A concentration of 0.67 mg/L in shallow water is likely to cause mortalities in the majority of fish species, based on the tests reviewed and results quoted in the ASTER database.

Effects on daphnia and other aquatic insects/invertebrates from direct overspray are likely to be severe, with Q = 670 for daphnia (using the most reliable result currently available, EC50 = 0.96 µg/L). Similarly, effects on other aquatic invertebrates are expected to be severe, based on results in Table 39.

5.3.2 Spray Drift

5.3.2.1 Second Tier — 10% Spray drift onto pond

Spray drift is of major concern for aquatic organisms. Using the US EPA assumption that 10% spray drift occurs (Urban and Cook, 1986), this provides a concentration of 67 µg/L for a shallow pond 15 cm deep (rate 1.0 kg/ha). This is significantly below the EC50 for the most sensitive fish in Table 38 (Common carp, EC50 = 2.16 mg/L) and similar to the most sensitive fish from the USEPA database, rainbow trout (Q = 0.74, see Table 40). The quotient for daphnia, the most sensitive organism in Table 39 with an acceptable endpoint (EC50 = 0.96 µg/L), is 70 and indicates a very high hazard. Using the most sensitive invertebrate species from the USEPA database, scud (EC50 = 0.2 µg/L), Q = 335.

At the typical rate for vegetables, 560 g/ha, the concentration in shallow water (15 cm) from 10% spray drift is 37 µg/L. There is a hazard to sensitive fish species (Q = 0.37) and a high hazard to aquatic invertebrates (Q = 39 for daphnia). At the higher rates used for macadamia nuts (2 kg ai/ha) the hazard from 10% spray drift is correspondingly 4 times higher.

The hazard to aquatic organisms from 10% spray drift is therefore considered unacceptable and further refinements to accurately determine the hazard is required.

5.3.3 Realistic Spray Drift Scenarios

5.3.3.1 Aerial Applications

Some considerations

The current labels give directions for aerial application for field crops and pastures, none of which have been identified in the agricultural assessment as current uses of diazinon. As these uses are on the current labels, they will be considered briefly (Tier 1 level in AgDRIFT only).

Vegetables, one of the uses identified as current, are sometimes aerially sprayed, in particular processing tomatoes and potatoes. The application rates given on the labels are 1 L/ha for potatoes and between 0.7 and 1.4 L/ha for tomatoes. These correspond to between 560 and 1120 g ai/ha. Of the vegetables that have been identified where diazinon is currently used, the draft report indicated only sweet corn would be expected to aerially sprayed when mature. This use will be considered in some detail.

Acute hazard

The US EPA has developed a computer based model for spray drift, AgDRIFT, based on the results of Bird *et al* (1996). Using this model and a range of possible water bodies {US EPA defined wetlands (15 cm deep) and a pond (2.0 m deep), as well as a small Australian river (30 cm deep and 3 m wide)}, Table 50 gives the concentration in the water and the quotient for daphnia for both fine (119 µm vdm) and medium (216 µm vdm) droplet sizes, which bracket the typical Australian droplet size. (Typical spraying in Australia uses droplets of between 150-200 µm vdm.) This is a Tier 1 assessment, as given in the AgDRIFT model (upper limit for fixed variables, reasonable but conservative assessment of spray drift) and no adjustment was made for Australian conditions, ie Micronair nozzles.

Droplets Sizes	Fine, 119 µm vdm			Medium, 216 µm vdm		
Distance Downwind, m	100	200	300	100	200	300
US EPA defined wetland	66.0 **68.8**	44.7 **46.6**	34.6 **36.0**	23.4 **24.4**	15.3 **15.9**	11.8 **12.3**
US EPA defined pond	4.9 **5.1**	3.35 **3.5**	2.5 **2.7**	1.76 **1.8**	1.15 **1.2**	0.88 **0.92**
Australian small river	38.7 **40.3**	24.5 **25.5**	18.5 **19.3**	14.4 **15.0**	8.38 **8.7**	6.39 **6.7**

Table 50. Concentration of diazinon in water as µg/L for defined waterbodies (US EPA defined wetlands (15 cm deep) and pond (2.0 m deep), as well as small Australian river (30 cm deep and 3 m wide) from application at 1.12 kg ai/ha and corresponding quotient for daphnia (in bold). Calculated from US EPA AgDRIFT model. Dark shading is Q > 0.5, light shading = 0.1<Q >0.5.

The results from the US EPA AgDRIFT model in Table 50 show that even at 300 metres, there is a high and unacceptable hazard to daphnia and there is potential for spray drift to significantly impact on the aquatic environment. It should be noted that this is for the maximum rate for field and pasture crops on the current labels, 1.4 L/ha. Using a more typical rate of 700 mL/ha (560 g ai/ha), the hazard in Table 48 is halved, but still represents a high hazard in all but very deep water (2 metres) and larger droplet sizes. Such deep water is not considered typical for the relatively dry Australian conditions.

Further Refinements to Hazard

The hazard will be refined for the current use in sweet corn, the only crop where aerial application could be expected.

As a further refinement in the US EPA AgDRIFT model, the spray drift from Micronair AU5000 nozzles, typical of those used in Australia, is modelled together with two hydraulic nozzles with medium size droplets (the Tier 2 modelling in AgDRIFT allows for 27 different nozzles to be modelled). The nozzles are at 0 degrees to the air stream. Table 51 gives the results at a distance of 300 metres using the same aquatic environments as for Table 50 for Micronairs (at 4000 rpm) and two different hydraulic nozzles (selected for vdm of around 250 and 400 µm) at the lowest rate for corn 560 g ai/ha.

Table 51 shows that even using placement spraying (vdm >250 µm), a 300 metre buffer would not protect aquatic invertebrates from the acute effects of diazinon. From AgDRIFT and using the D4-45 with a 600 metre buffer, the concentration in a small river (30 cm deep) from spray drift is 0.41 µg/L and for daphnia Q = 0.43. Given that the toxicity curve is very steep, ie LC50 of 0.96 µg/L and NOEC of 0.56 µg/L (see above), at a quotient of < 0.5 is considered to be acceptable.

Nozzle types	Micronair (vdm = 156 µm)	D4-45 (vdm = 272 µm)	CP 0.078 (vdm = 410 µm)
US EPA defined wetland	14.1	3.3	1.9
US EPA defined pond	1.1	0.25	0.15
Australian small river	7.5	1.8	1.0

Table 51. Quotient for daphnia in water at 300 metres away for US EPA defined wetlands (15 cm deep) and pond (2.0 m deep), as well as a small Australian river (30 cm deep and 3 m wide) from application of diazinon at 560 g ai/ha. Calculated from US EPA AgDRIFT Tier 2 modelling. Dark shading is Q > 0.5, light shading = 0.1<Q <0.5.

It should be noted that the hazard assessment is based on the *Daphnia magna* EC50 of 0.96 µg/L, which was used as it was the most reliable endpoint presented but is not the most sensitive species.

In refining the hazard, additional mitigating factors are considered. From the aquatic metabolism study, the dissipation (including adsorption to sediment) half-lives in water ranged from 7 to 15 days. The dissipation in water will not significantly reduce the acute toxicity in the first few days.

The above theoretical modelling is not the real world situation, which is very closely represented by the mesocosm studies, where the most sensitive organisms were those belonging to the order cladocerans, which include the daphnia. At the lowest test concentration, level 1, after exposure to the second treatment the average concentration in water was 1.99 µg/L and the cladoceran population was reduced to <10% of their pre-treatment levels when tested 6 days later. While this was not statistically significant in the analysis, due to high variation in the replicates and controls, it shows that significant effects on these organisms occurs at these levels and therefore mitigation of the laboratory toxicities in the open environment is unlikely.

As the above calculations indicate that an unacceptable hazard exists from aerial applications and there is currently only limited aerial application, Environment Australia recommended that aerial applications of diazinon should be banned.

Retention of Aerial Application for Seedling Maggot Control in Onions

In response to the above recommendation in the draft report, the onion industry indicated that the proposed removal of aerial application from all labels would seriously disadvantage them in respect of onion seedling maggot (OSM) control. The current label allows both ground and aerial application, and as OSM are often associated with wet soil, the loss of the latter could effectively remove diazinon as a viable control option.

The total area grown to onions in Australia is round 5000 hectares per annum (http://www.horticulture.com.au/aboutus/profiles3.cfm), with the major production in the States of SA and Tas. However, the need for aerial application is said not to be uniform across the industry, as it is not employed in the Tasmanian, Victorian and Western Australian production areas. Further, treatment in Queensland is unlikely as OSM is not considered a significant pest, and in South Australia the use of ground rigs is predominant as the sandy soil types allow rapid access following rain or irrigation. It is mainly in New South Wales when the clay soils are wet following rain or furrow irrigation that ground rig application could be problematic, and therefore aerial application most likely.

Two early season treatments within 3-4 weeks of germination and 10 days apart are usually applied. The maximum rate is 700 mL/ha (0.56 kg ai/ha) and, as both the infested soil and the emerged seedlings need to be treated, placement spraying with a medium to coarse droplet spectrum in the range of VMD >300 µm is considered desirable. To ensure adequate coverage and efficacy application volumes need to be between 20-40 L/ha. It is stated that the treated area is not likely to be large, with the average area of onion production per farm about 8 hectares. As it is unlikely that all areas will be planted simultaneously, the industry expects this will reduce the area to be treated to a few hectares per farm.

Table 51 covers the hazard of aerial application to sweet corn, considered at the time of the draft report to be the only crop where aerial application could be expected. The table estimates the hazard resulting from the aerial use of diazinon at 560 g/ha using of various types of nozzles with VDM = 156, 272 and 410 µm. It concludes that with the medium droplet size a buffer of 600 metres would be required to protect daphnia in a small 3 m wide by 30 cm deep river from the effects of spray drift. This was not the most sensitive organism, but the one with the most reliable end point.

Re-calculation using the newly available Tier 3 AgDRIFT model and using the extremes of the parameters suggested by the onion industry; VMD 439.39 µm (ASAE coarse to very coarse), application volume 20-40 L, wind speed 0-3 m/sec and temperature 30^{o}C and

50% RH) leads to the Q values listed in the following Tables 52 and 53 for an Australian creek 15 cm deep and 3 m wide, considered to be the most relevant for onion areas.

Distance (m)	Concentration (µg/L); 30 L & 0.5 m/s*	Q	Concentration (µg/L); 30 L & 3.0 m/s	Q
100	0.83	0.86	3.6	3.75
200	0.27	0.28	2.2	2.3
300	0.079	0.08	1.3	1.35
500	0.005	0.005	0.61	0.64
750	-	-	0.28	0.29

Distance (m)	Concentration (µg/L); 20 L & 0.5 m/s*	Q	Concentration (µg/L); 20 L & 3.0 m/s	Q
100	0.54	0.56	3.6	3.75
200	0.17	0.18	1.9	1.98
300	0.022	0.13	1.1	1.15
500	0.0008	0.0008	0.42	0.45

Distance (m)	Concentration (µg/L); 40 L & 0.5 m/s*	Q	Concentration (µg/L); 40 L & 3.0 m/s	Q
100	1.0	1.04	3.5	3.65
200	0.38	0.40	2.2	2.30
300	0.14	0.15	1.4	1.46
500	0.013	0.014	0.76	0.79
750	-	-	0.37	0.39

Table 52. Hazard resulting from aerial application to onions using extremes of industry's proposed parameters
* Minimum allowable wind speed in model

From the above it is clear that even at 750 metres (the range of the model) a hazard exists that needs to be mitigated. Indeed, even assuming a wind speed of 2 m/s the Q values -are only just acceptable at this distance (see table below).

Distance (m)	Concentration (µg/L); 40 L & 2.0 m/s	Q	Concentration (µg/L); 30 L & 2.0 m/s	Q
100	3.23	3.36	3.11	3.24
200	1.57	1.63	1.41	1.47
300	0.94	0.98	0.82	0.85
500	0.39	0.41	0.35	0.36
750	0.22	0.23	0.16	0.17

Table 53. Hazard resulting from aerial application to onions with a maximum wind speed of 2.0 m/sec

In conclusion and keeping in mind the ANZECC water quality criterion of 0.01 µg/L (despite the steep response curve there are clearly more sensitive organisms - see Tables 40 and 42 as well as Stuifzand *et al* in Section 4.2.3.2 above) and that mitigation through dissipation from water is not possible, a downwind buffer of 0.5 km using an application volume of not more than 30 L, a temperature <28^{o}C and a maximum wind speed of 2.0 m/s would be required to safely apply diazinon by air to onions for the control of onion seedling maggots. This should be coupled with the onion industry's proposal to include diazinon to the list of compounds targeted for testing by Murrumbidgee Irrigation, and the proposed communication strategy. However, based on the above, use of coarse droplets for ground application would appear to be acceptable with a label warning to control drift but without the need for any buffer zone (see Section 5.4.2.1 of this report).

The industry also notes that growers in the Murrumbidgee Irrigation Area (MIA) are complying with a recently developed Land and Water Management Plan which will manage surface water flows by retaining the equivalent of 25 mm rainfall or irrigation on farm for 7 days or more. While this will help minimise contamination of the riverine environment from run-off, the main concern here is with spray drift direct to natural waters following aerial application.

5.4 Ground Based Spraying

5.4.1 Orchard Spraying

While there is a range of orchard crops on the label, the agricultural assessment indicates that diazinon is not frequently used in orchard crops, except for bananas, macadamia nuts and pineapples. There could be some use in citrus in Queensland but the agricultural assessment indicates that this is not considered important.

5.4.1.1 Pome and Stone Fruit—Land Use Considerations

Pome fruits are grown in a number of locations with considerable variation in land use adjacent to these crops. No data exists for the occurrence of these crops close to waterbodies, but Environment Australia expects that ponds and drainage channels (both man-made/modified or natural) would be a common feature of the landscape in which pome fruits are grown, with subsequent movement into "natural" receiving waters such as swamps, marshes, lakes and rivers. Indeed, it is likely that man-made drainage channels would frequently be within 10 m of the crop, but are of less concern than natural waterbodies because of their expected lower biodiversity and ecological significance.

A similar situation occurs for stone fruit, with pome and stone fruit grown in the same regions, especially in the southern NSW and Victoria. As stone and pome fruits are of similar size, leaf shape and the applications rates are the same, they will be treated together in the hazard assessment.

Spraying of full canopy

For pome fruits, the label indicates use for scale pests before green tip and three applications after petal fall at 65 mL/100 L. Assuming that application is after petal fall at 3000 L per hectare (1.56 kg ai/ha), expected to be maximum rate for most trees, Table 50 gives the EEC in water and quotient for daphnia in shallow water from AgDRIFT using standard orchard air-blaster sprayer. It should be noted that large pears trees could be sprayed at higher volumes than used in Table 54.

Distance downwind, m	15	25	50	100
EEC, in water 15 cm deep µg/L	1.8	0.93	0.31	0.09
Quotient, daphnia EC50 = 0.96 µg/L	1.9	0.97	0.32	0.09

Table 54. Estimated concentration of spray drift from orchard air blaster using an EC formulation at 1.56 kg/ha together with acute quotient for daphnia. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

The water depth in permanent streams/rivers is expected to be greater than 15 cm and in the range 30-40 cm, therefore the hazard in Table 54 may be considered too high for a realistic Australian situation. Using a depth of 30 cm, the quotient in Table 54 is halved and considering that the toxicity curve is very steep, the hazard to daphnia in deeper, permanent flowing streams is considered acceptable at 25 metres and beyond.

In addition to the AgDRIFT results, there are German studies (Ganzelmeier and Rautmann, 2000) that specifically trialed orchard airblast sprayers according to strict protocols and standard conditions to test spray drift in grapes, fruit crops and hops, at both early and later growth stages, under GAP. Results give mean values for statistically treated data from repeated application trials on grapes (56 trials), orchards (78 trials) and hops (31 trials). Estimates for drift are given as the 95th percentile of mean values, quoted as % of the application rate.

The multiple trials on fruit trees appear useful in comparison with equivalent Australian crops. Apart from Australian weather conditions, where air temperatures are likely higher and humidity lower, the results should be useful in estimating drift in orchard situations under typical usage. Table 55 gives the results from Ganzelmeier and quotient in water 30 cm deep.

Distance downwind, m	10	30	50
Percent drift	5.05	0.37	0.11
EEC, in water 30 cm deep µg/L	26.26	1.92	0.57
Quotient, daphnia EC50 = 0.96 µg/L	27.35	2.00	0.60

Table 55. Estimated concentration of spray drift from orchard air blaster using an EC formulation at 1.56 kg/ha together with acute quotient for daphnia from Ganzelmeier. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

The hazard in Table 55 is approximately double that of Table 54 for the same distances despite the increased depth of water. Because the AgDRIFT results (normal) are modelled on data pooled from grapes (both conventional and wrap around sprayers) and apple orchards, they may not represent the typical spray drift from pome fruit orchards. (Note the Ganzelmeier results for grapevines show a lower drift compared to fruit crops.) Therefore the Ganzelmeier results are considered more reliable.

In addition, the species used for the analysis above, *D. magna*, is not the most sensitive, with ceriodaphnia and scud more sensitive (LC50 of 0.41 µg/L and 0.2 µg/L respectively). It should be noted that in Australia there are species of ceriodaphnia and therefore the analysis in Table 55 may underestimate the hazard under Australian situations. However, with repopulation of affected organisms from unaffected sites limiting any longer term effects and that the toxic data for invertebrates shows a steep response curve, a downwind buffer of 50 metres is considered just acceptable.

Use may be just acceptable provided care is taken to limit spray drift and that water bodies are >50 metres downwind from the application site, ie a 50 m downwind buffer.

Dormant Spraying

Spraying before green tip is the other orchard use on the label. It is normal in deciduous orchards to reduce the spray volume for early season spraying and assuming that 1500 L/ha is used, the application of diazinon is 0.78 kg ai/ha. Table 56 gives the concentration in water and spray drift for water 30 cm deep using AgDRIFT.

Distance downwind, m	15	30	50	100
AgDRIFT, EEC, µg/L	16.2	7.0	3.3	1.0
Quotient, daphnia	16.9	7.3	3.4	1.0
Ganzelmeier, EEC µg/L	14.90	2.66	0.76	-
Quotient, daphnia	15.52	2.77	0.79	-

Table 56. Estimated concentration of spray drift from orchard air blaster spraying during dormancy using an EC formulation at 0.76 kg/ha^{-}together with acute quotient for daphnia (EC50 = 0.96 µg/L) in water 30 cm deep. Results from AgDRIFT and Ganzelmeier. Dark shading is Q > 0.5, light shading = 0.1<Q <0.5.

Table 56 shows that dormant spraying of pome and stone fruit trees represents a significant hazard to aquatic invertebrates up to 100 metres away from the orchard using AgDRIFT. The Ganzelmeier results show the hazard is less but still high enough to be of concern at 50 metres. The higher hazard compared with spraying after petal fall reflects the lesser interception of spray with bare trees. The mitigation factors considered above would tend to balance out against the increased sensitivity of some species compared to *D. magna* and therefore the hazard at 50 metres downwind is considered high. As the agricultural assessment indicates that this use is not significant and represents a high hazard to aquatic invertebrates , it is recommended that this use should be removed from the label. If use is retained, a 50 metres buffer is required together with rates of <750 g ai/ha. It is noted that the Australian Apples and Pear Growers Association is not supporting continued use of diazinon.

5.4.1.2 Macadamia nuts

Brief Description

Macadamia nuts are native to eastern Australia and grow to 20 metres when fully mature. It is an evergreen with a large canopy. In commercial production the tree size is smaller than wild trees and are pruned to control size. Pests are relatively few and spraying is done by monitoring damage and spraying only when economic levels of damage occur. Macadamia nuts are commercially grown in NSW (mid North coast and Far North coast) and Queensland (Sunshine Coast, Bundaberg, Rockhampton, and Athernton Tablelands).

The Australian Macadamia Society indicates that more than 2million trees are currently planted across more than 20 000 hectares, and that one-third are immature indicating increasing production into the future.

At the time of European settlement, macadamias were rather rare trees because of their susceptibility to fire, usually being found in rainforest, rainforest margins and along creek banks. Macadamia trees grow best in deep well-drained soil such as found in rainforest areas. Most commercial production occurs within the boundaries of natural occurrence, the exceptions being the Atherton Tablelands in North Queensland and the Nambucca Valley on the mid-north coast of NSW. Macadamia plantations are likely to abut areas of high conservation value such as creek lines with remnant vegetation.

Diazinon is not considered the principal insecticide for control of pests, with its use in Macadamia orchard being occasional (Neil Treverrow, NSW Agriculture, personal communication). The rate used is 100 g ai/100 L and volumes used would not exceed 4000 L/ha (ie 4 kg ai/ha). Table 57 gives the concentration in water (Australian stream) and quotient for daphnia based in the AgDRIFT model at the maximum volume of 4000 L/ha.

Distance downwind, m	15	25	50	100	150	200
EEC, in water 30 cm deep µg/L	31.1	19.2	8.1	2.8	1.4	0.84
Quotient, daphnia EC50 = 0.96 µg/L	32.4	20.0	8.4	2.9	1.5	0.88

Table 57. Estimated concentration of spray drift for air blaster spraying of macadamia nut trees using an EC formulation at 4 kg/ha together with acute quotient for daphnia from AgDRIFT. Dark shading is $Q > 0.5$, light shading = $0.1<Q<0.5$.

Table 56 shows a high hazard to aquatic invertebrates, based on a worst case using AgDRIFT for dense trees (citrus and nut orchards) using high volume spraying and at the highest volume applied. Using a lower volume likely to be used with smaller trees, typical of modern orchard management practices, say 2000 L/ha, the hazard is reduced by half. Considering that this is a worst case scenario and the toxicity curve is very steep, the quotient of 1.5 at 100 metres could still indicate a potentially high hazard. However, in the regions were macadamias are grown, the streamside vegetation is expected to be luxuriant and should act as a buffer reducing the hazard. While it is not possible to model the effective capture rate for a stream side buffer, the paper by Salyani and Cromwell (1992) showed that the last two rows (rows 1 and 2) captured between 70-80% of the spray from rows 3 and 4. If a forested gully intercepts the spray drift similarly, then the hazard would be significantly reduced to a level that is closer to acceptable. In addition, its very rarely used in mature orchards, with the registered pests, felted coccid and leaf miner, being pests in young trees (Phil Wilk, NSW Agriculture, personal communication). Table 58 gives the quotients for reduced rates (2 kg ai/ha) and 70% interception by stream side vegetation.

Distance downwind, m	15	25	50	100	150	200
EEC, in water 30 cm deep µg/L	4.66	2.88	1.21	0.42	0.21	0.13
Quotient, daphnia EC50 = 0.96 µg/L	4.86	3	1.26	0.43	0.22	0.13

Table 58. Estimated concentration of spray drift for air blaster spraying of macadamia nut trees using an EC formulation at 2 kg/ha and assuming 70% interception by streamside vegetation together with acute quotient for daphnia. Dark shading is Q > 0.5, light shading = 0.1<Q <0.5

In considering the hazard in Table 58, it must be remembered there could be more sensitive organisms than *D. magna*. Therefore the hazard is considered as moderate to high at 100 metres and acceptable at 150 metres, noting as previously the steep toxicity curve. With repopulation of affected areas, and provided use remains occasional, Environment Australia would consider the current use pattern in macadamias as acceptable with a 100 m buffer. Note that not spraying the last 3 downwind rows (see below) would provided an additional margin of safety.

The Ganzelmeier results are not used as they were based on orchards in Germany (assumed to be pome and stone fruit orchards) and these trees are not likely to have a similar enough morphology to macadamia trees to allow extension of the spray drift data from one to the other.

5.4.1.3 Citrus

The agricultural assessment identified diazinon as having limited use in Queensland for citrus and therefore will be assessed briefly. The citrus industry is a low pesticide usage industry, with most growers only spraying once if required. Insecticide applications are frequently for scale and use the typical orchard rate (65 mL/100 L of spray, 52 g ai/100 L) and high volume application typically use 8000 L/ha (gives 4.2 kg ai/ha). Equipment used is orchard airblast, low volume or horizontal oscillating booms. The Australian citrus industry is in all mainland states, with most of the production in New South Wales (43%), South Australia (33%) and Victoria (13%) (Cope and Forsyth, 1995).

From the US EPA AgDRIFT information in Table 5 is for citrus (same as tall trees dense foliage, ie nut trees) at 4.2 kg ai/ha.

Distance downwind, m	15	25	50	100	150	200
EEC, in water 30 cm deep µg/L	32.7	20.2	8.50	2.94	1.47	0.88
Quotient, daphnia EC50 = 0.96 µg/L	34	21	8.9	3.1	1.5	0.92

Table 59. Estimated concentration of spray drift for air blaster spraying of citrus using an EC formulation at 4.2 kg/ha together with acute quotient for daphnia. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

While it is recognised that AgDRIFT is worst case and that the use is infrequent, the use in citrus represents a hazard for aquatic invertebrates. This is not able to be mitigated further as the major Queensland growing area in central Queensland, Gayndah and Mundubbera, is unlikely to have such luxuriant vegetation to intercept spray drift. This area is expected to rely on irrigation and therefore could be close to drainage systems and natural streams.

Given that citrus use is minimal and the hazard very high, it is recommended that use on citrus should be deleted from the label.

5.4.1.4 Grapes

The agricultural assessment identifies grapes as a crop that is currently treated with diazinon in Victoria to control mealy bugs. Vineyards occur near the coast and in river valleys, slopes and plains, under a wide range of temperature conditions, aridity, rainfall, relative humidity and sunshine hours, and on slopes ranging from relatively steep to very flat. Water management includes dryland and various methods of drip, spray and flood irrigation (Dry and Smart, 1988; Davidson, 1992).

Application rate is 30 mL/100 L, corresponding to 24 g ai/100 L with up to 1500 L/ha (worst case) being applied (360 g ai/ha). Davidson (1992) claims that most vignerons use application equipment delivering from 200-1,100 L/ha. The normal method of spraying grapes is by hand-held spray guns, one-sided and over-the-row boom sprayers, air-blast sprayers, and in some situations, aerial spraying from fixed wing aircraft or helicopters (Emmett et al., 1992). Aerial application is unusual and is only used in extreme conditions, ie flooding. It is expected that the majority of farmers will use trailer mounted air blast sprayers or vertical boom spray equipment, both with hollow cone nozzles.

Droplets with a volume mean diameter (vmd) < 100 µm (ie. mists and aerosols) are the most likely size to be used, although, application of a fine spray (vmd = 100-200 µm) is preferable to obtain a compromise between good coverage and reduced spray drift (Matthews, 1992). In practice, a significant proportion of small droplets may occur, depending on the equipment used, its calibration and the nozzle condition.

In the AgDRIFT model, grapes are pooled with pome fruit and stone fruit for the drift calculations and the results for treated at 360 g ai/ha are given in Table 60.

Distance downwind, m	15	30	50	100
AgDRIFT, EEC µg/L	0.21	0.08	0.04	0.01
Quotient, daphnia	0.22	0.08	0.04	0.01
Ganzelmeier, EEC,	0.95	0.37	0.19	-
Quotient, daphnia	0.99	0.39	0.20	-

Table 60. Estimated concentration of spray drift from orchard air blaster using an EC formulation at 360 g ai/ha for grapes together with acute quotient for daphnia in water 30 cm deep. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

As can be seen in Table 60, the hazard to daphnia from application to grapes is low. Even considering the more sensitive ceriodaphnia, the hazard at 30 metres is relatively low with the AgDRIFT modelling, mainly due to the relatively low application rate used. However, this is not the situation with the more reliable Ganzelmeier, where at 30 metres it is only just acceptable, but when the more sensitive ceriodaphnia is considered, the hazard extends to 50 metres. The AgDRIFT results appear to be lower that the Ganzelmeier for both orchards and grapes – a satisfactory explanation is not possible without further information on conditions used in the trials. With recovery of affected organism expected, use on grapes is considered acceptable with a label warning and minimum 30 metres downwind buffer.

5.4.1.5 Other Spray Equipment

Spray equipment other than the high volume conventional sprayers is increasingly being used by orchardists, with low volume methods being the main alternative to the traditional sprayers. The LV equipment that are increasingly being employed have smaller droplet sizes (vmd [volume median diameter] = 30-50 µm, Matthews, 1992) than the spray used to generate the AgDRIFT model. Non-electrostatic ULV applications are of particular concern due to the higher potential for spray drift from the smaller droplet size.

The US EPA AgDRIFT model does not include information for low volume spraying. However, the spray drift from low volume applications to citrus orchards has previously been studied and modelled (Salyani and Cromwell, 1992). The experimental data used for the model was obtained from low volume spraying in an orange orchard in Florida. There were three trials and the average spray drift was used to fit a quadratic equation to the spray drift curve. The high volume application was also tested and similarly modelled. (Fit to these equations of the data was good, $r^2 > 0.88$.) Using this model, Table 61 is generated for the spray drift to 30 cm deep water and the quotient for daphnia from macadamia trees.

Distance downwind, m	25	50	100	150	200
High Volume					
Spray drift, % of application rate	0.91	0.21	0.053	0.024	0.014
EEC, in water 30 cm deep µg/L	12.10	2.86	0.71	0.32	0.18
Quotient, daphnia EC50 = 0.96 µg/L	12.60	2.98	0.74	0.33	0.19
Low Volume					
Spray drift, % of application rate	0.72	0.25	0.083	0.043	0.027
EEC, in water 30 cm deep µg/L	9.56	3.30	1.11	0.58	0.36
Quotient, daphnia EC50 = 0.96 µg/L	9.95	3.43	1.15	0.60	0.38

Table 61. Estimated concentration of spray drift for air blaster spraying of macadamia nut trees using an EC formulation at 4 kg/ha together with acute quotient for daphnia. From Salyani and Cromwell, 1992. Dark shading is Q > 0.5, light shading = 0.1<Q<0.5.

Table 61 shows that the low volume spraying gives less drift than from high volume spraying and the AgDRIFT model (see Table 57). In addition, the high volume spray model from Salyani and Cromwell is also lower than the AgDRIFT results by a factor of approximately 3. However, it should be noted that the AgDRIFT is for the 90th percentile while the data in Table 61 is the average from 3 replicates. Therefore, the low volume spraying is unlikely to increase the hazard compared to high volume applications to macadamias as determined in the AgDRIFT model.

5.4.1.6 Other Considerations

The above predictions did not include any mitigation for the physical properties for diazinon when in water. For other chemicals, Environment Australia has used adsorption and other physical properties to mitigate the hazard but from the fate studies reviewed the adsorption of diazinon was low, with the concentration in water remaining close to initial values for the first 2 days (see Section 3.3.2). This was confirmed by the mesocosm study.

However, it must be noted that that the hazard from spray drift is a downwind phenomenon and is strongly dependent on timing with respect to atmospheric conditions and how the growers use chemicals, ie not spraying when the wind would allow spray drift to contaminate natural waterways. To limit the extent of spray drift in orchards, especially macadamias, spraying can be restricted to when the wind is blowing away from the water. However, if that is not possible, an in-crop buffer, ie the last 3 downwind rows not sprayed, should be used. These rows can be sprayed later when the wind direction is more favourable. This is based on evidence from citrus orchards indicating these rows are largely responsible for the majority of the spray drift (Salyani and Cromwell, 1992).

While the above hazard calculations are for ponds, a ‘pulse’ of contaminated water is likely in flowing streams and the acute hazard calculations are used as an approximation of this ‘pulse’. For ponds receiving runoff from orchards or from streams near orchards, further dilution is expected and as these ponds are likely to be significantly deeper, the hazard should be reduced. As this depends on the other land uses in the area, hazard calculations for such situations are site specific and a general case is difficult to derive. However, it is expected that the hazard will be less than that calculated for natural lentic ponds etc receiving water from streams near orchards.

5.4.2 Applications by Boom Spray.

5.4.2.1 Emulsifiable Concentrate—Low boom

Low booms are the normal method of spraying vegetables and other such crops. This has been identified as a significant agricultural use for diazinon, with most treated at 560 g ai/ha.

The AgDRIFT model gives the drift from boom sprayers, both low booms and high boom sprayers. The low boom sprayers are normally used for vegetables while high boom sprayers may be used for tall crops, eg sweet corn and pineapples. Table 62 is for low boom application to vegetables at 560 g ai/ha.

Distance in metres	10	25	50	100
EEC in water 30 cm deep µg/L	2.1	1.2	0.73	0.42
Quotient 25 daphnia EC50 = 0.96 µg ai/L	2.19	1.25	0.76	0.44

Table 62. Estimated concentration of spray drift from low boom sprayer using EC formulation at 560 g ai/ha together with acute quotient for daphnia. From US AgDRIFT model. Quotient is EEC/EC50. Dark shading is Q > 0.5, light shading = 0.1<Q <0.5.

Table 62 shows that there is a possible hazard to aquatic invertebrates from boom applications at 50 metres from the boom sprayer. It should be noted that this is modelled on average spray drift from the boom spray and is not worst case. Using the results for field crops (cereals) from Ganzelmeier as substitute for vegetables (which were not examined), averaged over early and late growing stages, Table 63 is generated.

Distance in metres	10	30	50	100
EEC in water 30 cm deep µg/L	0.45	0.22	0.13	0.07
Quotient 25 daphnia EC50 = 0.96 µg ai/L	0.47	0.23	0.14	0.08

Table 63. Estimated concentration of spray drift from low boom sprayer using EC formulation at 560 g ai/ha together with acute quotient for daphnia. From Ganzelmeier. Quotient is EEC/EC50. Dark shading is $Q > 0.5$, light shading = $0.1 < Q < 0.5$.

It is noted that the results from Tables 62 and 63 are not comparable and show a different level of drift. It is considered that this could be due to the different trial conditions and the different nozzles used, the AgDRIFT used hollow cone (fine spray, high drift) and the German studies used flat fan nozzles (medium spray, reduced drift). This emphasises the importance of using equipment that reduces the drift potential in areas where drift could be an environmental problem.

Given that most vegetable crops are expected to be greater than 5 metres from natural waterways, the Ganzelmeier results show that the average hazard would be moderate when medium spray is used. However, as AgDRIFT indicate a higher hazard for finer sprays, for those areas close to natural waterways, ie within 50 metres, low drift nozzles should be used.

Use of low booms sprays for application of diazinon are considered acceptable with a label warning to control drift and the use of low drift nozzles within 50 metres of natural waterways.

5.4.2.2 Boom Spraying of Diazinon to Pineapples

Pineapples were included in the High Boom spraying section of the draft report (Section 5.4.2.2). The industry believes that the assessment undertaken by Environment Australia in the draft report overestimated the level of risk to the aquatic environment, as the assumptions made were too conservative.

When using AgDrift (Table 60 of draft report) a high boom application is identified as 1.27 m high with a fine spray spectrum of 171 µm VMD, using hollow cone nozzles in the absence of a crop canopy. The industry notes that this does not describe normal application practices in pineapples, which are propagated from planted vegetative material. A crop height of approximately 1 m would be achieved at or near maturity, and for the majority of the growth period the crop would be below this height. The rough surface crop canopy is also likely to ensure efficient droplet capture. Therefore the industry believes that using the 'High Boom' AgDRIFT model would result in an overestimation of the possible risk.

Secondly, in their view the use of the Ganzelmeier tables derived from research on late season field crops such as 1 m high cereals (Section 5.4.2.2, Table 61 of the draft report), involving standard flat fan nozzles generating a medium spray spectrum, is also not appropriate. This work is European in origin, where common practice in field crop spraying are water volumes of 100-300 L/ha with a VMD in the order of 200-300 μm at pressures of 1.5-3 bar.

While the recommendation of 50 m buffer was understandable when using such parameters, the industry noted high water volumes and coarse droplet sizes are used in the application of diazinon to pineapples. Nozzles such as flood jets are commonly used, for which the proportion of droplets produced with a diameter of 200 μm, or below, is less than 1%. Thus the "driftable fraction" is minor, noting that a 200 μm droplet has a sedimentation velocity of 0.72 m/s.

Therefore, the industry believed that basing regulatory decisions on possible field crop extrapolations from existing models results in an overestimation of drift, and a reduced buffer zone of 20 m would suffice when coupled with the application of diazinon using coarse droplets in high volumes of water. For example, they indicated a label statement could read "Apply in a minimum spray volume of 2000 L/ha. Boom spray using low pressures and a very coarse droplet spectrum, e.g., turbo flood jet nozzles @ 1-2 bar should be used."

In addition, to ensure compliance it was proposed a grower education program would be implemented by the industry. The education program would include, for example, the distribution of fact sheets to growers, field days, farm walks, newsletters and individual farm visits. The purpose of these activities would be to communicate to growers what spray application techniques are acceptable and why.

Since the draft assessment, the Ganzelmeier tables have been revised (Ganzelmeier and Rautmann, 2000), and the amount of drift at 20 and 30 m for all field crops is now assumed to be 0.18 and 0.12% respectively, based on 34 additional outdoor drift trials (of a total 50). Therefore the Q values in Table 61 of the draft report for flat fan nozzles need to be amended to 1.13 and 0.75 at 20 and 30 metres respectively, and the Q would still be 0.44 at 50 metres (where 0.70% drifts) at the 1.8 kg/ha rate.

However, if one assumes that these drift figures were derived using standard flat fan nozzles, the proposed use of turbo flood jet nozzles should significantly reduce this amount of drift. Examination of page 91 of the Manufacturer's Manual[1] confirms that for Turbo FloodJet nozzles the percentage of droplets with a diameter of 200 μm, or below, is <1% at both 1.5 and 3 bar pressure. This may be compared with XR TeeJet Flat and DG TeeJet nozzles with a range of <1-14% at 1.5 bar and 12-34% at 3 bar pressure respectively. Given that the latter have far less drift potential than standard flat-fan nozzles[2], it may be in turn assumed that drift would be reduced to below 10% when turbo flood jet nozzles are used.

This would reduce the Q at 20 metres to an acceptable 0.11, and consequently industry's proposal is acceptable.

[1] Spraying Systems Agricultural Spray Products Catalogue 46M
[2] Spraying Solutions (A Resource of Spraying Systems Co) Bulletin No 423

5.4.2 Other applications

5.4.3.1 Mushrooms

The current use pattern is different to that on the current labels. The labels directions are for applications at spawning and after casting by spraying over the top. The current use is on mushroom casings, where diazinon mixed is with peatmoss, limestone and water in an indoor setting with no runoff. Similarly, when diazinon is used as a compost treatment, it is mixed during preparation in an indoor setting with no runoff. The casings and compost are used for three cropping cycles of mushroom (total of 63 days), after which there are unlikely to have any detectable residues of due to biodegradation, assuming the half life is between 4.5 and 8 days using the most reliable aerobic soil metabolism studies. The used mushroom castings are then used as garden compost, both commercially and domestically, where further degradation is expected. There is no EEC applicable for this use pattern.

5.4.3.2 Mosquitoes

The label directions for mosquitoes are for use by sprayer, misters and foggers with direction for use in mosquito breeding areas. This could lead to contamination of shallow water. The rates are 100 g ai/100 L for sprayers, 1.6 g per 100 m^2 (1600 g ai/ha) in diesel/kerosene for mister and 144 g ai/ha in fogging oil or distillate. Assuming a mister is used (maximum rate) and is applied to water at the given rate, then in water 15 cm deep, the concentration of diazinon is 1.1 mg/L and the hazard very high for aquatic organisms and moderate for fish (LC50 = 2.16 mg/L). However, when misters are used for mosquito control, the mist is allowed to drift over the waterbody. Assuming 10% of the application lands on any given area, then the concentration in water 15 cm deep is 110 µg/L and the hazard is still very high for invertebrates. As mosquito larvae are aquatic invertebrates, this is not surprising. The hazard would be expected to be higher from direct application to water by spraying but this cannot be calculated due to the lack of rate information on the label.

It should be noted that the agricultural assessment did not indicate that use for mosquitoes was a significant current use and one registrant has confirmed this. This use represents a high environmental hazard and should be removed from the labels. However, if this use is retained, further information will be required on the rate of application from spray application and type of equipment used.

5.4.4 Hazard to Algae

It should be noted that the agricultural assessment did not indicate that use for mosquitoes was a significant current use and one registrant has confirmed this. This used represents a high environmental hazard and should be removed from the labels. However, if this use is retained, further information will be required on the rate of application from spray application and type of equipment used.

5.4.5 Multiple applications

The Agricultural Assessment indicates the current usage is limited, with macadamias (occasional use), grapes (once only, perhaps one follow up), pineapples (every 2 months) and vegetables (every 10-14 days as required). Multiple applications are not expected, except for vegetables.

The above hazard analysis was for a single application but for orchards and vineyards these could theoretically occur within a day, ie 1 day between applications. It is expected that in most situations there would be at least 7 days between sprays. From the aquatic metabolism study (see Table 9) and assuming the worst case and the half-life in water is 15 days, then the increase in concentration after 10 days due to carryover is 66%. However, this is an extreme result and noting that diazinon use is more likely when insects are active, ie warmer weather, a more typical half-life would be 7 days from Table 9 and the carryover is approximately 37%. A significant increase in concentration in water is not expected or increased acute toxic effects on aquatic organisms from multiple applications, provided there is at least 10 days between applications. However, there could be chronic effects and thus an additional period is required (see below).

In the mesocosm study there was 7 days between each application 3 through to 6, the concentration in the water column only increased slightly and was some 50% above the target concentration for the final application. Target concentrations for treatments 4 and 6 (simulated runoff) were 1.53, 3.05, 6.13, 12.26 and 24.5 µg ai/L, for levels 1 through to 5 (0.37, 0.75, 1.5, 3.0 and 6.0 g ai/L for treatments 3 and 5-simulated spray drift) and final concentrations of 2.30, 4.30, 9.20, 12.5 and 29.7, µg ai/L levels 1 to 5. This clearly shows that while there could be an increase in concentration in water from multiple applications, the actual increase in concentration is relatively low, even under worst case conditions with a high level of multiple applications.

Due to current resistance management strategies, it is considered unlikely for more the 2 or 3 applications to occur one after the other and therefore the mesocosm study is worst case.

However, the main problem is repeated effects on organisms and 10 days between sprays may not allow affected populations to recover. This underlines the need to prevent contamination of natural waterways and every reasonable effort should be taken to minimise spray drift.

5.4.6 Chronic Effects

Once in the aquatic environment, diazinon is expected degrade. The range for the laboratory half-lives in natural water was 7-17 days (average 11 days) for the initial period of degradation. The field studies showed the degradation could be faster in environmental waters that are conditioned to diazinon ie rice paddies. In the mesocosm study, the half-lives ranged from 18.6 days to 10.7 days after the first two applications and after the sixth application, the half-lives reduced to between 8.6 days to 5.4 days. Given that after 21 days the concentration in water would be expected to be approximately one quarter of the initial value (using a half-life of 11 days), the mean concentrations in water would be 0.12

µg/L using spray drift at 10 metres for vegetables (Table 59, Ganzelmeier). Noting that the MATC for daphnia is 0.17-0.32 µg/L, chronic effects are unlikely from spray drift provided the spray interval is greater than 21 days.

In the mesocosm study, the sensitive cladocerans did not recover for some 9 weeks after the last application but the time taken was in part due to the time for recruitment to occur. Considering treatment level 1 only, there was some recruitment 48 days after the last treatment and the population was starting to slowly increase. It should be noted the concentration of diazinon after the 6th application in the level 1 in the mesocosm study (2.3 µg/L) is significantly higher than would be expected for spray drift and therefore organisms are expected to recover quicker from spray drift events.

For the microencapsulated products chronic effects cannot be ruled out. There was only one study presented on the metabolism and degradation of the microencapsulated formulation in aerobic soil, which showed significantly slower degradation than for the diazinon. A half-life was not calculated due to limited data. However, assuming that the reaction was first order and that the soil aerobic study will reflect the degradation in aerobic aquatic systems, the single point (26% degradation after 12 weeks) would tend to indicate that the half life is approximately 6 weeks and chronic effects are possible for aquatic invertebrates, based on Table 59 (assuming low boom spraying to lawn at 6 kg ai/ha, maximum rate). Until additional studies are done on the metabolism and degradation of the microencapsulated product, Environment Australia cannot accurately determine whether its use will constitute a significant chronic hazard or not.

5.4.7 Runoff and Leaching

Runoff from areas where diazinon has been applied for agricultural uses is not expected to be significantly contaminated. The K_{oc} indicates at least moderate binding to soil particles, which was confirmed in the column leaching studies. The relatively rapid degradation in soil will limit the time when erosion of soils treated with adsorbed diazinon is likely to be problematical. Further, significant erosion of contaminated soil is not expected due to modern orchard and vineyard management practices of including cover crops between rows. Erosion in horticultural (vegetable) crops is also not expected. The exception is mature macadamia nut orchards where there is canopy closure and little ground cover. However, diazinon is only rarely used in such orchards, with the registered pests, felted coccid and leaf miner, being pests in young trees where there are ground covers (Phil Wilk, NSW Agriculture, personal communication). If heavy rain occurs within days of application, expected to be a rare event, high dilution is likely which will limit environmental effects.

Domestic use of diazinon on turf could be a significant source of diazinon in urban streams. Diazinon was found in urban streams in the USA, where runoff from domestic lawn use was the major source of contamination of diazinon in urban streams (see Section 2.1.3.2, Environmental Occurrences). A similar situation is expected to occur in Australia but there is little direct evidence. Diazinon in Sydney sewers appears to be related to dog washes and disposal/cleaning from domestic uses rather than solely from turf use.

Leaching of diazinon to subsurface water is unlikely, as shown by the column leaching studies for the EC formulations.

5.4.8 Conclusions for Aquatic Hazard-Agricultural

Overall, the major hazard appears to be from spray drift, with some hazard during runoff events.

5.4.8.1 Aerial Application

Simple calculations show a very high hazard to aquatic invertebrates from both direct over spray and 10% spray drift at 1.09 kg ai/ha, but that the latter is marginal for fish. With more sophisticated modelling using the US EPA AgDRIFT model, the hazard to sensitive aquatic invertebrates is still unacceptable to beyond 300 metres (see Tables 48 and 49). Even when large droplet nozzles ('placement spraying') is used, there is a significant hazard to these organisms. It should be noted that the hazard assessment is based on *Daphnia magna* (EC50 of 0.96 µg/L), which was the most reliable study for which Environment Australia has data but it is not the most sensitive species, based on US EPA studies (see Table 41). Consideration of the results from aquatic metabolism and the mesocosm studies reveal that degradation of diazinon in water or dissipation to sediment does not occur at a sufficiently fast rate to mitigate this hazard.

As the above calculations indicate that an unacceptable hazard exists from aerial applications and as there is currently only limited aerial application, Environment Australia recommends that aerial application should be removed from all diazinon labels, except for onions.

If the onion industry wishes to maintain aerial application of diazinon to onions for the control of onion seedling maggots, a downwind buffer of 0.5 km using an application volume of not more than 30 L, a temperature <28°C and a maximum windspeed of 2.0 m/s would be required to allow this to be applied safely. Coupled to this, to ensure safe application by air, the onion industry should negotiate to add diazinon to the list of compounds targeted for testing by Murrumbidgee Irrigation, and implement their proposed communication strategy.

5.4.8.2 Orchard Air Blast Equipment

Calculations show the hazard to fish in shallow water is minimal from use of orchard air blast equipment. Based on the US EPA AgDRIFT model for spray drift, the hazard to daphnia is acceptable for normal pome fruit and stone fruit at 1.5 kg ai/ha, 65 mL/100 L of spray, 3000 L of spray per hectare, when these trees are in full leaf. Using the more accurate Ganzelmeier study for fruit trees, there was a hazard that extended to 50 metres, which was just acceptable at 50 metres away with additional label warning statements. For dormant spraying, used in the control of scale, there was a high and unacceptable hazard, even at low rates, which extended beyond 50 and 100 metres using the Ganzelmeier and AgDRIFT respectively. As this use represents a potential hazard to aquatic invertebrates and the agricultural assessment indicates that this use is not significant, it is recommended that this use should be removed from the label. It is further noted that the Australian Apples and Pear Growers Association is not supporting continued use of diazinon.

The hazard to daphnia from application to grapes was determined to be low based on the AgDRIFT modelling but using the more reliable Ganzelmeier results, the hazard that extended to 30 metres. When the more sensitive ceriodaphnia was considered, the hazard at 25 metres is relatively low. This is mainly due to the relatively low application rate used for grapes. Use on grapes is acceptable with additional label warning and a 30 metre downwind buffer.

For taller trees, such as macadamia nuts orchards, there is a high hazard to daphnia at 100 metres away in shallow water from typical drift levels at 4.0 kg ai/ha (125 mL/100 L at 4000 l/ha) from the AgDRIFT model. However, noting that diazinon is used mainly for young trees, where rates are lower, and that the growing areas often abut forested gullies that are likely to intercept spray drift (70% interception was assumed), the hazard was recalculated and considered as moderate to high at 50 metres and acceptable at 100 metres. With repopulation of affected areas, and provided use remains occasional, Environment Australia would consider the current use pattern in macadamias as acceptable. Note that not spraying the last 3 downwind rows (see below) would provide an additional margin of safety.

The Ganzelmeier results are not used as they were based on orchards in Germany, assumed to be pome and stone fruit orchards, and extension of the spray drift data to macadamia trees or other dense large trees, ie citrus, was not considered acceptable.

For citrus use, with very high applications volumes (8000 L/ha) and scale as the principal targeted pest, the hazard to aquatic invertebrates from spray drift was calculated to be high. While it is recognised that use is infrequent, the use in citrus represents a hazard for aquatic invertebrates. This was not mitigated further as several citrus areas rely on irrigation and therefore could be close to drainage systems and natural streams. Given that citrus use is minimal and the hazard very high, it is recommended that use on citrus should be deleted from the label.

Modern LV equipment used by some growers is of concern due to the higher potential for spray drift from the small droplet size used. However, comparative calculations based on literature results indicate that the spray drift from this type of equipment is somewhat lower than from conventional sprayers.

A recovery period is required to minimise the impact of repeated applications is highly desirable, and a minimum recovery period of 21 days between applications is highly desirable due to relative persistence of diazinon in the water column.

5.4.8.3 Boom Sprayers

Calculations based on AgDRIFT clearly show that the spray drift hazard from low boom sprayers is high and there are likely to be significant environmental effects. Estimates based on the more realistic German Ganzelmeier study using medium droplets show that waterbodies within 20 metres of the application site are unlikely to be significantly affected while the US EPA model (AgDRIFT) using fine droplets (worst case) show that effects are possible to 50 metres. Use of low booms sprays for application of diazinon are considered acceptable with a label warning to control drift and the use of low drift nozzles near waterways.

It is recommended that use on pineapples be allowed to continue at current label rates but with a 20 m buffer zone and the following label statement "Apply in a minimum spray volume of 2000 L/ha. Boom spray using low pressures and a very coarse droplet spectrum, e.g., turbo flood jet nozzles @ 1-2 bar should be used." This should be coupled to a grower education program as proposed.

Mosquito

Use of diazinon for control of mosquito larvae was shown to represent a high potential hazard to aquatic invertebrates. However, there was limited information presented on how diazinon is used for mosquito control, including the rate of application from spray application, and if use is to be maintained Environment Australia requires further information for a complete assessment. It should be noted that the agricultural assessment did not indicate that use for mosquitoes was a significant current use.

Mushrooms

The current use is on mushroom casings or as a compost treatment, where in both cases diazinon mixed is mixed during preparation in an indoor setting with no runoff. The casings and compost are used for three cropping cycles of mushroom (total of 63 days), after which these are unlikely to have any detectable residues of due to biodegradation. These are then used as garden compost, both commercially and domestically, where further degradation is expected. The exposure and hazard is expected to be minimal.

5.5 Veterinary Uses

Veterinary usage is the major use of diazinon, with most use on sheep by dipping (both plunge and shower dips) for short wool and jetting or pour-ons for both short and long wool treatments. Other significant uses are on cattle, goats, and pigs. In addition to the above uses in dips etc, diazinon is used for cattle in backrubbers and ear tags.

Diazinon is also used as wound dressing in sheep, cattle and horses. For domestic animals, diazinon is used in dog washes and in some cat and dog flea collars.

5.5.1 Sheep

The use of diazinon for dipping is the major use of diazinon by both value and amount of active used. The Di-Jet label for lice and ked (10-14 days off-shears) direct users to initially charge plunge and shower dips at 50 mL/100 L (10 g ai/100 L), then to reinforce at 130 mL per 100 L drop in dip level (26 g ai/100 L) before topping up at 50 mL/100 L. When used later (4-6 weeks off-shears) the label directs uses to double the amount of product used, presumably due to the increased amount of wool. The label directs using 200 mL/100 L (40 g ai/100 L) for jetting for control of blowfly, presumably a long wool treatment. Assuming that 2.5 L of solution per sheep is used to wet the animal, this equates to a maximum application rate of 1.0 g ai/sheep from jetting as a worst case. Note that plunge and shower dips are rarely, if ever, used for long wool treatments.

As treatment is normally carried out in concreted yards specially set up for the purpose, the environmental exposure during treatment is expected to be minimal. After treatment, animals are turned out into holding paddocks/yards where any drippings will contaminate the soil, although it is recognised that some yards are concreted and channel run-off away from soil. In Environment Australia's experience, up to two-thirds the applied amount will run-off from the sheep. However, due to the stripping nature of diazinon, proportionally more is expected to be retained in the fleece. Assuming approximately half the applied active ingredient runs off, 0.5 g ai/sheep will contaminate the soil of the fenced yard. At a temporary holding density of about 3 sheep/m^2 while treatment solution drips, this equates to an EEC of 11 mg ai/kg soil in the top 10 cm of soil with a density of 1.35 g/mL. This is significantly below the EC50 for earthworms (130 mg/kg) and below the tested level in the semi-field study of 20 mg/kg where there was no effect on earthworms. While there is likely to be effects on soil invertebrates (no data provided) in the holding yard, these will be localised to the holding yard and is not considered as significant. Soil degradation would then reduce the residues, with half-lives expected to be between 4.5-8 days. However, there could be a period when runoff could cause broader environmental concern.

Assuming that the runoff from a holding yard for 2000 sheep runs into a pond 1 ha in size and 15 cm deep and that diazinon runoffs in the runoff water at 5% of applied, then

Wt of diazinon in pond water	= 0.5 g ai/sheep X 5% X 2000
	= 50 g
Volume of water	= 10000 m^2 X .15 m X 1000 L/m^3
	= 1.5 ML
Concentration in pond	= 50 g ÷ 1.5 ML
	= 33 µg/L

The above calculation is very rough and can readily be further refined. For chlorfenvinphos, an organophosphate insecticide with similar chemical properties to diazinon, a US review reported runoff after rainfall was only 0.3-0.6% of applied (ATSDR, 1997). Using a figure of 0.5%, the EEC in water from runoff is 3.3 µg/L and for daphnia Q = 3.4, indicating a potential hazard to aquatic invertebrates. While this calculation does not allow for degradation in the soil or water column, runoff from dipping areas should not be allowed to contaminate natural waterways.

There is potential for significant environmental exposure from incorrect disposal of used dip and there are no label directions for the disposal of used dip on the registered labels. The normal industry practice for plunge dips is after stripping out the dip and reducing the volume of the dip, the dip is then covered. A similar practice is used for shower dips. When the dip is to be cleaned, normally done at the start of the next years dipping, the dip is pumped out and the water disposed of by pumping onto the ground. As the dip solution has stood for approximately a year, any diazinon is expected to have degraded, based on the aquatic metabolism study, and the environmental hazard low. This not the situation with mobile dips. Due to the mobility of these dips, after the dip is stripped out, the dipping solution is poured out onto paddocks. Assuming a 10,000 L dip is dipped out to 8000 L and that the reinforcement rate indicates the stripping rate (260 g/1000 L), then the dip contains solution at approximately 0.06 g ai/L. If this is just pumped out and allowed to flow over a paddock, this is a high localised concentration of diazinon and could represent an environmental hazard, especially if runoff occurs shortly afterwards. There should be label directions to limit such occurrences.

NSW Agriculture, the Woolmark Company and Qld DPI made a number of comments in respect of the practicality of proposed label statements for disposal of sheep dips, ie

"For dips that are pumped out shortly after use, after stripping, lime the dip to >pH 10 and then spray the used dip solution out over a paddock, away from watercourses and any drainage areas etc that could contaminate watercourses."

This recommendation was made before the Avcare draft Dip Disposal Guidelines were considered by the NRA's Registration Liaison Committee (RLC) in October 2000. Subsequent events have clarified that the proposed label statement is not acceptable, at least in the longer term as disposal to land is not considered to be a sustainable option by a number of States. The following comments are made:

- Environment Australia agrees that liming the dip prior to disposal may not be a practical option, particularly with a more frequent disposal regime. Examination of our technical report indicates that the only relevant data (Section 3.1.1.3) are from an old (1969) literature reference where the half-life at pH 10.4 was determined as 144.9 hours (approx 6 days). Apart from the difficulties noted by NSW Agriculture and Qld DPI about raising the pH above 10 with lime and ensuring an adequate mix, this would not result in sufficient degradation prior to disposal unless held for a considerable period;

- Acid hydrolysis may be more efficient in view of same reference quoting the half-life at pH 3.1 as being round 12 hours and other data indicating half-lives ranging from 3.8-31 days at pH 5. However, again it may not be easy for the farmer to achieve this pH with readily available chemicals. In both cases the hydrolysed solutions would likely need neutralisation prior to disposal;

- The State/Territory responses to the draft Avcare Dip Disposal Guidelines, including the discussion at RLC20 on 19 April 2001, made it clear that spraying used dip solution out over a paddock is not an acceptable or sustainable practice. Apart from the uncertainty about application rates there is a need to avoid exposure to grazing animals for residue considerations;

- The option of pumping the dip waste into separate truck mounted tanks for treatment and disposal off site is generally considered impractical as costs would be prohibitive; and

- This appears to leave the current practice of disposal of spent plunge and shower dips by emptying the dip sump into the area immediately adjacent to the dip site, with the solution flooding out over a restricted area, as the only available interim option.

In support of this option NSW Agriculture has undertaken some work on the degradation of diazinon in sheep dips (Levot and Lund, 2001). Spent dip wash and sludge from a mobile plunge dip, charged with diazinon at 200 mg/L, with constant replenishment and with over 3000 sheep put through in 2 days, was spread evenly as possible over a bunded 30X15 m area of slightly sloping land, at a rate of about 8.9 L/m^2. Soil was said to be a brown clay loam typical of the Cumnock area of NSW.

Measurements of diazinon residues in soil (8 cm deep) indicated these rapidly declined from a mean of 3.0 mg/kg one day after disposal to less than the limit of quantification (0.1 mg/kg) after 56 days, compared with the initial concentrations of 70 mg/L in dip wash and 320 mg/kg in the sludge. While the area sampled had also been used 6 months previously for diazinon dip wash disposal, residues pre treatment were below the level of quantitation. However, levels in samples in a boggy corner of the site actually increased until at least 14 days after disposal where the mean concentration was 5.2 mg/kg, but these had dropped to 0.7 mg/kg at day 56.

The above is consistent with the field dissipation results in Section 3.6 of the report, where a half-life of between 3-10 days might be expected under most situations. The reasons for the high levels in the boggy corner are unclear, with the authors speculating that it could have arisen through seepage and/or surface movement of water. Note that samples taken outside the bunded area at day 56 contained no detectable diazinon. Levels of the principal metabolite, G 275550 or oxypyrimidine (6-hydroxy-2-isopropyl-4-methylpyrimidine), do not seem to have been measured. Further work is being undertaken.

As noted above RLC has been considering the need for used dip disposal statements on labels and has recently agreed that a period of up to five (5) years should be given for data to be provided to the NRA leading to the approval of acceptable label statements for individual products. This should apply to all diazinon dipping and jetting products. During this period the following interim disposal statement, based on ongoing work by NSW Agriculture, should be added to all new products and when major changes are made to exisiting labels:

“Dispose of used dip solution and sludge over an area of dedicated and bunded flat land, away from watercourses and any drainage areas etc that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months”.

In generating the required data manufacturers are encouraged to liaise with producers and other stakeholders and to consult with the NSW Ectoparasite Steering Committee.

There are products for treatment of long wool that are pour-on formulations. Pour-on treatment would similarly have the sheep in holding yards after treatment but there is unlikely to be any contamination of the yard, and no need for disposal of spent dip.

Wound dressings

For the dressing of flystruck sheep there are several products using diazinon. These are formulated as powders (15 g ai/kg) or solutions (1.0 g ai/L) with similar directions to spray directly onto the struck area and surrounding skin. These products are also used after marking, mulesing and de-horning in the same manner. As the area to be dressed is generally less than the whole sheep, there is unlikely to be significant run-off and the number of sheep requiring dressing is usually minor in comparison to the whole flock, the environmental exposure from this use pattern is expected to be much lower compared to dipping/jetting.

5.5.3 Cattle, pigs, horses and goats

These animals are directed to be treated by hand spray at 50 mL/100 L (pigs, and goats) and at 250-400 mL/100 L water for cattle (0.50 g ai/ L), and for horses spray or swab liberally at 25 mL/10 L of water. Directions are to thoroughly wet goats and pigs, and for cattle the label instructs to use 5-10 L per animals (2.5-5.0 g ai/head). The amount of solution lost from a sheep's fleece is expected to be the worst case scenario for any of the animals registered for treatment (the hair on other animals is shorter and not expected to hold as much solution).

For cattle, no studies were submitted on the concentration of administered diazinon in faeces in order to determine safety to beneficial arthropods that breed in the excreta, eg dung beetles. Although cattle and other animals are treated dermally, there is potential for absorption as well as ingestion (and therefore excretion in the faeces) of diazinon as cows are noted to lick themselves periodically. However, a recent report states that diazinon is largely metabolised via cleavage of the phosphate and excreted through the kidneys as metabolites (McHenry, 1993). As the metabolites are considerably less toxic than the parent compound, these are unlikely to create an adverse impact on beneficial arthropods in dung. Environment Australia is not aware of any reports where OPs have been implicated in toxicity to dung dwelling invertebrates.

5.5.3.1 Backrubbers for buffalo fly on cattle

The application of diazinon by backrubbers is not expected to result in significant environmental exposure unless spilled. The backrubber is soaked in a mixture of oil and product, ie Di-Jet (500 mL/10 L of oil), then the backrubber placed outside so the cattle can walk under it. The EEC from this use pattern is expected to be much lower than from others above and therefore the hazard lower.

5.5.3.2 Cattle ear tags

These products use diazinon in a slow release solid formulations (some containing other actives) and there is expected to be minimal environmental exposure. During use there is not expected to significant exposure, with the tags normally staying with the animal. When the tags are changed, the used tags normally are disposed of to landfill or buried, where the residue diazinon in the solid formulations will slowly be released. The diazinon is expected to degrade due to the high biological activity within the landfill or in the soil. Any diazinon that is absorbed by the animal is expected to be metabolised before excretion and therefore be of low hazard.

The hazard from these ear tags is expected to be low.

5.5.3.3 Domestic animals

Pet collars

The pet collars are similar to the cattle ear tags above, in that there is a solid formulation containing the active that is then disposed of at landfill. Some of these collars could be lost when the animals lose then or remove their collars. As for the ear tags above, it is expected that the diazinon will slowly be released and then degrade in the landfill or environment. While there could be some environmental impacts for collars that are lost, these are expected to be very localised and randomly distributed and are not expect to cause broader environmental effects.

Dog washes

There are a number of dog wash products for use on dogs to control fleas, lice, mites and ticks on dogs. The rate is 2 g/3 L of water, ie 0.7 g/L. There is unlikely to be a significant environmental hazard provided the used wash is disposed of properly. However, there are no instructions for disposal of used wash on the Diatrol label and other labels are expected to be similar.

The disposal of dog washes could be a significant source of the diazinon that enters the Sydney STPs and is released in effluent. Other STPs throughout Australia are expected to be similarly affected with diazinon residues. The median concentration of diazinon in the effluent from the inland STP on the Hawkesbury–Nepean River catchments is 0.36 µg/L and is close to the LC50 of 0.36 µg/L for the Australian strain of *Ceriodaphnia dubia* (Sydney Water, 1999). The highest value of diazinon detected was 1.81 µg/L, and allowing for 1:3 dilution in receiving water, the concentration in receiving water is 0.6 µg/L and presents a high hazard to *C. dubia*. This would be expected to significantly affect a range of aquatic invertebrates and the hazard is unacceptable, noting that levels are up to >100 times the ANZECC Water Quality Guidleine of 0.01 µg/L. Further at many times during the year the river flow is insufficient to adequately dilute levels below this guideline.

It is unclear as to whether the disposal of used wash on gardens etc would be practical, given that it is normal for small and medium dogs to be washed inside, with larger dogs washed outside. In addition, veterinary surgeries, pet grooming establishments and mobile pet groomers all could be significant sources of diazinon residues in the STPs and label statements should be developed for these users as well.

In the draft report it was proposed a label statement such as 'Rinse waters, MUST be prevented from entering sewers, drains or waterways' should be included on these labels. However, the lack of a suitable alternative disposal option was subsequently identified, with disposal to garden soil or lawns not supported on health grounds, or impractical when dogs are washed in laundry tubs etc. Levels also remained high despite a pilot education program conducted by Sydney Water. Therefore it is recommended that these products be removed from the market.

5.5.4 Wool scouring

Diazinon represents a significant contaminant of the Australian wool clip and monitoring data in 1997/98 found a mean concentration of 5.4 mg ai/kg wool (Savage, 1998). In 1997/1998, 76% of the national flock was treated with diazinon which represented most of the OP residue in the clip of 5.8 mg/kg in the wool. Total OP residues from 1992 to 1998 ranged from 10.4 to 4.3 mg/kg and, as for 1997/98, it is assumed that most of these residues were due to diazinon.

The implications of these residues in the Australian wool clip have recently been reported for the Woolmark Company by Savage (1998). The report considers the use of a wide range of chemicals, including OPs, SPs, IGRs etc that are used in a variety of situations, eg off-shears and long wool, and examines the implications for residues in scouring effluents both in Australia and the UK. The report shows that the current levels of residues of diazinon exceed Australian and overseas requirements and a number of recommendations are made as to possible approaches to reduce the environmental contamination.

To this end, the NRA has announced new registration requirements for sheep ectoparasiticides, where registrants will have to propose maximum acceptable residue limits and wool harvesting intervals for both Australian and European environmental requirements (NRA Commonwealth Gazette, 7 September 1999). The NRA also announced a Special Review of selected sheep ectoparasiticides that give the highest potential environmental concentrations and for those products that make claims for use in long wool. This includes 18 diazinon products for long wool. While model calculations are available in Savage (1998) and some summary data on selected individual products are contained therein from the Avcare Task Force and Victorian Department of Agriculture, data was required for all individual products. Environment Australia is assessing these data packages for individual products, using the fate and toxicity data in this review and the methods described in Savage or updated version, in order to establish the maximum acceptable residue limits and wool harvesting intervals.

Savage also considers the wool scouring hazards from wound/blowfly strike dressings and concludes this is not a high priority at this stage. Environment Australia agrees.

5.5.5 Conclusion veterinary uses

Sheep

Dipping and jetting of sheep using diazinon to control sheep ectoparasiticides and blowflies is not expected to pose a significant environmental hazard. As treatment is normally carried out in concreted yards specially set up for the purpose, the environmental exposure during treatment is expected to be minimal. While calculations show that where sheep are allowed to drip-off after dipping or jetting there could be localised effects on soil invertebrates in the holding yard, these are not considered significant. Soil degradation would quickly degrade the residues, with a half-life between 4.5-8 days. However, there could be a period where runoff could cause broader environmental concern.

There is potential for significant environmental exposure from incorrect disposal of used dip and there are no label directions regarding this on the registered labels. The normal industry practice for plunge dips is after stripping out the dip and reducing the volume of the dip, the dip is then covered. A similar practice is used for shower dips. As this will allow the diazinon to degrade, the environmental hazard low. This not the situation with mobile dips were after the dip is stripped out, the dipping solution is poured out onto paddocks. A high localised concentration of diazinon is possible and could represent an environmental hazard, especially if runoff occurs shortly afterwards.

A number of comments were received on the proposal that the dip should be limed after use, then sprayed out over a paddock, away from watercourses and any drainage areas etc, in particulalr concerning difficulties in raising the pH above 10 and achieving an adequate mix.

The following interim disposal statement, based on ongoing work by NSW Agriculture, should be added to all new products and when major changes are made to exisiting labels while additional data are generated:

"Dispose of used dip solution and sludge over an area of dedicated and bunded flat land, away from watercourses and any drainage areas etc that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months".

In generating the required data manufacturers are encouraged to liaise with producers and other stakeholders and to consult with the NSW Ectoparasite Steering Committee.

The hazard resulting from the use of diazinon for wound dressing is acceptable. As the area treated by is generally significantly less than the whole sheep and the number of sheep requiring dressing is usually minor in comparison to the whole flock, the environmental exposure from this use pattern is expected to be much lower compared to dipping/jetting.

Wool scouring

Diazinon represents a significant contaminant of the Australia wool clip and the implications of these residues have recently been reported for the Woolmark Company. The report shows that the current levels of residues of diazinon exceed Australian and overseas requirements and a number of recommendations are made as to possible approaches to reduce the environmental contamination. To this end, the NRA has announced new registration requirements for sheep ectoparasiticides and a Special Review of existing products used in long wool, including diazinon (NRA Commonwealth Gazette, 7 September 1999). Environment Australia is assessing data packages for individual products, using the fate and toxicity data in this review, in order to establish the maximum acceptable residue limits and wool harvesting intervals for individual products.

Cattle, goats, horses and pigs
The use of diazinon for cattle, goats, horses and pigs is considered acceptable. The amount of solution lost from a sheep's fleece is expected to be the worst case scenario for any of the animals registered for treatment (the hair on other animals is shorter and not expected to hold as much solution).

Ear tags for cattle are not expected to pose a environmental hazard. When the tags are changed, the used tags normally are disposed of to landfill or buried, where the residue diazinon in the solid formulations will slowly be released and degraded within the landfill or in the soil.

Domestic animals

Pet collars are similar to the cattle ear tags above, in that there is a solid formulation containing the active that is then disposed of to landfill. Environmental impacts from collars that are lost are expected to be very localised and randomly distributed.

The disposal of dog washes could be a significant source for the diazinon that is released in Sydney sewage treatment plants (STPs) effluent. Levels of diazinon detected in sewage effluent by Sydney Water could significantly affect a range of aquatic invertebrates and are consdiered unacceptable as they are up to >100 times the ANZECC Water Quality Guideline of 0.01 μg/L. At many times during the year the river folw is insufficient to adequately dilute levels below this guideline. Other STPs throughout Australia are expected to be similarly affected.

The label statement "Do not dispose of used wash solutions or unused product down storm water drains or sewers" was proposed in the draft report. However, the lack of a suitable alternative disposal option was identified, with disposal to garden soil or lawns not supported on health grounds, or impractical when dogs are washed in laundry tubs etc. Levels also remained high despite a pilot program conducted by Sydney Water. Therefore it is recommended that these products be removed from the market.

5.6 Other Uses

5.6.1 In farm buildings etc

There are a range of uses given on several labels, including micro-encapsulated and EC formulations, for use in homes, flats, hotels, commercial buildings, industrial buildings (including kennels, stables and piggeries) and ships, and for spraying of skins and hides.

Use is for control of cockroaches, silverfish, carpet beetles and other household pests. The label directions are for several application types, including thermal foggers (50 g ai/L of fogging oil), sprayers (5 g ai/L of water or kerosene) and misters (12 g ai/L of water or kerosene). Given that the insects are likely to be controlled in the interior of these structures only, the environmental exposure is not expected to be high and no EEC is applicable.

For use in refuse areas, the directions of use has rates for sprayers (50 g ai/100 L), misters (15 g ai/L of either water or kerosene) and foggers (50 g/L of fogging oil or distillate). The user is directed to apply thoroughly to penetrate the refuse. As refuse and areas of garbage are likely to be of minimal environmental significance, the environmental exposure is not expected to be high and no EEC is applicable. However, runoff from treated areas could be hazardous and those labels that included application to refuse and garbage should include appropriate warning statements such as ‘Do not spray to runoff or onto exposed refuse if rain is expected within 24 hours’.

5.6.2 Domestic Uses

There are several labels for use in home gardens and lawns using EC and micro-encapsulated formulations and for control of various ants using powder formulations. Use in the domestic garden is unlikely to contaminate areas of environmental concern, apart from storm water runoff, with spray drift affecting other areas of the garden and runoff either going to other areas of the garden or to storm water drains. Similarly, use on domestic lawns is not expected to results in significant environmental exposures, apart for those due to runoff. The use for ants is as spot treatments of nests, tracks and other infested areas and the environmental exposure is not expected to be high. Powders are also expected to be far less hazardous to birds than granular formulation which may be ingested for use as grit in their crops.

The storm water drains are highly degraded systems but often run directly to streams etc untreated. In the US testing of the urban streams showed significant levels of diazinon, with approximately 70% of streams tested having >0.01 µg/L of diazinon and 30% >0.05 µg/L. In the US most of the residues are thought to be due to domestic uses of diazinon, in particular uses on lawns. A similar situation is expected for Australian urban streams. Using the chronic exposure value of 0.17 µg/L (NOEC) for *Daphnia magna* and the US information, approximately 30% of stream have residues of diazinon that are close to the chronic effects levels for invertebrates.

The disposal of unused domestic solutions and old containers of diazinon could contribute to the diazinon residues in the Sydney’s STP and other sewage treatments plants throughout Australia. This disposal issue should be addressed via label statements in the first place (see Disposal below).

5.6.3 Tanneries

Given that use on hides and skins to control skin and hide beetles is for use in tanneries etc, the environmental exposure is not expected to be high, as skins would be sprayed directly with little overspray, and no EEC is applicable.

5.7 Desirable terrestrial vegetation

Diazinon is stated to be non-phytotoxic when used as directed (Tomlin, 1997). In the phytoxicity studies, there were some relatively minor effects on seedling germination and emergence when tested at the highest rate used in the US (11.2 kg/ha). At rates likely to be used under in Australia, effects on non-target plants are expected to be minimal.

5.8 Hazard arising from formulation, handling and disposal

The hazard from formulation of the TGAC in Australia is expected to be minimal. This is expected to be done in suitable facilities, with relevant environmental controls to limit environmental exposure. Waste water expected to be treated before discharge to the sewer and environment. With dilution and adsorption, the environmental hazards are expected to be minimal. Any spills are expected to be cleaned up and treated according to the MSDS.

5.9 Controls/Labellling

Diazinon must not be allowed to contaminate waterways.

5.9.1 Transport

The material safety data sheet contains adequate information and instructions for containing and disposing of spills during transport.

5.9.2 Storage

With respect to storage, the labels are satisfactory.

5.9.3 Use

If registration is to continue for any formulation used in agriculture, the following warnings should be added to all labels under the heading of 'Use':

> Do not apply aerially (except for onions – see below).
>
> DO NOT apply under meteorological conditions or from spraying equipment that could be expected to cause spray to drift onto wetlands, natural surface waters,

> neighbouring properties or other sensitive areas. Diazinon is highly toxic and all efforts should be taken to minimise spray drift.
>
> Do not spray any plants in flower, including ground covers and adjacent foliage, or while bees are present. Spray drift is also highly toxic to bees and at considerable distance.
>
> For orchards a 50 m buffer should be observed upwind of sensitive areas when spraying pome and stone orchards. The buffer should be increased to 100 m when spraying dense foliage (such as macadamia) or large trees (such as mature pears).
>
> For boom spraying within 50 metres upwind of a sensitive area use low drift nozzles. With high application rates, greater than 1 kg ai/ha, low drift nozzles should be used within 100 metres upwind of a sensitive area together with a 50 metre buffer.

As use of diazinon on orchards is likely to be removed from labels, the last two environment warning statements are expected to become redundant. However, the following statements will need to be added to relevant labels.

If the onion industry wishes to maintain aerial application of diazinon to onions for the control of onion seedling maggots, a downwind buffer of 0.5 km using an application volume of not more than 30 L, a temperature $<28^{o}C$ and a maximum windspeed of 2.0 m/s would be required to allow this to be applied safely. In addition, the onion industry should negotiate to add diazinon to the list of compounds targeted for testing by Murrumbidgee Irrigation, and implement their proposed communication strategy.

For use on pineapples at current label rates a 20 m buffer zone is needed and the following statement should appear on the label "Apply in a minimum spray volume of 2000 L/ha. Boom spray using low pressures and a very coarse droplet spectrum, e.g., turbo flood jet nozzles @ 1-2 bar should be used." This should be coupled to the proposed grower education program.

5.9.8 Disposal

Some of the labels from different companies do not appear to comply to current labelling practices with respect to rinsing and disposal of used containers. All currently registered labels for agricultural use and currently sold products should comply with the current labelling requirements with respect to rinsing and disposal of containers, ie

> Triple rinse or pressure rinse empty containers before disposal. Add rinsings to the spray tank. Do not dispose of undiluted chemical on site. Break, crush or puncture and bury empty containers in a local authority landfill. If not available, bury the containers below 500 mm in a disposal pit specifically marked and set up for this purpose, clear of waterways, vegetation and roots. Empty containers and product should not be burnt.

For refillable containers the following should be added:

> Empty contents fully into application equipment. Close all valves and return to point of supply for refill or storage.

For all products likely to be used in domestic areas, labels should be updated to current disposal statements for domestic containers and dilute solutions. The following are suggested:

> Do not rinse out. Dispose of empty used container by wrapping in paper, then a plastic bag and placing into the domestic garbage.
>
> Do not dispose of solutions or unused product down drains or sewers. Avoid preparing excessive amounts of solutions and use what is prepared. Any prepared spray left should be sprayed out.

For products that include claims for use in refuse and garbage the following should be added:

> Do not spray refuse or garbage to runoff. Do not treated refuse areas or garbage that are exposed if rain is expected within 24 hours.

All veterinary products labels should be updated to ensure that they follow the current guidelines for disposal of used containers.

For the disposal of used sheep dip solutions, the following interim disposal statement should added to new or when major changes are made to existing labels, while additional data are being generated:

> Dispose of used dip solution and sludge over an area of dedicated and bunded flat land, away from watercourses and any drainage areas etc that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months

6 CONCLUSIONS AND RECOMMENDATIONS

Diazinon degrades in natural systems, with the first half-life of between 7-15 days in aerobic aqueous conditions depending on temperature. It degrades faster in soil, with a half-life between 4.5 to 8 days. Literature reports the half-life as between 2 to 4 weeks. Diazinon is moderately bound to soil and together with the rapid degradation is not expected to leach. However, the principal metabolite could leach. When sprayed over water, diazinon dissipates rapidly from the water column.

It is rated as very highly to moderately toxic to birds, moderately toxic to mammals and fish, and extremely toxic to aquatic invertebrates. Mammals are not expected to be significantly exposed to the chemical unless they enter an area recently sprayed.

Quality of the studies submitted

A comprehensive data package for fate and environmental toxicity has been submitted, and no specific additional studies are identified to complete the assessment, with the exception of regulatory studies on bees. While the lack of these additional studies did not affect the review, additional bee studies should be presented if agricultural uses are to be retained.

Terrestrial

The hazard to birds appears low from veterinary uses, moderate for agricultural uses and higher for lawn and turf uses. There are number of reports from overseas and in Australian of adverse effects, most of which relate to turf usage and grassed areas, ie golf courses involving water fowl, particularly geese, which Environment Australia understands is not currently a significant usage of diazinon, except for a micro-encapsulated product Pennside. A high hazard has been identified which is not supported by field reports, particularly in the US.

The hazard to bees is high, particularly from direct application, based on published reports, and there is a possible hazard to soil invertebrates but there are no toxicity data for these organisms. Terrestrial mammals are not expected to show significant effects when diazinon is used according to current label directions. It is recommended that the current warning label with regard to bees be strengthened.

Aquatic

Aerial application

Based on the US EPA AgDRIFT model, the hazard from aerial application to sensitive aquatic invertebrates is calculated as being unacceptable to beyond 300 metres. Even when large droplet nozzles ('placement spraying') is used, there is expected to be a significant hazard to these organisms. As there is currently only limited aerial application and an unacceptable hazard exists from aerial application, Environment Australia recommends that, except for onions, aerial application of diazinon should be removed from labels.

Orchard spraying

Based on the US EPA AgDRIFT model for spray drift, the hazard to fish in shallow water is minimal and the hazard to daphnia is acceptable for normal pome fruit and stone fruit when these trees are in full leaf. Using the more accurate Ganzelmeier study for fruit trees, there was a hazard that extended to 50 metres, which was just acceptable at 50 metres away with additional label warning statements. For dormant spraying, used in the control of scale, there was a high and unacceptable hazard which extent beyond 100 metres even at low rates. As this use represents a potential hazard to aquatic invertebrates and the agricultural assessment indicates that this use is not significant, it is recommended that this use should be removed from the label.

For taller trees there is a higher hazard to daphnia based on the AgDRIFT model. However, for macadamias and taking into consideration repopulation of affected areas, local factors and the current use pattern (young trees) with limited use, Environment Australia would consider the current use pattern as acceptable. If use were to increase, the hazard would then be considered unacceptable.

For citrus use, with very high applications volumes (8000 L/ha), the hazard to aquatic invertebrates from spray drift was calculated to be unacceptable, even considering that use is infrequent. This was not able to be mitigated further as several citrus areas rely on irrigation and therefore could be close to drainage systems and natural streams. Given that citrus use is minimal and the hazard very high, it is recommended that use on citrus should be deleted from the labels.

The hazard to daphnia from application to grapes was determined to be low based on the AgDRIFT modelling and Ganzelmeier data. The use in grapes is acceptable.

For all orchard uses, a recovery period is required to minimise the impact of repeated applications is highly desirable, and a minimum recovery period of 21 days between applications is recommended since diazinon levels in water degrade relatively slowly.

Boom spraying

Calculations for spray drift from low boom sprayers, based on realistic German field results using medium sprays, show that waterbodies within 20 metres of the application site were unlikely to be significantly affected. However, using the AgDRIFT model, which is based on fine sprays, the hazard extended to 50 metres. Use of low booms sprays for application of diazinon is considered acceptable with a label warning to control drift and the use of low drift nozzles near waterways.

With the clarification provided use on pineapples is acceptable provided a 20 m buffer and tightly defined spraying conditions are adopted.

Mosquitoes

Use of diazinon for control of mosquito larvae was shown to represent a high hazard to aquatic invertebrates. There is limited information presented on how diazinon is used for mosquito control and if use is to continue Environment Australia would requires further information for a complete assessment. It should be noted that the agricultural assessment did not indicate that use for mosquitoes was a significant current use.

Mushrooms

The exposure and hazard is expected to be minimal from the current use is on mushroom casings or as a compost treatment.

Veterinary uses

Sheep

The dipping and jetting of sheep with diazinon for control of sheep ectoparasiticides and blowflies is not expected to pose a significant environmental hazard during treatment nor from the dripping to soil after treatment. However, there could be a period where runoff from yards where sheep are held after treatment could cause broader environmental concern.

There is potential for significant environmental exposure from incorrect disposal of used dip and there are no label directions for the disposal of used dip on the registered labels. For the disposal of used sheep dip solutions, the following interim disposal statement should added to new or when major changes are made to existing labels, while additional data are being generated:

> Dispose of used dip solution and sludge over an area of dedicated and bunded flat land, away from watercourses and any drainage areas etc that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months

The use of diazinon for wound dressing is acceptable.

Wool scouring

Following concerns over residues in the Australian wool clip, including diazinon, and the impact of effluent from scourers, the NRA has announced new registration requirements for sheep ectoparasiticides and a Special Review of existing products used in long wool (NRA Commonwealth Gazette, 7 September 1999). Consequently, Environment Australia is assessing data packages for individual products, using the fate and toxicity data in this review, in order to establish the maximum acceptable residue limits and wool harvesting intervals for individual products.

Cattle, goats, horses and pigs

The use of diazinon for cattle, goats, horses and pigs is considered acceptable. Ear tags for cattle are not expected to pose a environmental hazard.

Domestic animals

Pet collars are similar to the cattle ear tags above and are not expected to pose a significant environmental hazard.

The disposal of dog washes is a significant source for the diazinon that enters the Sydney sewage treatment plants (STPs) and is then discharged in the effluent. Levels of diazinon detected in sewage effluent by Sydney Water could be expected to significantly affect a range of aquatic invertebrates and is unacceptable. Other STPs throughout Australia are expected to be similarly affected.

The label statement "Do not dispose of used wash solutions or unused product down storm water drains or sewers" was proposed in the draft report. However, the lack of a suitable alternative disposal option was identified, with disposal to garden soil or lawns not supported on health grounds, or impractical when dogs are washed in laundry tubs etc. Levels also remained high despite a pilot education program conducted by Sydney Water. Therefore it is recommended that these products be removed from the market.

Other Uses

There are several labels for control of various insects in domestic and commercial buildings as well as ships. Given that the insects are likely to be controlled in the interior of these structures only, the environmental exposure is expected to be low. However, there are uses for refuse areas where runoff could be hazardous and those labels that included application to refuse and garbage areas should include appropriate warning statements.

There are several labels with uses in home gardens and lawns. Use in the domestic gardens and lawns are unlikely to contaminate areas of environmental concern, apart from storm water runoff and sewers. In the US testing of the urban streams showed significant levels of diazinon, which are thought to be due to domestic uses of diazinon, in particular uses on lawns, and a similar situation is expected in Australia.

The disposal of unused domestic solutions and old containers of diazinon could contribute to the diazinon residues in the Sydney's STP and other sewage treatments plants throughout Australia. This disposal issue should be addressed via appropriate label statements and an education program in the first place.

Summary

The following current uses are supported on environmental grounds:

> Pome and stone fruit in full leaf; grapes; occasional uses in macadamias,
> low booms for vegetables and for pineapples with additional label statements.
> Most veterinary uses, on the understanding that long wool sheep use is being assessed in the Special Review.
> Most domestic uses with additional labels statements.

The following uses lead to undue risks:

> Aerial applications to any crop (except onions), dormant spraying of deciduous trees and use in citrus at current rates.

In addition, it is strongly recommended that discontinued use patterns, such as for control of locusts in pastures, cotton, sugar cane and rice should be deleted from labels. Should proposals arise for retention of any of these uses, additional hazard assessments will be required.

Particular concerns arise in urban areas. Use of companion animal products and other domestic uses appears to give rise to excessive concentrations in sewage effluent in the Sydney region and probably in other cities. As this cannot be dealt with by the inclusion of appropriate label statements, it is recommended this use be removed from labels.

The micro-encapsulated product (Pennside) is used mainly on golf and bowling greens in Austalia. Assessment of the hazard to birds from this use indicates that this is high, in particular to the grass and herbage eating Australian wood duck. This appears to contrast with the US experience that this formulation poses much less of a risk than granulated or emulsified concentrate forms of diazinon when used in this situation. Noting there have been at least two well publicised local bird kill incidents from use in these situations, it is recommended that a watching brief be maintained, and Environment Australia will take appropriate action if new information such as further bird poisoning incidents comes to hand through the use of the micro-encapsulated diazinon formulation.

Labels

The following warnings should be added to all labels for agriculture uses under the heading of 'Use':

> DO NOT apply under meteorological conditions or from spraying equipment which could be expected to cause spray drift onto natural streams, rivers or waterways. The use of low drift nozzles near waterways and other sensitive areas is recommended. Diazinon is highly toxic and all efforts should be taken to minimise spray drift.
> Do not spray any plants in flower, including ground covers and adjacent foliage, or while bees are present. Spray drift is also highly toxic to bees and at considerable distance.

All currently registered labels for agricultural use and currently sold products should comply with the current labelling requirements with respect to rinsing and disposal of containers, ie

> Triple rinse or pressure rinse empty containers before disposal. Add rinsings to the spray tank. Do not dispose of undiluted chemical on site. Break, crush or puncture and bury empty containers in a local authority landfill. If not available, bury the containers below 500 mm in a disposal pit specifically marked and set up for this purpose, clear of waterways, vegetation and roots. Empty containers and product should not be burnt.

For refillable containers the following should be added:

> Empty contents fully into application equipment. Close all valves and return to point of supply for refill or storage.

For all products likely to be used in domestic areas, labels should be updated to current disposal statements for domestic containers and dilute solutions. The following are suggested:

> Do not rinse out. Dispose of empty used container by wrapping in paper, then a plastic bag and placing into the domestic garbage.
>
> Do not dispose of solutions or unused product down drains or sewers. Avoid preparing excessive amounts of solutions and use what is prepared. Any prepared spray left should be sprayed out.

For products that include claims for use in refuse and garbage the following should be added:

> Do not spray refuse or garbage to runoff. Do not treated refuse areas or garbage that are exposed if rain is expected within 24 hours.

All veterinary products labels should be updated to ensure that they follow the current guidelines for disposal of used containers.

For the disposal of used sheep dip solutions, the following interim disposal statement should added while additional data are being generated:

> Dispose of used dip solution and sludge over an area of dedicated and bunded flat land, away from watercourses and any drainage areas etc that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months

Environment Australia 2 September 2002

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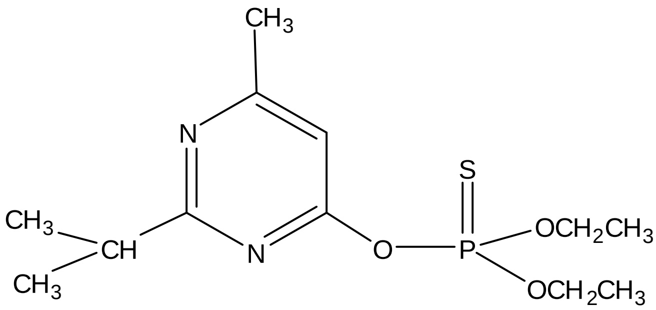
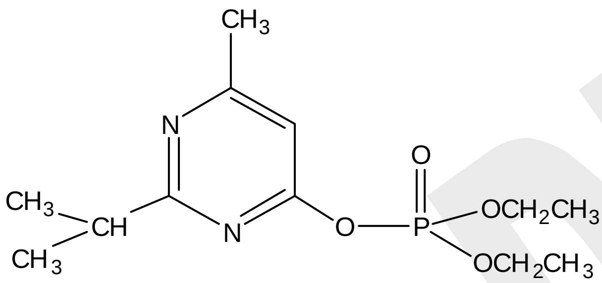
APPENDIX 1

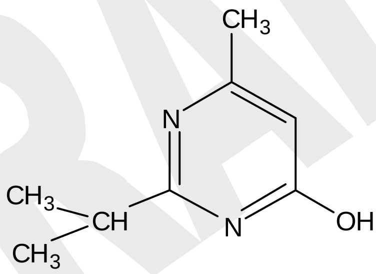
Chemical structures of diazinon and its metabolites, G 24576, G 27550, demethylated G 27550 and GS 31144.



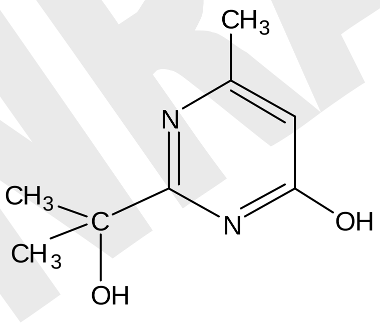
Diazinon



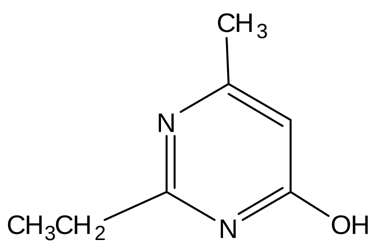
Diazoxon, G 24576



Oxypyrimidene, G 27550



G 31144



Demethylated G 27550

APPENDIX 2

Summary of literature review of the effect of diazinon on beneficial insects.

Insects	Rate used		Effect on Beneficial insects
Predator complex	2500 g/ha 0.05%	A + I A+I	Reduced predators: anthocorids, chrysopa, damsel bugs, spiders and beetles Diazinon reduced beneficial arthropods significantly after 24 h. Anthocorids 80-92%, mirids 91-95% Chrysopa 59-95%, beetles 57-91%, parasitoids 66-88%, spiders 57-79%
Anthocorids	0.1%	A + I	66% and 68% reduction
Hymenopt. parasitoids	0.1% 0.06% 0.06% 0.075% 0.06% 0.062%	A A A I, P, A A	66% reduction Diazinon could not be integrated with use of the parasitoid *Encarsia forosa* for control of whiteflies in greenhouses. Adverse for biological control of pine needle miner in forests Tremendous reduction in parasitoids. Most toxic chemical of 5 tested Reduced numbers of parasitoids at 3 day intervals, not at 10 day intervals
Chrysopa ssp	0.1%	A + I,	88% reduction
spiders	0.1% 200, 1000 g/ha 600 g/ha and 1000 g/ha 600 g/ha and 1000 g/ha	A + I, A+I A+I A+I	27% reduction At 200 g/ha no significance difference to control; at 1000 g/ha not particularly harmful. no effect on spiders after two applications Safe after 7 applications
Predatory. mite	0.1% 0.06% 1% in oil 0.04% 0.05%	A + I, A + I A A + I A+I	6% mortality Minimal effects on resistant mites Sprayed at green tip. Population reduction of 85%, 21 DAT; 98%43 DAT and 40% 92 DAT compatible with resistant mites with sufficient time between sprays Diazinon did not effect integrated mite control
Syrphids	0.06%	I,	reduced syrphids by prey suppression
Coccinellid	0.075% 500 g/ha	A A	Tremendous reduction in beneficial beetles. Reduced the convergent lady beetles, in part by prey suppression
Predatory Beetles	9000 g/ha	A	50-60% reduction 5 weeks after treatment
Rove beetle (Staphylinidea)	2500 g/ha ni ni	A A+I A+I	No adults from pupa Parasitism of cabbage maggot by beetles not affected by diazinon. Very toxic to parasitoid beetles

A = adults, I = immature, p = pupa, ni = no information.

APPENDIX 3

Summary of the toxicity of diazinon to a range of beneficial insects. Taken from IOBC/WPRS working Group (Hassan, S.A., , *et al* 1988).

	Insect Species	Laboratory exposed	Laboratory protected	Semi-field initial	Semi-field persistence	Field
WASPS	*Trichogramma cacoeciae**	4	4		2	
	*Encarsia formosa**	4	1		4	
	*Aphidius matricariae**	4	4			
	Cales noacki	2				
	Leptomastix dactylopii	3				
	Phygadeuon trichops	4				
	Coccygomimus turionellae	4			2	
MITES	*Phytoseiulus persimilis* R	1				
	*Phytoseiulus persimilis**			4		
	*Amblyseius potentillae**	4				
	*Amblyseius finlandicus**					4
	*Typhlodromus pyri**	4				
	Typhlodromus pyri R	1				
	Chiracanthium mildei	4				
INSECTS	*Chrysopa carnea**	4		2		
	*Syrphus corollae**	4				
	Semiadalia 11-notata	4	3			
	*Harmonia axyridis**	1				
	*Bembidion lampros**	3				
	*Pterostichus cupreus**	4				
	Anthocoris nemoralis	1	1			
	*Coccinella septempunctata**			1		

Laboratory Toxicity (mortality): 1=<50%, 2=50-79%, 3=80-99%, 4=>99%. Field, Semi-field initial (mortality): 1=<25%, 2=25-50%, 3=51-75%, 4=>75%. Semi-field, persistence (duration of harmful effects): 1=<5 days, 2=5-15 days, 3=16-30 days, 4=>30 days. *Indicates that insect is used as part of IPM programs in Australia. R = resistant strain.

Laboratory "exposed" life stage (adults of parasites and larvae of predators) —exposed to residues on glass, leaf or soil at the recommended application rate. Four evaluations categories from 1 = (harmless, <50% mortalities) to 4 = harmful (>99% mortalities).

Laboratory "protected" life stage or "less exposed" (parasites with in the host or adults of predators) —exposed directly at the recommended concentration and evaluated as above.

Semi-field initial toxicity—exposure to freshly dried residues on foliage sprayed to point-of-drip at the recommended concentration. Four evaluation categories from 1= harmless (<25% mortalities) to 4 = harmful (>75% mortalities).

Semi-field duration of toxicity—exposed to residues aged for up to one month under field or simulated field conditions. Again four evaluation categories from 1= short lived (<5 days) to 4 = persistent (>30 days).

Field application—crops with beneficial insects at sprayed at recommended rates and a number of retreatments following good agricultural practice. Four evaluation categories as for 3 above.