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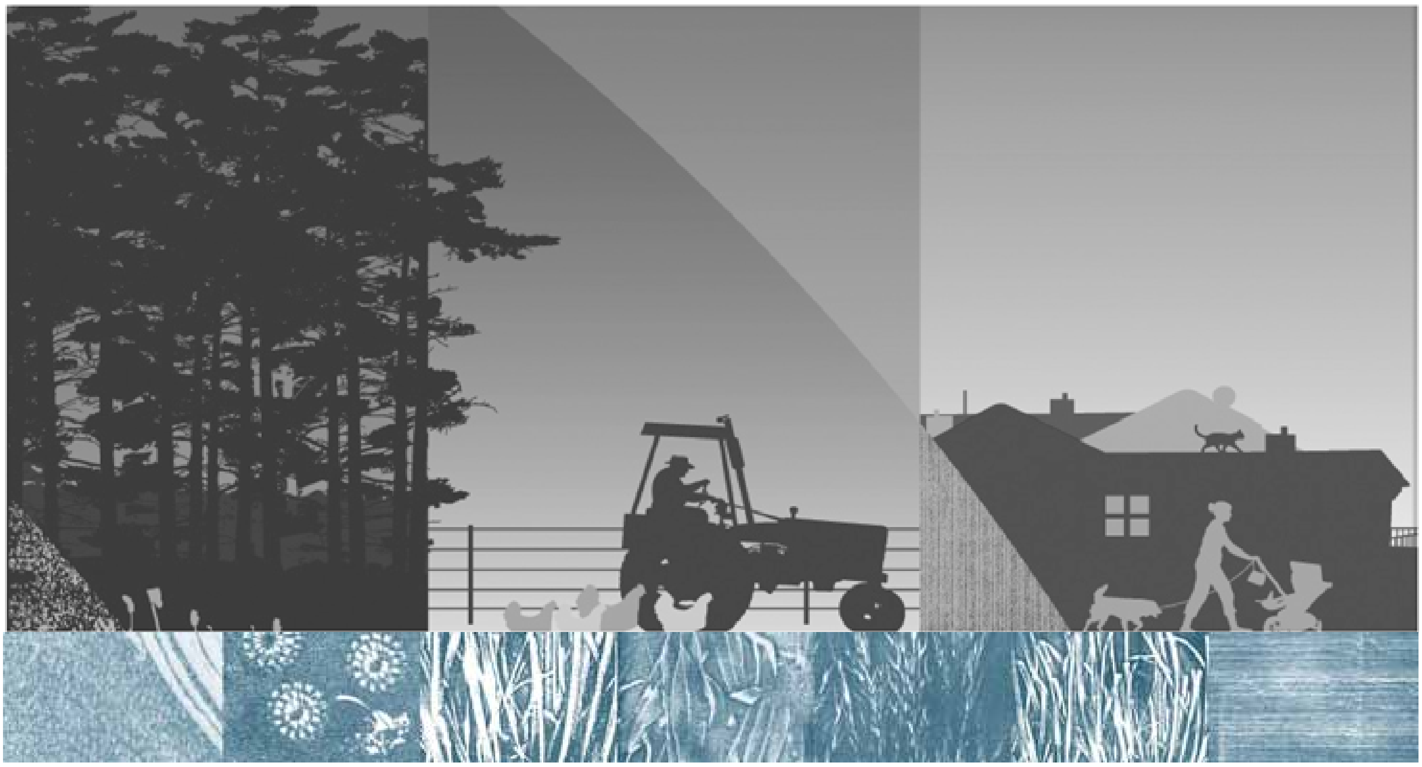

DICHLORVOS
Environmental Assessment

The reconsideration of approvals of the
active constituent, registrations of products containing
dichlorvos and approvals of their associated labels

June 2008

The Australian Pesticides & Veterinary Medicines Authority publishes this review report for oral, intramammary and injectable products, which contain dichlorvos and their associated approved labels. For further information about this review or the Chemical Review Program, contact:

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Introduction

The active constituent (ac) dichlorvos was nominated for assessment in the second round of the Existing Chemical Review Program (ECRP). Dichlorvos is an organophosphate insecticide and acaricide with respiratory, contact and stomach action and which gives rapid knockdown (Tomlin 1997). It acts by inhibiting the activity of cholinesterase enzymes which normally block nerve transmissions after they are sent. Its vapour pressure is sufficiently high to give it high insecticidal activity in the vapour phase and its main importance is based on its fumigant-type action and knockdown ability: Howard (1991) commented that it is one of the more volatile organophosphates. Formulations in which dichlorvos has been available therefore include a pressurised gas formulation with CO_2 propellant, ready to use liquid formulations, plastic or naphthalene matrices providing sustained release, and a paste formulation for dosing horses, as well as emulsifiable concentrate and liquid concentrate formulations.

As explained in the Agricultural Assessment Section of this review, the major current and/or recent uses in Australia (either registered or via permit) include disinfestation of stored product facilities and stored products and control of household and public health pests in a wide range of situations. Apart from use in stored crops (flour, grain, potatoes) and treatment of animal houses and manure, agricultural uses appear to be minor and limited to control of western flower thrips in cut flowers and flowering plants (potentially plants in greenhouses and in the field), control of sciarid flies in mushrooms, and in a tank mixture with chlorpyrifos, to control leaf rollers in avocados. There may also have been years for some minor use in recent pests in glasshouses and greenhouses, and treatment of posts in dormant apple orchards to control codling moth. Veterinary uses include flea collars for domestic pets and as an ingredient in an oral formulation for control of bot fly larvae and worms in horses.

Dichlorvos has been commercially manufactured and used throughout the world since 1961 (WHO 1989) and has been used in Australia since the early 1960's. An "Environmental Health Criteria" review of dichlorvos was published by WHO in 1989 (WHO 1989). Dichlorvos is produced as a metabolite of the insecticide naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate) in some situations (eg in plants – US EPA 1995), but there are no current registrations for naled in Australia. Dichlorvos may also be produced as an initial degradation product of the insecticide trichlorfon (dimethyl 2,2,2-trichloro-1-hydroxyethylphophonate) under neutral to alkaline conditions (Muehlmann and Schrader 1957; Tomlin 1997) and may in fact be responsible for the insecticidal effect of trichlorfon (Samuelsen 1987). As trichlorfon is registered in Australia for various agricultural and veterinary purposes, some contribution of dichlorvos to the environment may occur indirectly through this source.

Overseas regulatory activity:

In 1988, the US EPA commenced a Special Review of dichlorvos and in June 2006 issued its Interim Reregistration Eligibiility Decision (IRED) for dichlorvos (US EPA, 2006). The only agricultural field uses remaining on US labels (lawn, turf and ornamentals) have been deleted voluntarily by the registrants. Because of environmental concerns regarding contamination of surface water with use in greenhouse culture, agricultural (but not domestic or veterinary) uses of this pesticide were banned in 1996 under Dutch pesticide legislation, reinforced by a decision of the Dutch Board of Appeal for Industry (BNA 1999; Section 4.3). Environmental concerns have also been expressed regarding the use of dichlorvos to control ectoparasites in finfish culture (eg Scotland – Davies 1995). This has led to consideration of alternative control measures and to proposals for Environmental Quality Standards for Scottish sea lochs (McHenery et al. 1992; Section 7.3.1.4).

1 CHEMICAL IDENTITY

Common Name: Dichlorvos

Chemical Name: 2,2-dichlorovinyl dimethylphosphate (IUPAC)
2,2-dichloroethenyl dimethylphosphate (Chemical Abstracts)

Other names: Bayer-19149, DDVF, DDVP, ENT 20738, OMS-14, SD 1750, C-177

Tradenames: Various

CAS number: 62-73-7

Molecular formula: $C_4H_7Cl_2O_4P$

Molecular weight: 220.98

Structural formula:

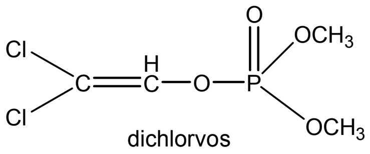

Figure 1. Structural formula of dichlorvos.

Purity of active constituent: Should not be less than 970 g/L, the impurities depending on the manufacturing process used (WHO 1989). Stabilisers are usually not required for the active constituent with modern production methods, but have been used in the past (WHO 1989).

2 PHYSICO-CHEMICAL PROPERTIES

While published values for various properties are reasonably consistent, in some cases (particularly vapour pressure) they vary significantly

Physical form:	Pure substance: colourless liquid Active constituent: colourless to amber liquid with a mild, non-specific aromatic odour
Boiling Point:	35˚C at 0.05 mm Hg (Ciba-Geigy 1988; WHO 1989) 74˚C at 1 mm Hg (Tomlin 1997; WHO 1989) 234˚C at 750 mm Hg (Tomlin 1997)
Thermal stability:	Differential thermal analysis indicated exothermic decomposition commencing at 180˚C, and thermogravimetric analysis indicated weight loss over the temperature range 40-200˚C, but with evaporation, not decomposition, below 150˚C (Klusacek and Krasemann 1985).
Specific Gravity:	1.425 at 20˚C (Tomlin 1997)
Vapour Pressure:	1.6 Pa (0.0120 mm Hg) at 20˚C (WHO 1989; Ciba-Geigy 1988; Teunissen-Ordelman and Schrap 1997) 2.1 Pa (0.016 mm Hg) at 25˚C (Tomlin 1997) 7.03 Pa (0.0527 mm Hg) at 25˚C (Howard 1991)
Water Solubility:	8.8 g/L at 20˚C (Bayer 1988a) ~10 g/L at 20˚C (Ciba-Geigy 1988; WHO 1989; Teunissen-Ordelman and Schrap 1997) 16 g/L at 25˚C (Howard 1991) ~18 g/L at 25˚C (Tomlin 1997)
Solubility in other solvents:	Completely miscible with aromatic hydrocarbons and alcohols; moderately soluble in diesel oil, kerosene, isoparaffinic hydrocarbons and mineral oils.
Volatility from water and moist surfaces:	Henry's Law Constant (K in Pa·m^3/mole) and as the dimensionless partition coefficient (H): K = 9.71 X 10^{-2} Pa·m^3/mole at 25˚C (H = 3.92 X 10^{-5}) (Howard 1991 – calculated from solubility and vapour pressure data at 25°C) K = 3.54 X 10^{-2} Pa·m^3/mole (H=1.45 X 10^{-5}) (calculated by the Department of the Environment and Water Resources [DEW] for 20°C from solubility and vapour pressure data at 20°C, agrees with Bayer 1988b) K = 7 X 10^{-3} Pa·m^3/mole (H = 2.82 X 10^{-6}) (Tomlin 1997) K = 1.9 X 10^{-1} Pa·m^3/mole (H = 7.8 X 10^{-5}) (Teunissen-Ordelman and Schrap 1997 – evidently calculated from the lowest solubility and highest vapour pressure values reported)

n-Octanol/Water Partition Coefficient:	Log K_{OW}	= 1.16 (Howard 1991) = 1.43 (Bayer 1988a; Tomlin 1997; Teunissen-Ordelman and Schrap 1997) = 1.47 (WHO 1989) = 1.90 (Tomlin 1997 – HPLC method) = 1.99 (Ciba-Geigy 1988 – HPLC method)

2.1 Comments on Physico-Chemical Properties

According to classifications of physico-chemical properties listed by Mensink *et al.* (1995), dichlorvos is readily soluble in water (water solubility at 20-25ºC $\geq$ 1000 mg/L) and volatile from dry surfaces (vapour pressure at 20-25ºC = 1-100 Pa), but is only very slightly to moderately volatile from moist surfaces and water (dimensionless Henry's Law Constant H = $1 \times 10^{-5} - 3 \times 10^{-2}$ or $< 1 \times 10^{-5}$, respectively). Howard (1991) comments that the Henry's Law Constant indicates that volatilisation of the substance from water and moist soil should generally be slow, and that if released into the atmosphere, it is expected to exist almost entirely in the vapour phase in ambient air.

g the Mackay Level 1 fugacity model (through a US EPA ASTER Ecotoxicity Profile, using available data for 25°CDEW). According to this model, environmental partitioning of dichlorvos would be approximately 98.6% to water, 1.0% to air, 0.2% to soil and 0.2% to sediment. The model as fitted by ASTER appears to relate to an area near a large body of water. Using a similar model (Trent University 1998) with parameters estimated for an inland area in Australia near a relatively small volume of water (Connell and Hawker 19DEW has estimated partitioning of dichlorvos in the environment usin86), DEW estimates that environmental partitioning would be approximately 6.9% to air, 88.3% to water, 4.2% to soil, 0.4% to sediment and 0.2% to aerosols.

3 ENVIRONMENTAL EXPOSURE

3.1 Environmental Release

3.1.1 Volume

In 1997/98 a total of approximately 42 t of dichlorvos active ingredient was imported, either already formulated or as active constituent for formulation in Australia.

3.1.2 Use pattern

The registered and permitted uses of dichlorvos in Australia have been discussed in the agricultural assessment section of this review. On the basis of approved labels as of 12 July 2007, the uses of dichlorvos products in Australia are presented in Table 1, with the approximate percentage of active ingredient going to broad end uses indicated as they were at the time the review commenced. Apart from use after harvest and during storage, it appears that little dichlorvos is currently used in Australia in field or glasshouse/greenhouse agricultural situations, use evidently being restricted to purposes where the volatility and quick knockdown of this insecticide is a necessary advantage. Some products available at the time of the initial review are no longer available, including pet collars for flea control and combination products with propoxur, chlorpyrifos and pyrethrins/piperonyl butoxide.

3.1.3 Methods of use

As discussed in the agricultural assessment section, methods of application in Australia include:
"ready to use" (resin strips or slow release blocks for treatment of confined areas, and aerosol with CO_2 propellant for treatment of closed-up areas);
coarse wet spray (application to the floor and around doorways and windows by watering can or as a very coarse spray, relying on volatilisation to fumigate the air space and penetrate less accessible areas);
surface spray (application to the surface of manure heaps, potato bag surfaces, grain piles, grain elevators, wasp nests etc);
space spray (released from pressurised cylinders via spray gun or EC diluted in water and released into the building air space as a fine spray);

Table 1.1. Approved use patterns of dichlorvos in Australia for products containing dichlorvos as the sole active ingredient.

Situations	Formulation and maximum rate of active	Application method and

(crop/animal/use)	**ingredient per application and frequency of application**[1]	**comments**
Glasshouse and field crops (~1.7% of ac used)		
Avocados	EC: 500 g ac/ha (tank mixed with 1 kg chlorpyrifos/ha) repeated as necessary	spray – apply at first sign of pest activity before larvae move to fruit
Greenhouses, glasshouses	EC: 6.7-7.5 g ac/100 m^3 PG: 200 g ac/300 m^3; whenever necessary or unspecified	EC: spray, fog, wooden block method PG: spray into air space
Mushroom houses	EC: 6.7-7.5 g ac/100 m^3; PG: 200 g/300 m^3; whenever necessary or unspecified	EC: spray, fog, wooden block method PG: spray into air space
Direct animal treatment and animal housing (~2.4% of ac used)		
Animal house and pens	EC: 10 g/10 L water at 15 L/100 m^2 (15 g/100 m^2); frequency unspecified	spray on walls and other surfaces or into air as a mist
Stables and piggeries	EC: 35 g/1000 m^3	space spray or mist
Dairies, cattle sheds	EC: 25 g/ 10L at 600 mL/50 m^2 (6 g/100 m^2)	coarse spray on floor and around doorways and windows
Poultry manure	EC: 30 g/10 L water applied to 12 m of manure under cages, repeated every 3 weeks	spray for control of fly maggots
Crop storage areas and stored product treatment (~55% of ac used)		
Stored grains	EC: 25-50 g/100 m^2 grain surfaces; frequency unspecified	spray grain surface
Infested grain held by flour millers	EC: 60-120 g/10 L water (1 L spray/t – 6-12 ppm on grain); frequency unspecified	spray during movement on elevator – higher rate for lesser grain borer
Bagged and stored potatoes	EC: 25 g/5 L water to treat 16 bags; frequency unspecified	spray bag surfaces
Warehouse	EC: 100 g/1000 m^3 repeated as necessary	spray or fogging
Empty silos	EC: 50 g/10 L water; frequency unspecified	spray inside wall and chutes to run-off
Stored product facilities (warehouses, silos, farm machinery, storage bins etc)	PG: 200 g/300 m^3 (stored product moths & flour beetles); 400 g/300 m^3 (tobacco beetle & tobacco moth); frequency unspecified	spray into air space
Domestic uses, recreational areas, industrial areas etc (~41% of ac used)		
Domestic, recreational and industrial areas	EC: 6 g/L water; PG: 200 g/300m^3; frequency unspecified	EC: spray to treat bee and wasp nests PG: spray into air space
Flies etc in domestic areas, moths and silverfish in linen cupboards etc	SR: 20 g SR plastic strip (186 g/kg), to treat 3 m^3; continuous release with 4 months claimed effective life	hang or place in cupboard or other confined space to be protected
Rubbish bins	SO (with naphthalene): One 55 g unit per wheelie bin; continuous release with 3 months claimed effective life	hang unit inside wheelie bin
Household	EC: 6 g/L water; frequency unspecified	spray or sprinkle where pests occur
Factories stores, mills, food warehouses	EC: 17.5-75 g/1000 m^3; repeated as necessary for flies etc; twice per week for moths etc	space or surface spray or fogging 2.5 g + 50 g sugar/L at 0.6-0.7 L/50 m^2 spray in strips or patches as a liquid bait
Wineries (vinegar fly)	EC: 70 g/1000 m^3 or 10-10.5 g/10 L water at 10 L/50 m^2 – 20-21 g/100 m^2; frequency	coarse wet spray on floor and around doorways and

	unspecified	windows, or as a space spray or fog
Meatworks (non-product areas)/abattoirs	EC: 10 g/10 L water at 15 L/100 m^2; frequency unspecified	coarse spray to walls and other surfaces or into air as a mist
Garbage dumps, picnic and recreational areas	EC: 150 g/ha; frequency unspecified	space spray, mist or fog
European wasps	EC: 6-10 g/L; PG: 200 g/300 m^3; frequency unspecified	EC: spray in and around entrance holes at 1 L per nest (less for very small nests) PG: direct nozzle into cavity or nest

[1] Formulation - EC Emulsifiable Concentrate; PG Pressurised Gas; SR Sustained Release; SO Solid.

fogging (similar to space spray, but EC released into building air space as a fog, using kerosene, diesoline or similar carrier);
liquid bait (application with sugar as a coarse spray or paint close to insect harbouring areas);
wooden board method (undiluted spray sprinkled on wooden boards placed in closed-up stores or glasshouses);
agricultural spray for avocados;
application to horses by syringe into the mouth as a paste.

Equipment used to apply the material may therefore range from slow release matrices, controlled release pressurised gas, misters and foggers, to hand held sprayers, pressurised knapsacks, spray guns and potentially spray booms.

Table 1.2. Use patterns of dichlorvos in Australia for products containing dichlorvos together with other active ingredients.

Product and use situations	Formulation and maximum rate of active ingredient per application and frequency of application[1]	Application method and comments
dichlorvos + oxibendazole oral worm and bot paste for horses	PA: 0.5 g/100 kg, twice per year or as required (4 weekly intervals during the bot fly season)	oral administration

[1] Formulation – PA Paste.

3.1.4 Implications for environmental exposure

Dichlorvos may potentially reach non-target areas directly:

- via sprayed dichlorvos solutions;
- as vapours released from slow release matrices or aerosol dispensers;

or indirectly

- through movement of directly released vapours or dichlorvos volatilising from sprayed surfaces
- in spray drift
- in water draining from treated areas after washing, irrigation or rain
- on treated material such as stored products, cut flowers or manure
- in excrement from treated horses
- through residues remaining in containers or slow release matrices.

Thus use of dichlorvos in Australia occurs predominantly in protected environments, where the main means by which the substance is likely to reach the external environment is as vapour, unless treated material is disposed of or treated surfaces are washed or reached by irrigation water before residues have dissipated to the atmosphere, degraded or have been absorbed. Where the substance is applied external surfaces or sprayed on crops direct spray or spray drift may also contribute to environmental contamination.

3.2 Formulation, handling and disposal

All dichlorvos active constituent manufacture occurs outside Australia and technical dichlorvos is shipped to Australia in 140-220 L steel drums in sealed shipping containers. With the exception of impregnated plastic strips, most (if not all) the end use products appear to be formulated and packed in Australia.

Formulations currently available in Australia and available package sizes include:
compressed gas concentrate containing 50 g dichlorvos/kg with the balance CO_2 propellant (cylinders with a net weight of 6 kg and 31 kg);
concentrates containing 1140 g dichlorvos/L (>90% by weight) with emulsifier (2.4 L to 20 L);
emulsifiable concentrate formulations containing 500 g dichlorvos/L with hydrocarbon solvents, surfactants and other additives (1 L-50 L);
slow release pest strips containing 186 g dichlorvos/kg in plastic resin (pack sizes 2-10 X 20 g strips, claimed to provide continuous release for up to 4 months in confined areas;
a slow release formulation with 80 g dichlorvos/kg and 800 g naphthalene/kg, plus other ingredients (1 X 55 g tablets per domestic pack); and
an oral worm and bot paste for horses containing 2.5 g dichlorvos and 5.0 g oxibendazole per 25 mL plastic injector.

Details are not available for most products, but it is presumed that formulating most of the above products from the imported active constituent is a straightforward process of mixing the chemical with other ingredients and transferring the product into the relevant containers. It is expected that appropriate equipment and procedures are used during these processes to minimise the chances of a significant spill and ensure that should a spill occur, it can be contained safely. Impregnated plastic strips are formulated and packed overseas, hence there is no potential exposure of the Australian environment during manufacture of these products.

Any spills during formulation, packing or transport are expected to be treated according to the relevant MSDS.The Novartis active constituent MSDS provided when this review commenced advised minimising further leakage, sweeping up spills by use of absorbent materials, shovelling into specially marked drums, adding hydrated lime (presumably based on the rapid hydrolysis of dichlorvos under alkaline conditions) and topping with soil, with the affected area to be decontaminated with water containing soda, soap or detergent and the washings collected to avoid any contamination of surface or ground water, water supplies or drains, with heavily contaminated soil to be dug out and removed, and with all contaminated material to be disposed of at an approved secure landfill site, with no re-use of spilt product. Currently available (July 2007) MSDSs for the end use products contain advice such as prevent spill from entering drains or water courses, stop leak and contain spill, absorb onto sand, vermiculite or other absorbent material, collect and place in sealable containers for disposal, if indoors wash contaminated areas with mild bleach solution (sodium hypochlorite). DEW
Container disposal statements on current labels are generally satisfactory, indicating that:
compressed gas cylinders remain the property of the manufacturer and must be returned for refilling,
domestic and veterinary product containers should be wrapped and disposed of in garbage (hence ending up in landfill), and
containers for EC and concentrate products should be triple or preferably pressure rinsed before disposal and recycled or broken, crushed or punctured and buried in a local authority landfill or buried deeper than 500 mm in a specifically marked disposal pit set up for this purpose clear of waterways, desirable vegetation and tree roots.

3.3 Environmental monitoring

In pesticide monitoring in the Netherlands, Teunissen-Ordelman and Schrap (1997) reported dichlorvos was detected at maximum concentrations in the range 10-100 μg/L in “regional” surface water (i.e. in or near agricultural areas) and 0.1-1 μg/L in rainwater. Concentrations detected in regional, “national fresh,” “transboundary,” marine and rain water exceeded the Maximum Permissible Concentration (MPC - 95% of species protected), whereas no dichlorvos was detected in groundwater. In contrast to the minor amount of agricultural use in Australia for outdoor or protected cultivation, approximately 80% of Dutch dichlorvos use was in greenhouses, with a comparable volume (>49 t in 1993, 7.1 t 1985, 32-41 t 1988, 1991, 1994) to the total used in Australia. Relevant emission routes for greenhouse cultivation were identified as run-off of condensation containing pesticides deposited on the inner surfaces after crops have been treated, water flowing after greenhouse walls and roofs are sprayed clean, and water draining from sprinklers located high up in greenhouses via draining valves (i.e. when chemicals have been applied via sprinkler irrigation). Dichlorvos rated 5th highest “risk emission” and action has since been taken to ban agricultural use of dichlorvos in the Netherlands (Section 1).

Dichlorvos concentration in four European river/estuary systems (the Western Scheldt, Louros, Ebro and Rhone Rivers, respectively in The Netherlands, Spain, Greece and France) were evaluated on two to three occasions over different seasons in each system (Steen *et al.* 1999). In none of these cases was dichlorvos detected (detection limit = 10 ng/L).

DEW is not aware of any reports of dichlorvos being detected in Australian waters.

4 ENVIRONMENTAL CHEMISTRY AND FATE

In addition to the data package provided by respondents to the NRA call-out on dichlorvos, DEW has consulted published literature referring to the substance and unpublished reports included in previous submissions on the substance provided by Bayer Australia Ltd Agricultural Division and Ciba-Geigy Australia Limited for active constituent Clearance purposes under the system/s operating in the 1980s.

4.1 Hydrolysis

Several studies which investigated the hydrolysis of dichlorvos were considered, as summarised in the various parts of Table 2 and discussed further below.

4.1.1 Rate of hydrolysis - effect of pH, temperature and ionic strength

Suter (1981) examined the hydrolysis of dichlorvos in aqueous acidic, neutral and basic media at various temperatures (pH buffer for pH 5, 7 and 9; 0.1N HCl and 0.1N NaOH, respectively, for pH 1 and 13; 30, 50 and 70°C for pH 1, 5, 7 and 9; 20°C for pH 7 and 13). A range of ionic strengths was evaluated for pH 7 at 70°C (1, 10, 25 and 50 mM phosphate buffer) and 30°C (1 and 10 mM), whereas the pH 7 buffer used for the main part of the study was approximately 120 mM and the ionic strength at other pHs was 90-150 mM (calculated by DEW from the stated buffer compositions). The experiments were conducted in sealed brown glass ampoules to prevent volatilisation of the substance. Incubation time varied according to the test conditions, from as short as 70 seconds (pH 13 at 20°C) to as long as 336 hours (pH 7 at 30°C and 1mM ionic strength). Analysis was conducted using an HPLC technique.

Table 2.1 Hydrolysis half-life of dichlorvos under various pH and temperature conditions, and for pH 7 at 30 and 70°C, with differing buffer ionic strengths (Suter 1981).

pH[a]	Half-life (h)			
	20°C	30°C	50°C	70°C
1	-	73.5	27.1	5.4
5	77 (estimated)	50.5	16.7	2.75
7	31.4	17.6[a], 73.1[b], 108[c]	11.5	1.21[a], 1.69[d], 2.81[e], 4.39[b], 4.23[c]
9	19 (estimated)	16.2	14.7	0.649
13	-	1.29×10^{-2}	-	-

[a] Standard buffer - DEWDEW calculates that the ionic strength of the standard pH 7 buffer used was approximately 120 mM; [b] ionic strength of buffer 10 mM; [c] ionic strength of buffer 1 mM; [d] ionic strength of buffer 25 mM; [e] ionic strength of buffer 50 mM.

Fitted kinetic data showed that both temperature and pH had an effect on the rate of hydrolysis (Table 2.1). There was evidence that degradation at pH 7 was strongly dependent on ionic strength, the half-life being longest at 1 mM at both 30 and 70°C (Table 2.1). While first order kinetics evidently applied at 20-50°C at pH 7, a non-linear relationship in the Arrhenius plot was indicated at 70°C at all pHs tested at that temperature (possibly associated with vapour phase effects). Hence the estimated half-lives at 20°C for pH 5 and 9 were each based on extrapolation from only two fitted values (DEW would prefer at least 3 values to confirm linearity in each case).

The rate of hydrolysis increased with increasing pH to be very fast under highly alkaline conditions (Table 2.1). Based on the estimated or measured hydrolysis half-lives in standard buffers at pH 5-9 and 20°C, dichlorvos would be classified as hydrolysing “readily” (DT50 in range 1-4 days) to “very rapidly” (DT50 < 1 days - Mensink *et al.*1995).

4.1.2 Rate of hydrolysis - effect of pH and temperature

A study reported by Bayer (1982a) investigated the rate of hydrolysis of dichlorvos at pH 4, 7 and 9 at temperatures of 28 or 30 and 40°C (Table 2.2). In this study, the substance was incubated in sealed glass ampoules, using commercial buffer solutions diluted 1:1 (v/v), with the procedure stated to follow the OECD Method “Hydrolysis as a function of pH” (analysis was by GC). Estimated hydrolysis half-lives at 22°C were again based on extrapolation from only two fitted values.

Table 2.2 Hydrolysis half-life of dichlorvos under various pH and temperature conditions (Bayer 1982a).

pH	Half-life (h)			
	22°C	28°C	30°C	40°C
4	766 (est.)	-	305	101
7	69.6 (est.)	43.3	-	17.6
9	48.0 (est.)	27.1	-	9.3

As indicated in Table 2.2, the estimated hydrolysis half-life at 22°C (again based on extrapolation from only two fitted values) was > 30 days (720 h) at pH 4, i.e. "slightly hydrolysing" (Mensink *et al.*1995), whereas the estimated half lives at pH 7 and 9 were approximately 2-3 days ("readily hydrolysing"). Thus the estimated half-lives at 22°C were somewhat longer at pH 7 and 9 and much longer at acid pH than those estimated at 20°C by Suter (1981).

4.1.3 Rate of hydrolysis – effect of pH

Lamoreaux and Newland (1978) reported a study of the degradation rate of dichlorvos in buffered, oil-free aqueous solutions at a range of pH values (borate buffer; temperature conditions and other details of incubation not stated, but presumably room temperature; residual dichlorvos determined by GLC at 24 hour intervals). DEW has fitted equations to the four available data points (24-96 hours) for each pH, assuming first order kinetics (Table 2.3). The results (statistically significant in several cases - Table 2.3) indicate very slow hydrolysis under very acid conditions ("slightly hydrolysing" DT50 > 30 days, Mensink *et al.* 1995). Based on the estimated half-lives, the substance was "moderately hydrolysing" at pH 6.2-6.9 (DT50 in the range 10-30 days – Mensink *et al.* 1995), ranging to "readily" hydrolysing (DT50 1-4 days) at pH 7.8-8.2 and "very rapidly hydrolysing" at pH 8.7-9.3.

Table 2.3 Hydrolysis half-life of dichlorvos under various pH conditions (Lamoreaux and Newland 1978).

pH	2	3.3	6.2	6.9	7.8	8.2	8.7	9.3
slope	0.00078	-	0.0019	0.0027	0.0075	0.017	0.048	0.336
r^2	0.48 (ns)	-	0.94^*	0.80 (ns)	1.00^*	0.96^*	0.98^*	0.84 (ns)
half-life (h)	(887)	stable	369	(258)	92.0	41.8	14.3	(2.1)

* statistically significant ($P < 0.05$); ns: not significant (half-life based on fitted slope shown in parentheses)

4.1.4 Hydrolysis of dichlorvos under various conditions and in natural waters

Drevenkar *et al.* (1976) reported a hydrolysis study conducted to explore reasons for a "much faster" observed rate of hydrolysis in water from the Kupa River than three other Yugoslavian rivers. Incubation was conducted in deionised and distilled water or buffer solutions prepared there from, in glass-stopped glass flasks, which were exposed to sunlight and artificial light during the experiment (full details not provided). Analysis was by a GC method. DEW notes that direct photolysis of dichlorvos is unlikely to have occurred from exposure to sunlight (see phototransformation, below), but that indirect photolysis or effects of sunlight on metabolites cannot be excluded.

Table 2.4 Hydrolysis half-life of dichlorvos at various concentrations at room temperature (Table 2.4.1), a range of pH conditions (Table 2.4.2) and at pH 8 at various temperatures with different buffers (Table 2.4.3) (Drevenkar et al.1976).

Table 2.4.1

pH 8.9	Temperature 20°C	Dichlorvos concentration (µg/L)	75	150	750	1500
		Half life (h)	23	24	20	19

Table 2.4.2

pH	6.6	7.0	7.6	8.0
Half-life (h)	79	46	32	27

Table 2.4.3

pH 8.0 in	Half-life (h)		
	4°C	15°C	25°C
borate buffer	1422	205	61
bicarbonate solution	130	98	49
phosphate buffer	165	50	17

Results of various experiments were as follows (Table 2.4):

The authors stated that hydrolysis of dichlorvos to phosphate ester actually follows second order kinetics, but can be considered to be pseudo-first order if one of the reactants is in large excess or its concentration is kept constant. They found fitted first order half-lives of 19-24 hours (“very rapidly hydrolysing”) from initial dichlorvos concentrations of 75-1500 µg/L (pH 8.9, at room temperature – Table 2.4.1).

They found a strong influence of pH within the pH range expected in natural waters: fitted half-lives at pH 6.6, 7.0, 7.6 and 8.0 were 79, 46, 32 and 27 hours, respectively (“readily hydrolysing” - Table 2.4.2).

There was a strong influence of temperature and also evidently from the type of buffer solution used (Table 2.4.3), with the results indicating that at 15-25°C, dichlorvos ranged from “fairly hydrolysing” (DT50 in the range 4-10 days) to “very rapidly” hydrolysing (from Mensink *et al*. 1995). However, the authors noted that the evident enhancement in degradation rate with phosphate buffer was in the presence of high concentrations of dihydrogen phosphate ion, and they found practically negligible deviations in the degradation rate of dichlorvos in borate buffer at pH 8 and room temperature with the addition of 63 µg/L P in the form of sodium dihydrogen phosphate to the borate buffer. Hence the authors concluded that ion species could affect hydrolysis rate significantly “only if present in large quantities.”

There was little difference in hydrolysis rate in untreated Kupa River water compared to Kupa River water which had been percolated through activated carbon (half-lives approximately 85-90 h – readily hydrolysing), suggesting that organic components had little influence on the rate of hydrolysis.

Drevenkar *et al.* (1976) concluded that differences in temperature and alkalinity may significantly affect the rate of hydrolysis in natural streams, but noted that measurements indicated little difference in these parameters between the Kupa and Sava River waters at the time of the study. Hence they attributed the observed rate differences between these natural streams to differences in biological and bacteriological properties (several other studies pertaining to hydrolysis are discussed later in this review under “Degradation in aquatic situations”).

4.1.5 Rate of hydrolysis - effect of pH and temperature

Dedek, Georgi and Grahl (1979) investigated the rate of hydrolysis of ^{32}P-labelled dichlorvos and related organophosphates in a range of buffer solutions at 25 and 40 °C (Table 2.5). The half-life of dichlorvos again decreased with increasing pH and at pH 5-8 ranged from 34.5 hours to 10.3 days at 25°C.

Table 2.5 Hydrolysis half-life of dichlorvos under various pH and temperature conditions (Dedek, Georgi and Grahl 1979)

	Half-life (h or d)					
pH	2	5	6	7	8	10
25°C	22.4 d	10.3 d	5.0 d	2.44 d	34.5 h	5.7 h
40°C	4.6 d	3.2 d	37.5 h	16 h	8.2 h	1.5 h

5.1.5 Other hydrolysis studies

Yasuno *et al.* (1965) estimated residues of dichlorvos in pH buffer solutions ranging from pH 3 to 10 after 16 days incubation at 27°C. From an initial application level of 20 ppm, residues had declined to 0 ppm at pH 7-10, 2 ppm at pH 6 and 8-12 ppm at pH 3-5, confirming greater instability to hydrolysis at alkaline pH.

Muehlmann and Schrader (1957) estimated the half-life of dichlorvos under acid conditions (pH in the range 1 to 5) at 240, 61.5, 17.3 and 5.8 hours, respectively, at 10, 20, 30 and 40°C.

4.1.6 Proposed hydrolysis pathway

Muehlmann and Schrader (1957) indicate that hydrolysis of dichlorvos produces dimethylphosphoric acid and dichloroacetaldehyde (via dichlorovinyl alcohol as an unstable intermediate). Ciba-Geigy Australia Limited (1988) adds that both these products are degraded further under alkaline conditions and that the demethylation product desmethyldichlorvos (Figure 2, Section 5.3) also occurs.

4.1.7 Summary and conclusions regarding hydrolysis

The hydrolysis of dichlorvos has been studied under a wide range of conditions, particularly in regard to incubation temperature and pH of the test solution. Dichlorvos has been shown to hydrolyse readily (DT50 in range 1-4 days) to moderately (DT50 in range 10-30 days) at 15-30°C at pH values expected under ambient conditions (pH 4-9). The rate of hydrolysis increases with increasing pH, being very slow under very acid conditions, but very rapid under alkaline conditions (i.e. it is evidently favoured by the presence of OH^- ions). Differences between studies in estimated half-life under similar temperature and pH (particularly at acid pH) are difficult to explain, but contributory factors may have included differences in ionic strength and composition of the buffers used.

4.2 Phototransformation

Several studies which investigated the direct or indirect photolysis of dichlorvos were considered, as summarised in Table 3 and discussed further below.

Table 3. Photolysis of dichlorvos in solution and on glass plates, and estimates of the indirect photochemical transformation of the substance in the vapour phase.

Reference	Estimated half-lives and comments
Aqueous	
Wilmes (1982)	No degradation detected after 7 h exposure of a 22 mg dichlorvos/L solution to high-pressure mercury vapour lamps – absorption spectrum indicates that direct photolysis should not occur under normal environmental conditions at the earth's surface.
Guth and Voss (1970)	Half-life under test conditions approximately 7 h at 100 ppm in water (based on a cholinesterase inhibition assay), but stable in methanol (6 h exposure to a filtered UV light source) – degradation presumably due to hydrolysis in water.
On glass plates	
Chen *et al.* (1984) [cited by WHO (1989)]	Half-life for dichlorvos on glass plates at UV wavelengths ~300 nm approximately 7.3 h
Dedek, Georgi and Grahl (1979)	<5 h with substance on glass plates exposed to "UV" radiation, <20 h with exposure to "sunlight" radiation. Metabolites identified.
Indirect photochemical transformation	
Howard (1991)	Estimated half-life due largely to hydroxyl radical reactions 2 d
Environment Defense Fund (1999)	Estimated half-life due largely to hydroxyl radical reactions 1 d
Calculated by DEW	Estimated half-life due largely to hydroxyl radical reactions < 0.5 d

4.2.1 Aqueous photolysis

A preliminary study of light stability of dichlorvos in water was reported by Wilmes (1982). UV adsorption of the substance in water was found to drop relatively steeply from a maximum below 200 nm, with adsorption no longer detectable at 250 nm, i.e. below UV wavelengths reaching the earth's surface. No photodegradation was detected in a solution of 22 mg/L dichlorvos in double distilled water irradiated at 17°C for 7 hours using high-pressure mercury vapour lamps. Thus direct photolysis of dichlorvos is not expected under normal environmental conditions, but indirect photolysis in the presence of sensitisers cannot be excluded. In addition, Howard (1991) cites Gore *et al.* (1971 – not seen by DEW) that dichlorvos does not absorb UV light above 240 nm and hence is not a candidate for photolysis.

A brief report with few experimental details was provided of a study by Guth and Voss (1970) of the photodecomposition of a number of organophosphate insecticides in water (presumably distilled or deionised) and methanol. In both cases the pure substance at a concentration of 100 ppm was illuminated for a maximum of 6 hours at ~20°C with a UV/light source claimed to have a minimum effective wavelength of 290 nm. No degradation was found in methanol, but in water the concentration of dichlorvos analysed by a cholinesterase inhibition technique fell after an initial one-hour lag period to 55 ppm after 6 hours of exposure, presumably due to hydrolysis rather than photolysis. The overall half-life in irradiated water calculated by DEW was 415 minutes (~7 hours; $r^2 = 0.91$, 8 data points).

4.2.2 Photolysis on glass plates

WHO (1989) cites Chen *et al.* (1984) as finding a photochemical degradation rate constant of 265×10^{-7}/s at environmentally important wavelengths (around 300 nm) and a concentration of dichlorvos of 0.67 μg/cm^2 of glass plate. The calculated photolysis half-life for dichlorvos on glass plates was therefore approximately 7.3 hours.

Dedek, Georgi and Grahl (1979) briefly reported a study where photodegradation of dichlorvos and related organophosphates was examined on glass plates. The substance was found to have been totally degraded after 5 hours exposure to "UV" irradiation, identified metabolites being desmethyldichlorvos and dimethyl and monomethyl phosphate. After 20 hours "sunlight" irradiation, dichlorvos had degraded by 75%, with dimethyl phosphate and inorganic phosphate identified, but no desmethyl dichlorvos.

These results suggest that dichlorvos is susceptible to photodegradation on the surface of glass plates, but the results are difficult to interpret in the absence of experimental detail, particularly the wavelengths and intensity of the "UV" and "sunlight" irradiation used and steps taken to avoid loss by volatilisation and hydrolysis.

4.2.3 Photochemical transformation in air by ozone and free radicals

Howard (1991) noted that no experimental data could be found on the photodegradation of dichlorvos by reactive atmospheric species, but predicted that the molecule would be attacked by both ozone and hydroxyl radicals, primarily by addition to the double bond. Howard [based on Atkinson (1987) and Atkinson and Carter (1984)] provided estimates of the rate constants for the vapour-phase reaction of dichlorvos with photochemically produced hydroxyl radicals (using an estimate of 5×10^5 hydroxyl radicals per cm^3) and with ozone (using an estimate of 7×10^{11} ozone molecules per cm^3) indicating half-lives of about 2 days and 320 days, respectively. However, these estimates apply to air in the troposphere exposed to sunlight, and Howard notes that they may not be appropriate for indoor air, where dichlorvos is most used. An estimated atmospheric half-life (largely from reactions with hydroxyl radicals) of 1 day was reported by Environmental Defense Fund (1999), based on Kwok and Atkinson (1995). DEW estimates from OECD (1992) methods and Kwok and Atkinson (1995) that as well as addition reactions at the C to C double bond in the dichlorvos molecule, abstraction of H is also possible and may be more important than addition, with a half-life less than 0.5 day indicated at the same hydroxyl radical concentration as above.

4.2.4 Summary and conclusions regarding photochemical transformation

The UV-adsorption spectrum for dichlorvos indicates that direct photolysis of the substance should not occur under normal environmental conditions at the earth's surface and this is confirmed by two rather old and poorly described aqueous photolysis studies. Similar studies of the photolysis of dichlorvos on glass plates indicated that the substance did degrade in the presence of UV radiation or sunlight, with a half-life of <20 h under sunlight. While direct photolysis of dichlorvos is not expected under normal environmental conditions, indirect photolysis may occur in the presence of sensitisers in water or on various surfaces. In outside air, dichlorvos is likely to be readily degraded (half-life <0.5 d to 2 d) by reaction with hydroxyl radicals produced by photochemical reactions.

4.3 Soil Metabolism

Several studies which investigated the fate of dichlorvos in soil were considered, as summarised in Table 4 and discussed further below. While its vapour pressure indicates that dichlorvos is likely to be volatile from dry soil, the calculated Henry's Law values indicate that it is expected to volatilise relatively slowly from moist soil. Hence only slow loss by volatilisation is expected during soil incubation, despite intermittent or continuous exposure to the atmosphere (some volatilisation could also occur during preparation, eg where the substance was added in non-aqueous solvent to air-dry soil). There was no indication of significant loss by volatilisation in the ^{14}C-labelled dichlorvos studies discussed below, at least under non-sterile conditions (total recovery of radioactivity = 90-103% and % applied radioactivity recovered as volatile compounds other than $^{14}CO_2$ <0.1% in non-sterile samples, ≤1.4% in sterile samples).

Table 4. Degradation of dichlorvos in soil.

Reference	Estimated half-life and other comments
Getzin & Rosefield (1968)	<<1 d in non-sterile and irradiated soil at 25°C. 99, 88 and 17% degradation after 24 h at 25°C in non-sterile, irradiated and autoclaved soil, respectively (soil characteristics not stated in this paper).
Bayer (1975, 1982b)	1 h and 16 h, respectively, in soils with pH 6.8 and 5.2 at 20-24°C.
Lamoreaux & Newland (1978)	3.9 and 10 d, respectively, in non-sterile and sterile soil perfusion systems (soil pH 6.2-7.4, temperature ~26°C). Estimated 70% of total degradation in the non-sterile system was due to hydrolysis in this soil.
Sattar (1990)	Average ~16 d (range 12.3-19.3 d, with no clear difference between the soils) in two soils (pH 5.5 and 6.9) at 10, 100 and 1000 ppm and 25°C.
Fritz (1987a)	<<2 d in two non-sterile soils (pH 5.7 and 6.05 - <2% applied radioactivity remaining at 2 d) at 22°C and 8.7 d in sterile soil (pH 5.7), with rapid initial degradation and a high degree of mineralisation after 60 d incubation in the non-sterile soils, but not the sterile soil ($^{14}CO_2$ 73-75% and <1% of applied radioactivity, respectively, in non-sterile and sterile soils).
Fritz & Brauner (1987)	<<1 d (dichlorvos 62% applied radioactivity after 10-15 minutes incubation and not detectable after 1 d), with rapid mineralisation (65% applied radioactivity recovered as $^{14}CO_2$ at 1 d) in a soil with pH 5.8 (22°C).
Guerguis and Shafik (1975) cited by Howard (1991 – not seen by DEW)	Half-life of dichlorvos in autoclaved clay and calcareous soil was 0.9 and 0.85 days, respectively, reduced by the presence of micro-organisms to 0.75 and 0.70 days
Nowak *et al.* (1972) cited by Bayer (1982b – not seen by DEW)	At 15°C the dichlorvos content of treated soil was reduced to 36-68% of the initial value within 7 days, compared to 3 days at 40°C

4.3.1 Rapid loss in non-sterile and irradiated soil

Getzin and Rosefield (1968) compared the extent of degradation after 24 hours of a range of organophosphate insecticides added to moist non-sterile soil, gamma-irradiated soil and autoclaved irradiated soil (sterility of irradiated and of autoclaved soil was confirmed). Recovery of dichlorvos from fortified autoclaved soil was 80-95%, whereas only 60-70% recovery of “unstable” insecticides (presumably including dichlorvos) was obtained from non-sterile soil extracted immediately after treatment (recovery from gamma-irradiated soil was not indicated). The claimed extent of degradation for dichlorvos after incubation for 24 hours at 25°C was 99% in non-sterile soil, 88% in irradiated soil and 17% in autoclaved soil.

The authors attributed the difference between the amount of insecticide decomposed in irradiated soil and in autoclaved soil to the presence of non-viable, heat-labile substances (possibly exoenzymes). However, from experimental evidence, Lamoreaux and Newland (1978) concluded that adsorption may have contributed to the rapid initial disappearance of the substance in an autoclaved soil (see Section 5.3.3, below). As it is conceivable that soil adsorption characteristics were affected to differing extents by autoclaving and irradiation, it cannot be excluded from the information given that adsorption effects may also have contributed to apparent loss of the test substance in the Getzin and Rosefield (1968) study.

4.3.2 Half-life in two soils

A brief summary (Bayer 1975, 1982b) of a laboratory study conducted according to 1973 German standards (20-24°C) indicated half-lives of 1 hour in standard soil 2.1 [pH 6.8, 2.6% organic carbon (OC); recovery 54%] and 16 hours in standard soil 2.2 (pH 5.2, 0.6% OC; recovery 82%). Poor recovery in the first soil was stated to be the result of fast degradation, and the difference in degradation rate between the soils was presumed to have been due to higher pH in the first soil. DEW regards these results as indicative only, but similarly rapid degradation occurred in the Getzin and Rosefield (1968) study (above) and in studies by Fritz (1987) and Fritz and Brauner (1987) (below).

4.3.3 Contributions of adsorption, hydrolysis and microbial degradation to loss in soil

Lamoreaux and Newland (1978) examined the fate of dichlorvos in Houston Black Clay soil [pH = 7.7-8.0 in 1:1 soil to distilled water suspension, but measured pH = 6.2-7.4 during incubation; organic matter (OM) content 3.3%]. Incubation was carried out at (evidently at a room temperature of 26°C) for 10 days in a soil column perfusion system (a column of soil continually perfused with an aqueous solution containing 1000 mg dichlorvos/L), using sterile (autoclaved) soil with and without added *Bacillus cereus*.

Apparent loss of dichlorvos in soil extracts after 10 days reached 71% and 50%, respectively, with and without the added bacteria, and greater loss in the presence of the bacteria was associated with a measured increase in bacterial growth. Calculated dichlorvos half-lives for the non-sterile and sterile systems were 3.9 and 10 days, respectively. A comparison of dichlorvos degradation in filtered sterilised soil extract with that in sterile soil suggested that adsorption contributed to the rapid initial disappearance of the substance in sterile soil. The authors estimated that 70% of total degradation in the non-sterile system was due to chemical mechanisms (i.e. degradation occurring in the sterile system, presumably due to adsorption together with hydrolysis and other means of abiotic degradation) and 30% due to bacteriological mechanisms.

4.3.4 Degradation rates in two soils at a range of initial dichlorvos concentrations

Sattar (1990) investigated the degradation rate of dichlorvos in a silty clay soil (pH 5.5, 0.9% OM) and a less acidic, sandy clay soil (pH 6.9, 1.1% OM). Dichlorvos (purity 99-100%) and various other organophosphates were applied in hexane to air-dried soil at 10, 100 and 1000 ppm and brought to field capacity moisture content (~25 g water/100 g soil). Treated samples were incubated in glass containers fitted with lids at 25±3°C for up to 80 days. Samples were extracted with a solvent mixture and analysed by GLC. The author indicated average half-lives over all concentrations of 16 days in both soils. DEW calculates the half-lives for 10, 100 and 1000 ppm to be 12.9, 18.5 and 19.3 days (average 16.9 days), and 12.3, 17.8 and 18.2 days (average 16.1 days), respectively, in the silty clay and the sandy clay. Thus there was little apparent influence of soil type on the degradation rate with the two soils tested (both air-dried before use, but not sterilised), and degradation was significantly slower in this study than in other soil studies under non-sterile conditions (Table 4).

4.3.5 Studies using ^{14}C-labelled dichlorvos

4.3.5.1 Degradation rate

Fritz (1987a) reported an aerobic soil metabolism study using [1-^{14}C]-labelled dichlorvos, based on German protocols. The study was carried out with German standard soil Speyer 2.1 (slightly humous sand; pH 5.7, 0.65% OC, maximum water holding capacity 18.2 g/100 g; microbial biomass initially and during study 159 and 95-259 mg microbial C/kg dry soil, respectively) and a field soil from Höfchen (sandy silt; pH 6.05, 2.17% OC, maximum water holding capacity 36.7 g/100 g; microbial biomass initially and during study 1283 and 569-1098 mg microbial C/kg dry soil, respectively). In addition to these “biologically active” soils (air-dried), autoclaved Speyer 2.1 soil was used to investigate degradation under “sterile” conditions (no biological activity was detected during the study period). Dichlorvos was applied at 1 mg/kg dry soil (added in isopropanol to air dried soil), and the soil moisture content adjusted to 40% of the maximum water capacity. Incubations were continued at 22°C in the dark for up to 60 days, in flasks fitted with absorption columns for CO_2 and other volatiles (the airspace was flushed through the column by compressed air when the flask was sampled). Soil samples were extracted using a methanol/ water procedure.

Measured concentrations of dichlorvos at time 0 were approximately 91, 53 and 78% of applied radioactivity, respectively, in the sterile Speyer 2.1, non-sterile Speyer 2.1 and non-sterile Höfchen soils, presumably indicating rapid degradation in the presence of micro-organisms during the preparation and extraction period [recovery was satisfactory in each case (88-103%) and the balance of radioactivity was largely in the extracted fraction, with no $^{14}CO_2$ and little unextracted material]. The dichlorvos concentration fell to approximately 86% and 1% of applied radioactivity after 2 days (the next sampling occasion) in the sterile and non-sterile Speyer 2.1 soil and to undetectable levels in the non-sterile Höfchen soil. Over the same period, approximately 60% of applied radioactivity was recovered as $^{14}CO_2$ from both non-sterile soils but <0.1% of applied radioactivity in the sterile soil. CO_2 emitted after 60 days reached approximately 73-77% of applied radioactivity in the non-sterile soils, but <1% applied radioactivity in the sterile soil. Other volatile components were recovered in trace or very minor quantities (<0.1% applied radioactivity in non-sterile soils, ≤1.4% in sterile soil), suggesting that little or no volatilisation of dichlorvos occurred. Unextracted radioactivity was similar in magnitude in the three soils, at approximately 14-22% of applied radioactivity after 60 days incubation.

Thus dichlorvos was metabolised very rapidly in both non-sterile soils, with degradation half-lives well below 2 days and rapid mineralisation to $^{14}CO_2$ of much of the applied substance. Degradation in the sterile soil was much slower, with a calculated half-life of 8.7 days, and little mineralisation to $^{14}CO_2$ occurred even after 60 days incubation. Presumably degradation in the sterile soil occurred by abiotic hydrolysis, as conditions remained sterile and autoclaving would have destroyed heat-labile substances potentially capable of degrading dichlorvos (Getzin and Rosefield 1968 – discussed above).

4.3.5.2 Metabolites produced

Fritz and Brauner (1987) examined the metabolites produced from dichlorvos degrading in soil using non-sterile Speyer 2.2 soil (loamy sand; pH 5.8, 2.42% OC, maximum water holding capacity 27.5 g/100 g; microbial biomass initially 345 mg microbial C/kg dry soil). ^{14}C-labelled dichlorvos was applied at 2 mg/kg dry soil and soil samples incubated similarly to the above study for up to 10 days (sterile and non-sterile Speyer 2.1 and 2.2 soil incubation systems containing higher initial concentrations of dichlorvos were also used to generate larger quantities of metabolites for structure elucidation).

Dichlorvos was again found to break down rapidly in a comparable fashion to the above study, with recovery of radioactivity again satisfactory (90-98% of applied). Only 62% of applied radioactivity was detected as parent substance after 10-15 minutes incubation (time 0) and no unchanged dichlorvos was detectable after 1 day incubation. At this time, approximately 65% of applied radioactivity was found to be $^{14}CO_2$, <0.1% applied radioactivity as other volatiles (again suggesting that little or no volatilisation of dichlorvos occurred) and 21% was in the unextracted fraction, and there was relatively little change in these figures after 10 days incubation (70% CO_2, <0.1% other volatiles, 18% unextracted).

Three metabolites were positively identified in the main study:

- desmethyldichlorvos (peak approximately 14% of applied radioactivity at time 0 and 1% on day 1, not detectable thereafter)
- 2,2-dichloroacetaldehyde (peak approximately 12% of applied radioactivity at time 0, not detectable thereafter)
- 2,2-dichloroethanol (approximately 2-4% of applied radioactivity over time 0-day 4, not detectable at day 10).

A fourth metabolite (dichloroacetic acid) was only detectable when a higher concentration of dichlorvos was applied and is thought to be a very short lived intermediate product in soil. The structures of these short-lived metabolites and hypothesised degradation pathway for dichlorvos in soil are shown in Figure 2.

4.3.6 Other laboratory soil studies

Howard (1991) cites Guerguis and Shafik (1975 – not seen by DEW) as finding that the half-life of dichlorvos in autoclaved clay and calcareous soil was 0.9 and 0.85 days, respectively, and that this was reduced by the presence of micro-organisms to 0.75 and 0.70 days.

Bayer (1982b) cite Nowak *et al.* (1972 – not seen by DEW) as finding that the rate of dichlorvos degradation increased with increasing carbon content and incubation temperature: at 15°C the dichlorvos content of treated soil was reduced to 36-68% of the initial value within 7 days, compared to 3 days at 40°C.

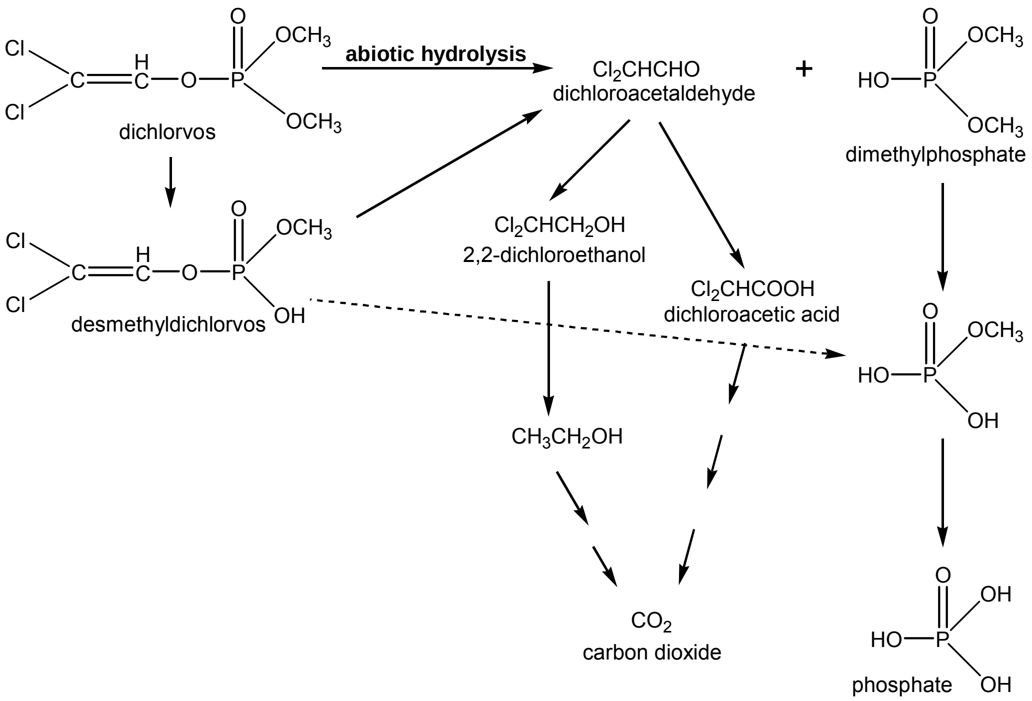

Figure 2. Proposed pathway for the breakdown of dichlorvos in soil and in water/sediment systems, including abiotic hydrolysis and microbial degradation steps.

4.3.7 Summary and conclusions regarding degradation in soil

Two aerobic soil degradation studies conducted with ^{14}C-labelled dichlorvos to reasonably modern protocols with a total of 3 soils indicated that under aerobic conditions at 22°C, degradation of dichlorvos occurred rapidly, with half-lives less than 1-2 days under non-sterile conditions. A high degree of mineralisation (breakdown to release $^{14}CO_2$) occurred rapidly, with intermediate metabolites including desmethyldichlorvos, 2,2,-dichloroacetaldehyde and dichloroethanol.

Similarly rapid degradation (< 1 day) under non-sterile conditions at 20-25°C was reported in 3 other earlier studies. Two other studies indicated slightly longer half-lives in non-sterile soil: of the order of 3 days at 40°C and 7 days at 15°C in one study; and 3.9 days in a second study using an unusual soil perfusion incubation system (at ~26°C). A further study indicated a somewhat longer dichlorvos half-life of ~16 days in 2 soils. Reasons for the slower degradation rate in the latter study particularly are not clear, but possible explanations could include the treatment of soil between sampling and use in the study (eg the extent of drying, duration and conditions of storage) and incubation conditions (eg extent of aeration).

Some of these studies also evaluated degradation in soil which had been sterilised by autoclaving or irradiation prior to treatment. In the ^{14}C-labelled dichlorvos study, in the one soil which was autoclaved, degradation was slower than in the presence of biological activity (half-life = 3.9 days) and little mineralisation occurred during the 60 day incubation period in the dark. In another study, the degradation half-life was only ~25% longer in the absence of biological activity, and still less than one day. Possible effects from non-viable, heat-labile substances and/or adsorption were indicated in a study where degradation was evaluated in non-sterile soil, soil sterilised by gamma irradiation and soil sterilised by autoclaving, there being 99, 88 and 17% degradation, respectively, after 24 hours incubation at 25°C.

4.4 Degradation by micro-organisms in culture and by sewage sludge

In vitro studies by Lamoreaux and Newland (1978) showed that the bacteria *Bacillus cereus* (isolated from soil) is capable of using dichlorvos as a sole or additional carbon source, but not as the sole source of phosphorus. Laveglia and Dahm (1977) cite evidence that dichlorvos is degraded by various other identified species of bacteria. Matsumura and Boush (1968) found evidence that dichlorvos is degraded by the soil fungus *Trichoderma viride*.

Lieberman and Alexander (1981) determined that dichlorvos had little or no toxicity to sewage sludge micro-organisms at 0.1-100 mg/L, but that little degradation occurred of dichlorvos provided as the sole carbon source (< 5% of available O_2 over ~7 days incubation). Lieberman and Alexander (1983) obtained from sewage sludge a “microbial enrichment” capable of metabolising dichlorvos as the main carbon source in the presence of a vitamin supplement.

They determined that *Pseudomonas* bacteria and a (tentatively identified) *Bacillus* were among the microbes contributing to dichlorvos degradation.

Lieberman and Alexander (1983) isolated microbial cells by centrifugation from a supplemented microbial culture and used them to investigate the metabolites produced from dichlorvos by biotic and abiotic processes (similar initial pathway to that shown in Figure 2but with the formation of ethyl dichloroacetate and ethyl acetate).

Thus dichlorvos evidently has little or no toxicity to various micro-organisms in soil and sewage sludge and may provide a sole or supplemental nutrient source (see also pp 52-53).

4.5 Degradation in Aquatic Situations

Several studies which investigated the fate of dichlorvos in aquatic situations were considered, as summarised in Table 5 and discussed further below.

Table 5. The fate of dichlorvos in aquatic situations.

Reference	Estimated half-lives and comments
Fritz (1987b)	Half-life approximately 1 d or less in two water/sediment systems (pH of water slightly alkaline in both cases); $^{14}CO_2$ = 69-76% of applied radioactivity after 16 d.
Horváth *et al.* (1982)	Half-life in water of natural origin (a Hungarian lake) was approximately 1 d, compared to 8 d in distilled water (incubation conditions and pH not indicated).
Grahl (1979) [cited by WHO (1989) and Howard (1991)]	Half-life in two ponds treated with dichlorvos = 34 and 24 h. Half-life approximately 100 h in a German lake with pH < 6 and temperature < 25°C.
Samuelsen (1987)	Half-life in seawater 93-195 h at 4.5-13.5°C, pH 7.7-8.0 and +/- aeration.
Drevenkar *et al.* (1975) [cited by Howard (1991)]	Half-life in water from 3 Yugoslav rivers < 72 h.
Drevenkar *et al.* (1976)	Half-life in water from the Kupa River with and without carbon filtration approximately 85-90 h.

4.5.1 Laboratory Water/Sediment Study

Fritz (1987b) evaluated the metabolism of ^{14}C-labelled dichlorvos in two water/sediment systems from the Netherlands (1 mg dichlorvos/L, cf. 1 kg ac/ha to water 10 cm deep; the test system held 500 mL water, with 10% w/w sediment). Water and sediment samples were obtained from an orchard drainage ditch (IJzendoorn: %sand/silt/clay = 44.1/36.9/18.9; pH 7.1; 2.5% OC; 15,000 mg $CaCO_3$/kg) and a reclaimed gravel pit (Lienden: %sand/silt/clay = 78.1/10.3/11.6; pH 7.4; 0.8% OC; 11,500 mg $CaCO_3$).

Measurements showed that over the experimental period, aerobic conditions were maintained adequately in the surface water of the incubation systems (Redox potential = +139-272 mV, dissolved O_2 = 45-95% of saturation metabolites produced), and the authors stated that microbial counts on surface waters indicated the systems remained biologically active throughout both experiments. The pH of the surface water remained slightly alkaline (pH = 7.5-8.8 and 7.4-8.6 in the IJzendoorn and Lienden systems, respectively), with no clear trends in pH over time.

Degradation of dichlorvos in these aquatic systems occurred rapidly, with a half-life of approximately one day or less in both cases (50-55% of the applied dose remained as dichlorvos at 1 h, 7-31% at 1 d and $\leq$ 1% by 7 days). Similar short-lived metabolites were identified to those found in the soil degradation study by Fritz and Brauner (1987), and as in the soil study these were rapidly mineralised to carbon dioxide and phosphate (Figure 2). Most of the applied radioactivity was ultimately recovered as $^{14}CO_2$ (total approximately 69 and 76% of applied radioactivity, respectively, after 16 days in the IJzendoorn and Lienden systems).

4.5.2 Other aquatic studies

Yasuno *et al.* (1965) reported tests showing that the rate of degradation in water is hastened slightly by the presence of the bacteria *Bacillus subtilis*. Horvàth *et al.* (1982) evaluated the degradation of dichlorvos in water of natural origin (from a Hungarian lake) and in distilled water and found it was much faster in natural water (half-life approximately 1 day compared to approximately 8 days in distilled water – incubation conditions and water pH were not indicated).

WHO (1989) cites a study by Grahl (1979) where two ponds containing 9200 and 25,000 μg plankton/L water, respectively, were treated with dichlorvos sprayed under the surface of the water to give an initial concentration of 325 μg/L water. The half-life of dichlorvos in these ponds was 34 and 24 hours, respectively. Howard (1991) cites what is evidently the same report (Grahl 1979) as indicating that the half-life of dichlorvos in a German lake whose pH was <6 and temperature <5°C was approximately 100 hours.

Samuelsen (1987) found that the half-life of dichlorvos in seawater was 93-195 hours, depending upon water temperature (4.5 or 13.5°C), pH (7.7 or 8.0) and the presence or absence of aeration. Howard (1991) cites Drevenkar *et al.* (1975) that the half-life of dichlorvos in water from 3 Yugoslav rivers was less than 72 h. A subsequent study reported by Drevenkar *et al.* (1976) (discussed in more detail earlier in this review under “Hydrolysis”) indicated that the half-life of dichlorvos in water from the Kupa River with and without carbon filtration was approximately 85-90 h.

4.5.3 Summary and conclusions regarding degradation in aquatic situations

An aquatic metabolism study with dichlorvos in two water/sediment systems indicated rapid degradation of dichlorvos (half-life ≤ 1 d in both cases). Similar intermediate metabolites were identified to those found in soil studies and a high degree of mineralisation occurred within 16 d of application. Several studies suggest that in unsterilised water, degradation may be somewhat faster than occurs due to hydrolysis alone, and micro-organisms enable the products of hydrolysis to degrade further.

4.6 Mobility in soil

4.6.1 Adsorption to organic carbon

Kenaga (1980) predicted the K_{OC} of dichlorvos from its water solubility, the predicted value being 28 (from water solubility of 10,000 ppm, using the regression equation log K_{OC} = -0.55 log WS + 3.64, where WS is the water solubility in mg/L). DEW notes that a predicted value for the K_{OC} of 150 is obtained if an alternative regression equation for estimating K_{OC} (Lyman 1982) based on the octanol:water partition coefficient is used (K_{OC} = 0.544 X log K_{OW} + 1.377; log K_{OW} = 1.47). Teunissen-Ordelman and Schrap (1997) indicate a log K_{OC} of 1.4 (K_{OC} = 25 – this may simply be a calculated value, there being no indication of its source). These estimates indicate that dichlorvos can be classified as having high (K_{OC} 50-150) to very high (K_{OC} 0-50) mobility in soil (McCall *et al.* 1980).

4.6.2 Column leaching studies

Three brief reports summarised simple column leaching studies with dichlorvos applied as a 50% EC formulation (Bayer 1974a,b,c). The substance was applied at a rate equivalent to 500 g ac/ha to the top of 30 cm columns (5 cm diameter) containing sand-sandy loam soils varying in pH (pH 5.2-7.0), %OC (0.6-2.6%) and clay content (4-20%). The columns were then leached with the equivalent of 190 mm rain over a 2.25 day period. No dichlorvos was detected in the leachate from any of the three soils (detection limit = 0.002 μg/L). DEW finds this study to be deficient, as it is likely that extensive hydrolysis and microbial degradation of dichlorvos may have occurred during leaching and prior to measurement, yet metabolites of dichlorvos were not evaluated. DEW expects the highly water soluble metabolites of dichlorvos would be even more mobile than dichlorvos itself, but that to some extent downward movement of metabolites may be limited by mineralisation to release CO_2.

4.6.3 Other data

Howard (1991) cited a field experiment reported by Petrova and Novozhilov (1980), which found that 18-20% of the dichlorvos which was sprayed on the ground had penetrated the soil to a depth of 30 cm within 5 days, suggesting that the substance has significant mobility in soil. Howard (1991) also cited Khan and Khan (1986) as reporting R_f values ranging from 0.36 to 0.74 from thin layer chromatography (TLC) measurements with dichlorvos in soil, indicating the substance is in the “intermediate” (R_f-range 0.35-0.64) to “mobile” (R_f-range 0.65-0.89) mobility classes of Helling and Turner (1968).

4.6.4 Summary and conclusions regarding mobility in soil

Estimates calculated from the physicochemical characteristics of dichlorvos indicate that dichlorvos has high (K_{OC} 50-150) to very high (K_{OC} 0-50) mobility in soil. Thin layer chromatography values for dichlorvos in soil also suggest dichlorvos may have at least intermediate mobility in soil. Brief reports of column leaching studies indicated that no dichlorvos was found in leachate, suggesting limited mobility in soil despite leaching with the equivalent of 190 mm rain over a 2.25 d period, but it is likely that extensive hydrolysis and microbial degradation of dichlorvos may have occurred during leaching and prior to measurement. DEW expects that the highly water soluble metabolites of dichlorvos may be even more mobile than the parent substance, though to some extent downward movement of metabolites may be limited by mineralisation to release CO_2. A field experiment found dichlorvos penetrated to a depth of 30 cm within 5 d of application, suggesting significant mobility in soil. DEW concludes that while dichlorvos may be mobile in soil, it is unlikely to reach watertable or persist because of its rate of degradation through hydrolysis and microbial activity.

4.7 Volatilisation

As indicated earlier, according to classifications of physico-chemical properties listed by Mensink *et al.* (1995), dichlorvos is volatile from dry surfaces (vapour pressure at 20-25ºC in the range 1-100 Pa), but is only very slightly to moderately volatile from moist surfaces or water (dimensionless Henry's Law Constant H in the range 1×10^{-5} to 3×10^{-2}, or $< 1 \times 10^{-5}$, respectively).

Dedek, Georgi and Grahl (1979) provided some evidence that significant loss of dichlorvos by evaporation may occur through volatilisation in a study with ^{32}P-labelled dichlorvos applied to leaf surfaces and glass plates exposed to an air stream for 8 hours, but the results were reported too briefly for adequate interpretation, except that evaporative loss of dichlorvos was maximal after 3 hours exposure and continued relatively high compared to the related organophosphates butonate and trichlorfon.

WHO (1989) cites FAO/WHO "Pesticide residues in food" reports as stating that dichlorvos is rapidly lost from leaf surfaces by volatilisation and by hydrolysis, with a laboratory half-life of the order of a few hours, and with a small percentage of the deposited substance penetrating into the waxy layers of plant tissues where it persists longer before being hydrolysed.

Howard (1991) indicates that the volatilisation half-life from a model river (1 m deep flowing 1 m/s with a wind speed of 3 m/s) has been estimated to be about 57 days [(calculated according to Thomas (1982)], while that from a model pond, where the effect of adsorption is considered, has been estimated to be over 400 days (calculated using US EPA EXAMS II Computer Simulation, 1987). Thus these estimates indicate that the rate of volatilisation from water is very minor compared to the rate of hydrolysis.

Thus the physico-chemical properties of dichlorvos indicate that it is volatile from dry surfaces, making dichlorvos one of the more volatile organophosphates. However, it is also readily soluble in water and hence only very slightly to moderately volatile from moist surfaces or water.

4.8 Field Dissipation

4.8.1 Studies of dissipation in mushroom houses and from various treated surfaces

Hussey and Hughes (1963) and Hussey and Hughes (1964) reported studies of the concentration of dichlorvos and/or aldehyde degradation products of dichlorvos in the air of mushroom houses where various surfaces were treated with dichlorvos (analysis by a colorimetric method). These data presumably reflect both partitioning of the substance and its aldehyde metabolites between the air and other surfaces and degradation of these substances by hydrolysis in the humid air (stated to be 85% relative humidity, rising to 95% in spawn-running rooms) contained in the houses and potentially by microbial degradation in soil etc.

In one study, the 50% EC was applied in a fine spray at 48 mL in the 4000 cu ft (113.2 m^3) house. DEW calculates this to be equivalent to 212 µg ac/L air, if all the dichlorvos volatilised without loss. Measured atmospheric concentrations of dichlorvos plus aldehydes in the closed, unventilated house fell from 24.00 µg/L over 0-30 minutes, to 4.95 µg/L at 30 minutes-1.5 hours, 1.05 µg/L at 1.5-2.5 hours and 0.30 µg/L by 6.5-17 hours.

In a second study, the 50% EC was applied by watering can on the floor at 1 US gallon (4.55 L) of a 10% solution in a 4000 cu ft (113.2 m^3) house, with a view to obtaining persistence of fumigant action without continuous or repeated release. DEW calculates this to be equivalent to 2010 µg ac/L air, if all the dichlorvos volatilised without loss. Measured atmospheric concentrations of dichlorvos in the house fell from 0.80 µg/L air over 0-17 hours to 0.31 µg/L over 40-57 hours and 0.03-0.10 µg/L over days 4 to 8, and dichlorvos was present at ≤0.02 µg/L at days 11 and 14-15 after application, with effective insecticidal action remaining for at least 5 days. Corresponding concentrations of the metabolite dichloroacetaldehyde were 1.18, 1.23, 0.55-1.11 and 0.18-0.37 µg/L, respectively.

Thus in both these studies the peak concentration recorded from the sampling intervals used was well below the potential peak concentration if all the applied dichlorvos volatilised rapidly without loss, and then declined. While much of the decline in concentration is likely to have been due to degradation in the air, water, soil and on various surfaces, the measured concentrations were also potentially affected by incomplete and relatively slow volatilisation of the applied substance, incomplete sealing of the glasshouse leading to air exchange, dichlorvos loss in water through drainage, and the insensitivity of the measurements due to the relatively large sampling intervals.

In a further study discussed by Hussey and Hughes (1964), the relative persistence of dichlorvos on various surfaces was investigated. Dilute (5%) emulsifiable concentrate was applied to glass slides, small cement blocks, pieces of wooden board, and moist loam soil (pH 6.45 - in glass-stoppered flasks). Less than 1% of the applied dichlorvos remained on the cement after 1 hour, whereas on glass, 18% of the applied dichlorvos remained after 1 day and approximately 1% after 3 days. In soil, approximately 84% of the applied dichlorvos remained after 1 day and 35% after 3 days, while on wood, approximately 61% of the applied dichlorvos remained at 7 hours, 45-55% at days 2-18 and 39% at day 33. Peak concentrations of the metabolite dichloroacetaldehyde detected were approximately 8%, 2%, 9% and 7%, respectively, on cement, glass, soil and wood. Rapid dissipation from cement was presumed to have been due to alkaline hydrolysis. Thus the fate and rate of dissipation of dichlorvos applied in a mushroom house is affected by the nature of the surface/s treated.

4.8.2 Summary and conclusions regarding field dissipation

Information is available on the concentration of dichlorvos and/or its aldehyde degradation products in the air of unventilated mushroom houses following application by various means. In that situation, peak concentrations of dichlorvos plus aldehydes recorded in the air of the houses were well below the potential peak concentration if all the applied dichlorvos volatilised rapidly without loss, indicating incomplete and relatively slow volatilisation. Concentrations in air declined rapidly over the measurement period with application by a fine spray to the air of the house, but remained at effective insecticidal concentrations for at least 5 days when dichlorvos was applied at a high rate to the floor. The rate of dissipation was also shown to be affected by the nature of the surface/s treated, with dissipation most rapid from cement (half-life < 1 h, presumably hastened by alkaline hydrolysis) and glass, slower from soil (half-life < 3d) and much slower from wood (39% remaining after 33 d).

There is little specific information regarding field dissipation of dichlorvos, but from the available evidence DEW concurs with the conclusion by WHO (1989) that “direct application of dichlorvos on crops or animals will result in residues disappearing rapidly by volatilisation and hydrolysis. Airborne dichlorvos arising from fogging, spraying, or volatilisation from impregnated strips is hydrolysed in the atmosphere to dimethylphosphate and dichloroacetaldehyde. Losses occur through ventilation and by absorption and hydrolysis on surfaces. Depending on the material, dichlorvos may be absorbed and diffuse into the material, or it may be hydrolysed on the surface.”

4.9 Uptake and Metabolism in Plants

Dedek, Georgi and Grahl (1979) found that addition of plant homogenates did not reduce the degradation half-life of dichlorvos compared to hydrolysis at the same pH. They found that the half-life for dichlorvos on leaf surfaces of various species was 4.6-6.8 hours, presumably due to losses by volatilisation as well as degradation.

Rowlands (1971) reported that dichlorvos has been shown to break down rapidly on the surface of wheat grain to give mainly dimethyl phosphate and phosphorylated protein derivatives, with lesser amounts of desmethyldichlorvos, monomethyl phosphate and phosphoric acid. Degradation rate has been found to be rapid even in dry grain, but the proportion of these metabolites differed with the moisture content of the wheat. Tests of the phosphorylated protein fractions from dichlorvos-treated wheat found that none were toxic to adult *Oryzaephilus surinamensis* (saw-toothed grain beetle), but germination of the wheat was slightly impaired at the 10 ppm level and seriously affected when saturated with dichlorvos. Rowlands (1970) reported that dichlorvos topically applied to wheat grains was taken up rapidly, the uptake rate decreasing once all protein had been phosphorylated (“saturation”), after which excess dichlorvos could be lost by volatilisation in addition to the rapid degradation taking place on the grain surface.

Rowlands (1975) reported evidence that the storage temperature is important as a factor influencing degradation rate. For example, they cite a study where half-lives in wheat treated with dichlorvos at 50 ppm and 9, 11, 13 or 14% moisture content were 20, 15, 8 and 7 days, respectively, at 21°C and 3-5 days at 35°C, whereas degradation was much slower at -15°C (still 34-49 ppm after 11 months). The author commented that no attempt was made in this study to differentiate between chemical or enzymic breakdown, loss by volatilisation or inextractability, and noted that it is not clear ‘whether the high initial losses recorded by many workers … are due to volatilisation or drift during spraying and mixing, actual chemical or enzymatic breakdown, vapour-phase loss from the treated grain, or failure to extract “bound” residues.’

Desmarchelier (1977) reported that in regard to initial measured residues of dichlorvos on wheat, on average about 10% (0-20%) of the insecticide applied was lost by processes including missing of target, volatility losses, specific enzyme reactions occurring only immediately after application, and incomplete extraction of aged residues.

Thus dichlorvos has been found to dissipate rapidly from treated leaf surfaces, with a half-life of 4.6-6.8 h, presumably due principally to volatilisation and hydrolysis. Enzymatic breakdown may also occur, but a test using plant homogenates showed they did not hasten degradation. Dissipation rate from treated grain has been found to increase with increasing moisture content and increasing storage temperature: eg one study indicated half-lives ranging from 7-20 d at 21°C and a moisture content of 9-14%.

4.10 Metabolism and Excretion in Mammals

WHO (1989) indicate that dichlorvos is readily absorbed by mammals by all routes of exposure and is rapidly hydrolysed and metabolised. Hence DEW presumes that in horses orally dosed with dichlorvos for control of bot fly larvae, provided it is in a readily available form, a high proportion would be absorbed and metabolised or hydrolysed in the animal, or hydrolysed during passage through the gut and in freshly evacuated manure. However, DEW notes that levels toxic to birds have been reported from dichlorvos supplied to horses in a pelleted formulation – see "Avian toxicity reported in the field," Section 6.2.5.

4.11 Bioconcentration

Kenaga (1980) predicted the bioconcentration factor for dichlorvos from its water solubility, the predicted value being 3 (from log BCF = 2.791 – 0.564 X log WS, where WS is the water solubility of 10,000 mg/L). Moreover, DEW notes that the substance hydrolyses readily at relevant pHs, further limiting the possibility of bioaccumulation.

This prediction is highly consistent with the results of a bioconcentration and excretion study of a range of organophosphates with the fish species willow shiner (*Gnathopogon caerulescens*) reported by Tsuda *et al.* (1992). Fish were exposed to dichlorvos in a continuous flow through system for 168 hours, followed by a depuration period of 72 hours. The mean measured dichlorvos concentration (± standard deviation) was 2.3±0.3 μg/L (water pH 7.0-7.1, temperature 21±1°C). Calculated bioconcentration factors (BCFs) for dichlorvos at 24, 72, 120 and 168 hours were 0.8, 0.4, 1.2 and 0.8. The low concentrations of dichlorvos in the fish decreased rapidly during depuration and were below the limit of detection by 6 hours.

Thus both calculation using an equation relating the bioconcentration factor to water solubility and the results of a bioconcentration and excretion study with dichlorvos and the fish species willow shiner (*Gnathopogon caerulescens*) indicate low bioconcentration factors (BCFs) for the substance (BCF = 3 and ≤ 1.2, respectively). Hence dichlorvos is not expected to bioaccumulate in fish exposed to residues in water.

4.12 Summary and conclusions regarding environmental chemistry and fate

4.12.1 Hydrolysis

The hydrolysis of dichlorvos has been studied under a wide range of conditions, particularly in regard to incubation temperature and pH of the test solution. DEW concludes that dichlorvos hydrolyses readily (DT50 in range 1-4 days) to moderately (DT50 in range 10-30 days) at 15-30°C at pH values expected under ambient conditions (pH 4-9). The rate of hydrolysis increases with increasing pH, being very slow under very acid conditions, but very rapid under alkaline conditions (i.e. it is evidently favoured by the presence of OH^- ions). Differences between studies in estimated half-life under similar temperature and pH (particularly at acid pH) are difficult to explain, but contributory factors may have included differences in ionic strength and composition of the buffers used.

4.12.2 Photochemical transformation

The UV-adsorption spectrum for dichlorvos indicates that direct photolysis of the substance should not occur under normal environmental conditions at the earth's surface and this is confirmed by two rather old and poorly described aqueous photolysis studies. Similar studies of the photolysis of dichlorvos on glass plates indicated that the substance did degrade in the presence of UV radiation or sunlight, with a half-life of <20 h under sunlight. While direct photolysis of dichlorvos is not expected under normal environmental conditions, indirect photolysis may occur in the presence of sensitisers in water or on various surfaces. In outside air, dichlorvos is likely to be readily degraded (half-life <0.5 d to 2 d) by reaction with hydroxyl radicals produced by photochemical reactions.

4.12.3 Degradation in soil

Two aerobic soil degradation studies conducted with ^{14}C-labelled dichlorvos to reasonably modern protocols with a total of 3 soils indicated that under aerobic conditions at 22°C, degradation of dichlorvos occurred rapidly, with half-lives less than 1-2 days under non-sterile conditions. A high degree of mineralisation (breakdown to release $^{14}CO_2$) occurred rapidly, with intermediate metabolites including desmethyldichlorvos, 2,2,-dichloroacetaldehyde and dichloroethanol.

Similarly rapid degradation (< 1 day) under non-sterile conditions at 20-25°C was reported in 3 other earlier studies. Two other studies indicated slightly longer half-lives in non-sterile soil: of the order of 3 days at 40°C and 7 days at 15°C in one study; and 3.9 days in a second study using an unusual soil perfusion incubation system (at ~26°C). A further study indicated a somewhat longer dichlorvos half-life of ~16 days in 2 soils. Reasons for the slower degradation rate in the latter study particularly are not clear, but possible explanations could include the treatment of soil between sampling and use in the study (eg the extent of drying, duration and conditions of storage) and incubation conditions (eg extent of aeration).

Some of these studies also evaluated degradation in soil which had been sterilised by autoclaving or irradiation prior to treatment. In the ^{14}C-labelled dichlorvos study, in the one soil which was autoclaved, degradation was slower than in the presence of biological activity (half-life = 3.9 days) and little mineralisation occurred during the 60 day incubation period in the dark. In another study, the degradation half-life was only ~25% longer in the absence of biological activity, and still less than one day. Possible effects from non-viable, heat-labile substances and/or adsorption were indicated in a study where degradation was evaluated in non-sterile soil, soil sterilised by gamma irradiation and soil sterilised by autoclaving, there being 99, 88 and 17% degradation, respectively, after 24 hours incubation at 25°C.

4.12.4 Degradation in sewage

Evidence indicates that dichlorvos has little or no toxicity to various micro-organisms and may provide a sole or supplemental nutrient source to them.

4.12.5 Degradation in water

An aquatic metabolism study with dichlorvos in two water/sediment systems indicated rapid degradation of dichlorvos (half-life ≤ 1 d in both cases). Similar intermediate metabolites were identified to those found in soil studies and a high degree of mineralisation occurred within 16 d of application. Several studies suggest that in unsterilised water, degradation may be somewhat faster than occurs due to hydrolysis alone, and micro-organisms enable the products of hydrolysis to degrade further.

4.12.6 Mobility

Estimates calculated from the physicochemical characteristics of dichlorvos indicate that dichlorvos has high (K_{OC} 50-150) to very high (K_{OC} 0-50) mobility in soil. Thin layer chromatography values for dichlorvos in soil also suggest dichlorvos may have at least intermediate mobility in soil. Brief reports of column leaching studies indicated that no dichlorvos was found in leachate, suggesting limited mobility in soil despite leaching with the equivalent of 190 mm rain over a 2.25 d period, but it is likely that extensive hydrolysis and microbial degradation of dichlorvos may have occurred during leaching and prior to measurement. The highly water soluble metabolites of dichlorvos may be even more mobile than the parent substance, though to some extent downward movement of metabolites may be limited by mineralisation to release CO_2. A field experiment found dichlorvos penetrated to a depth of 30 cm within 5 d of application, suggesting significant mobility in soil. While dichlorvos may be mobile in soil, it is unlikely to reach water tables or persist because of its rate of degradation through hydrolysis and microbial activity.

The physico-chemical properties of dichlorvos indicate that it is volatile from dry surfaces, making dichlorvos one of the more volatile organophosphates. However, it is also readily soluble in water and hence only very slightly to moderately volatile from moist surfaces or water.

4.12.7 Glasshouse and field dissipation

Information is available on the concentration of dichlorvos and/or its aldehyde degradation products in the air of unventilated mushroom houses following application by various means. In that situation, peak concentrations of dichlorvos plus aldehydes recorded in the air of the houses were well below the potential peak concentration if all the applied dichlorvos volatilised rapidly without loss, indicating incomplete and relatively slow volatilisation.

Concentrations in air declined rapidly over the measurement period with application by a fine spray to the air of the house, but remained at effective insecticidal concentrations for at least 5 days when dichlorvos was applied at a high rate to the floor. The rate of dissipation was also shown to be affected by the nature of the surface/s treated, with dissipation most rapid from cement (half-life < 1 h, presumably hastened by alkaline hydrolysis) and glass, slower from soil (half-life < 3d) and much slower from wood (39% remaining after 33 d).

There is little specific information regarding field dissipation of dichlorvos, but from the available evidence, as concluded by a WHO review: "direct application of dichlorvos on crops or animals will result in residues disappearing rapidly by volatilisation and hydrolysis. Airborne dichlorvos arising from fogging, spraying, or volatilisation from impregnated strips is hydrolysed in the atmosphere to dimethylphosphate and dichloroacetaldehyde. Losses occur through ventilation and by absorption and hydrolysis on surfaces. Depending on the material, dichlorvos may be absorbed and diffuse into the material, or it may be hydrolysed on the surface."

4.12.8 Uptake and metabolism by plants

Dichlorvos has been found to dissipate rapidly from treated leaf surfaces, with a half-life of 4.6-6.8 h, presumably due principally to volatilisation and hydrolysis. Enzymatic breakdown may also occur, but a test using plant homogenates showed they did not hasten degradation. Dissipation rate from treated grain has been found to increase with increasing moisture content and increasing storage temperature: eg one study indicated half-lives ranging from 7-20 d at 21°C and a moisture content of 9-1.

4.12.9 Metabolism and excretion in mammals

Dichlorvos is readily absorbed by mammals by all routes of exposure and is rapidly hydrolysed and metabolised. Hence it is expected that little or no dichlorvos would be excreted by horses dosed orally with the substance (i.e. for control of bot fly larvae) provided it is in a readily available form. However, toxic levels in excreted pellets have been reported from dichlorvos supplied to horses in a pelleted formulation.

4.12.10 Bioaccumulation

Both calculation using an equation relating the bioconcentration factor to water solubility and the results of a bioconcentration and excretion study with dichlorvos and the fish species willow shiner (*Gnathopogon caerulescens*) indicate low bioconcentration factors (BCFs) for the substance (BCF = 3 and $\leq$ 1.2, respectively). Hence dichlorvos is not expected to bioaccumulate in fish exposed to residues in water.

4.12.11 Conclusions

Dichlorvos is likely to dissipate rapidly in most situations where it is exposed to air, soil and/or water, due to volatilisation, hydrolysis and microbial degradation. Dichlorvos vapours are not expected to persist in air due to OH radical attack, and residues in soil and water are expected to hydrolyse to less toxic metabolites due to hydrolysis and microbial degradation, with the latter leading to mineralisation to CO_2 and phosphate.

5 ENVIRONMENTAL TOXICOLOGY

5.1 Introductory comments

Information on the environmental toxicology of dichlorvos provided by the respondents to the ECRP data call-in included few reports of studies conducted to accepted modern guidelines, though other relevant information was included, often with few details of methodology. DEW has obtained further data from earlier active constituent submissions and the scientific literature (again often with little indication of methods used or with citation of results only, and/or by methods which fall short of current guidelines for regulatory purposes).

Data available to Environment have been rated by DEW as being "reliable", "acceptable" or "for information" as indications of toxicity. These ratings can be described as:

Reliable: There is a high level of confidence in the results. The study has been performed satisfactorily, with at most only minor problems unlikely to have affected the results (cf. US EPA "core" studies).
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/s or lack of critical information (cf. US EPA "supplemental" studies). Often the results are in terms of nominal concentration only.

For information: There are sufficient departures in the test from standard guidelines to make its reliability uncertain in terms of those guidelines, or insufficient information available to DEW for a judgment to be made.

DEW also used a database from the Ecological Fate and Effects Division of the Office of Pesticide Programs, US EPA (US EPA 1998), which contains the 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. In a few cases, DEW has had access to a copy of the reviewer's report, gaining a greater appreciation of the methods used and details such as the formulation tested.

The studies are ranked as either *core* or *supplemental* (similar to *reliable* and *acceptable* described above). As these studies have been reviewed and accepted by the US EPA, DEW has referred to this database rather than the wider AQUIRE aquatic toxicity database also managed by the US EPA (US EPA 1999), except where adequate data are otherwise lacking. However, in most cases DEW has not seen the original report or the US EPA reviewer's report, and care is then needed in interpreting the results for risk assessment (eg the database indicates specific values for each LC50 or LD50 listed and does not indicate where a value is unbounded, and results are expressed in terms of the material tested, not as active ingredient, with the composition of formulations tested not always clear).

5.2 Avian Toxicity

5.2.1 Acute oral toxicity

The available results for acute oral avian toxicity of dichlorvos are summarised in Table 6.1. In the studies or literature reports seen by DEW, LD50s from a single oral dose of dichlorvos to a wide range of bird species (from the Orders Anseriformes, Galliformes, Passeriformes and Columbiformes) ranged from ~5 mg/kg body weight (for a canary study) to 42.1 mg/kg body weight (for a study with starlings).

These results are consistent with those of regulatory studies reviewed by the US EPA and classified as *core* studies in regard to their Test Guideline 71-1, but which were not seen by DEW: i.e. a study with the active constituent and bobwhite quail (LD50 = 8.8 mg/kg bodyweight) and a 0.46% formulation and mallard duck LD50 > 21.4 mg ac/kg bodyweight). Thus dichlorvos is highly to very highly toxic to birds (LD50 in the range 10-50 or <10 mg/kg bodyweight, respectively) with acute oral exposure.

WHO (1989) notes that signs of acute oral dichlorvos intoxication in birds are typical of organophosphate poisoning. These include salivation, lachrymation, tremors, and terminal convulsions, and these signs usually appear shortly after dosing, lethal doses causing death within 1 h. Survivors appear to recover completely, though various internal haemorrhages were found in surviving treated birds sacrificed for autopsy of both species tested by Tucker and Crabtree (1970).

Table 6.1. Acute oral toxicity of dichlorvos to birds (single dose by gastric lavage or capsule).

Species	Rating (DEW or US EPA)	Test substance purity	Age of birds	Study duration	LD50 (mg/kg bodyweight)[1]	Study date (authors where available)
Studies seen by DEW						
Mallard duck (*Anas platyrhynchos*)	Guideline 71-1a – SUPPLEMENTAL	93%	5 mths	14 d	Male 7.8 (6.0-10.1)	1984 (Hudson *et al.*)
Quail (*Coturnix coturnix*)	ACCEPTABLE	96	NR	NR	Female 23.7 (*NC*)	1979 (Schafer & Brunton)
Japanese quail (*Coturnix c. japonica*)	FOR INFORMATION	NR	NR	NR	Male 22; Female 26	1974 (Hattori *et al.*[2])
Domestic fowl (*Gallus domesticus*)	FOR INFORMATION	NR	21 d	NR	6.5	1978 (Naidu *et al.*[2])
	FOR INFORMATION	NR	6-8 mths	NR	30	1975 (Dmitriev & Kozhemyakin[2])
	FOR INFORMATION	NR	‘Chick’	NR	14.8	1963 (DeCino)
Ring-necked pheasant (*Phasianus colchicus*)	Guideline 71-1 – SUPPLEMENTAL	93%	3 mths	14 d	Male 11.3 (9.0-14.3)	1984 (Hudson *et al.*)
Canary (*Serinus canarius*)	ACCEPTABLE	97.4%	NR	7 d	Female in the range 2.5-10	1982c (Bayer)
Common grackle (*Quiscalus quiscula*)	ACCEPTABLE	96	wild trapped	NR	13.3 (*NC*)	1979 (Schafer & Brunton)
Red-winged blackbird (*Agelaius phoeniceus*)	ACCEPTABLE	96	wild trapped	NR	Male 13.3 (*NC*)	1979 (Schafer & Brunton)
	FOR INFORMATION	NR	wild trapped	NR	17	1972 (Schafer)
	FOR INFORMATION	NR	NR	NR	12-22	1963 (DeCino)
House sparrow (*Passer domesticus*)	ACCEPTABLE	96	wild trapped	NR	17.8 (10.0-31.6)	1979 (Schafer & Brunton)
Starling (*Sturnus vulgaris*)	ACCEPTABLE	96	wild trapped	NR	42.1 (*NC*)	1979 (Schafer & Brunton)
	FOR INFORMATION	NR	wild trapped	NR	12	1972 (Schafer)
	FOR INFORMATION	NR	NR	NR	7-22	1963 (DeCino)
Common pigeon (*Columba livia*)	ACCEPTABLE	96	wild trapped	NR	23.7 (13.3-42.1)	1979 (Schafer & Brunton)
	FOR INFORMATION	NR	NR	NR	16.8	1974 (Hattori)
Studies on the US EPA Reviewed Studies Database additional to those seen by DEW						
Mallard duck (*Anas platyrhynchos*)	Guideline 71-1 – CORE	0.46%	NR	14 d	> 4650 (> 21.4 as ac)	1973
Bobwhite quail (*Colinus virginianus*)	Guideline 71-1a – CORE	96.5%	17 wks	14 d	8.8 (6.2-13.4)	1988[3]

[1] 95% confidence limits indicated in parentheses where when they were provided - *NC* indicates where confidence limits were declared not to be calculable, otherwise this information was not provided; [2] Not seen by DEW – listed in WHO (1989).

[3] A copy of the Data Evaluation Record for this study by US EPA was seen, but not the study itself.

Brief additional comments on the reports summarised in Table 6.1 follow.

The canary study (Bayer 1982c) was reported only briefly. There were only 3 test concentrations, but 6 birds were tested at each concentration, with the substance applied by stomach tube after 1 h fasting, followed by a 7 d observation period. No symptoms or mortality were observed with a 2.5 mg/kg body weight dose, vomiting and 50% mortality were observed at 5 mg/kg body weight and 100% mortality at the 10 mg/kg body weight dose. Hence probit analysis could not be used to estimate the LD50, but it was in the range 2.5-10 mg/kg body weight and probably close to 5 mg/kg bodyweight. Rated by DEW as *acceptable*.

A copy of a letter and accompanying table from DeCino (1963) indicates the oral and dermal toxicity of dichlorvos to starling, redwing and “other - chick” (presumably domestic fowl chickens). It appears that for oral dosing the toxicant was administered using treated ground poultry feed in gelatin capsules, and for dermal exposure was administered in acetone, but details of methodology were unclear or lacking in the information provided. The stated oral LD50s for starling, redwing and “chick” were 7-22, 12-22 and 14.8 mg/kg bodyweight, respectively, and the stated dermal LD50s for starling and redwing were 5.6 and 32 mg/kg bodyweight. Rated by DEW as *for information*.

DEW only saw an abstract of a Japanese literature report of the pigeon study by Hattori (1974). Four dose rates (15-120 mg/kg bodyweight) of dichlorvos or two other insecticides were administered in an emulsion by stomach tube to 2 birds per dose level. The claimed LD50 for dichlorvos was 16.8 mg/kg bodyweight. Rated by DEW as *for information*.

An extract from a paper reporting the toxicity of a large number of chemicals to various species of wild bird (Schafer 1972) was provided in the ECRP submission. The study was conducted by the Denver (Colorado) Wildlife Research Center, Bureau of Sport Fisheries and Wildlife, US Department of the Interior, but the paper provided little experimental detail. Wild-trapped birds were preconditioned to captivity for 2-6 wks, then dosed, usually by gavage, with suspensions or solutions of the test chemicals in propylene glycol. LD50s reported for starling and redwing were 12 and 17 mg/kg bodyweight, respectively. Rated by DEW as *for information*.

Schafer and Brunton (1979) reported results obtained using the Recommended Practice for Determining Acute Oral LD50 for Testing Vertebrate Control Agents (E555-75) of the American Society of Testing and Materials. This is the basis of the current US EPA methods and as such is considered acceptable within the constraint that the method is older and results refer to nominal concentrations. Rated by DEW as *acceptable*.

Hudson, Tucker and Haegele (1984) summarised the results of studies conducted at the Denver (Colorado) Wildlife Research Center (Bureau of Sport Fisheries and Wildlife, US Department of the Interior) of the toxicity of dichlorvos to mallard ducks and pheasants. These studies were reviewed by the US EPA and rated as *supplemental* in regard to their Test Guideline 71-1.

In addition to citing data from Schafer (1972), Schafer and Brunton (1979) and Tucker and Crabtree (1970), WHO (1989) lists values for the LD50 of dichlorvos to some bird species from reports by Dmitriev and Kozemjakjn (1975), Hattori *et al*. (1974) and Naidu *et al*. (1978). DEW has not itself seen any of these reports and few details were provided in the WHO (1989) summary, hence DEW rates these three reports as *for information*.

5.2.2 Dietary toxicity

5.2.2.1 Lethal effects

The available results for acute/subacute avian dietary toxicity of dichlorvos are summarised in Table 6.2. The studies or literature reports available to DEW indicate LC50s in the diet ranging from 298 to >5000 ppm (mg/kg diet) for the standard 8 day study period (5 days dietary exposure followed by 3 days observation) or for domestic fowl, a 28 day period. Two of these studies were assessed by the US EPA as *core* studies in regard to their Guideline 71-2: i.e. studies with mallard duck and ring-necked pheasant, indicating LC50s of >1317 and 568 ppm., respectively. These results indicate that dichlorvos is moderately to highly toxic (LC50 in the range 501-1000 and 51-500 ppm diet, respectively) to Japanese quail, ring-necked pheasant and domestic fowl, and slightly toxic to mallard duck (LC50 in the range 1001-5000 ppm diet).

A further study assessed as a *core* study for Guideline 71-2 by the US EPA and which has not been seen at all by DEW indicated an LC50 for a 0.46% formulation of dichlorvos to bobwhite quail of ≥ 4640 ppm, or ≥ 21.3 ppm in terms of active ingredient. Thus this study indicates that dichlorvos provided as the 0.46% formulation may be very highly toxic to bobwhite quail: if the value is not unbounded and DEW has correctly interpreted the % active ingredient in the formulation, the dietary toxicity of dichlorvos in this formulation to this species is much higher than found in other avian dietary studies.

5.2.2.2 Sub-lethal effects

WHO (1989) indicates that in the Naidu *et al.* (1978) study (not seen by DEW) with 7 d old male chicks, weight loss and 50% mortality occurred with 500 ppm dichlorvos in the diet, marked, dose-related inhibition of brain acetylcholinesterase activity occurred at 50, 100 and 500 ppm diet, but no effects were noted at 10 ppm dichlorvos in the diet.

A series of experiments reported by Pym *et al.* (1984) examined sub-lethal effects to laying hens exposed to dichlorvos and other insecticides in their diets for 28 d. The authors reported no statistically significant depression of egg production at 80 ppm dichlorvos alone, whereas food consumption was significantly reduced by dietary dichlorvos concentrations as low as 30 ppm and blood plasma cholinesterase level was reduced by about 70% after 4 weeks at 30 ppm. They cited an earlier paper by the same principal author (Pym *et al.* 1976) which reported significant effects on egg production at 40 ppm, and they suggested that the absence of a statistically significant effect in the more recent study was due to lower sensitivity in statistical comparisons (fewer replicates).

Table 6.2. Dietary toxicity of dichlorvos to birds (usually 5 d exposure to treated diet followed by 3 d observation).

Species	Rating	Test substance purity	Age of birds	Study duration	Toxicity (ppm diet)	Study date (authors where available)
Studies seen by DEW						
Mallard duck (*Anas platyrhynchos*)	Guideline 71-2b – CORE	94.8%	5 d	8 d	LC50 > 1317 (1043-1674)	1975 (Hill *et al.*)
	Guideline 71-2b – SUPPLEMENTAL	94.8%	16 d	8 d	LC50 > 5000	1975 (Hill *et al.*)
Japanese quail (*Coturnix c. japonica*)	Guideline 71-2a – SUPPLEMENTAL	94.8%	14 d	8 d	LC50 = 298 (257-345)	1975 (Hill *et al.*)
Ring-necked pheasant (*Phasianus colchicus*)	Guideline 71-2a – CORE	94.8%	10 d	8 d	LC50 = 568 (473-675)	1975 (Hill *et al.*)
Domestic fowl (*Gallus domesticus*)	FOR INFORMATION	NR	7 d	28 d	LC50 = 500; LOEC = 50; NOEC = 10	1978 (Naidu *et al.*[1])
	FOR INFORMATION	EC (ac conc. not stated)	28 d	28 d	LOEC = 40 ppm (egg production)	1976 (Pym *et al.*)[2]
	FOR INFORMATION	EC (ac conc. not stated)	28 d	28 d	LOEC = 30 ppm (food consumption, AchE[3])	1984 (Pym *et al.*)
Studies on the US EPA Reviewed Studies Database additional to those seen by DEW						
Bobwhite quail (*Colinus virginianus*)	Guideline 71-2a – CORE	0.46%	NR	8 d	LC50 > 4640 (> 21.3 ppm ac)	1973

[1] Full original reference not seen by DEW – listed in WHO (1989). [2] Not seen by DEW – cited in Pym *et al.* (1984). [3] Blood plasma cholinesterase level.

5.2.3 Early life/reproductive toxicity

The available results for early life/reproductive toxicity of dichlorvos to birds are summarised in Table 6.3. No early life/reproductive study was seen by DEW. However, the 28 d dietary study by Pym *et al.* (1976) described in the previous section indicated depression of egg production in laying hens by dichlorvos at dietary concentrations of 40 ppm, and that by Pym *et al.* (1984) showed reduced food consumption and blood plasma acetylcholinesterase levels as low as 30 ppm. Similarly, the 28 d domestic fowl study starting with 7 d old male chicks (Naidu *et al.* 1978) indicated a NOEC of 10 ppm and LOEC of 50 ppm. These results suggest that the LOEC and NOEC for prolonged dietary exposure to dichlorvos (eg similar to an early life/reproductive study) would be ≤ 30 ppm.

Toxicity of similar magnitude to these results with 28 d exposure was indicated in studies not seen by DEW, but reported on the US EPA Reviewed Studies Database. A study assessed by US EPA as a *core* study to their Guideline 71-4 (exposure commenced as treated birds approached their first breeding season and observations continued for about 20 weeks, following surviving offspring to 14 d old) indicated a NOEC of 30 ppm to bobwhite quail. Studies rated as *supplemental* to this Guideline indicated a NOEC of < 12 ppm to mallard duck in a study with the active constituent, and a NOEC = 20 ppm to Japanese quail and < 2 ppm to mallard duck with a 0.46% formulation (evidently much higher toxicity than the above, assuming these results are in terms of the test substance rather than ac).

Table 6.3. Early life/reproductive toxicity of dichlorvos to birds (dietary exposure continuing for at least 10 weeks prior to egg laying).

Species	Rating	Test substance purity	Study duration	LOEC, NOEC (ppm diet)	Study date
Studies on the US EPA Reviewed Studies Database additional to those seen by DEW					
Bobwhite quail (*Colinus virginianus*)	71-4a – CORE	98%	20 wks	LOEC = 100 ppm NOEC = 30 ppm	1996[1]
Japanese quail (*Coturnix coturnix japonica*)	71-4a – SUPPLEMENTAL	0.46%	1 generation	LOEC > 20 ppm NOEC = 20 ppm = 0.09 ppm as ai	1974
Mallard duck (*Anas platyrhynchos*)	71-4b – SUPPLEMENTAL	0.46%	1 generation	LOEC = 2 ppm NOEC < 2 ppm < 0.01 ppm as ai	1974
	71-4b – SUPPLEMENTAL	98%	22 wks	LOEC = 12 ppm NOEC < 12 ppm	1996[1]

[1] Copies of the Data Evaluation Records for these studies by US EPA were seen, but not the actual studies.

5.2.4 Inhalation toxicity

5.2.4.1 Cage birds

WHO (1989) summarises a report by Brown *et al*. (1968) (not seen by DEW) which indicated that no overt signs of intoxication were observed in canaries, Indian finches and budgerigars continuously exposed for 5 d to dichlorvos vapour at 0.14 mg/m^3. However, in canaries and Indian finches, there was a reduction observed in plasma and brain acetylcholinesterase levels.

5.2.4.2 Birds at a zoo

A report by Haas (1970) suggested that most bird species tolerated exposure to dichlorvos from slow-release strips in a confined room. In one experiment, 18 birds from 5 species in the Wuppertal Zoological Gardens were exposed for 4 weeks (2 fresh strips designed for treating 80 m^3 air space in a 67 m^3 room which was ventilated daily for 30 minutes by opening a window), with observations continued for 10 d after exposure ceased. In a second experiment with 35 birds from 18 species, three similar fresh strips were hung in the same room and exposure continued for up to 7 weeks (10 minutes ventilation per day) followed by 10 d observation. There was no true replication nor untreated controls for comparison, and dichlorvos concentrations in the air were not measured.

Six birds in the second experiment were observed to have ruffled plumage and other symptoms 2 d after treatment commenced, but most subsequently recovered. While some mortalities occurred in both experiments (2 of 18 birds in the first experiment and 5 of 35 birds in the second), at least 3 of these appeared to be due to non-treatment effects. From the limited information available it was concluded that mortality was only elevated among the green avadavats (*Amandava formosa* - 1 out of 3 birds dying in the first experiment and 2 out of 2 in the second, dying in the first 3 days after treatment commenced).

5.2.5 Avian toxicity reported in the field

WHO (1989) summarises several reports in the literature of incidents where deaths of birds occurred following accidental exposure to dichlorvos in grain or feed, water or pellets for animal treatment (the original reports cited in the WHO report were not seen by DEW):

adult mallards feeding near horse mangers containing dichlorvos-treated feed were found dead within a short time;
domestic fowl died within 24 h after picking out dichlorvos pellets from the faeces of a horse dosed with the pellets;
mass poisoning of chickens followed consumption of drinking water contaminated accidentally with dichlorvos;
English game bantams died after eating wheat contaminated with 300 mg dichlorvos/kg wheat.

5.2.6 Conclusions — Avian Toxicity

Dichlorvos rates as highly to very highly toxic (LD50 in the range 10-50 or <10 mg/kg bodyweight, respectively) to birds by a single oral dose, with LD50s ranging from ~5 to 42 mg/kg body weight for all studies (11 species). No full GLP reports of studies meeting modern acute oral toxicity guidelines were available to DEW, but those available included two rated as supplemental by the US EPA. The available results were also consistent with two studies rated as *core* to US EPA Guideline 71-1, not seen by DEW. Studies available to DEW indicate that the LC50 with the standard 8 day dietary exposure test (5 d exposure followed by 3 d observation) ranged from 298 to 568 ppm for Japanese quail and ring-necked pheasant, to >1317 and >5000 ppm for mallard ducks. Studies with domestic fowl exposed to dichlorvos in their diets for 28 d indicated a dietary LC50 value of 500 ppm, but a LOEC for non-lethal effects as low as 30 ppm. Thus the acute/subacute dietary toxicity of dichlorvos to birds ranges from slight (LC50 in the range 1001-5000 ppm) to high toxicity (LC50 in the range 51-500 ppm). A further test not provided to DEW rated as *core* to US EPA Guideline 71-2 apparently indicated much higher toxicity to bobwhite quail, but DEW has not seen the original report for confirmation.

No early life/reproductive studies were provided to DEW, but the 28 d dietary studies with domestic fowls indicated effects such as reduced food consumption and/or depression of egg production at dietary concentrations as low as 30-50 ppm. Toxicity of similar magnitude to these results with 28 d exposure was indicated in a study using bobwhite quail not seen by DEW, but reported on the US EPA Reviewed Studies Database as a *core* study to their Guideline 71-4 (exposure commencing as treated birds approached their first breeding season and observations continued for about 20 weeks, following surviving offspring to 14 d old).

Studies gave some indication of the toxicity of dichlorvos by inhalation, but did not indicate specific values for harmful concentrations. There have been reports of mortality in domestic fowl, mallard ducks and English game bantams arising from accidental exposure to residues in grain or feed, water or pellets present in horse manure, indicating the need for caution in handling and using dichlorvos in situations where birds might be exposed.

5.3 Aquatic toxicity

5.3.1 Fish

5.3.1.1 Acute toxicity of active constituent and formulations to fish

Results of various studies indicating the acute toxicity of dichlorvos (active constituent and various formulations) to fish are summarised in Table 6.4, with the results of additional studies summarised in WHO (1989) listed in Table 6.5. The listed reports generally indicate that dichlorvos is highly toxic (LC50 in the range 0.1-1 mg/L) to moderately toxic (LC50 in the range 1 to 10 mg/L) to fish, with a few reports indicating slight toxicity (LC50 in the range 10-100 mg/L). The range in acute toxicity (LC50) of dichlorvos to fish from these studies was ~0.2 mg/L to >40 mg/L, with the lowest value being 0.122 mg/L for larvae of the herring.

No full GLP (Good Laboratory Practice protocols) reports were provided of studies listed as *supplemental* or *core* under Test Guidelines 72-1 or 72-3 in the US EPA database, but a scientific paper was found reporting a GLP study which DEW rates as *reliable* as an acute estuarine/marine fish toxicity study on the information available (this study is in the AQUIRE database (US EPA, 1999), but was not on the US EPA core/supplemental database). However, the available data are generally consistent with results listed in that database (Table 6.6). The range in acute toxicity from studies classified as *core* studies was 0.17 mg/L to 11.6 mg/L.

Brief additional comments on the reports summarised in Tables 6.4-6.6 follow.

A brief report (Bayer 1980) of a study with a 50EC formulation of dichlorvos (555 g ac/L) indicated that the 96 h LC50 of the product to rainbow trout was 0.93 (95% confidence limits = 0.85-1.04) mg product/L, a dose which would result in a dichlorvos concentration of approximately 0.5 mg ac/L. A similar study (Bayer 1981) with golden orfe indicated a 96 h LC50 of 0.45 (95% confidence limits = 0.40-0.52) mg product/L, a dose which would result in a dichlorvos concentration of approximately 0.2 mg ac/L. Both tests were rated as *acceptable* by DEW (respectively, control + 4 dose levels with 10 or 20 fish at each concentration, and control + 7 dose levels, with 10 fish at each concentration, but concentrations not measured).

Lewallen and Wilder (1962) reported that dichlorvos (evidently active constituent added in acetone) was not lethal to either 1 week old or 1 month old fry of rainbow trout at 1 mg/L, but caused 100% lethality at 10 mg/L. In a paper describing Japanese aquatic toxicity testing methods, Nishiuchi (1974) indicated that the 48 h LC50 of dichlorvos to carp is in the range 0.5-10 mg/L. As both papers only indicate ranges these results are rated as *for information*.

Spehar *et al.* (1981) cited Rath and Misra (1979) (not seen by DEW) as reporting 96 h LC50 values ranging from 1.4 to 1.9 mg/L for dichlorvos to three size groups of Mozambique tilapia, with the smaller fish being more sensitive. Rated by DEW as *for information* as the original paper has not been seen and no details of methodology are available indicated.

Yoshida & Nishimura (1972) indicated the toxicity of dichlorvos or formulations of it to a range of fish species, using methods claimed to follow UK (MAFF) guidelines. However, some important information is unclear, such as details of formulations tested and the units in which the results are presented (evidently mg/L from citations elsewhere of this publication and from other publications containing what appear to be the same data). Hence DEW rates the data as *for information* only. Toxicity values listed included 48 h LC50s for the active constituent to carp and goldfish of >40 and 10-40 mg/L, respectively; and 48 h LC50s for an EC formulation to medaka and weather fish of 18 and 2.2 mg/L (apparently in terms of ac).

An excerpt from Anon (1968) listed 24 h LC50 values for dichlorvos to rainbow trout and bluegill sunfish of 0.5 and 1.0 mg/L, respectively, from studies at the Fish-Pesticide Research Laboratory, US Department of the Interior, Denver, Colorado and Columbia, Missouri. In the absence of additional information, DEW rates these results as *for information* only.

Verma, Tonk and Dalela (1981d) reported a 96 h LC50 for dichlorvos active constituent to carp (3 day old fry) of 0.34 mg/L, based on an experiment where 7 concentrations were tested, with solution renewal every 24 h. Limited information on methodology is presented and solution concentrations were not measured, but DEW regards the study as *acceptable*.

Koesoemadinata (1983) examined the toxicity of a 500 g/L formulation (presumably EC) of dichlorvos to common and Java carp. The 24, 48 and 96 h LC50 values and corresponding 95% confidence intervals for common carp were 3.80 (3.52-4.10), 2.70 (2.41-3.02), 2.30 (2.04-2.59) mg product/L. Those for Java carp were 4.10 (3.90-4.30), 4.00 (3.70-4.40), 3.70 (2.50-3.90) mg product/L, respectively. The concentrations of product for the 96 h LC50s would result in concentrations of approximately 1.15 and 1.85 mg ac/L, respectively. DEW rates the results as *acceptable* (duplicated with at least 5 concentrations plus control with 10 fish per test container, but concentrations not measured).

An excerpt from Alabaster (1969) provided the results of tests conducted at the Salmon and Freshwater Fisheries Laboratory (evidently in the UK), to standardised procedures (presumably UK MAFF). Median lethal concentrations of a formulation containing ~83% dichlorvos to harlequin fish were 12 mg product/L at 24 h and 7.8 mg/L at 48 h. These concentrations would result in dichlorvos concentrations of approximately 10 and 6.5 mg/L, respectively. In the absence of details on the methods used for the tests, DEW rates this item as *for information*.

Pimentel (1971) cited earlier reports as finding a 48 h LC50 from dichlorvos to bluegill sunfish of 0.70 mg/L and 24 h LC50s to bluegill and harlequin fish of 1 mg/L and 10 mg/L, respectively. Kenaga (1979) reported 96 h LC50's for dichlorvos to bluegills and spot of 0.48 mg/L and 0.55 mg/L, respectively. Insufficient experimental details were available for either report, hence they have been rated by DEW as *for information* only.

McHenery *et al.* (1991) reported studies conducted with post yolk sac herring larvae with larvae of the herring. The tests were conducted under static renewal conditions (50% of solution changed every 24 h), with dichlorvos concentrations measured at the start and end of each 24 h period. Mean dichlorvos concentrations at the end of each 24 h period were 87.5% of initial values, indicating relatively slow degradation of dichlorvos under the test conditions (10.3°C, pH 7.9, salinity 34 parts per thousand), presumably due to slower hydrolysis (though favourable pH) and low biological activity at the cool temperature (Sections 5.1 and 5.5). The calculated 12, 24, 48 and 96 h LC50 values (and 95% confidence limits) for dichlorvos to the herring larvae were >1000, 657 (186-890), 240 (192-300) and 122 (95-157) μg/L. DEW notes that this trend of increasing toxicity with increasing time of exposure is relatively steep and appears not to have plateaued. The authors of this published scientific paper state that the study was conducted according to Good Laboratory Practice (GLP) principles; thorough measurements were reported of various parameters (including ac concentration) and control mortality in this experiment was acceptable (they were too high in a similar experiment with yolk sac larvae). DEW therefore considers the study *reliable*.

WHO (1989) summarised further acute fish toxicity data for freshwater and estuarine fish from sources not seen by DEW, as listed in Table 6.5. Studies listed on the US EPA Reviewed Studies database are summarised in Table 6.7. There appears to be some studies in common between the two tables.

5.3.1.2 Chronic toxicity of active constituent and formulations to fish

Verma, Tonk and Dalela (1981d) reported an estimated Maximum Acceptable Toxicant Concentration (MATC) for dichlorvos to carp of 16-20 μg/L, based on the total weight of live fish at 60 days divided by the original number of exposed fry (evidently with exposure continuing under similar conditions of solution renewal). While limited information on methodology is presented and solution concentrations were not measured, DEW will regard the study as *acceptable*.

WHO (1989) cited various papers by Verma *et al.* (1981b,c; 1983, 1984) reporting studies with African catfish exposed to sublethal concentrations of dichlorvos (45, 90 μg/L) for 30 d. Effects were observed on blood chemistry and levels of various enzymes and from the results a No Observed Adverse Effect Concentration of 30 μg/L was derived. It was not clear how this was obtained if only the above 2 doses were tested, but if it is an actual rather than calculated value, the MATC for these studies is 36.7 μg/L. DEW has not seen the original scientific papers and considers the results as *for information* only.

The MATC values from these studies are consistent with the results for rainbow trout listed in the US EPA Reviewed Studies database (Table 6.6 – 61 d MATC = 7.2 μg/L), but lower than the result on the same database for an “early life” study with sheepshead minnow with a shorter exposure duration (34 d MATC = 1329 μg/L).

5.3.1.3 Other data on fish toxicity

In an experiment at the Wuppertal Zoological Gardens described by Haas (1970), mortality of 3 species of fish in aquaria exposed to dichlorvos from slow-release strips in a confined room was similar to that found normally. Three fresh strips designed for treating 80 m^3 air space were hung in a 67 m^3 room which was ventilated daily for 10 minutes. The lids were left off the aquaria and air for the pumps was obtained from the experimental room. Exposure continued for up to 7 weeks followed by 10 d observation. There was no true replication nor untreated controls for comparison, and dichlorvos concentrations in the air were not measured.

Table 6.4. Toxicity to fish - reports seen by DEW.

Species	Rating	Test material & method^1	Toxicity^2	Source
Freshwater species				
Rainbow trout (*Oncorhynchus mykiss*)	ACCEPTABLE	555 g/L; static, nominal; 4-5.5 cm, 1.1-1.5 g	96 h LC50 ≈ 0.5 mg /L	Bayer (1980)
	FOR INFORMATION	Evidently ac; static, nominal	24 h LC50 in the range 1-10 mg/L	Lewallen & Wilder (1962)
	FOR INFORMATION	Not indicated	24 h LC50 = 0.50 mg/L	Anon (1968)
Bluegill sunfish (*Lepomis macrochirus*)	FOR INFORMATION	Not indicated	24 h LC50 = 1.00 mg/L	Anon (1968)
	FOR INFORMATION	Not indicated	48 h LC50 = 0.70 mg/L	Pimentel (1968)
	FOR INFORMATION	Not indicated	96 h LC50 = 0.48 mg/L	Kenaga (1979)
Golden orfe (*Leuciscus idus melanotus*)	ACCEPTABLE	555 g/L; static, nominal; 6-6.6 cm, 2.4-2.7 g	96 h LC50 ≈ 0.2 mg/L	Bayer (1981)
Medaka fish (*Oryzias latipes*)	FOR INFORMATION	EC; static, nominal; 2.5 cm	48 h LC50 = 18 mg/L	Yoshida & Nishimura (1972)
Weather fish (*Misgurnus anguillicaudatus*)	FOR INFORMATION	EC; static, nominal; 10 cm	48 h LC50 = 2.2 mg/L	Yoshida & Nishimura (1972)
Tilapia mozambica	FOR INFORMATION	Presumably ac; static; 3 size ranges	96 h LC50 = 1.4-1.9 mg/L	Rath & Misra (1979)
Goldfish (*Carassius auratus*)	FOR INFORMATION	ac; static, nominal; 4 cm	48 h LC50 = 10-40 mg/L	Yoshida & Nishimura (1972)
Common carp (*Cyprinus carpio*)	ACCEPTABLE	Evidently ac; static, nominal; 3 d old fry	96 h LC50 = 0.34 mg/L 60 d MATC = 16-20 µg/L	Verma, Tonk & Dalela (1981d)
	ACCEPTABLE	500 g/L; static, nominal; ~2 g & 5 cm	96 h LC50 ≈ 1.15 mg/L	Koesoemadinata (1983)
	FOR INFORMATION	Static, nominal; 5 cm	48 h LC50 in the range 0.5-10 mg/L	Nishiuchi (1974)
	FOR INFORMATION	ac; static, nominal; 5 cm	48 h LC50 > 40 mg/L	Yoshida & Nishimura (1972)
Java carp (*Puntius gonionotus*)	ACCEPTABLE	500 g/L; static, nominal; ~2 g & 5 cm	96 h LC50 ≈ 1.85 mg/L	Koesoemadinata (1983)
Harlequin fish (*Rasbora heteromorpha*)	FOR INFORMATION	Purity ~83%; static	48 h LC50 ≈ 6.5 mg/L	Alabaster (1969)
Estuarine/marine species				

Herring (*Clupea harengus*)	RELIABLE	500 EC formulation (50.84% ac)	96 h LC50 to larvae = 0.122 mg ac/L	McHenery *et al.* (1991)
Spot (*Leiostomus xanthurus*)	FOR INFORMATION	Presumably ac	96 h LC50 = 0.55 mg/L	Kenaga (1979)

[1] Exposure conditions static or flow-through, concentrations nominal or measured; size of fish. [2] DEW recognises that formulations may differ in toxicity from the active ingredient because of the presence of other ingredients, but for comparative purposes has converted the toxicity values to the equivalent concentration of ac.

Table 6.5. Toxicity to fish - reports listed in WHO (1989) not seen by DEW.

Species	Size	Toxicity	Original source
Freshwater species			
Bluegill sunfish (*Lepomis macrochirus*)	1.5 g	96 h LC50 = 0.9 mg/L	Johnson & Finley (1980)
Cutthroat trout (*Salmo clarkii*)	2.5 g	96 h LC50 = 0.2 mg/L	
Lake trout (*Salvelinus namaycush*)	0.3 g	96 h LC50 = 0.2 mg/L	
Mosquito fish (*Gambusia affinis*)	0.2 g	96 h LC50 = 5.3 mg/L	
Fathead minnow (*Pimephales promelas*)	0.7 g	96 h LC50 = 12 mg/L	
Carp (*Cyprinus carpio*)	6 g, 8 mm	24 h LC50 = 20 mg/L	Yamane *et al.* (1974)
Snakehead (*Ophiopcephalus punctatus*)	40-55 g	96 h LC50 = 2.3 mg/L	Verma *et al.* (1981a)
Singii (*Saccobranchus fossilis*)	5-10 g	96 h LC50 = 6.6 mg/L	Verma *et al.* (1982a)
Walking catfish (*Clarias batrachus*)	26-31 g	96 h LC50 = 8.9 mg/L	Verma *et al.* (1983)
African catfish (*Mystus vittatus*)	6-10 g	96 h LC50 = 0.5 mg/L	Verma *et al.* (1980, 1981a)
	not stated	30 d NOAEC[1] = 30 μg/L, 30 d LOEC = 45 μg/L	Verma *et al.* (1981b,c; 1983, 1984)
Estuarine/marine species			
American eel (*Anguilla rostrata*)	0.14 g	96 h LC50 = 1.8 mg/L	Eisler (1970)
Mummichog (*Fundulus heteroclitus*)	1.7 g	96 h LC50 = 2.7 mg/L	
Striped killifish (*Fundulus majalis*)	0.92 g	96 h LC50 = 2.3 mg/L	
Atlantic silverside (*Menidia menidia*)	0.8 g	96 h LC50 = 1.3 mg/L	
Striped mullet (*Mugil cephalus*)	1-6 g	96 h LC50 = 0.23 mg/L	
Northern puffer (*Sphaeroidus maculatus*)	100 g	96 h LC50 = 2.3 mg/L	
Bluehead (*Thalassoma bifasciatum*)	5.4 g	96 h LC50 = 1.4 mg/L	

[1] No Observed Adverse Effect Concentration

5.3.1.4 Use of dichlorvos in fish farming

Dichlorvos is much less toxic to fish species such as salmon than it is to fish parasites such as the salmon louse *Lepeophtheirus salmonis* (24-48 h LC50 < 5 μg/L to 40 μg/L according to the US EPA AQUIRE database) and the freshwater isopod *Alitropus typus* (48 h LC50 = 9.25 μg/L - Nair and Nair 1982). Hence dichlorvos has been widely used to control ectoparasites in finfish culture, though this use may have declined due to problems with louse resistance (Ross 1989) and environmental concerns (Davies 1995). Trichlorfon, which degrades to dichlorvos in water, has also been used for the same purpose (Samuelsen 1987). The recommended treatment in the UK involved surrounding the fish pen with a tarpaulin to restrict through flow, adding a diluted dichlorvos formulation to reach an active ingredient concentration of 1 mg/L, and maintaining the tarpaulin in place for 1 hour before the treatment solution is released, though treatment methodology, duration and frequency varied considerably (Ross 1989). By this method, a treated volume of approximately 500-1000 m^3 of seawater containing 1 mg/L dichlorvos is released per cage.

Reports of serious fish losses during treatment with dichlorvos (and trichlorfon) and recognition of the potential for environmental harm from careless or inappropriate use of dichlorvos led to action to control use of these substances (Egidius and Moster 1987; Samuelsen 1987; Ross 1989; Dobson and Tack 1991; McHenery *et al.* 1992). In Scotland, Environmental Quality Standards were proposed to regulate the amount of dichlorvos which could be administered each day per site in sea lochs (McHenery *et al.* 1992). The values to be set were an average annual value of 40 ng/L (1/100 X 96 h LC50 value for the sand shrimp, or 1/5 X MATC for effect on lobster

Table 6.6. Toxicity to fish - reports listed on the US EPA Reviewed Studies Database.

Species	Size	Guideline	Conditions	Test material[1]	Toxicity (mg test material/L)	NOEC	date
Freshwater species							
Bluegill sunfish (*Lepomis macrochirus*)	1.5 g	72-1 – CORE	Static	100	96 h LC50 = 0.87 (0.7-1.0) mg/L	N.R.	1986[3]
	1.7 g	72-1 – SUPP	Static	98.1	64 h LC50 = 1.35 mg/L	< 1.35	1968
	0.4 g	72-1 – SUPP	Static	0.04	96 h LC50 > 180 mg/L (>0.072 mg ac/L)	< 180	1976
	0.8 g	72-1 – SUPP	Static	0.46	96 h LC50 = 0.8 (0.6-1.0) mg/L (~0.0037 mg ac/L)	< 0.32	1976
	0.09 g	72-1 – CORE	Flow-through	4-E (42.4% ac)	96 h LC50 = 4.3 (3.7-4.9) mg/L (~1.8 mg ac/L)	< 0.9	1994
Cutthroat trout (Oncorhynchus clarkii)	0.17 g	72-1 – SUPP	Static	90	96 h LC50 = 0.213 (0.141-0.321) mg/L	N.R.	1973
	2.5 g	72-1 – CORE	Static	100	96 h LC50 = 0.17 (0.14-0.206) mg/L	N.R.	1986[3]
Fathead minnow (Pimephales promelas)	0.7 g	72-1 – CORE	Static	100	96 h LC50 = 11.6 (7.8-17.2) mg/L	N.R.	1986[3]
Guppy (Poecilia reticulata)	3.0 g	72-1 – SUPP	Static	FORM	24 h LC50 = 5.81 mg/L	N.R.	1968
Lake trout (Salvelinus namaycush)	4.2 g	72-1 – SUPP	Static	90	96 h LC50 = 0.183 (0.093-0.363) mg/L	N.R.	1973
	0.3 g	72-1 – CORE	Static	100	96 h LC50 = 0.187 (0.11-0.32) mg/L	N.R.	1986[3]
Mosquitofish (Gambusia affinis)	0.2 g	72-1 – SUPP	Static	100	96 h LC50 = 5.27 (2.6-10.4) mg/L	N.R.	1986[3]
Rainbow trout (Oncorhynchus mykiss)	N.R.	72-1 – SUPP	Static	100	96 h LC50 = 0.1 mg/L	N.R.	N.R.
	2.3 g	72-1 – SUPP	Static	98.1	96 h LC50 = 0.1 mg/L	< 0.10	1968
	1.0 g	72-1 – SUPP	Static	100	24 h LC50 = 0.5 mg/L	N.R.	1986
	0.28 g	72-1 – SUPP	Flow-though	4-E (42.4% ac)	96 h LC50 = 0.75 (0.6-0.9) mg/L (~0.32 mg ac/L)	0.25	1994
	Early Life	72-4a – CORE	Flow-though	98	61 d LOEC = 10.1 µg/L 61 d MATC = 7.2 µg/L[2]	5.2	1995
Estuarine/marine species							
Atlantic silverside (*Menidia menidia*)	2.1 g	72-3 – SUPP	Static	90	24 h LC50 = 9.6 mg/L	N.R.	1964
Mummichog (Fundulus heteroclitus)	4.0 g	72-3 – SUPP	Static	90	96 h LC50 = 3.2 mg/L	N.R.	1964
Northern pipefish (*Syngnathus fuscus*)	1.1 g	72-3 – SUPP	Static	90	96 h LC50 = 2.2 mg/L	N.R.	1964
Spot (Leiostomus xanthurus)	N.R.	72-3 – SUPP	Static	90	24 h LC50 < 1.0 mg/L	0.1	1963
	Juv	72-3a – SUPP	Flow-though	98	48 h LC50 = 0.32 mg/L	N.R.	1986
Striped killifish (*Fundulus majalis*)	0.9 g	72-3 – SUPP	Static	90	96 h LC50 = 2.3 mg/L	N.R.	1964
Striped mullet (*Mugil cephalus*)	Juv	72-3a – SUPP	Flow-though	98	48h LC50 = 0.32 mg/L	N.R.	1986
Sheepshead minnow (Cyprinodon variegatus)	Early Life	72-4a – CORE	Flow-though	98	34 d LOEC = 1840 µg/L 34 d MATC = 1329 µg/L[2]	960	1995

[1] % dichlorvos or other indication of formulation or ac used. [2] Calculated by DEW. [3] These results appear to be the same as those ascribed to Johnson & Finley (1980) in Table 6.5, evidently from a later publication of the data. larvae acetylcholinesterase levels over 23 d exposure) and a 24 h value of 600 ng/L (1/5 X MATC for effect on lobster larvae acetylcholinesterase levels over 24 h exposure).

5.3.2 Aquatic invertebrates

5.3.2.1 Acute toxicity of active constituent and formulations to aquatic invertebrates

Results of various studies indicating the acute toxicity of dichlorvos (active constituent and various formulations) to aquatic invertebrates are summarised in Table 6.7, with the results of additional studies summarised in WHO (1989) listed in Table 6.8. The range in acute toxicity (LC50) of dichlorvos to aquatic invertebrates from these studies was 0.066 μg/L to 881 μg/L for exposure of 24-96 h, indicating that dichlorvos was very highly toxic (LC50 < 0.1 mg/L) to highly toxic (LC50 in the range 0.1 to 1 mg/L) to the species tested.

No full GLP (Good Laboratory Practice protocols) reports were provided of studies listed as *supplemental* or *core* under Test Guidelines 72-2 or 72-3 in the US EPA database, but DEW rates the one GLP study which was provided as an *acceptable* study of acute freshwater invertebrate toxicity (cf. Guideline 72-2). On the information available, DEW also rates a scientific paper reporting a GLP study as *reliable* as an evaluation of acute freshwater invertebrate toxicity: this study is in the AQUIRE database (US EPA 1999), but does not appear to be listed on the US EPA core/supplemental database (US EPA 1998). With one exception the available data are consistent with results listed in the US EPA database (Table 6.9). The range in acute toxicity from studies classified as *core* studies was 0.066 μg/L to 1.0 μg/L, with the exception of an amphipod study where a much higher LC50 value was listed, which DEW suspects is a database entry error.

WHO (1989) described the acute toxicity of dichlorvos to aquatic insects and crustaceans as extremely high and notes that freshwater crustaceans are particularly sensitive. The review adds that as may be expected from an organophosphate insecticide, aquatic invertebrates are about three orders of magnitude more susceptible to dichlorvos than are fish. McHenery *et al.* (1992) comment in regard to fisheries use that because of dispersion dichlorvos in the water column, planktonic, rather than benthic, organisms are at greatest risk: DEW notes that this is probably also true of water contamination arising by other means, due to the water solubility of dichlorvos.

WHO (1989) also noted a report by Grahl *et al.* (1981) that treating eutrophic carp ponds with 325 μg/L killed *Cladocera* (predominantly *Bosmina* and *Daphnia* species) and decreased *Copepoda* (mainly *Cyclops*). However, the total plankton biomass changed only slightly, as the decrease was offset by increased development of *Rotatoria* and phytoplankton.

Brief additional comments on the reports summarised in Tables 6.7-6.9 follow.

Table 6.7a. Toxicity to aquatic invertebrates - reports seen by DEW.

Species	Rating	Test material & method[1]	Toxicity[2]	Source
Freshwater species				
Water flea (*Daphnia magna*)	ACCEPTABLE	ac; static, nominal; juveniles	48 h EC50 = 0.19 µg/L MATC = 0.075 µg/L	Heimbach (1986)
	RELIABLE	ac; static renewal, stock solution/1st dilution measured	21 d NOEC = 0.00016 µg/L (time to 1st brood); 21 d NOEC = 0.00256 µg/L (adult, juvenile mortality; cumulative reproduction)	Vial (1992)
Water flea (*Daphnia pulex*)	FOR INFORMATION	not indicated	48 h EC50 = 0.26 µg/L	Pimentel (1971)
	FOR INFORMATION	ac; static, nominal; 11 cm adult	3 h EC50 = 2800 µg/L	Yoshida & Nishimura (1972)
Water flea (*Moina macrocopa*)	FOR INFORMATION	ac; static, nominal; 11 cm adult	3 h EC50 = 3500 µg/L	Yoshida & Nishimura (1972)
Water flea (*Simocephalus serrulatus*)	FOR INFORMATION	not indicated	48 h EC50 = 0.066 µg/L	Pimentel (1971)
Crayfish (*Procambarus clarkii*)	FOR INFORMATION	ac; static, nominal; 11 cm adult	48 h LC50 = 880 µg/L	Yoshida & Nishimura (1972)
Freshwater prawn (*Macrobrachium lamarrei*)	FOR INFORMATION	not indicated	96 h LC50 = 881 µg/L	Nikunen *et al.* (1990)
	FOR INFORMATION	not indicated	72 h LC50 = 5.8 µg/L	Nikunen *et al.* (1990)
Isopod (*Alitropus typus*)	ACCEPTABLE	ac; static, nominal; juveniles	48 h LC50 = 9.25 µg/L	Nair & Nair (1982)
Estuarine/marine species				
Lobster (*Homarus gammarus*)	RELIABLE	Stage 5 larvae, static renewal, measured concentrations	96 h LC50 = 5.7 µg ac/L	McHenery *et al.* (1991)
	ACCEPTABLE	Stage 4 larvae, static renewal	96 h LC50 = 8.7 µg/L; 23 d LC50 = 1.25 µg/L, 23 d NOEC = 0.63 µg/L (multiple effects)	McHenery *et al.* (1996)
Pink shrimp (*Palaemon serratus*)	FOR INFORMATION	not translated	96 h LC50 = 6 µg/L, respectively	Messager & Esnault (1992)
Amphipods	FOR INFORMATION	not indicated in citation by McHenery *et al.* (1996)	96 h LC50 = 9 µg/L	McHenery *et al.* (1990)
Barnacle nauplii	FOR INFORMATION		96 h LC50 = 4500 µg/L	
Planktonic copepods	FOR INFORMATION		24 h LC50 = 141 µg/L	
Mussels (*Mytilus edulis*)	FOR INFORMATION		24 h LC50 = 1000 µg/L	

[1] Exposure conditions static or flow-through, concentrations nominal or measured; size. [2] DEW recognises that formulations may differ in toxicity from the active ingredient because of the presence of other ingredients, but for comparative purposes has converted the toxicity values to the equivalent concentration of ac.

Heimbach (1986) [ECRP Submission – Protected Registration Data] described a study of the acute toxicity of dichlorvos (ac) to the water flea *Daphnia magna* conducted according to OECD Guideline 202 (Guideline for Testing of Chemicals, *Daphnia* sp. – Acute Immobilisation Test and Reproduction Test, Part I, adopted 4 April 1984), with a 48 h exposure period under static conditions to nominal concentrations of 0.010-0.320 μg ac/L (temperature 20.3°C, pH 8.0). The resulting EC50s (immobilisation) were 0.3-0.5 μg ac/L at 24 h and 0.19 (95% confidence limits 0.15-0.25) μg ac/L at 48 h, and the NOEC and LOEC were 0.056 μg ac/L and 0.1 μg ac/L, respectively. This study is rated as *acceptable* by DEW (the study appears satisfactory, except that concentrations in neither the stock nor test solutions were measured).

Table 6.7b. Toxicity to aquatic invertebrates - reports seen by DEW.

Aquatic insects				
Water bug (*Sigara substriata*)	FOR INFORMATION	EC formulation; static, nominal; 6 mm early stage larvae	48 h LC50 = 65 μg/L	Nishiuchi (1981)
Water bug (*Micronecta sedula*)	FOR INFORMATION	EC formulation; static, nominal; 3.2 mm early stage larvae	48 h LC50 = 55 μg/L	
Mayfly (*Cloeon dipterum*)	FOR INFORMATION	EC formulation; static, nominal; 9.3 mm early stage larvae	48 h LC50 = 28 μg/L	
Dragonfly (*Orthetrum albistylum speciosum*)	FOR INFORMATION	EC formulation; static, nominal; 2.5 cm late stage larvae	48 h LC50 = 14 μg/L	
Dragonfly (*Sympetrum frequens*)	FOR INFORMATION	EC formulation; static, nominal; 2.1 cm late stage larvae	48 h LC50 = 100 μg/L	

Table 6.8. Toxicity to aquatic invertebrates - reports listed in WHO (1989) not seen by DEW.

Species	Toxicity	Source
Freshwater		
Water flea (*Daphnia pulex*)	48 h EC50 = 0.07 μg/L	Johnson & Finley (1980)
Water flea (*Simocephalus serrulatus*)	48 h EC50 = 0.28 μg/L	
Amphipod, scud (*Gammarus lacustris*)	96 h LC50 = 0.5 μg/L	
Estuarine/marine		
Sand shrimp (*Crangon septemspinosa*)	48 h LC50 = 12 μg/L; 96 h LC50 = 4 μg/L	Eisler (1969)
Grass shrimp (*Palaemonetes vulgaris*)	48 h LC50 = 300 μg/L; 96 h LC50 = 15 μg/L	
Hermit crab (*Pagurus longicarpus*)	48 h LC50 = 52 μg/L; 96 h LC50 = 45 μg/L	

Yoshida and Nishimura (1972) indicated the toxicity of dichlorvos to a range of aquatic invertebrates, using methods claimed to follow UK (MAFF) guidelines. However, some important information was unclear, hence DEW rates the data as *for information* only. The 3 h EC50s for the active constituent to the water fleas *Daphnia pulex* and *Moina macrocopa* were 2800 and 3500 μg/L, respectively; and the 72 h LC50 of the active constituent to adults of the freshwater crayfish *Procambarus clarkii* was 880 μg/L.

Nishiuchi (1981) presented the results of tests of the toxicity of various chemicals to a range of aquatic insects. 48 h LC50 values with a dichlorvos EC formulation ranged from 0.028 mg ac/L for early stage larvae of the mayfly *Cloeon dipterum* to 0.14 mg ac/L for late stage larvae of the dragonfly *Orthetrum albistylum speciosum* (Table 6.7b). Experimental details are unclear and DEW rates these results as *for information* only.

Pimentel (1971) cited Sanders and Cope (1966) as finding a 48 h EC50 from dichlorvos to the water fleas *Simocephalus serrulatus* and *Daphnia pulex* of 0.066 μg/L and 0.26 μg/L, respectively, but these values are listed in the reverse order on the US EPA Reviewed Studies Database, where both are indicated as *core* studies.. Nikunen *et al.* (1990) cite Omkar and Shukla (1985) as reporting a 96 h LC50 of 881 μg/L to the freshwater prawn *Macrobrachium* *lamarrei* and Mary *et al.* (1986) as reporting much lower 1, 2 and 3 d LC50 values of 13.1, 8.3 and 5.8 µg/L, respectively.

Table 6.9. Toxicity to aquatic invertebrates - reports listed on the US EPA Reviewed Studies Database.

Species	**Size**	**Guideline**	**Conditions**	**Test material[1]**	**Toxicity (mg test material/L)**	**NOEC**	**date**
Freshwater species							
Water flea (*Daphnia magna*)	N.R.	72-2 – CORE	Static	0.46	48 EC50 = 1.0 (0.8-1.4) µg/L	75 µg/L	1976
Water flea (Daphnia pulex)	1st instar	72-2 – CORE	Static	100	48 h EC50 = 0.066 (0.05-0.09) µg/L	N.R.	1986[2]
Water flea (Simocephalus serrulatus)	1st instar	72-2 – CORE	Static	100	48 h EC50 = 0.26 (0.16-0.42) µg/L	N.R.	1986[2]
Amphipod, scud (Gammarus lacustris)	Adult	72-2 – SUPP	Static	100	96 h LC50 = 0.50 (0.37-0.70) µg/L	N.R.	1986[2]
Amphipod, scud (Gammarus fasciatus)	N.R.	72-2 – CORE	Static	Tech.	96 h LC50 = 400,000 (320,000-490,000) µg/L[5]	N.R.	1972
Mud snail (Massa obsoleta)	0.63 g	72-2 – SUPP	Static	90	96 h LC50 = 25.7 µg/L	N.R.	1964
Stone fly (Pteronarcys californica)	Year Class 2	72-2 – CORE	Static	100	96 h LC50 = 0.10 (0.07-0.15) µg/L	N.R.	1986
Estuarine/marine species							
Pink shrimp (*Penaeus duorum*)	Juvenile	72-3 – SUPP	Flow-through	98	48 H LC50 = 24 µg/L	N.R.	1986
Shore (grass) shrimp (Palaemonetes vulgaris)	0.8 g	72-2[4] – SUPP	Static	N.R.	96 h LC50 = 15 µg/L	N.R.	1969[3]
Sand shrimp (*Crangon septemspinosa*)	N.R.	72-3 – SUPP	Static	N.R.	96 h LC50 = 4 µg/L	N.R.	1969[3]
Hermit crab (*Pagurus longicarpus*)	N.R.	72-3 – SUPP	Static	N.R.	96 h LC50 = 45 µg/L	N.R.	1969[3]
Eastern oyster (*Crassostrea virginica*)	Spat	72-3 – CORE	Flow-through	98	96 h LC50 = 1000 µg/L	N.R.	1986

[1] % dichlorvos or other indication of formulation or ac used. [2] These results appear to be the same as those ascribed to Johnson & Finley (1980) in Table 6.8, evidently from a later publication of the data. [3] These results appear to be the same as those ascribed to Eisler (1969) in Table 6.8. [4] This is the guideline indicated on the database: DEW understands that this species is estuarine, but has a high tolerance for freshwater. [5] DEW suspects that this value is a mis-entry and should be 0.4 µg/L, corresponding to an entry in Nikunen *et al.* (1990).

Nair and Nair (1982) reported studies of the toxicity of dichlorvos and other insecticides to juveniles of the freshwater isopod *Alitropus typus*, a fish parasite. A static bioassay procedure was used (5 concentrations selected after a range-finding test, 10 juveniles per concentration), but concentrations were not measured, and DEW rates this report as *acceptable*. The 48 h LC50 to this species was found to be 9.25 µg/L as technical dichlorvos. The authors commented that this value is much lower than the toxicity reported for some freshwater fishes, and that while a similar concentration has also been reported to eradicate some predacious insects, food organisms such as *Cyclops*, *Ceriodaphnia*, *Diaptomus* and *Brachionus* are not affected by 500 µg/L or lower (however, DEW notes that the data in Tables 6.7-6.9 show dichlorvos is in fact very highly toxic to many aquatic invertebrate species). According to the US EPA AQUIRE database, dichlorvos is also very highly toxic to the salmon louse *Lepeophtheirus salmonis* (24-48 h LC50 < 5 µg/L to 40 µg/L). Hence dichlorvos has been used as a selective poison in fish farming.

Messager and Esnault (1992) indicated that among crustacean from the local environment in seawater used for rearing rainbow trout, the pink shrimp *Palaemon serratus* was found to be particularly susceptible to dichlorvos, with 24 h, 48 h and 96 h LC50s of 36, 15 and 6 µg/L, respectively. In the absence of a translation of the full scientific article, DEW rates this report as *for information*.

McHenery *et al.* (1991) reported studies conducted with stage 5 larvae of the lobster *Homarus gammarus*, described as the “transitional” stage at which the animals adapt from a pelagic (upper layers of the open sea) to benthic (bottom of the sea) existence. The tests were conducted under static renewal conditions (50% of solution changed every 24 h), with dichlorvos concentrations measured at the start and end of each 24 h period. Mean dichlorvos concentrations at the end of each 24 h period were 98.8% of initial values, indicating surprisingly slow degradation of dichlorvos under the test conditions (10.3°C, pH 7.9, salinity 34 parts per thousand; 87.5% of initial concentrations were found under similar conditions with a herring study - Section 6.3.1.1). The calculated 12, 24, 48 and 96 h LC50 values (and 95% confidence limits) for dichlorvos to the herring larvae were 53.1 (45-62.6), 28.3 (24.2-33.2), 10.8 (9.6-12.2) and 5.7 (4.6-7) μg ac/L, again showing a steep rise in toxicity with time, without a plateau being reached. The 96 h EC50 for behaviour/activity effects was 3.3 μg ac/L and the corresponding NOEC was 1.56 μg ac/L, but the authors commented that lobsters exposed even to this concentration appeared to have difficulty completing ecdysis and suggested a possible toxicity threshold between 0.78 and 1.56 μg/L.

With 24 h exposure in the above experiment, acetylcholinesterase activity was significantly lower than the control group at 10 and 100 μg ac/L, with 50% inhibition of acetylcholinesterase activity estimated to occur at 2.7 μg ac/L (activity was significantly higher at 0.01 μg ac/L, evidently hormesis– i.e. an effect where a toxic substance acts like a stimulant in small doses, but is an inhibitor in large doses). All animals exposed to 10 μg ac/L were still surviving at that time, making this enzyme system potentially useful in assessing exposure to the insecticide. The authors of this published scientific paper claim the study was conducted according to GLP principles; thorough measurements were reported of various parameters (including ac concentration) and control mortality in this experiment was acceptable. DEW therefore considers the main study *reliable*.

McHenery *et al.* (1996) reported a 96 h LC50 of 8.7 μg/L from a further experiment with stage 4 of the same lobster species (similar procedures to the above paper, but no details of dichlorvos concentration measurements were reported - rated as *acceptable* by DEW). They cite McHenery *et al.* (1990) as finding LC50s for dichlorvos to amphipods, barnacle nauplii, planktonic copepods (taxonomic names not indicated) and mussels (*Mytilus edulis*) of 9 μg/L (96 h), 4500 μg/L (96 h), 141 μg/L (24 h) and 1000 μg/L (24 h), respectively (rated as *for information* in the absence of the original paper).

WHO (1989) summarised further acute toxicity data for freshwater and estuarine aquatic invertebrates from sources not seen by DEW, as listed in Table 6.8, several of which appear to be common to the US EPA Reviewed Studies Database.

5.3.2.2 Chronic toxicity of active constituent and formulations to aquatic invertebrates

Vial (1992) [ECRP Submission – Protected Registration Data] reported a study of the chronic/reproductive toxicity of dichlorvos (technical) to the water flea *Daphnia magna* conducted according to OECD Guideline 202 (Guideline for Testing of Chemicals, *Daphnia* sp. – Acute Immobilisation Test and Reproduction Test, Part II, 1984, modified according to OECD-ringtest 1985-86). Daphnids were exposed to nominal concentrations of dichlorvos of 0.00001-0.00256 μg/L under semi-static conditions (thrice weekly renewal) for 21 d. Measured concentrations in the stock solution (nominally 10 mg/L) and first dilution (0.01 mg/L) at days 0, 7, 14 and 21 varied between 67-83% (mean 74.9%) of nominal in the stock solution and 65-131% (mean 100.5%) of nominal in the first dilution. There were no treatment related mortalities (immobilisation) of adults at any of the concentrations tested (NOEC for adult immobilisation = 0.00256 μg/L). The data for total cumulative number of young were analysed by nonparametric statistical methods as they were not normally distributed, the test indicating a NOEC of 0.00256 μg/L. There were no dead young, but there was a significant effect of dichlorvos on the length of time for the appearance of the first brood (NOEC = 0.00016 μg/L, LOEC = 0.00064 μg/L, EC50 > 0.00256 μg/L – 10/10 daphnids having brooded before day 10 in the control and 10/10 brooding on or after day 12 at the highest rate). DEW rates this report as *reliable*, given that low concentrations in all test solutions could not have been accurately measured.

McHenery *et al.* (1996) reported a 23 d LC50 for stage 4 lobster larvae of 1.25 μg/L and 23 d NOEC of 0.63 μg/L. 100% mortality occurred by 12 d at 2.5-10 μg/L, compared to 29% mortality by 23 d at 1.25 μg/L and comparable mortality to the control (3/24 larvae) at 0.08-0.63 μg/L. Progressive behaviour/activity changes before death with exposure to 2.5-10 μg/L were not evident at lower concentrations. At the end of the exposure period, 10 larvae (or half the survivors) from each treatment were assayed for acetylcholinesterase activity: this indicated significantly lower levels than the control with exposure to ≥ 0.31 μg/L. Most or all remaining animals survived when placed in flowing sea water in recovery tanks for 11 d post exposure, though with most treatments acetylcholinesterase activities had not fully recovered to the control level. The study appears to have been well conducted, but details such as concentration measurements (if they were made) have not been provided, hence it is rated by DEW as *acceptable*.

No chronic/reproductive daphnid or mysid studies (Test Guideline 72-4) were reported on the US EPA supplemental/core studies database (US EPA 1998).

5.3.2.3 Other data on aquatic invertebrate toxicity

WHO (1989) cited Kuwabara *et al.* (1980) as reporting no effect at 10 mg dichlorvos/L in an aqueous system on the "hatchability" of brine shrimp (*Artemia salina*) dry eggs. WHO (1989) also cited Omkar and Shukla (1984) as reporting biochemical effects in freshwater prawns (*Macrobrachium lamarrei*) exposed to dichlorvos concentrations of 0.31 or 0.62 mg/L for 96 h. Nikunen *et al.* (1990) cite Srinavasamoorthy *et al.* (1986) as reporting biochemical effects in the freshwater mussel *Lamellidens marginalis* from dichlorvos at 5 mg/L for 2 d.

In tests with small numbers of animals intended to imitate conditions after treatment with trichlorfon or dichlorvos on a fish farm rather than estimate LC50 values, Egidius and Moster (1987) showed lobster (*Homarus gammarus*) was by far the most susceptible to =both substances of several invertebrate species tested. Adult lobsters survived 24 h exposure to dichlorvos at 10 µg/L, but died within 30 minutes at 1000 µg/L, after 3.5 h at 500 µg/L, and at or within 7.5 h at 100 µg/L. The other species tested with dichlorvos were the European rock crab *Cancer pagurus*, (the 4 crabs tested survived 10 h at 1000 µg/L, but one out of 4 crabs died with 24 h exposure at 1000 µg/L); European shore crab *Carcinus maenas* (crabs survived 10 h at 1000 µg/L) and common bay mussel *Mytilus edulis* (mussels survived 24 h at both 100 and 1000 µg/L).

5.3.3 Algae and aquatic plants

Only one study pertaining to algae was seen by DEW, but the study was rated by DEW as *reliable*. The result (EC50 based on 96 h biomass production = 52.8 mg ac/L for *Scenedesmus subspicatus*) is consistent with values listed by the US EPA (48 h EC50 = 14-100 mg/L for four algal or diatom species - studies rated as *supplemental* rather than *core*) and indicates dichlorvos is only slightly toxic to algae (EC50 in the range 10-100 mg/L) and typical of organophosphate insecticides. Somewhat higher toxicity (50% growth inhibition at 3.5 mg/L) was indicated to the unicellular alga *Euglena gracilis* in a study by Butler (1977) reported by WHO (1989). Phytoplankton (mainly *Scenedesmus* and *Pediastrum* species) were unaffected by treatment of eutrophic ponds at 0.325 mg/L, a dose which killed *Cladocera* (WHO 1989, citing Grahl *et al.* 1981). No studies with dichlorvos and aquatic plants are available, but DEW expects similar toxicity to aquatic plants to that found with algae. These results are summarised in Tables 6.10-6.11 and the study seen by DEW is discussed further below.

Heimbach (1985) reported an algal growth inhibition test based on the relevant ISO Guideline (June 1984) and OECD Guideline No. 201 (Alga, Growth Inhibition Test, June 1984), evaluating the toxicity of dichlorvos technical to the freshwater green alga *Scenedesmus subspicatus*. The pH of the medium at test initiation was 8.1, i.e. alkaline conditions (temperature 22.0-22.5°C), favouring hydrolysis (Section 5.1). Hence it is likely that a high percentage (possibly > 75%) of the substance degraded over the 96 h duration of the test, thus the test results are in terms of nominal initial concentrations. The 96 h EC50s for biomass increase (E_bC50) and growth rate (E_rC50) were 52.8 mg ac/L and 159.6 mg ac/L, respectively, and the corresponding NOECs were 18 mg ac/L and 32 mg ac/L. DEW rates this study as *reliable* (lack of measured concentrations acceptable given the difficulty of measuring concentrations in media and 96 h exposure adequate given expected rate of degradation).

Table 6.10. Toxicity to algae - reports seen by DEW.

Species	Rating	Test material & method	Toxicity	Source
Freshwater crustacea				
Green alga (Scenedesmus subspicatus)	RELIABLE	ac; static, nominal	96 h E_bC50[1] = 52.8 mg/L 96 h E_rC50[1] = 159.6 mg/L	Heimbach (1985)

[1] E_bC50, E_rC50 = EC50 for biomass and growth rate, respectively, both as nominal initial concentrations.

Table 6.11. Toxicity to algae - - reports listed in WHO (1989) not seen by DEW.

Species	Toxicity	Source
Unicellular alga (*Euglena gracilis*)	50% growth inhibition dose = 3.5 mg/L	Butler (1977)

Table 6.11. Toxicity to algae - reports listed on the US EPA Reviewed Studies Database.

Species	Guideline	Conditions	Test material[1]	Toxicity (mg test material/L)	date
Estuarine/marine species					
Golden alga (Isochrysis galbana)	122-2 – SUPP	Static	98	48 EC50 = 14 mg/L	1986

Green alga (Dunaliella tertiolecta)				48 h EC50 = 100 mg/L	
Diatom (Skeletonema costatum)				48 h EC50 = 28 mg/L	
Diatom (Thalassiosira pseudonana)				48 h LC50 = 17 mg/L	

[1] % dichlorvos or other indication of formulation or active constituent used.

5.3.4 Amphibians

Yoshida and Nishimura (1972) indicated the toxicity of an EC formulation of dichlorvos to tadpoles of the toad *Bufo bufo japonicus*, using methods claimed to follow UK (MAFF) guidelines. The composition of the EC was not indicated, but it appears that the 48 h LC50 to the toad of 76 mg/L was expressed in terms of ac concentration. DEW rates the data as *for information* only. The US EPA AQUIRE database lists 48 h LC50 values to the frog species *Rana hexadactyla* and *Rana limnocharis* of 9.7 and 10 mg/L, respectively, but DEW has not seen the original references for these studies. This limited evidence suggests that dichlorvos is slightly to moderately toxic to amphibians (LC50 in the range 10-100 mg/L or 1-10 mg/L, respectively), i.e. comparable toxicity to that to fish.

5.3.5 Conclusions – Aquatic Toxicity

5.3.5.1 Fish

The range in acute toxicity (LC50) of dichlorvos (as active constituent or various formulations) to a wide range of freshwater and estuarine/marine species of fish from various studies was ~0.2 mg/L to >40 mg/L. In general, studies show that dichlorvos is highly toxic (LC50 in the range 0.1-1 mg/L) to moderately toxic (LC50 in the range 1 to 10 mg/L) to fish, with a few reports indicating slight toxicity (LC50 in the range 10-100 mg/L). No full GLP reports of fish studies listed as *core* or *supplemental* by the US EPA were provided, but DEW found a scientific paper reporting a GLP study which was rated as a *reliable* study of acute estuarine/marine fish toxicity (cf. US EPA Test Guideline 72-3). The available data are consistent with studies listed as *core* under Test Guideline 72-1 by the US EPA (range 0.17 mg/L to 11.6 mg/L). Data available on the chronic toxicity of dichlorvos indicate a 60 day Maximum Acceptable Toxicant Concentration (MATC) to carp of 16-20 µg/L, and a 30 day MATC for African catfish of 36.7 µg/L. These MATC values are comparable with a 61 d MATC = 7.2 µg/L for rainbow trout listed by the US EPA, but lower than a 34 d MATC = 1329 µg/L listed for sheepshead minnow (both listed as *core* studies). Various studies show biochemical effects on fish at sublethal concentrations. However, as dichlorvos was found to be much less toxic to fish species such as salmon than to parasites such as salmon louse, it has been used widely to control parasites in finfish culture, though not yet in Australia.

5.3.5.2 Aquatic invertebrates

The range in acute toxicity (LC50) of dichlorvos to aquatic invertebrates from studies with a range of freshwater and estuarine/marine crustacea, molluscs and aquatic insects was 0.066 µg/L to 881 µg/L for exposure of 24-96 h. Hence dichlorvos was highly toxic (LC50 in the range 0.1 to 1 mg/L) or in most cases, very highly toxic (LC50 < 0.1 mg/L) to the species tested. No full GLP reports of studies listed under Test Guideline 72-2 or 72-3 in the US EPA database were provided to DEW, but DEW rated the one GLP study which was provided as an *acceptable* study of acute freshwater invertebrate toxicity (cf. Guideline 72-2) and two detailed studies reported in the literature as *reliable* in one case and *acceptable* in the other. With one exception, the available data are consistent with results listed in the US EPA database, where the range in acute toxicity from studies classified as *core* studies was 0.066 µg/L to 1.0 µg/L, with the exception being an amphipod study where a much higher LC50 value was listed (DEW suspects was a database entry error). Thus the acute toxicity of dichlorvos is in most cases much higher to aquatic invertebrates than it is to fish.

Available data on the chronic or reproductive toxicity of dichlorvos to aquatic invertebrates includes a study with the water flea *Daphnia magna*, where the no observed effect concentration (NOEC) for adult immobilisation, total cumulative number of young and mortality of young up to 14 d was the highest concentration tested, 0.00256 µg/L, but where there was a significant delaying effect of dichlorvos on the length of time for the appearance of the first brood (NOEC = 0.00016 µg/L, LOEC = 0.00064 µg/L, EC50 > 0.00256 µg/L). Thus dichlorvos may have subtle effects on aquatic invertebrate populations at concentrations well below lethal levels. This GLP study was rated by DEW as a *reliable* study of chronic/reproductive toxicity to freshwater invertebrates: no studies to the relevant Test Guideline (72-4) were listed on the US EPA database. Studies with the common lobster *Homarus gammarus* indicated a 23 d LC50 of 1.25 µg/L and 23 d NOEC of 0.63 µg/L (rated as *acceptable* by DEW). Various studies have also shown biochemical effects on other aquatic invertebrates at sublethal concentrations.

5.3.5.3 Algae and aquatic plants

Only one study pertaining to algae was seen by DEW, a full GLP report rated as *reliable* by DEW, but not listed by the US EPA as a *core* or *supplemental* study. The result (EC50 based on 96 h biomass production = 52.8 mg ac/L for *Scenedesmus subspicatus*) is consistent with values listed as *supplemental* by the US EPA (48 h EC50 = 14-100 mg/L for four algal/diatom species) and indicates dichlorvos is only slightly toxic to algae (EC50 in the range 10-100 mg/L). No studies with dichlorvos and aquatic plants are available, but DEW expects similar toxicity to aquatic plants to that found with algae.

5.3.5.4 Amphibians

A study seen by DEW indicated a 48 h LC50 for an EC formulation of dichlorvos to tadpoles of the toad *Bufo bufo japonicus* of 76 mg/L, presumably expressed in terms of ac concentration. The US EPA AQUIRE database lists 48 h LC50 values to the frog species *Rana hexadactyla* and *Rana limnocharis* of 9.7 and10 mg/L, respectively. This limited evidence suggests that dichlorvos residues in water are slightly to moderately toxic to amphibians (LC50 in the range 10-100 mg/L or 1-10 mg/L, respectively).

5.4 Terrestrial Invertebrates

5.4.1 Bees

Atkins and Anderson (1967) indicated a 48 h LD50 value for dichlorvos to honey bees of 0.495 μg/bee with contact exposure by a dusting method (pesticide blended with pyrolite as a diluent). Kenaga (1979) listed an acute contact LD50 value for honey bees of 0.52 μg/bee using a similar method. Kudamatsu (1977) determined a 24 h LD50 value of 0.052 μg/bee for contact exposure of honey bees to dichlorvos active constituent (95% ac) applied in acetone to the dorsal surface of the bees. DEW rates these studies as *acceptable*, as they appear to have been conducted to standard guidelines, but with limited details provided.

WHO (1989) cited Beran (1979) as obtaining an LD50 with topical application of 0.65 μg/g body weight and an oral LD50 of 0.29 μg/g body weight (respectively, approximately 0.9 μg/bee and 0.4 μg/bee, assuming a mean body weight of ~140 mg for *Apis mellifera* - Helson *et al.* 1994).

Three studies not seen by DEW are listed on the US EPA Reviewed Studies Database, all rated as *core* studies. These include a study with dichlorvos active constituent and adult bees to Guideline 141-1 (Honey Bee - Acute Contact LD50), for which the result (48 h LD50 = 0.5 μg/bee) is consistent with the above reports for contact toxicity. Two studies are also listed for Guideline 141-2 (Honey Bee - Toxicity of Residues on Foliage), for which DEW has seen no other reports. The results for foliar toxicity, both to worker bees, were 24 h LD50s of 0.35 kg product/ha for a 50 EC formulation and 0.56 kg product/ha for a 42.4% ac formulation, corresponding to approximately 0.18 kg ac/ha and 0.24 kg ac/ha, respectively.

The above results for contact toxicity all indicate that dichlorvos is highly toxic (LD50 < 1.0 μg ac/bee) according to Felton *et al.* (1986). Anderson and Atkins (1967) also rated dichlorvos as “highly toxic” to honey bees as determined by laboratory and field tests in California, based on LD50 contact values < 2 μg toxicant/bee.

Anon (unknown date) rated both the direct and field application toxicity of dichlorvos to honey bees as “very high,” with a residual effect lasting > 1 d and classification as “hazardous to bees at any time on blooming crops." Johansen (1979) indicated that for minimal hazard to honeybees, dichlorvos should not be applied to blooming crops or weeds and that residual toxicity may remain for longer than 10 h. At mosquito abatement rates, Johansen indicated that dichlorvos should be applied only during the late evening, night or early morning, and that residual toxicity at this rate was usually low within 3 h. Johansen also cited earlier reports warning against the use of slow-release strips in honey houses, as vapours of dichlorvos from slow-release strips are absorbed by beeswax and remain a toxic hazard for some time. Anderson *et al.* (unknown date) rated dichlorvos as “highly toxic” to bees and indicated that severe losses may be expected if the insecticide is used when bees are present at treatment time or within a few days thereafter.

5.4.2 Earthworms

Vial (1991) [ECRP submission - PRD] reported a 14 d study of the acute toxicity of dichlorvos active constituent (purity 99.8%) to the earthworm *Eisenia foetida foetida*. The test was based on OECD Guideline No. 207, April 1984 (Earthworm – Acute Toxicity Tests), with the worms exposed to dichlorvos at nominal concentrations of 12.3-1000 mg/kg dry artificial soil substrate (dichlorvos would be expected to degrade significantly over the test period). There was 7.5% mortality in the control and a decline in average live weight in the control and at all dose levels, and a deviation from the guideline in that the initial average live weight of worms at all dose levels (237-262 g) was lower than that in the control (386 g). Because of the latter, DEW rates this study as *acceptable* rather than *reliable*. The 14d LC50 was 80.9 mg/kg dry soil (95% confidence limits 61.9-106.7 mg/kg), with a NOEC stated to be < 12.3 mg/kg. This result indicates that dichlorvos is moderately toxic to earthworms (LC50 in the range 10-100 mg/kg dry soil) according to the scale of Mensink *et al.* (1995).

5.4.3 Non-target insects and mites

Mani and Krishnamoorthy (1984) reported a study of the toxicity of dichlorvos and other insecticides to *Apanteles plutellae*, a parasite of the diamond back moth (*Plutella xylostella*). A 100 EC formulation of dichlorvos was tested at the spray concentration recommended for use by the manufacturers (0.05% in water). One-day-old adults were exposed to the dried spray on filter paper placed into glass vials, where they were held for 6 h, transferred to clean vials and observed for a further 24 h. One-day-old cocoons were spread uniformly on glass plates and sprayed with a glass atomiser, dried and kept for observation in clean glass vials. Results were not provided in the excerpt of the paper supplied, but the abstract indicates that dichlorvos was “highly toxic” to adults, but “relatively safe” for the cocooned stages.

WHO (1989) cited Shinkaji and Adachi (1978) as finding dichlorvos to be highly toxic to the predatory mite *Amblyseius longispinosus* in contact trials, residual toxicity disappearing within 6 days.

No other data on the toxicity of dichlorvos to insect and mite predators and parasites or other non-target species were available to DEW, but the above results show that dichlorvos is highly toxic to aquatic insects, bees and insect and mite predators. Tomlin (1997) indicates that dichlorvos is an insecticide and acaricide used to control a wide range of insect and mite species with respiratory, contact and stomach action. Australian product labels also claim that it can kill spiders. DEW therefore expects that in general, dichlorvos will be highly toxic to insects, mites and spiders directly exposed to its vapours or residues, unless they have inherent resistance to it.

5.4.4 Conclusions – Terrestrial Invertebrates

Dichlorvos is an insecticide and acaricide used to control a wide range of arthropod pest species with respiratory, contact and stomach action. Laboratory tests (details not seen) show that it is highly toxic (LD50 < 1.0 μg/bee) to honey bees (*Apis mellifera*), with topical application or oral dosing giving LD50 values ranging from 0.052 μg per bee to approximately 0.9 μg/bee, and the LD50 from residues on foliage being approximately 0.2 kg ac/ha. A laboratory study based on OECD Guideline No. 207 indicated a 14d LC50 of dichlorvos to the earthworm *Eisenia foetida foetida* of 80.9 mg/kg dry soil (95% confidence limits 61.9-106.7 mg/kg), with a NOEC stated to be < 12.3 mg/kg. Because the weights of the control and treatment worms differed significantly at the start of the test, DEW rates this study as *acceptable* rather than *reliable*. Literature reports also indicate that dichlorvos is highly toxic to *Apanteles plutellae*, a parasite of the diamond back moth, and to the predatory mite *Amblyseius longispinosus.* DEW expects that in general, dichlorvos will be highly toxic to insects, mites and spiders directly exposed to its vapours or undegraded residues, unless they have inherent resistance to it.

5.5 Terrestrial Plants

No studies on the toxicity of dichlorvos to terrestrial plants are available. DEW notes that while dichlorvos is used in some situations where plants are directly sprayed (eg avocados), dichlorvos itself and/or the solvent in some formulations may be phytotoxic, as indicated by warnings on some product labels, eg:

“Do not spray directly onto plants – phytotoxicity may occur following use on young tomatoes, cucumbers and chrysanthemums. Do not apply directly onto mushrooms as solvent damage may result.” (Vapona™ label in regard to greenhouses, glasshouses, mushroom houses); and

“Spray into air space. Avoid phytotoxicity by not spraying in direct sunlight. Should only be sprayed onto known dichlorvos tolerant species. Plants should not be under stress at time of application.” (Insectigas™ D in relation to greenhouses).

Tomlin (1997) indicates that dichlorvos is rapidly decomposed in plants. DEW concludes that dichlorvos may be phytotoxic to some species in some circumstances.

5.6 Micro-organisms

As discussed earlier (Degradation by micro-organisms in culture and by sewage sludge, Section 5.4), several studies indicate that dichlorvos has little or no toxicity to various micro-organisms from sewage and soil, including *Bacillus* and *Pseudomonas* species and the soil fungus *Trichoderma viride*.

WHO (1989) cited various studies which also show low toxicity to bacteria, including:-

no influence of dichlorvos on the overall metabolic processes of the bacteria *Escherischia coli* and *Enterobacter aerogenes* at doses up to 250 mg/L (Grahl *et al.* 1980);
dichlorvos was not toxic to a sewage isolate at up to 10 mg/L (Rosenberg *et al.* 1979);
concentrations of dichlorvos of 100 and 1000 mg/L did not significantly reduce coliform populations in poultry effluent slurry, whereas 10,000 mg/L caused almost complete death (Ballington *et al.* 1978) – nonetheless, WHO (1989) indicates that the author claimed that residues of dichlorvos used for fly control in layer houses can significantly reduce enteric coliform populations essential to the conversion of organic nitrogen in poultry waste effluent;
the growth of *Bacillus thuringiensis* var *thuringiensis* was not inhibited by dichlorvos (Dougherty *et al.* 1971);
dichlorvos does not appear to be utilised by ruminal bacteria or ciliated protozoa under anaerobic conditions, does not stimulate endogenous gas production, but may in some circumstances affect volatile fatty acid production (Williams 1977).

WHO (1989) also discussed evidence from published scientific papers showing some effects of dichlorvos on various fungi, though generally at relatively high concentrations:

citric acid fermentation in the fungus *Aspergillus niger* was evaluated with 10-80 mg dichlorvos/L in an artificial medium and found to be markedly affected at 40 and 80 mg dichlorvos /L, possibly through effects on oxidative metabolism (Rahmatullah *et al.* 1978; Ali *et al.* 1979);
in one case where effects were evident at relatively low concentrations, citrinin production by the fungus *Penicillium citrinum* was inhibited to the extent of 76% by dichlorvos at 100 µg/L and 48% at 10 µg/L (Draughton and Ayres 1978);
the threshold value for effects on the survival time and membrane potential of the slime mould *Physarum polycephalum* in a laboratory test system was 300 mg/L for technical dichlorvos and 30 mg/L for the pure chemical (Terayama *et al.* 1978);
dose levels of dichlorvos at 10-120 mg/kg to 17 soil fungi cultivated in artificial medium generally led to a growth depression during a 21 d test period, the extent of depression depending on the fungal strain and in some cases growth being unaffected or even stimulated (Jakubowska and Novak 1973).

5.7 Mammals

Dichlorvos is moderately to highly toxic to mammals by the single dose oral route, with the acute oral LD50 to rats being 30-110 mg/kg body weight, depending on the solvent used (WHO 1989). Toxicity to mammals is discussed thoroughly in the human health section of this report.

5.8 Summary of Environmental Toxicology

5.8.1 Birds

Dichlorvos rates as highly to very highly toxic (LD50 in the range 10-50 or <10 mg/kg bodyweight, respectively) to birds by a single oral dose, with LD50s ranging from ~5 to 42 mg/kg body weight for all studies (11 species). No full GLP reports of studies meeting modern acute oral toxicity guidelines were available to DEW, but those available included two rated as supplemental by the US EPA. The available results were also consistent with two studies rated as *core* to US EPA Guideline 71-1, not seen by DEW. Studies available to DEW indicate that the LC50 with the standard 8 day dietary exposure test (5 d exposure followed by 3 d observation) ranged from 298 to 568 ppm for Japanese quail and ring-necked pheasant, to >1317 and >5000 ppm for mallard ducks. Studies with domestic fowl exposed to dichlorvos in their diets for 28 d indicated a dietary LC50 value of 500 ppm, but a LOEC for non-lethal effects as low as 30 ppm. Thus the acute/subacute dietary toxicity of dichlorvos to birds ranges from slight (LC50 in the range 1001-5000 ppm) to high toxicity (LC50 in the range 51-500 ppm). A further test not provided to DEW rated as *core* to US EPA Guideline 71-2 apparently indicated much higher toxicity to bobwhite quail, but DEW has not seen the original report for confirmation.

No early life/reproductive studies were provided to DEW, but the 28 d dietary studies with domestic fowls indicated effects such as reduced food consumption and/or depression of egg production at dietary concentrations as low as 30-50 ppm. Toxicity of similar magnitude to these results with 28 d exposure was indicated in a study using bobwhite quail not seen by DEW, but reported on the US EPA Reviewed Studies Database as a *core* study to their Guideline 71-4 (exposure commencing as treated birds approached their first breeding season and observations continued for about 20 weeks, following surviving offspring to 14 d old).

Studies gave some indication of the toxicity of dichlorvos by inhalation, but did not indicate specific values for harmful concentrations. There have been reports of mortality in domestic fowl, mallard ducks and English game bantams arising from accidental exposure to residues in grain or feed, water or pellets present in horse manure, indicating the need for caution in handling and using dichlorvos in situations where birds might be exposed.

5.8.2 Aquatic organisms

5.8.2.1 Fish

The range in acute toxicity (LC50) of dichlorvos (as active constituent or various formulations) to a wide range of freshwater and estuarine/marine species of fish from various studies was ~0.2 mg/L to >40 mg/L. In general, studies show that dichlorvos is highly toxic (LC50 in the range 0.1-1 mg/L) to moderately toxic (LC50 in the range 1 to 10 mg/L) to fish, with a few reports indicating slight toxicity (LC50 in the range 10-100 mg/L). No full GLP reports of fish studies listed as *core* or *supplemental* by the US EPA were provided, but DEW found a scientific paper reporting a GLP study which was rated as a *reliable* study of acute estuarine/marine fish toxicity (cf. US EPA Test Guideline 72-3). The available data are consistent with studies listed as *core* under Test Guideline 72-1 by the US EPA (range 0.17 mg/L to 11.6 mg/L). Data available on the chronic toxicity of dichlorvos indicate a 60 day Maximum Acceptable Toxicant Concentration (MATC) to carp of 16-20 μg/L, and a 30 day MATC for African catfish of 36.7 μg/L. These MATC values are comparable with a 61 d MATC = 7.2 μg/L for rainbow trout listed by the US EPA, but lower than a 34 d MATC = 1329 μg/L listed for sheepshead minnow (both listed as *core* studies). Various studies show biochemical effects on fish at sublethal concentrations. However, as dichlorvos was found to be much less toxic to fish species such as salmon than to parasites such as salmon louse, it has been used widely to control parasites in finfish culture, though not yet in Australia.

5.8.2.2 Aquatic invertebrates

The range in acute toxicity (LC50) of dichlorvos to aquatic invertebrates from studies with a range of freshwater and estuarine/marine crustacea, molluscs and aquatic insects was 0.066 μg/L to 881 μg/L for exposure of 24-96 h. Hence dichlorvos was highly toxic (LC50 in the range 0.1 to 1 mg/L) or in most cases, very highly toxic (LC50 < 0.1 mg/L) to the species tested. No full GLP reports of studies listed under Test Guideline 72-2 or 72-3 in the US EPA database were provided to DEW, but DEW rated the one GLP study which was provided as an *acceptable* study of acute freshwater invertebrate toxicity (cf. Guideline 72-2) and two detailed studies reported in the literature as *reliable* in one case and *acceptable* in the other. With one exception, the available data are consistent with results listed in the US EPA database, where the range in acute toxicity from studies classified as *core* studies was 0.066 μg/L to 1.0 μg/L, with the exception being an amphipod study where a much higher LC50 value was listed (DEW suspects was a database entry error). Thus the acute toxicity of dichlorvos is in most cases much higher to aquatic invertebrates than it is to fish.

Available data on the chronic or reproductive toxicity of dichlorvos to aquatic invertebrates includes a study with the water flea *Daphnia magna*, where the no observed effect concentration (NOEC) for adult immobilisation, total cumulative number of young and mortality of young up to 14 d was the highest concentration tested, 0.00256 μg/L, but where there was a significant delaying effect of dichlorvos on the length of time for the appearance of the first brood (NOEC = 0.00016 μg/L, LOEC = 0.00064 μg/L, EC50 > 0.00256 μg/L). Thus dichlorvos may have subtle effects on aquatic invertebrate populations at concentrations well below lethal levels. This GLP study was rated by DEW as a *reliable* study of chronic/reproductive toxicity to freshwater invertebrates: no studies to the relevant Test Guideline (72-4) were listed on the US EPA database. Studies with the common lobster *Homarus gammarus* indicated a 23 d LC50 of 1.25 μg/L and 23 d NOEC of 0.63 μg/L (rated as *acceptable* by DEW). Various studies have also shown biochemical effects on other aquatic invertebrates at sublethal concentrations.

5.8.2.3 Algae and aquatic plants

Only one study pertaining to algae was seen by DEW, a full GLP report rated as *reliable* by DEW, but not listed by the US EPA as a *core* or *supplemental* study. The result (EC50 based on 96 h biomass production = 52.8 mg ac/L for *Scenedesmus subspicatus*) is consistent with values listed as *supplemental* by the US EPA (48 h EC50 = 14-100 mg/L for four algal/diatom species) and indicates dichlorvos is only slightly toxic to algae (EC50 in the range 10-100 mg/L). No studies with dichlorvos and aquatic plants are available, but DEW expects similar toxicity to aquatic plants to that found with algae.

5.8.2.4 Amphibians

A study seen by DEW indicated a 48 h LC50 for an EC formulation of dichlorvos to tadpoles of the toad *Bufo bufo japonicus* of 76 mg/L, presumably expressed in terms of ac concentration. The US EPA AQUIRE database lists 48 h LC50 values to the frog species *Rana hexadactyla* and *Rana limnocharis* of 9.7 and 10 mg/L, respectively. This limited evidence suggests that dichlorvos residues in water are slightly to moderately toxic to amphibians (LC50 in the range 10-100 mg/L or 1-10 mg/L, respectively).

5.8.3 Terrestrial invertebrates

Dichlorvos is an insecticide and acaricide used to control a wide range of arthropod pest species with respiratory, contact and stomach action. Laboratory tests (details not seen) show that it is highly toxic (LD50 < 1.0 μg/bee) to honey bees (*Apis mellifera*), with topical application or oral dosing giving LD50 values ranging from 0.052 μg per bee to approximately 0.9 μg/bee, and the LD50 from residues on foliage being approximately 0.2 kg ac/ha. A laboratory study based on OECD Guideline No. 207 indicated a 14d LC50 of dichlorvos to the earthworm *Eisenia foetida foetida* of 80.9 mg/kg dry soil (95% confidence limits 61.9-106.7 mg/kg), with a NOEC stated to be < 12.3 mg/kg. Because the weights of the control and treatment worms differed significantly at the start of the test, DEW rates this study as *acceptable* rather than *reliable*, but the study suggests moderate toxicity to earthworms. Literature reports also indicate that dichlorvos is highly toxic to *Apanteles plutellae*, a parasite of the diamond back moth, and to the predatory mite *Amblyseius longispinosus.* DEW expects that in general, dichlorvos will be highly toxic to insects, mites and spiders directly exposed to its vapours or undegraded residues, unless they have inherent resistance to it.

5.8.4 Terrestrial plants

While dichlorvos is used in some situations where plants are directly sprayed, warnings on some product labels indicate that dichlorvos itself and/or the solvent in some formulations may be phytotoxic.

5.8.5 Micro-organisms

From a range of evidence, it may be concluded that dichlorvos generally has low toxicity to soil and sewage micro-organisms, though in some cases it may have specific effects at relatively low concentrations.

5.8.6 Mammals

Diazinon is moderately to highly toxic to mammals by the single dose oral route, with the acute oral LD50 to rats being 30-110 mg/kg body weight. Toxicity to mammals is discussed thoroughly in the human health section of this report.

5.8.7 Conclusions

Dichlorvos is highly to very highly toxic to birds following a single oral dose and generally has slight to high avian toxicity with acute/subacute dietary exposure. With acute exposure (24-96 h), dichlorvos generally has moderate to high acute toxicity to fish, but in most cases is highly to very highly toxic to aquatic invertebrates (48 h EC50 to water fleas as low as 0.066 μg/L). It is only slightly toxic to algae and generally has low toxicity to soil and sewage micro-organisms, but may be toxic to terrestrial plant species in some circumstances. Dichlorvos is an insecticide and acaricide used to control a wide range of arthropod pest species with respiratory, contact and stomach action and is therefore expected to be toxic to a wide range of terrestrial arthropods coming in contact with the spray, vapours or fresh residues. High toxicity to honey bees by topical application or oral dosing and to certain parasitic/predatory species has been confirmed. Tests indicate that dichlorvos is moderately toxic to earthworms exposed to soil residues.

6 ENVIRONMENTAL RISK ASSESSMENT

6.1 Introductory remarks

In Australia, dichlorvos is a pesticide used to a large extent in non-agricultural situations and/or in enclosed areas or slow release formulations. Use on crops in the field is very minor and restricted to specific pests on avocados (leaf rollers). Use on crops in protected environments is also minor and includes control of phorids in mushrooms and control of pests of glasshouses and greenhouses. Use on animals is restricted to use as one of two active ingredients in an orally-administered paste for bot fly and worm control in horses.

Much greater use occurs to disinfest harvested and stored products (grain, potatoes, tobacco) and to treat produce storage and handling areas (silos, warehouses etc), wineries, grain mills, animal housing, manure heaps and abattoirs/meatworks (non-food production areas). Major uses also include space spray, surface or spot treatment and slow release methods for the control of a wide range of pests (flies, mosquitoes, moths, spiders) in domestic, recreational and industrial areas. These may range from confined spaces such as clothes cupboards and rubbish bins, to specific areas such as the vicinity of European wasp nests, to treatment of open areas such as rubbish dumps.

DEW will firstly consider the general risk from release of dichlorvos to the atmosphere from all sources and then consider the risks arising from individual use situations.

6.2 Risk from vapour release to the atmosphere

Because of the volatility of dichlorvos, a significant proportion of the substance applied by various means is expected to vaporise and enter the external atmosphere directly from dry or drying surfaces, or as confined air exchanges. While much dichlorvos use occurs in relatively protected areas, usage situations include storages with limited air exchange for an indefinite period (eg clothes cupboards), areas which may be largely air tight when treated but are ventilated after a lock-up period (eg mushroom houses or glasshouses), areas which are not air tight or where produce is treated as it is stored (eg in the grains industry, where current use of dichlorvos is almost exclusively as a disinfestant, often in situations where storage is not air-tight - Agricultural Assessment, Section 1.2), and spaces with relatively free ventilation (eg refuse tips, animal houses).

DEW expects that emissions of dichlorvos to the external atmosphere will dissipate rapidly through dilution, degradation and removal in precipitation. Dichlorvos degrades in sunlight with a half-life of the order of 0.5-1 day through reaction with OH radicals (Section 5.2.3). Dichlorvos in the atmosphere may also partition to droplets of moisture, where it would be susceptible to hydrolysis and may be removed in precipitation. Hence, outside treated areas or the immediate vicinity downwind of a treated area during application or post treatment ventilation, DEW expects the concentration of dichlorvos in air will be very low, well below toxic levels. Air concentrations in exposed areas are expected to drop rapidly after release ceases.

Dichlorvos has been detected at 0.1-1 μg/L in rainwater in the Netherlands in one of three years where rainwater was monitored (Section 4.3), but contamination at this level is unlikely in Australia, particularly given widely dispersed use in Australia, lower overall use in the southern hemisphere, and different use patterns to the Netherlands. Concentrations reached in streams etc from atmospheric sources would be expected to be minimal and to dissipate rapidly through hydrolysis and microbial metabolism. DEW therefore considers the risk to the environment from dichlorvos release into the atmosphere from use in Australia not to be significant.

6.3 Risk from residues reaching water, soil, produce etc.

The sole current Australian use of dichlorvos on plants growing in the field is on avocados (the only other recent use was under past permits for use to control Western flower thrips in ornamentals). The advantage sought in using dichlorvos is its transitory, fumigant effect. As a worst case, DEW will consider treatment of an avocado orchard for leaf rollers, at a rate of 1 L/ha 50% EC (500 g ac/ha) by orchard air blaster. Because of the short half-life of dichlorvos in natural waters and soil, it would not be expected to persist or accumulate from repeated spraying, hence acute rather than chronic toxicity indicators will be used for risk assessment.

6.3.1 Use in avocado orchards

6.3.1.1 Background to industry

The avocado is indigenous to upland and lowland areas of tropical America, but various varieties are adapted to a wide range of latitudes and altitudes, from temperate to tropical areas (Purseglove 1968; Bolton 1995; Anon 1999). Key requirements include good drainage to discourage rootrot diseases, suitable temperatures for fruit setting and freedom from frost and wind damage during establishment. Areas with low rainfall require irrigation, typically by under tree sprinklers. The Australian Avocado Growers Federation Inc. lists 15 avocado growing areas, including Pemberton, Perth and Carnarvon in WA, the Riverland of SA and Sunraysia district of Vic., Mid and Far North Coast of NSW and areas in Queensland from the south east of the state to Bundaberg to the Atherton Tablelands. A range of varieties across these locations enables production in Australia to be maintained around the year. Fruit takes 6 or more months to mature after flowering and ripens after it is picked from the tree, hence birds and animals such as flying foxes are not greatly attracted to consume them.

Avocados can have a very large canopy, but growers usually limit tree size to ~6 m to facilitate picking. It is common practice to leave forested gullies and to plant trees along creek lines, though other trees may often be removed. Dichlorvos is seen as useful in controlling certain pests of avocados because of its fumigant action. It is rarely used in most areas, but still seen by the industry as very useful in occasional years when the pests reach problem levels, when two sprays 10 days apart would normally be applied and (personal communications 9 and 10 Nov 1999, John Wilkie, Wilkie Fleming & Associates Pty Ltd, Alstonville NSW and Peter Rigden, Department of Primary Industries, Nambour, Queensland).

6.3.1.2 Risk to birds and mammals

Japanese quail were the most sensitive bird species in regard to dietary toxicity, with an LC50 (standard 8 d test, with 5 d dietary exposure) of 298 ppm (Section 6.2.2). Although this species is not native to Australia, it can be used as a surrogate for estimating the risk to sensitive native species. The EEC in potential food items can be estimated from the maximum application rate of dichlorvos of 500 g ac/ha to avocados and the updated Kenaga nomogram (Urban and Cook 1986, US EPA 1993, Fletcher *et al.* 1994, Pfleeger *et al.* 1996). Assuming a diet of 70% grain/30% small insects, the dietary EEC is calculated as follows:

Quail diet = 70% grain + 30% small insects
EEC of dichlorvos on grain = 49 mg ac/kg food
EEC of dichlorvos on small insects = 60 mg ac/kg food
Dietary EEC of dichlorvos = 0.7 X 49 + 0.3 X 60 mg ac/kg food
= 52.3 mg ac/kg food

This estimated dietary EEC values is less than the LC50 for Japanese quail of 298 ppm. Furthermore, the initial concentration of dichlorvos on food sources is likely to decline relatively rapidly due to volatilisation, hydrolysis and metabolism. It is also unlikely that the entire diet of native birds would be based in areas reached by the spray, though it is possible that insects affected by spray may initially attract birds to feed, and some feeding may occur in adjacent areas affected by lower dichlorvos concentrations from spray drift. DEW will therefore assume that the average dietary EEC is ≤ 50% of the above figure. The calculated Q value (EEC/LC50) for Japanese quail is then < 0.1, indicating an acceptable dietary risk for birds from dichlorvos. However, DEW notes that chlorpyrifos is also added to the tank mix with dichlorvos for leaf roller control in avocados and that this would add to the concurrent exposure of birds to organophosphates through the diet.

Dichlorvos is highly to very highly toxic to birds by acute oral exposure, may be toxic by inhalation and is readily absorbed through the skin. As with other organophosphate insecticides, it may cause temporary sublethal effects which make the bird more susceptible to other sources of harm, such as predators. Birds remaining in a sprayed area, reached by spray drift, or entering an area that has been recently sprayed could be exposed either dermally or orally from preening contaminated feathers (Driver *et al.*, 1991). The extent to which these means of exposure add to the overall risk would depend on the extent to which birds remain in the vicinity of orchards during spraying and how early they return, and whether or not they receive repeat exposure from a second spray. However, on each spraying occasion the risk of exposure to dichlorvos is only expected to be transitory as it should dissipate rapidly.

Avocados are not native to Australia and do not carry ripe fruit likely to attract birds and mammals. Hence DEW concludes that the overall risk to birds and mammals such as flying foxes from dichlorvos used on avocados is acceptable.

6.3.1.3 Risk to aquatic organisms

6.3.1.3.1 Method of assessment

DEW assesses the environmental risk from acute exposure in an aquatic contamination situation by calculating the Environmental Risk Quotient (Q = EEC/LC50 or EC50, based on Urban and Cook, 1986), using the EEC (expected environmental concentration) from spray reaching lentic water 15 cm deep (as a worst case situation in regard to water depth) and acute toxicity data for the most sensitive aquatic species. DEW generally considers the following as an appropriate guide for the establishment of risk:

• $Q > 0.5$:	risk is unacceptable
• $0.1 \leq Q \leq 0.5$:	risk may be able to be mitigated by some form of risk management, such as label restraints for a specific use and an identified risk arising from that use
• $Q < 0.1$:	risk is considered low (and may or may not require some form of risk management, such as general label restraints).

DEW notes that the reported range of acute toxicity for dichlorvos to freshwater invertebrates is 0.066 μg/L to 881 μg/L (Section 6.3.2). DEW will use the 48 h EC50 of 0.066 μg/L for *Daphnia magna* , as used by Teunissen-Ordelman and Schrap (1997) as a toxicity value for freshwater crustacea in Dutch risk assessments, presumably from the EC50 to the water flea *Daphnia pulex* and also used as the freshwater aquatic invertebrate endpoint for the US EPA risk assessment of dichlorvos. EC50/LC50 values reported for other sensitive aquatic invertebrate species are in the range 0.19-0.50 μg/L).

Dichlorvos is much less toxic to most species of fish (reported range 200 μg/L to > 40,000 μg/L – Section 6.3.1) and also appears to be less toxic to algae and aquatic plants and to amphibians than it is to aquatic invertebrates (Sections 6.3.3 and 6.3.4). For freshwater fish, DEW will use an LC50 value of 170 μg/L, as used by Teunissen-Ordelman and Schrap (1997) as a toxicity value for freshwater fish in Dutch risk assessments (a value of 183 μg/L for lake trout was used for the US assessment). This value is listed for cutthroat trout (*Oncorhynchus clarkii*) on the US EPA database and is close to the value of 200 μg/L common to several sensitive freshwater fish species in other studies seen by DEW or listed in WHO (1989). A reliable lower value of 122 μg/L is indicated for larvae of herring by McHenery *et al.* (1991), but use of dichlorvos on avocados is not expected to impact on marine species.

6.3.1.3.2 Direct overspray situation

In the event that direct over spraying with dichlorvos occurred, DEW calculates that the expected environmental concentration (EEC) of dichlorvos which could be reached in a shallow (15 cm deep) lentic water body at a rate of 0.5 kg ac/ha is 333 μg/L. This concentration is far above concentrations found to be harmful to many aquatic invertebrates, with the calculated Q value for *Daphnia pulex* being 5050. It also indicates an unacceptable risk to fish (Q for cutthroat trout = 2.0). Hence direct contamination of natural streams or water bodies with dichlorvos is clearly unacceptable and this should be indicated on product labels.

6.3.1.3.3 Spray drift situation

Spray drift is of major concern for aquatic organisms. Using the US EPA worst case assumption that 10% spray drift reaches water (Urban and Cook, 1986), this would result in a concentration of 33.3 µg/L for a shallow pond 15 cm deep (application rate 0.5 kg/ha). This indicates a mitigable risk for fish (Q = 0.2), but the risk to aquatic invertebrates remains unacceptable (Q = 505). Hence more refined assessment of the risk from spray drift to aquatic organisms is required.

To more realistically assess the spray drift risk from expected methods of ground application, DEW models the amount of drift from orchard/air- blast equipment using the AgDRIFT® model (Version 2.0.07, Tier I Orchard/Air- blast; US EPA, 1997), and where appropriate supplements this with evaluation according to the "Ganzelmeier tables" (Rautmann *et al*., 2001), consistent with proposed APVMA policy (APVMA, 2006). The AgDRIFT® model for orchard/air blast application is based on applications to a range of orchard crops and crop situations and the results have been pooled into three groups: normal (grapes wrap-around sprayer, pome fruit and grapes with air blast), dense (citrus [air blast and mister] and nut trees) and sparse (small trees and dormant trees). For avocadoes, DEW considers the results for dense foliage most appropriate, and the Ganzelmeier tables as inappropriate as they do not cover such species.

Table 7.1 summarises these results for dichlorvos at a rate of 0.5 kg ac/ha, with spray drift to a water 15 cm deep in a 3 m wide pond. Risk quotients are shown for fish (LC50 = 170 µg/L) and daphnia (EC50 = 0.066 µg/L). These indicate an acceptable risk for fish at 25 m downwind, but an unacceptable risk remains to daphnids, even at 200 m downwind.

This is the case even if the second lowest daphnid endpoint of 0.19 µg/L is used (also shown in Table 7.1). Repeated spraying after a 10 day interval (or "as necessary" according to the label) is unlikely to lead to increased concentrations as dichlorvos is likely to have largely or completely dissipated between spray events, but may add to the risk as organisms may be unable to recover between spray events.

Table 7.1. Spray drift estimates for dichlorvos from air blast sprayers in an avocado orchard from AgDRIFT® at 0.5 kg ac/ha in a water body 3 m wide and 15 cm deep at the distances shown. The shading indicates Q > 0.5 (unacceptable risk).

Distance (m)	**% drift**	**EEC (µg/L)**	**Q, Fish (LC50 = 170 µg/L)**	**Q, *Daphnia pulex* (EC50 = 0.066 µg/L)**	**Q, *Daphnia magna* (EC50 = 0.19 µg/L)**
25	0.78	2.60	0.015	39.4	13.7
50	0.33	1.09	0.006	16.5	5.7
75	0.20	0.67	0.004	10.2	3.5
100	0.15	0.49	0.003	7.4	2.6
150	0.10	0.32	0.002	4.8	1.7
200	0.07	0.24	0.001	3.6	1.3

The depth of water is a significant factor in determining the concentration in water from spray drift, eg the risk quotients in Table 7.1 are halved if the water depth were 30 cm instead of 15 cm. Some allowance may also be given for dissipation of dichlorvos from a contaminated water body. However, even if a fourfold reduction in predicted concentrations is allowed for these two factors, the Q value for daphnids at 200 m remains unacceptably high for *Daphnia pulex* (Q = 0.9) and for *Daphnia magna* is unacceptable at 100 m and still not in the acceptable range at 200 m (Q = 0.65 and 0.33, respectively).

A factor which might be thought to mitigate the risk to aquatic environments from spray drift of dichlorvos is its volatility, but this factor does not operate significantly during spraying as the Henry's Law value shows that dichlorvos is only very slightly to moderately volatile from water due to its high solubility.

With current knowledge it is not considered that interception of drift by windbreaks or streamside vegetation can be relied upon as generally applicable protective measures, as there are too many variables and uncertainties involved as to the location and nature of vegetation that may be present and the effectiveness such vegetation as is present may have in intercepting drift. A paper by Salyani and Cromwell (1992) showed that the last two rows (rows 1 and 2) in an orchard situation captured between 70-80% of the spray from rows 3 and 4, but DEW's understanding is that the approach of not spraying end rows is not considered practical by growers, and it would require further investigation for regulatory use.

For these reasons DEW considers that an impracticably long downwind buffer would be required to protect aquatic areas from spray drift. Hence it is recommended that use for leaf roller control on avocados should be deleted from dichlorvos labels.

Aerial application is not regarded as the normal practice for applying pesticides to orchards in Australia, though it is not prohibited on the dichlorvos labels. If use on avocados is maintained, a restraint against aerial application should be added to product labels indicating that use.

6.3.1.3.4 Run-off

Dichlorvos is water soluble and does not bind strongly to soil, but residues on surfaces in the open air are expected to dissipate rapidly due to volatilisation as droplets evaporate, and degradation on moist soil and plant surfaces. However, the above figures indicate that dichlorvos could present a risk to aquatic invertebrates if it were to enter streams or other water bodies in run-off water. Thus there is a short-term risk from rainfall following soon after application leading to leaching of dichlorvos from plant surfaces and soil into run-off water.

DEW concludes that there is a potential risk to aquatic invertebrates from run-off if rain follows before the applied spray has dried. Hence if the avocado use is maintained, product labels should indicate that the product should not be used if rain is expected within 4 hours.

6.3.1.4 Risk to terrestrial invertebrates

6.3.1.4.1 Bees and other non-target arthropods

The use of dichlorvos in avocado orchards as described is likely to be toxic to any arthropods exposed to it in the orchard canopy, including bees and insect predators and parasites. However, the risk from dichlorvos is only expected to be transitory and confined to the area directly exposed or reached by spray drift. Hence for any product with field uses, an appropriate label warning should be provided to indicate that dichlorvos is dangerous to bees and will kill bees foraging in the crop to be treated or in hives which are over-sprayed or reached by spray drift. Use of the spray tank mix may impact upon IPM programs, but the effects of dichlorvos itself are expected to be short term due to its transitory, fumigant action.

6.3.1.4.2 Earthworms

Expected concentrations in soil reached directly by spray at the rate of 500 g dichlorvos/ha would be ~0.7 mg/kg if confined to the surface 5 cm of soil (bulk density 1.4 g/cm^3). Furthermore, dichlorvos is likely to dissipate rapidly from the soil and foliage surfaces, minimising residues moving into the soil. The expected soil concentration is 2 orders of magnitude below the 14 d LC50 of 80.9 mg/kg soil for dichlorvos to the earthworm *Eisenia eisenia foetida*, hence DEW concludes that the risk to earthworms from this use of dichlorvos is acceptable.

6.3.1.5 Terrestrial plants

Dichlorvos is evidently not phytotoxic to avocados at the recommended rate, and direct application to non-target plants is unlikely with ground-based application. Lower rates from drift would have presumably have less likelihood of causing phytotoxicity.

6.3.1.6 Conclusions regarding use of dichlorvos on avocados

When used as an insecticide in the open air, dichlorvos has a transitory, fumigant action and residues on foliage or soil are expected to dissipate rapidly as water droplets evaporate. DEW concludes that the use of dichlorvos in avocado orchards as described presents a risk to birds and mammals such as flying foxes if they are directly exposed to spray or spray drift or enter freshly sprayed trees while they are still wet. However, this risk is relatively low, as avocados are not Australian natives and do not carry attractive ripe fruit, birds present are likely to be disturbed by the noise and disruption from spraying, and residues are likely to dissipate rapidly.

Concentrations of dichlorvos harmful to aquatic organisms (particularly invertebrates) may result from direct overspray, or from spray drift, and DEW considers that an impracticably long spray drift buffer would be needed to protect aquatic invertebrates in downwind areas. Hence DEW recommends that use for leaf roller control on avocados should be deleted from dichlorvos labels. DEW is advised that use of dichlorvos on avocados now occurs rarely and this use is currently only registered in NSW, Queensland and WA only, although the crop is grown in other States. Dichlorvos in spray or spray drift is also likely to be harmful to bees and other arthropods, particularly those in the exposed canopy. Hence label advice for products where field exposure may occur should indicate that dichlorvos is dangerous to bees and will kill bees foraging in the crop to be treated or in hives which are over-sprayed or reached by spray drift. Use of the spray may impact upon IPM programs, but the effects of dichlorvos itself are expected to be short term due to its transitory, fumigant action: the possibility of impacts on IPM programs should also be indicated on the label.

If use on avocados is allowed to continue, product labels should also provide more comprehensive and restrictive advice on the frequency of use (the current advice is simply “Apply at first sign of pest activity before larvae move to fruit … repeat as necessary”).

6.3.2 Use in mushroom houses

Dichlorvos is one of two insecticides (the other being permethrin) currently used to control adult sciarid flies, particularly during the two weeks prior to casing of the compost in which mushroom spores are seeded, but also at other growth stages. For this purpose, dichlorvos is applied in a form intended to treat the air of the mushroom house, rather than being applied to the mushrooms, casing or compost directly. Other insecticides (eg diazinon, triflumuron and fipronil) are used as casing treatments or in the compost.

Dichlorvos is applied in mushroom houses as a space spray or fog, or via the wooden board method (concentrate applied to a wooden board to provide sustained release of dichlorvos vapour for a few hours/days). Hence limited contamination of casings, compost or internal mushroom house surfaces would be expected and no immediate contamination of the external environment from spray drift or run-off would be expected. Mushroom casings and compost are used for three cropping cycles (total of 63 days), after which they are used as garden compost, both commercially and domestically. Significant residues of dichlorvos would not be expected to occur in this material, and any dichlorvos reaching casing or compost material would be expected to degrade before or soon after disposal through hydrolysis and microbial activity.

DEW concludes that the use of dichlorvos as described in mushroom houses is unlikely to cause contamination of soil or water in the external environment.

6.3.3 Use in glasshouses and greenhouses

In Australia, the only methods of use for dichlorvos in glasshouses and greenhouses referred to on labels are space spraying/fog application or the wooden board method. Application via the watering system (“chemigation”) and spraying of the glasshouse surfaces are not recommended on current Australian labels, and the choices of method available are in any case limited by the risk of phytotoxicity when sensitive plants are present.

Contamination of adjacent areas by the direct spray or spray drift is likely to be minimised by the protective structures, though less so in greenhouses. Degradation of dichlorvos residues by hydrolysis and microbial activity and loss by volatilisation are likely to reduce dichlorvos residues relatively rapidly in these environments. However, dichlorvos residues on surfaces reached directly by the spray/fog or from vapour deposition in water droplets may wash off and enter drainage before they degrade, eg with spray irrigation subsequent to treatment. Hence significant losses of dichlorvos to the external environment may occur through drainage water.

In contrast to the situation in the Netherlands prior to banning of agricultural uses of dichlorvos (Sections 1 and 4.3), the use of dichlorvos in glasshouses and greenhouses in Australia is very minor, and such facilities are spread over a wider geographical area than is the case in the Netherlands. However, localised impacts could occur to streams reached by drainage water, particularly near large facilities. Hence drainage from treated glasshouses should not be allowed to reach aquatic areas before degradation has occurred, and DEW recommends that a caution be placed on relevant labels against direct aquatic contamination with glasshouse drainage water.

6.3.4 Use in slow release formulations for flea collars, cupboards, bins etc.

The use of dichlorvos in slow release products for purposes such as moth control in clothes cupboards or fly control in rubbish bins is not expected to pose a risk to the environment. These products are solid formulations and are expected to remain in place in a largely confined space, gradually releasing active ingredient.

At disposal only low concentrations of dichlorvos are likely to remain. The product labels advise that for disposal, they should be wrapped in paper, placed in a plastic bag and put in the garbage. Thus after removal, the used products would normally be disposed of to landfill. DEW concludes that significant contamination of soil and water is unlikely to arise from these uses.

6.3.5 Use in bot fly/worming paste for horses

Dichlorvos is used in a worming and bot fly paste for horses at a dose rate of 0.5 g dichlorvos/100 kg body weight, potentially as often as once per month in the bot fly season (DEW understands that in practice, regular treatment every 6 weeks may occur, with a change to a different active ingredient every 6 months - K Daniels, pers. comm. 21 Oct 1999). DEW has no specific information on the metabolism of dichlorvos in horses, but from the available animal metabolism studies (Section 4.1 of Chemistry and Residue Evaluation) expects that with this type of formulation a high proportion of the administered dose would be absorbed and metabolised or hydrolysed in the animal. Dichlorvos which has not been absorbed may hydrolyse to some degree during passage through the gut (though at a slow rate under highly acidic conditions), be metabolised by gut microflora (possibly only to a limited degree - Section 6.7), and be hydrolysed and/or metabolised in evacuated manure. For example, in a ^{32}P-labelled dichlorvos study with cows and goats (Casida *et al.* 1962) 34% of the orally dosed dichlorvos was excreted in faeces and "The ^{32}P in the faeces of treated cows was present predominantly (greater than 95%), if not entirely, as ionic DDVP derivatives" (faeces samples collected at or for the period 144 hours after dosing).

Concentrations of dichlorvos toxic to birds may evidently remain in freshly evacuated manure where an animal has been dosed with dichlorvos supplied in a pelleted formulation (Section 6.2.5). A metabolism study (Potter *et al.* 1973) with pigs given a single dose of ^{14}C-vinyl labelled dichlorvos in a slow release pellet formulation found 62% of administered radioactivity was recovered in pellets in faeces (presumably largely as unchanged dichlorvos), with an additional 6% of radioactivity in the remainder of the faeces (Section 4.1.3 of Chemistry and Residue Evaluation). Information provided by the paste manufacturer on a pellet formulation containing dichlorvos (source not stated) indicates that horse wormer pellets are non-digestible and may be observed in manure from treated horses as soon as 10 h following administration, with an average time to first appearance in manure of 24 h and presence of pellets in faeces for up to 5 d following treatment.

In addition to being toxic to birds attracted to eat the pellets, such residues may also be toxic to dung beetles and particularly their larvae emerging in the manure. However, the only oral formulation of dichlorvos available in Australia is a paste formulation, in which dichlorvos should be freely available for absorption and degradation (DEW notes that there are also several worm/bot fly control products for horses containing the organophosphate trichlorfon, which initially breaks down to form dichlorvos, including one “palatable granule” formulation).

Hence very little or no dichlorvos is expected to remain in faeces from application in worming paste and DEW concludes that little or no toxicity is expected to dung beetles and/or their larvae from residues in horse manure. Even if some toxicity to larvae were to occur with this use, the risk on each treatment occasion would be short term and localised and would not be expected to affect overall populations of dung beetles. Furthermore, aside from breeding and training establishments, horses generally are not present in large numbers or high concentrations per hectare of land, whereas protection of dung beetles is more crucial with cattle.

Small quantities of the paste may remain in the syringe after use. The label appropriately indicates that the syringe (which is not sharp) should be disposed of by wrapping with paper and putting in garbage, thus any such residues would be expected to end up in landfill or burial on site.

6.3.6 Use in animal housing, meatworks and on poultry manure

The recommendation for using dichlorvos to control flies, mosquitoes and fleas in situations such as animal housing and meatworks is to apply a coarse spray to walls and other surfaces at 15 g dichlorvos in 15 L water/100 m^2, i.e. 0.15 g dichlorvos/m^2 treated surface. The recommended rate for fly control in poultry manure is 30 g dichlorvos in 10 L water per 12 m of manure under cages, or 2.5 g dichlorvos per m^2 manure, assuming a treated width of 1 m. The latter use on manure could result in a concentration in the manure of the order of 50 mg/kg in the surface 5 cm layer of manure. If 12 t/ha of manure containing residues at this level were applied to land and incorporated to a depth of 15 cm in soil, the resulting dichlorvos concentration in soil would be < 0.3 mg/kg (assuming soil bulk density = 1.4 g/cm^3). Thus even if no dissipation occurred from manure before distribution in the field, soil concentrations would be well below toxic levels to earthworms (LC50 = 80.9 mg/kg soil for *Eisenia foetida*, Section 6.4.2). Rapid dissipation would be expected once manure was composted or applied to soil, if not in situ in the poultry shed.

Dichlorvos residues on treated surfaces would be expected to dissipate within a few days by volatilisation (dry surfaces), and by hydrolysis and microbial degradation (moist surfaces and possibly manure). Residues remaining in manure when it is removed would be expected to dissipate rapidly in subsequent composting or field application. Significant concentrations of dichlorvos could result in drainage water if treated surfaces are washed while residues are relatively fresh (eg up to 150 mg/L if washed with 1 L water/m^2), but minimum re-entry periods for occupational health and safety reasons should suffice to prevent this occurring and manure under cages is unlikely to be deliberately wetted.

Non-target organisms in the vicinity of the treated area are likely to be directly or indirectly exposed to dichlorvos, but residues of dichlorvos are not expected to persist and any such effects are expected to be short term and localised. However, repeated application every 3 weeks as recommended to poultry manure could presumably affect non-target insect and mite species which can develop in poultry manure (potentially including various insect and mite predators and parasites of fly life stages).

DEW presumes that effluent and drainage ponds would be installed at meatworks and for most animal housing situations, at least with modern and/or large facilities. Any residues removed in washing water or effluent would be expected to be diluted and degraded rapidly in these ponds and should not be harmful to most micro-organisms present. In the event that interception ponds are not present, freshly treated surfaces should not be washed, or drainage water which might contain residues of dichlorvos should not be allowed to enter directly into natural watercourses such as creeks etc., as such residues could be harmful to fish and particularly, aquatic invertebrates. Current label statements need to be amended to address such mechanisms of aquatic contamination.

6.3.7 Use on stored products and storage/handling areas

Products and their storage areas which may be treated range from flowers to potatoes to grains. DEW will consider the case of wheat, where residues on treated grain may potentially affect birds.

Desmarchelier (1977) reported that the commercial rate for dichlorvos in grain (in NSW) was 6 ppm (mg/kg) and this rate is indicated on some labels for treatment of “infested grain held by flour millers,” by application to the grain on the elevator. A comparable rate results in the surface 5 cm of treated grain if the surface of wheat in storage is treated at a rate of 25 g ac/100 m^2, assuming a wheat bulk density of 0.8 g/cm^3. A higher treatment rate of 12 ppm is used to treat lesser grain borer. Thus initial residues on bulk wheat grain are expected to be 12 ppm or less, declining with a half-life of 3-20 days at 20-35°C and more slowly at lower temperatures, depending on moisture content (Section 5.9).

Concentrations on bulk grain freshly treated with dichlorvos are therefore expected to be well below dietary LD50s to birds ($\geq$ 300 ppm) and comparable in magnitude to the NOEC from various dietary and reproductive studies (Sections 6.2.2-6.2.3). Nonetheless, there have been reports in the literature of fatalities occurring with birds fed grain treated with dichlorvos (Section 6.2.5). DEW concludes that such harmful exposure may have followed accidental or deliberate contamination of grain at much higher concentrations than those normally used (eg one instance noted a concentration of 300 ppm), or consumption of freshly treated grain from only the surface layer of grain. Care to clean up spilt grain (eg around augers) is therefore indicated, while adequate safety to birds or other animals should be provided where treated grain is not moved until the withholding period for human or animal feed consumption is reached.

Residues of dichlorvos as high as 250 ppm have been reported in the past in silo dust (Pym *et al.* 1984). High levels in silo dust possibly arose because residues are concentrated on the epidermis of the grain, which presumably contributes to much of the silo dust, and may be very dry and contain significant residues if the contents of the silo are shipped shortly after treatment. High residues in dust could also arise from treatment of the silo surfaces if they are not cleaned thoroughly prior to application. Thorough cleaning is mentioned on some, but not all product labels in reference to treatment of empty silos. However, DEW expects that silo dust would normally be dumped on farm or conveyed to landfill, where any remaining dichlorvos residues would be expected to degrade within a few days to weeks under moist conditions.

In addition to treatment of grain in storage, surfaces of buildings, bins and machinery used for grain storage and movement may be treated. Limited release into the environment should occur in this process. In the absence of spillage or other accidental release, DEW expects that the applied dichlorvos will degrade on the grain or in the external atmosphere after volatilising from the grain and treated surfaces. Freshly treated grain and silo or other surfaces are unlikely to be exposed to rain or washed.

DEW concludes that significant contamination of soil and water is not expected to arise from use on stored grain and grain storage areas, as freshly treated material or surfaces are not expected to be exposed to rain or washed and contaminated dust would normally be expected to be conveyed to landfill. The risk to birds from treated grain is acceptable, provided birds do not have access to freshly treated grain. Spilt grain would be expected to be cleaned up promptly to avoid waste and attracting pests such as rats, and should minimise the risk of birds consuming treated grain, but a statement to protect birds from exposure to contaminated spilt grain should be placed on product labels with these uses.

6.3.8 Use in domestic, recreational and industrial areas

There are a range of uses given on several labels with various formulations (some in combination with other active ingredients), for use in domestic, recreational, commercial and industrial areas to control a wide range of pests. The label directions are for several application methods, ranging from fog or mist to a spray or sprinkle to bait (solution with sugar in water).

Where these uses pertain to the interior of structures or areas immediately surrounding buildings, the environmental exposure is not expected to be high. Minimum re-entry periods for occupational health and safety reasons should be sufficient for surfaces to dry before action such as washing occurs in interior areas. However, labels should generally caution against washing treated surfaces before applied product has dried to minimise the risk of residues being leached into drainage water.

For use in some outdoors situations, the directions of use have rates for foggers (undiluted 50% EC at 150 g ac/ha) or misters (75 g ac/ ha as a 0.05% solution of 50% EC in water). Foggers and misters produce fine spray droplets with high potential for drift, but the rates used are relatively low and residues of dichlorvos are expected to dissipate rapidly in such open air situations. The discussion regarding use on avocados indicates the potential risks to birds and non-target terrestrial arthropods exposed to the spray or spray drift, and the high risk to aquatic invertebrates if drift reaches natural water bodies, though the duration of the risk from each application is likely to be short term.

Refuse and areas of garbage are likely to be of minimal environmental significance, provided wind does not carry drift to sensitive areas. The potential impact of use in picnic and recreational areas would depend on the location, eg near sensitive areas or in highly modified areas, and the scale and frequency of application. In both cases, product labels should include a caution that aquatic areas should not be treated and that spraying should not be undertaken under conditions likely to cause drift onto sensitive areas, including native vegetation and aquatic areas. To prevent residues entering run-off, product labels should also carry a warning that the product should not be used if areas are to be washed down or if rain is expected before the applied product has dried.

6.3.9 Use for European wasp control

Dichlorvos is also used for the control of European wasps, where there is a specific need for a fumigant action with rapid knockdown. For this purpose, the spray mixture is applied to all the entrance holes of the nest. Some labels simply advise “spray in and around the entrances of nests,” while one label indicates that the spray mixture should be applied to all the entrance holes of the nest and warns that the product should not be applied to other areas, including trees, ground, rockeries or buildings. Presumably the latter comment is intended to prevent users unnecessarily drenching the general vicinity of the nest: similar advice on the method to be used for European wasp control should be added to all labels recommending this use. Rates used are up to 1 L mixture (6-10 g ac) per nest.

Environmental exposure from this source is not expected to be high and residues of dichlorvos would be expected to degrade rapidly in soil or water. Harm to terrestrial invertebrates should be confined to the immediate vicinity of the treated area, including soil into which the mixture drains. Application if watering or rain are expected before surface residues have dried should be forbidden on the label, to minimise the risk of residues leaching into natural water.

6.4 Summary of Environmental Risk Assessment

Most uses of dichlorvos in Australia involve relatively little risk of exposure of terrestrial and aquatic environments, as this pesticide is used to a large extent in non-agricultural situations and/or in enclosed areas or slow release formulations. Use on crops in the field is very minor and restricted to one specific pest in one crop – leaf rollers in avocados. Use on crops in protected crop environments is also minor. Use directly on animals is restricted to administration as one of two active ingredients in an orally-administered paste for bot fly and worm control in horses. More significant uses include disinfestation of harvested and stored products and treatment of produce storage and handling areas, wineries, grain mills, animal housing, manure heaps and abattoirs/meatworks. Major uses also include control of a wide range of pests in domestic, recreational and industrial areas. These may range from confined spaces such as clothes cupboards and rubbish bins, to specific areas such as the vicinity of European wasp nests, to treatment of open areas such as rubbish dumps.

6.4.1 Risk from vapour release to the atmosphere

Dichlorvos is volatile and a significant proportion of the applied substance is expected to vaporise and enter the external atmosphere, but it is expected that emissions of dichlorvos to the external atmosphere will dissipate rapidly through dilution, degradation and removal in precipitation and that atmospheric concentrations will remain well below toxic levels.

6.4.2 Risks to birds and mammals

6.4.2.1 Agricultural spray application and outdoor misting/fogging applications

Dichlorvos may be toxic to birds by inhalation, absorption through the skin and ingestion through preening of contaminated feathers or consumption of contaminated fruit, foliage or insects. A risk assessment of the use of dichlorvos in avocados indicates that residues of dichlorvos in treated orchards are unlikely to result in toxicity to birds or mammals by dietary exposure. It is concluded that the use of dichlorvos in avocado orchards as described may present a risk to birds and mammals such as flying foxes if they are directly exposed to spray or spray drift or enter freshly sprayed trees while they are still wet. However, this risk is relatively low, as avocados are not Australian natives and do not carry attractive ripe fruit, birds present are likely to be disturbed by the noise and disruption from spraying, and residues are likely to dissipate rapidly.

Some risk to birds could also arise with fogging or misting of dichlorvos in outdoor situations such as refuse and garbage areas and picnic and recreational areas, but again the presence of people and disruption from spraying operations is likely to deter birds in the vicinity, at least during spraying. Refuse/garbage areas are likely to be of minimal environmental significance, provided wind does not carry drift to sensitive areas, though in some cases recreational/picnic areas could be near sensitive environmental locations.

6.4.2.2 Other uses

There are reports of birds having been poisoned through consuming grain treated with dichlorvos, drinking water containing dichlorvos, and in one case, through consuming pellets containing dichlorvos deposited in manure.

Concentrations on bulk grain freshly treated with dichlorvos are expected to be well below dietary LD50s to birds comparable in magnitude to the NOEC from various dietary and reproductive studies. It appears that harmful exposure may have followed accidental or deliberate contamination of grain at much higher concentrations than those normally used, or consumption of freshly treated grain from only the surface layer of grain. Care to clean up spilt grain (eg around augers) is therefore indicated, while adequate safety to birds or other animals should be provided where treated grain is not moved until the withholding period for human or animal feed consumption is reached.

The only oral dosing formulation of dichlorvos used in Australia is a paste, in which dichlorvos should be freely available for absorption and degradation. Very little or no dichlorvos is expected to remain in faeces from application in worming paste, and any residues would not be concentrated in potentially attractive pellets and are unlikely to be harmful to birds.

6.4.3 Risk to aquatic organisms

DEW has assessed the risk to aquatic organisms from dichlorvos based on its use in avocados at an application rate of 500 g ac/ha through an air blast sprayer. Direct application to a shallow water body presented an unacceptable risk of harm to aquatic invertebrates and also potentially to fish, and a 10% drift scenario presented an unacceptable risk to aquatic invertebrates, but a mitigable risk to fish. Concentrations in a 15 cm deep water body downwind of a sprayed area were estimated using the AgDRIFT™ model. At 100 m and 200 m downwind, respectively, estimated dichlorvos concentrations were 0.49 and 0.24 μg/L (0.15% and 0.07% drift) respectively, exceeding the EC50 for the most sensitive organism (water fleas, 48 h EC50 = 0.07 μg/L) by a factor of 7.4 and 3.6, respectively, but well below toxic levels to fish. Consideration of mitigating factors such as deeper water (30 cm) and dissipation from the contaminated water did not reduce the risk to aquatic invertebrates from spray drift adequately and it is considered that the longer buffer distance that would be needed to protect aquatic organisms from drift would be impracticable. Hence it is recommended that use of dichlorvos for leaf roller control in avocados be deleted from product labels.

Dissipation of dichlorvos from leaf and soil surfaces is likely to minimise the risk of aquatic contamination by run-off unless rain follows within a few hours of application. Hence the product label should indicate that the product should not be used if rain is expected within 4 hours.

A similar risk to aquatic invertebrates pertains to any other use of dichlorvos where residues may reach water, either by spray drift or wash off or leaching of residues before they have volatilised or degraded.

6.4.4 Risk to non-target terrestrial invertebrates

6.4.4.1 Bees and other non-target arthropods

The use of dichlorvos in field situations (orchards, refuse/garbage areas, recreational/picnic areas) is likely to be toxic to any arthropods exposed to it, including bees and insect predators and parasites, predominantly in the air and in plant canopies. However, the risk from dichlorvos is only expected to be transitory and confined to the sprayed area and adjacent areas reached by drift. Hence labels should warn dichlorvos is dangerous to bees and will kill bees and other pollinators foraging in the area sprayed or in hives which are over-sprayed or reached by spray drift Use of the spray may impact upon IPM programs, but the effects of dichlorvos itself are expected to be short term due to its transitory, fumigant action.

A risk to non-target arthropods may also occur with uses in any other situation, but this is generally not expected to be of concern. A possible exception could be pollinators or IPM programs in glasshouses/greenhouses, but DEW presumes this is unlikely with the nature of use in these situations. A suitable label warning may still be appropriate to cover such situations.

Very little or no dichlorvos is expected to remain in horse faeces from application in worming paste and any residues would continue to decline rapidly due to hydrolysis and microbial degradation. Hence it is concluded that little or no toxicity is expected to dung beetles and/or their larvae from residues in horse manure, with at most minor effects on local populations despite repeated treatment.

6.4.4.2 Earthworms

Expected concentrations in soil reached directly by spray at the rate of 500 g dichlorvos/ha would be ~0.7 mg/kg if confined to the surface 5 cm of soil. Furthermore, dichlorvos is likely to dissipate rapidly from the soil and foliage surfaces, minimising residues moving into the soil. In the case of application to poultry manure, even if dichlorvos did not dissipate before spreading and incorporation into soil, soil concentrations would be similarly low. In both cases, the expected maximum soil concentration is well below the 14 d LC50 of dichlorvos to the earthworm *Eisenia eisenia foetida*. Hence DEW concludes that little risk pertains to earthworms from field use of dichlorvos or use on manure. With other uses of dichlorvos the potential for contamination is low and a low risk to earthworms is again indica

6.4.5 Terrestrial plants

There is little risk of spray reaching terrestrial plants with many uses of dichlorvos and labels for glasshouse/greenhouse uses caution against spraying directly onto plants. In the only field situation where the substance is used on plants, direct application from ground-based equipment is unlikely to lead to direct overspray of non-target vegetation and lower rates from drift would have less likelihood of causing phytotoxicity.

6.4.6 Risk arising from formulation, handling and disposal

The risk from formulation of the active constituent into end user products in Australia is expected to be minimal, as this is expected to be done in suitable facilities, with relevant environmental controls to limit environmental exposure and with waste water treated before discharge to the environment (dichlorvos is expected to degrade during normal sewage treatment). Any spills are expected to be cleaned up and treated according to the MSDS.

7 REFERENCES

Alabaster JS (1969). Survival of fish in 164 herbicides, insecticides, fungicides, wetting agents and miscellaneous substances. Intern. Pest Control 11(2): 25-35.

Ali SF et al. (1979). Effect of DDVP (insecticide) on citric acid fermentation in Aspergillus niger. Enzyme Microb. Technol. 1: 127-128. [Cited by WHO (1989) – NOT SEEN by DEW.]

AMGA (Australian Mushroom Growers Association Ltd 1995) Mushrooms. In: Coombs B (ed), Horticulture Australia: The Complete Reference of the Australian Horticultural Industry, pp 234-239. Morescope Publishing Pty Ltd, Hawthorn East, Victoria.

Anderson LD & Atkins EL (1967). Toxicity of pesticides to honey bees in the field. University of California Agricultural Extension Service, AXT-251.

Anderson LD et al. (unknown date). Toxicity of pesticides to honey bees. ECRP Submission, unpublished extension report.

Anon (1968). Suggested guide for the use of insecticides to control insects affecting crops, livestock, households, stored products, forests, and forest products 1968. US Department of Agriculture, Agriculture Handbook No. 331 (excerpt only).

Anon (1999). Daleys Fruit Tree Nursery. Avocado. Internet “fact sheet” http://www.nor.com.au/business/daleys/facavo.html

Anon (unknown date). The bee poisoning hazard from pesticides. Washington Agricultural Experiment Station, Bulletin 709. (Excerpt only).

Atkins EL & Anderson LD (1967). Toxicity of pesticides and other agricultural chemicals to honey bees. Laboratory studies. University of California Agricultural Extension Service, Circular M-16.

Atkinson R (1987). A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. International Journal of Chemical Kinetics 19:799-828.
Atkinson R & Carter WPL (1984) Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. Chemical Reviews 84:437-470.

Ballington et al. (1978). Response of coliform populations in poultry waste digesters to three insecticides. J Environ. Qual. 7(2): 262-264. [Cited by WHO (1989) – NOT SEEN by DEW.]

Bayer (1974a). Pesticide residues in the leachate (laboratory leaching test). Report 2702/74. Bayer AG, Leverkusen, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, p 6:142. Unpublished Report.

Bayer (1974b). Pesticide residues in the leachate (laboratory leaching test). Report 2703/74. Bayer AG, Leverkusen, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, p 6:143. Unpublished Report.

Bayer (1974c). Pesticide residues in the leachate (laboratory leaching test). Report 2704/74. Bayer AG, Leverkusen, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, p 6:144. Unpublished Report.

Bayer (1975). Behaviour of plant protection materials in soil (laboratory experiment in breakdown). Dichlorvos. Report 2700/75. Plant Protection Application Technology, Biological Research, Bayer AG, Leverkusen, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, pp 6:145-146. Unpublished Report.

Bayer (1980). Toxicity to fish. Report No. FF-110. Crop Protection Application Technology, Chemical Product Development and Ecobiology, Bayer AG, Leverkusen, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book X, Part 7: Environmental toxicology, pp 7:058-060. Unpublished Report. Unpublished Report.

Bayer (1981). Toxicity to fish. Report No. FO-373. Crop Protection Application Technology, Chemical Product Development and Ecobiology, Bayer AG, Leverkusen, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book X, Part 7: Environmental toxicology, pp 7:065-068. Unpublished Report.

Bayer (1982a). Action of plant protection agents in water – hydrolytic decomposition of dichlorvos. Report WLF H 034. Federal Biological Institute for Agriculture and Forestry, Division of Plant Protection Agents and Application Technology, Braunschweig, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, pp 6:158-164. Unpublished Report.

Bayer (1982b). The behaviour of dichlorvos residue in soil. Report RA 678/93B. Plant Protection Division, Application Technology CE, Institute for Metabolic Research and Residue Analytics, Leverkusen, Germany. Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, pp 6:057-058. Unpublished Report.

Bayer (1982c). Acute oral toxicity/bird: canary (Serinus canarius). Report No. VK-207. Plant Protection Application Technology, Chemical Product Development and Ecobiology, Bayer AG, Leverkusen, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book X, Part 7: Environmental toxicology, p 7:006. Unpublished Report.

Bayer Australia Ltd Agricultural Division (1988a). Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book I, Part 1: Submission summary. Unpublished Report.

Bayer Australia Ltd Agricultural Division (1988b). Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book II, Part 1: Chemical data. Unpublished Report.

Beran (1979). [Present knowledge on the toxicity of our pesticides to bees.] Gesunde Pflanz. 22(2): 21-31. [Cited by WHO (1989) – NOT SEEN by DEW.]

BNA (1999). Use of insecticide dichlorvos ruled illegal by Dutch Board for Industry. International Environment Reporter 22(11):455. Bureau of National Affairs, Inc., Washington DC.

Bolton (1995). Avocados. In: Coombs B (ed), Horticulture Australia: The Complete Reference of the Australian Horticultural Industry. Morescope Publishing Pty Ltd, Hawthorn East, Victoria, pp 353-358. Morescope Publishing Co. Hawthorn East, Victoria, Australia.

Brown VKH et al. (1968). The toxicity of low concentrations of dichlorvos by inhalation in rodent and avian species. Sittingbourne, Shell Research Ltd. Report No. TLGR.0015.68. Unpublished.

Butler GL (1977). Algae and pesticides. Residue Review 66: 40. [Cited by WHO (1989) – NOT SEEN by DEW.]

Casida JE et al. (1962). Metabolism of 2,2-dichlorovinyl dimethyl phosphate in relation to residues in milk and mammalian tissues. Journal of Agricultural and Food Chemistry 10: 370-377.

Chen ZM, Zabik MJ and Leavitt RA (1984). Comparative study of thin film photodegradative rates for 36 pesticides. Ind. Eng. Chem. Prod. Res. Dev. 23:5-11. [Cited by WHO (1989) – NOT SEEN by DEW.]

Ciba-Geigy Australia Limited (1988). Technical Dichlorvos Submission. Part I – Submission summary. Unpublished.

Connell DW (1990) Evaluation of the bioconcentration factor, biomagnification factor, and related physicochemical properties of organic compounds. In: Connell DW ed, Bioaccumulation of Xenobiotic Compounds. CRC Press, Boca Raton, USA.

Connell D and Hawker D (1986). Predicting the Distribution of Persistent Organic Chemicals in the Environment. In Chemistry in Australia. December 1986. pp 428-431.

Davies IM (1995). Pesticide usage in modern fish farming – the role of the chemist. In Best G and Ruthven (eds), Pesticides: developments, impacts, and controls, pp 135-140. Royal Society of Chemistry, Cambridge, UK.

DeCino TJ (1963). Letter dated Mar 27 1963 (with attached table) to WM Zeck of Vero Beach Laboratories, Inc, Vero Beach, Florida from TJ DeCino of United States Department of the Interior Fish and Wildlife Service, Wildlife Research Center, Denver Colorado. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book X, Part 7: Environmental toxicology, pp 7:004-005. Unpublished.

Dedek W, Georgi W and Grahl R (1979). Comparative degradation and metabolism of ^{32}P-labelled butonate, trichlorphone and dichlorvos in crop plants. Biochem. Physiol. Pflanzen 174:707-722.

Desmarchelier JM (1977). A model of the breakdown of dichlorvos on grain. Australian Journal of Experimental Agriculture and Animal Husbandry 17:818-825.

Dmitriev AI and Kozemjakjn NG (1975). [Veterinary expert report on the meat of chicken poisoned by dichlorvos.] Veterinarija 1975(1):90-92.

Dobson DP & Tack TJ (1991). Evaluation of the dispersion of treatment solutions of dichlorvos from marine salmon pens. Aquaculture 95(1): 15-32.

Dougherty EM et al. (1971). Sensitivity of Bacillus thuringiensis var. thuringiensis to various insecticides and herbicides. J Invertebr. Pathol. 17: 292-293. [Cited by WHO (1989) – NOT SEEN by DEW.]

Draughton FA and Ayres JC (1978). Effect of selected pesticides on growth and citrinin production by Penicillium citrinum. J Food Science 43: 576-578. [Cited by WHO (1989) – NOT SEEN by DEW.]

Drevenkar V et al. (1975). Archiv Za Higyino Roda I Toksikologiju 26:257-266. [Cited by Howard (1991) – NOT SEEN by DEW.]

Drevenkar V et al. (1976). The fate of pesticides in aquatic environment. II. Hydrolysis of dichlorvos in a model system and in river water. Archiv Za Higyino Roda I Toksikologiju 27:297-305.

Driver, C J, Ligotke, M W, Voris, P V, McVeety, B D, Greenspan, G J and Drown, D B (1991). Routes of Uptake and their Relative Contribution to the Toxicologic Response of Northern Bobwhite (Colinus virginianus) to an Organophosphate Pesticide. Environ. Toxicol. Chem. 10: 21-33.

Egidius E & Moster B (1987). Effect of Neguvon and Nuvan treatment on crabs (Cancer parugus, C. moenas) lobster (Homarus gammarus) and the blue mussel (Mytilus edulis). Aquaculture 60: 165-168.

Eisler (1969). Acute toxicities of insecticides to marine decapod crustaceans. Crustaceana 16: 302-310. [Cited by WHO (1989) – NOT SEEN by DEW.]

Eisler (1970). Acute toxicities of organochlorine and organophosphorus insecticides to estuarine fish. Technical Paper No. 46, US Department of the Interior, Fish and Wildlife Service, Bureau of Sports Fisheries and Wildlife. Washington DC, USA. [Cited by WHO (1989) – NOT SEEN by DEW.]

Environmental Defense Fund (1999). Dichlorvos. Scorecard Chemical Profile. Internet http://scorecard.org/chemical-profiles/html/dichlorvos.html.

Felton JC, Oomen PA and Stevenson JH (1986). Toxicity and hazard of pesticides to honeybees: harmonisation of test methods. Bee World 67(3): 114-124.

Fletcher JS, Nellessen JE & Pfleeger TG (1994). Literature review and evaluation of EPA food-chain (Kenaga) nomogram, an instrument for estimating pesticide residues on plants. Environmental Toxicology and Chemistry 13(9):1338-1391.

Fritz R (1987a). Degradation of [1-^{14}C]dichlorvos in soils under aerobic conditions. $^{14}CO_2$ study. Bayer AG Geschäftsbereich Pflanzenschutz Forschung CE, Institut für Metabolismusforschung, Monheim, Germany. Report PF No. 2836. ECRP Submission, Unpublished Report.

Fritz R (1987b). Aerobic metabolism of dichlorvos in an aquatic ecosystem model. Bayer AG Geschäftsbereich Pflanzenschutz Forschung CE, Institut für Metabolismusforschung, Monheim, Germany. Report PF No. 2893. ECRP Submission, Unpublished Report.

Fritz R and Brauner A (1987). Study on the metabolism of dichlorvos in soils under aerobic conditions. Bayer AG Geschäftsbereich Pflanzenschutz Forschung CE, Institut für Metabolismusforschung, Monheim, Germany. Report PF No. 2857. ECRP Submission, Unpublished Report.

Ganzelmeier H et al. (1995). Studies on the spray drift of plant protection products. Results of a test program carried out throughout the Federal Republic of Germany. Mitteilungen aus der Biologischen Bundenastalt für Land- und Fortwirtschaft, Berlin-Dahlem, H. 305.

GESAMP [IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection] (1997). Towards safe and effective use of chemicals in coastal aquaculture. Reports and Studies No. 65. Food and Agriculture Organisation of the United Nations, Rome.

Getzin LW and Rosefield I (1968). Organophosphorus insecticide degradation by heat-labile substances in soil. Journal of Agricultural and Food Chemistry 16(4):598-601.

Gore RC et al. (1971). J Assoc Off Anal Chem 54:1040-1082.

Grahl K (1979). [The persistence of trichlorfon and dichlorvos in ponds.] Z. Binnenfisch. DDR 25(10):312-316. [Cited by WHO (1989) and Howard (1991) – NOT SEEN by DEW.]

Grahl K et al. (1980). [Toxicity of butonate, trichlorfon, and dichlorvos to Escherischia coli and Enterobacter aerogenes.] Acta Hydrochim. Hydrobiol. 8: 19-28.] [Cited by WHO (1989) – NOT SEEN by DEW.]

Grahl K et al. (1981). [Effect of butonate, trichlorfon, and dichlorvos on plankton populations.] Acta Hydrochim. Hydrobiol. 9(2): 147-161.] [Cited by WHO (1989) – NOT SEEN by DEW.]

Guerguis and Shafik (1975). Bull Entomol Soc Egypt Econ Ser 8:29-32. [Cited by Howard (1991) – NOT SEEN by DEW.]

Guth JA and Voss G (1970). Photodecomposition of dichlorvos, phosphamidon, dicrotophos, monocrotophos, dioxacarb, C-10015, and C-17018 in aqueous and methanoic solutions. Report SPR 09/70 mow. Agrochemical Division, CIBA Limited, Basle, Switzerland. ECRP Submission, Unpublished Report.

Haas G (1970). Appraisal of the tolerance of Mafu Strip (manufactured by Farbenfebriken Bayer AG) for birds, fish and small mammals. Zoologischer Garten Wuppertal, Germany. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book X, Part 7: Environmental toxicology, pp 7:008-014. Unpublished Report.

Hattori K (1974). [Toxicological studies on the effects of chemicals on birds, part 2. Acute oral toxicity of fenitrothion, trichlorfon, and dichlorvos in the common pigeon.] Hokkaidoritsu Eisei Kenkyusho Ho (Rep. Hokkaido Inst. Pub. Health) 24:154 (Toxicology & Pharmacology Abstract No. 75-.3830).

Hattori K et al. (1974). [Toxicological studies on the effects of chemicals on birds, part 1. Acute oral toxicity and cholinesterase inhibition of three organophosphate insecticides in Japanese quail.] Hokkaidoritsu Eisei Kenkyusho Ho (Rep. Hokkaido Inst. Pub. Health) 24:35-38.

Heimbach F (1985). Trial report. Growth inhibition on green algae (Scenedesmus subspicatus) by dichlorvos (techn.). Bayer AG, Plant Protection Application Technology, Institute for Ecobiology, Leverkusen, Germany. Report HBF/Al 17. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book X, Part 7: Environmental toxicology, pp 7:208-222. Unpublished Report.

Heimbach F (1986). Test report. Acute toxicity of dichlorvos (technical) to waterfleas. Bayer AG, Pflanzenschutz Anwendungstechnik, Institut für Ökobiologie, Leverkusen, Germany. Report HBF/Dm 54. ECRP Submission, Unpublished Report.

Helling CS and Turner BC (1968). Pesticide mobility: determination by soil thin-layer chromatography. Science 12:562-563. [Cited by Howard (1991) – NOT SEEN by DEW.]

Helson BV et al. (1994). Laboratory toxicology of six forestry insecticides to four species of bee (Hymenoptera: Apoidea). Arch. Environ. Contam. Toxicol. 27: 107-114.

Hill EF & Heath RG (1975). Lethal dietary toxicities of environmental pollutants to birds. United States Department of the Interior Fish and Wildlife Service. Special Scientific Report – Wildlife No. 191. Washington D.C.

Horváth L et al. (1982). Application of a radiometric enzymic method for monitoring organophosphorus and carbamate insecticide residues in water of the Danube River. In Horváth L (1982). Persistence of organophosphorus pesticides in aquatic environments. Final Report for the Period 1976-07-01 – 1982-07-31. Institute of Isotopes. Hungarian Academy of Sciences, Budapest, Hungary. International Atomic Energy Agency, Vienna. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, pp 6:102-110. Unpublished Report.

Howard PH (ed) (1991). Handbook of Environmental fate and Exposure data for Organic Chemicals. Volume III, Pesticides, pp 251-258. Lewis Publishers Chelsea, Michigan, USA.

Hudson RH, Tucker RK & Haegele MA (1984). Handbook of Toxicity of Pesticides to Wildlife 2^{nd} Edition. United States Department of the Interior Fish and Wildlife Service. Resource Publication 153. Washington D.C.

Hussey NW and Hughes JT (1963). Report on observation made following the application of DDVP in mushroom houses and Report on observations made on use of DDVP to control mushroom flies at GHCRI Littlehampton. Glasshouse Crops Research Unit. ECRP Submission, Unpublished Report.

Hussey NW and Hughes JT (1964). Investigations on the use of dichlorvos in the control of the mushroom phorid, Megaselia halterata (Wood). Annals of Applied Biology 54:129-139.

Jakubowska and Nowak (1973). [The effect of organophosphorus and carbamate insecticides on the development of soil fungi.] Zesz. Nauk. Akad. Roln. Szczecinie 39(10): 141-150. [Cited by WHO (1989) – NOT SEEN by DEW.]

Johansen CA (1979). Honeybee poisoning by chemicals: signs, contributing factors, current problems and prevention. Bee World 60(3): 109-127.

Johnson WW & Finley MT (1980). Handbook of acute toxicity of chemicals to fish and aquatic invertebrates. Resource Publication No. 137, US Department of the Interior, Fish and Wildlife Service. Washington DC, USA. [Cited by WHO (1989) – NOT SEEN by DEW.]

Kenaga EE (1979). Acute and chronic toxicity of 75 pesticides to various animal species. Down to Earth 35(2): 25-31.

Kenaga EE (1980). Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. Ecotoxicology and Environmental Safety 4:26-38.

Khan S and Khan NN (1986). Soil Science 142:214-222. [Cited by Howard (1991) – NOT SEEN by DEW.]

Klusacek H and Krasemann R (1985). Thermal stability of the agrochemical active ingredient dichlorvos. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book II, Part 1: Chemical data, pp 1:014-018. Unpublished Report.

Koesoemadinata S (1983). Lethal toxicity of 24 insecticide formulations commonly used for rice pest control in irrigated rice field to two Indonesian freshwater fish species, Cyprinus carpio and Puntius gonionotus. Badan Pelelitian dan Pengembangan Pertanian, Balai Penelitian Perikanan Darat (Research Institute for Inland Fisheries, Bogor, Indonesia).

Kudamatsu A (1977). Bee toxicity of pesticides. Nihon Tokushu Noyaku Seizo K.K. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book X, Part 7: Environmental toxicology, p 7:196. Unpublished Report.

Kuwabara K, Nakamura A & Kashimoto T (1980). Effect of petroleum oil, pesticides, PCBs, and other environmental contaminants on the hatchability of Artemia salina dry eggs. Bull. Environ. Contam. Toxicol. 25: 69-74. [Cited by WHO (1989) – NOT SEEN by DEW.]

Kwok ESC and Atkinson R (1995). Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update. Atmospheric Environment 29(14):1685-1695.

Lamoreaux RJ and Newland LW (1978). The fate of dichlorvos in soil. Chemosphere 7(10):807-814.

Laveglia J and Dahm PA (1977). Degradation of organophosphorus and carbamate insecticides in the soil and by microorganisms. Annual Review of Entomology 22:483-513.

Lewallen LL & Wilder WH (1962). Toxicity of certain organophosphorus and carbamate insecticides to rainbow trout. Mosquito News 22(4): 369-372.

Lieberman MT and Alexander M (1981). Effects of pesticides on decomposition of organic matter and nitrification in sewage. Bulletin Environm. Contam. Toxicol. 26:554-560.

Lieberman MT and Alexander M (1983). Microbial and nonenzymatic steps in the decomposition of dichlorvos (2,2-dichlorovinyl O,O-dimethyl phosphate). Journal of Agricultural and Food Chemistry 31:265-267.

Lyman WJ (1982). Adsorption coefficient for soils and sediments. Chapter 4 (pp 4-1 to 4-33) in Lyman WJ, Reehl WF and Rosenblatt DH, eds, Handbook of chemical property estimation methods. Environmental behavior of organic compounds. McGraw-Hill Book Company New York.

Mani M & Krishnamoorthy A (1984). Toxicity of some insecticides to Apanteles plutellae, a parasite of the diamond back moth. Tropical Pest Management 30(2): 130-132.

Mary Sr.A et al. (1986). Toxicity evaluation of organophosphorus and chlorinated hydrocarbon pesticides in freshwater prawn Macrobrachium lamarrei. J. Environ. Biol. 7: 189. [Cited by Nikunen et al. (1990) – NOT SEEN by DEW.]

Matsumura F and Boush GM (1968). Degradation of insecticides by a soil fungus, Trichoderma viride. Journal of Economic Entomology 61(3):610-612.

McCall PJ et al. (1980). Estimation of chemical mobility in soil from liquid chromatographic retention times. Bulletin of Environmental Contamination and Toxicology 24:190-195.

McHenery JG et al. (1990). Comparative toxicity of dichlorvos to marine invertebrates. Scot. Fish. Work. Pap. No. 7/90. [Cited by McHenery et al. (1992, 1996) – NOT SEEN by DEW.]

McHenery JG et al. (1991). Lethal and sublethal effects of the salmon delousing agent dichlorvos on the larvae of the lobster (Homarus gammarus) and herring (Clupea harengus). Aquaculture 98: 331-347.

McHenery JG et al. (1992). Control of the use of the insecticide dichlorvos in Atlantic salmon farming. In Michel C & Alderman DJ (eds) “Chemotherapy in Aquaculture: from Theory to Reality.” Symposium, Paris, 12-15 March 1991, pp 179-186.

McHenery JG et al. (1996). Threshold toxicity and repeated exposure studies of dichlorvos to the larvae of the common lobster (Homarus gammarus L.). Aquat. Toxicol. 34(3):237-251[Cited on US EPA AQUIRE database – NOT SEEN by DEW.]

Mensink BJWG, Montforts M, Wijkhuizen-Maslankiewicz L, Tibosch H & Linders JBHJ (1995) Manual for summarising and evaluating the environmental aspects of pesticides. Report No. 679101022. National Institute of Public Health and the Environment, The Netherlands.

Messager JL & Esnault F (1992). [Treatment with dichlorvos of copepod infections in rainbow trout reared in seawater: modes of treatment adapted to French environmental conditions]. In Michel C & Alderman DJ (eds) “Chemotherapy in Aquaculture: from Theory to Reality.” Symposium, Paris, 12-15 March 1991, pp 195 et seq.

Muehlmann R and Schrader G (1957). The hydrolysis of phosphoric ester insecticides. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book IX, Part 6: Environmental chemistry and fate, pp 6:078-098. Unpublished Report.

Naidu NV et al. (1978). Toxicological investigation of dichlorvos in chicks. Indian Journal of Pharmacology 10(14):323-326.

Nair GA & Nair NB (1982). Effect of certain organophosphate biocides on the juveniles of the isopod, Alitropus typus M. Edwards (Crustacea:Flabellifera:Aegidae). J Anim. Morphol. Physiol. 29: 265-271.

Nikunen E, Leionen R & Kultamaa A (1990). Environmental Properties of Chemicals. Ministry of the Environment, Environmental Protection Department, Research Report 91. VAPK-Publishing, Helsinki, Finland.

Nishiuchi Y (1974). Testing methods for the toxicity of agricultural chemicals to aquatic organisms. Japan Pesticide Information No. 19: 15-19.

Nishiuchi Y (1981). Toxicity of pesticides to some aquatic organisms – I Toxicity of pesticides to some aquatic insects. English translation from Seitai Kagaku 4(2): 31-46.

Nowak A, Sevarcewicz M and Wyieralski J (1972). Wplyw zawartosci wegla organicznego w glebiei temperatura na dynamike zanikania Nogosu 50 EC. Zesz. Nauk. Akad. Roln. Szczecinie 38:293-298. [Cited by Bayer (1982b) – NOT SEEN by DEW.]

OECD (1992). The rate of photochemical transformation of gaseous organic compounds in air under tropospheric conditions. Environment Monograph No.61. Organisation for Economic Co-operation and Development, Paris. GD 92 (172).

Omkar & Shukla GS (1984). Alteration in carbohydrate metabolism of fresh-water prawn Macrobrachium lamarrei after dichlorvos exposure. Ind. Health 22: 133-136. [Cited by WHO (1989) – NOT SEEN by DEW.]

Omkar & Shukla GS (1985). Toxicity of insecticides to Macrobrachium lamarrei (H. Milne Edwards) (Decapoda, Palaemonidae). Crustaceana 48: 1. [Cited by Nikunen et al. (1990) – NOT SEEN by DEW.]

Petrova TM & Novozhilov KV (1980). Migr Zagryaz Vishchestv Pochvakh Sopredil'nykh Sridakh Tr Vses Soveshch 2: 136-143. [Cited by Howard (1991) – NOT SEEN by DEW.]

Pfleeger TG, Fong A, Hayes R, Ratsch H & Wiskliff C (1996). Field evaluation of the EPA (Kenaga) nomogram, a method for estimating wildlife exposure to pesticide residues on plants. Environmental Toxicology and Chemistry 15(4):535-543.

Pimentel D (1971). Ecological effects of pesticides on non-target species. Executive Office of the President, Office of Science and Technology. US Government Printing Office, Washington DC, USA, Stock No. 4106-0029 (excerpt only).

Potter JC et al. (1973). Carbon-14 balance and residues of dichlorvos and its metabolites in pigs dosed with dichlorvos-^{14}C. Journal of Agricultural and Food Chemistry 21: 163-166.

Purseglove JW (1968). Tropical Crops. Dicotyledons Vol. I, pp 192-198. Longmans, Green and Co. Ltd, London and Harlow.

Pym RAE et al. (1984). Effects of dichlorvos, maldison and pirimiphos-methyl on food consumption, egg production, egg and tissue residues, and plasma acetylcholinesterase inhibition in layer strain hens. Australian Journal of Experimental Agriculture and Animal Husbandry 24:83-92.

Pym RAE et al. (1976). The effect of dichlorvos (DDVP) as a contaminant in the feed of laying hens. Proceedings of the First Australian Poultry and Stock Feed Convention, Melbourne 2:313-316.

Rahmatullah M et al. (1978). Effect of organophosphorus insecticides on fermentation processes in Aspergillus niger. J Ferment. Technol. 56: 169-172. [Cited by WHO (1989) – NOT SEEN by DEW.]

Rath S & Misra BN (1979). Relative toxicity of dichlorvos (DDVP) to Tilapia mossambica Peters of 3 different age groups. Exp. Gerontol. 14: 307-309. [Cited by Spehar et al. (1981) – NOT SEEN by DEW.]

Rosenberg A et al. (1979). Microbial degradation of pesticides. PB 79-123156, US National Technical Information Service, Springfield, Virginia.

Ross A (1989). Nuvan use in salmon farming. The antithesis of the precautionary principle. Marine Pollution Bulletin 20(8): 372-3374.

Rowlands DG (1970). The metabolic fate of dichlorvos on stored wheat grains. Journal of Stored Product Research 6(1):19-32 - Abstract only. Insecticide Department, Pest Infestation Laboratory, Slough, UK.

Rowlands DG (1971). The metabolism of contact insecticides in stored grains. II. 1966-1969. In Gunther FR (ed), Residue Reviews 34.

Rowlands DG (1975). The metabolism of contact insecticides in stored grains. III. 1970-74. *In* Gunther FR (ed), Residue Reviews 58.

Salyani, M and Cromwell, R P (1992). Spray Drift from Ground and Aerial Applications. Transactions of the ASAE [American Society of Agricultural Engineers], 1992, 35, 1113-1120.

Samuelsen OB (1987). Aeration rate, pH and temperature effects on the degradation of trichlorfon to DDVP and the half-lives of trichlorfon and DDVP in seawater. Aquaculture 66:373-80.

Sanders HO & Cope OB (1966). Toxicities of several pesticides to two species of cladocerans. Trans. Am. Fish. Soc. 95(2): 165-169.

Sattar MA (1990). Fate of organophosphorus pesticides in soil. Chemosphere 20(3/4):387-396.

Schafer EW (1972). The acute oral toxicity of 369 pesticidal, pharmaceutical and other chemicals to wild birds. Toxicology and Applied Pharmacology 21(3):315-330.

Schafer EW & Brunton RB (1979). Indicator bird species for toxicity determinations: is the technique usable in test method development? Vertebrate Pest Control and Management Materials. In JR Beck JR (Ed.) ASTM (American Society for Testing and Materials) Special Technical Publication No. 680, pp 157-168.

Shinkaji N & Adachi T (1978). [The effect of certain pesticides on the predaceous mite Amblyseius longispinosus (Evans) (Acarina: Phytoseiidae).] Akitsu 2: 99-108. [Cited by WHO (1989) – NOT SEEN by DEW.]

Spehar RL et al. (1981). Effects of pollution on freshwater fish. Journal WPCF 53(6): 1028-1076.

Spray Drift Task Force (1997). AgDRIFT™ spray model: a tiered approach for the assessment of spray drift of pesticides, Version 1.05, November 1997. Spray Drift Task Force, c/o Stewart Agricultural Research Services Inc., Macon, Missouri, USA.

Srinavasamoorthy K et al. (1986). Dichlorvos induced metabolic changes in tissues of fresh water mussel, Lamellidens marginalis. J. Environ. Biol. 7:101. [Cited by Nikunen et al. (1990) – NOT SEEN by DEW.]

Steen RJCA et al. (1999). Ecological risk assessment of agrochemicals in European estuaries. Environmental Toxicology and Chemistry 18(7): 1574-1581.

Suter P (1981). Rate of hydrolysis of dichlorvos (Nogos®, Nuvan®) under laboratory conditions. Project Report 29/81. Biochemistry, Department R & D Plant Protection, Agricultural Division, Ciba-Geigy Limited, Basle, Switzerland. ECRP Submission, Unpublished Report.

Terayama K et al. (1978). Toxicity of heavy metals and insecticides on slime mold Physarum polycephalum. J Toxicol. Sci 3: 293-304. [Cited by WHO (1989) – NOT SEEN by DEW.]

Teunissen-Ordelman HGK and Schrap SM (1997). 1996 Aquatic Outlook. An analysis of issues pertaining to aquatic environments. Pesticides. RIZA Policy Document No. 97.038. Netherlands Ministry of Transport, Public Works and Water Management, Directorate-General for public Works and Water Management – Translation: Foreign Affairs, Amsterdam).

Thomas RG (1982). Volatilization from water. Chapter 15 (pp 15-1 to 15-34) in Lyman WJ, Reehl WF and Rosenblatt DH, eds, Handbook of chemical property estimation methods. Environmental behaviour of organic compounds. McGraw-Hill Book Company New York.

Tomlin CDS ed (1997) The pesticide manual: a world compendium. Eleventh edition, pp 372-374. British Crop Protection Council, Surrey, UK.

Trent University (1998). Level 1 Fugacity Based Environmental Equilibrium Partitioning Model, Version 2.1. Trent University, Environmental Modelling Centre, Ontario, Canada.

Tsuda, T et al. (1992). Accumulation and excretion of organophosphorous pesticides by willow shiner. Chemosphere 25(12):1945-1951.

Urban DJ & Cook NJ (1986) Hazard Evaluation Division Standard Evaluation Procedure: Ecological risk assessment. EPA 540/9-85-001. Office of Pesticide Programs, United States Environmental Protection Agency, Washington, D.C.

US EPA (1993). Wildlife exposure factors handbook. EPA/600/R93/187. United States Environmental Protection Agency, Washington, D.C.

US EPA (2006). Interim Reregistration Eligibility Decision for Dichlorvos (DDVP). United States Environmental Protection Agency, Prevention, Pesticides and Toxic Substances. EPA 738-R-06-013. http://www.epa.gov/pesticides/reregistration/ddvp/

US EPA (1998). Reviewed studies ecological toxicity endpoints database of Ecological Effects Branch, Environmental Fate and Effects Division, Office of Pesticide Programs, Office of Prevention, Pesticides and Toxic Substances, United States Environment Protection Agency, Washington, D.C. July 1998 draft version.

US EPA (1999). AQUIRE (AQUatic toxicity Information Retrieval) database, United States Environmental Protection Agency (US EPA), Mid-Continent Ecology Division, Duluth, MN (MED-Duluth). Now located via the Internet on http://www.epa.gov/ecotox/.

Verma SR et al. (1980). Effects of the pesticides thiotox, dichlorvos, and carbofuran on the test fish Mystus vittatus. Water Air Soil Pollut. 13(2): 229-234. [Cited by WHO (1989) – NOT SEEN by DEW.]

Verma et al. (1981a). Evaluation of the comparative toxicity of thiotox, dichlorvos, and carbofuran to two fresh water teleosts Ophiocephalus punctatus and Mystus vittatus. Acta Hydrochem. Hydrobiol. 9(2): 119-129. [Cited by WHO (1989) – NOT SEEN by DEW.]

Verma et al. (1981b). Isolated and combined effects of pesticides on serum transaminases in Mystus vittatus (African catfish). Toxicol. Lett. 8: 67-71. [Cited by WHO (1989) – NOT SEEN by DEW.]

Verma et al. (1981c). Pesticide-induced physiological alterations in certain tissues of a fish Mystus vittatus. Toxicol. Lett. 9: 327-332. [Cited by WHO (1989) – NOT SEEN by DEW.]

Verma et al. (1981d). Determination of the maximum acceptable toxicant concentration (MATC) and the safe concentration for certain aquatic pollutants. Acta Hydrochem. Hydrobiol. 9(3): 247-254.

Verma et al. (1982a). Bioassay trials with twenty-three pesticides to a fresh water teleost Saccobranchus fossilis. Water Res. 16: 525-529. [Cited by WHO (1989) – NOT SEEN by DEW.]

Verma et al. (1982b). Indicators of stress induced by pesticides in Mystus vittatus: haematological parameters. Indian J Environ. Health 24(1): 58-64. [Cited by WHO (1989) – NOT SEEN by DEW.]

Verma et al. (1983). Pesticide-induced dysfunction in carbohydrate metabolism in three fresh water fishes. Environ. Res. 32: 127-133. [Cited by WHO (1989) – NOT SEEN by DEW.]

Verma SR et al. (1984). Effects of pesticides and their combinations on three serum phosphatases of Mystus vittatus. Water Air Soil Pollut. 21: 9-14. [Cited by WHO (1989) – NOT SEEN by DEW.]

Vial A (1991). Report on the acute toxicity test of C177 technical to earthworm (Eisenia eisenia foetida). Ciba-Geigy Ltd, Product Safety, Ecotoxicology, Basel, Switzerland. Test No. 918079. ECRP Submission, Unpublished Report.

Vial A (1992). Report on the reproduction test of C177 technical to Daphnia (Daphnia magna Straus 1820). Ciba-Geigy Ltd, Product Safety, Ecotoxicology, Basel, Switzerland. Test No. 918078. ECRP Submission, Unpublished Report.

WHO (1989). Dichlorvos. Environmental Health Criteria 79. World Health Organisation, Geneva, Switzerland.

Williams PP (1977). Metabolism of synthetic organic pesticides by anaerobic microorganisms. Residue Rev. 66: 102.

Wilmes R (1982). Preliminary study on light stability. Report WLF OL 034. Bayer Australia Ltd Agricultural Division, Dichlorvos TGAC Submission to the Technical Committee on Agricultural Chemicals. Book II, Part 1: Chemical data, pp 1:012-013. Unpublished Report.

Yamane S et al. (1974). Histochemical demonstration of cholinesterase activity in tissues of the carp and effect of DDVP on its activity in situ. Acta Histochem. Cytochem. 7(2): 167-174. [Cited by WHO (1989) – NOT SEEN by DEW.]

Yasuno M et al. (1965). Inactivation of some organophoshorous insecticides by bacteria in polluted water. Japan. J. Exp. Med. 35(6):545-563.

Yoshida K & Nishimura Y (1972). Toxicity of pesticides to some water organisms. Translated from Bulletin of the Agricultural Chemicals Inspection Station No. 12: 122-128.