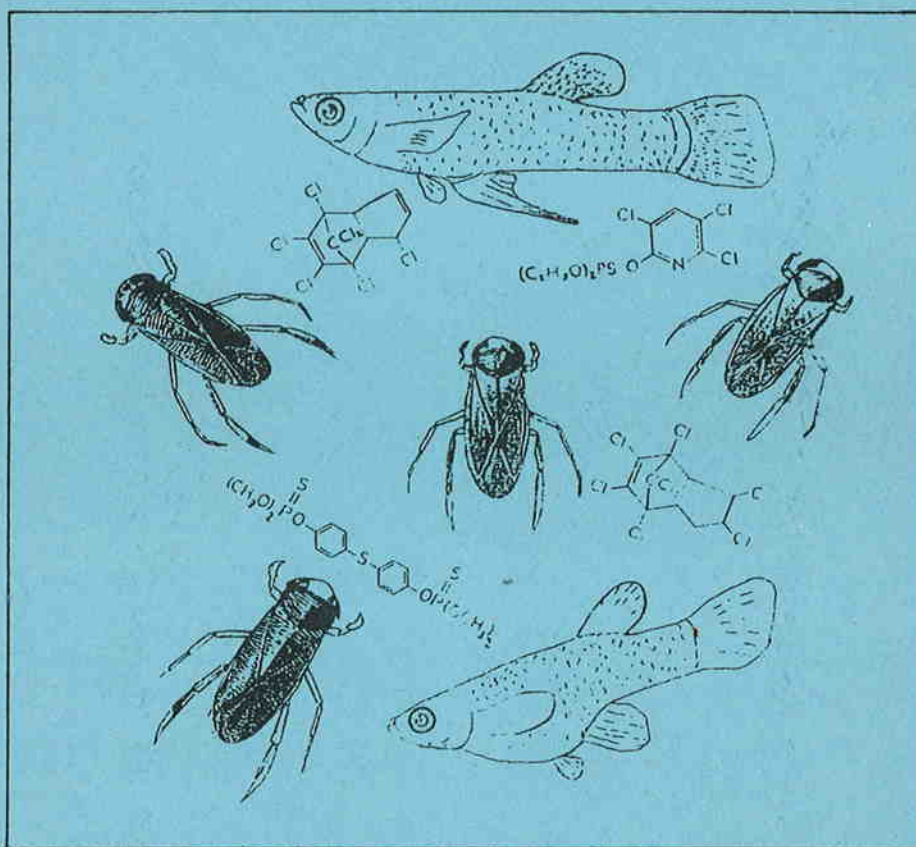


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HERDSMAN LAKE PESTICIDE STUDY

LITERATURE REVIEW



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Herdsmen Lake Pesticide Study

Literature Review

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For:

The Department of Conservation
and Land Management

The State Planning Commission

The Department of Agriculture

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1. INTRODUCTION

1A. Objectives of Review

This review was undertaken in conjunction with a study to monitor the environmental effects of spraying to control Argentine ants in the northeastern surrounds of Herdsman Lake in March and April, 1986.

The aims of the review were to describe:

- i) The chemical structure and residual products of the pesticides used.
- ii) The common uses (and target organisms) of these pesticides.
- iii) The recorded levels of these pesticides in water, sediments, aquatic invertebrates and fish.
- iv) The effects of various levels of these pesticides on the aquatic invertebrate and fish fauna.

In addition, this review endeavours to put into perspective the current spraying programme in relation to previous spraying and residue monitoring in and around the Perth metropolitan area.

2. PESTICIDE CHEMISTRY

2A. Pesticides used at Herdsman Lake

The 1986 spraying programme for the control of the Argentine ants at Herdsman Lake (conducted over the period 21 March to 11 April 1986) involved the use of an organochlorine compound, heptachlor, and two organophosphates, temephos (Abate) and chlorpyrifos (Dursban). Previous sprayings undertaken at the lake as part of the same Argentine ant control programme (see Section 6) involved the use of dieldrin (1955 to 1969) and heptachlor (1970 to present) (Shewchuk, 1981). In addition, chlordane was used between 1955 and 1973, and DDT, Mirex bait, diazinon, endosulphin and chlorpyrifos have all been tested at various times (Porter, 1982).

Heptachlor, together with chlordane, dieldrin, aldrin and endrin, belong to the cyclodiene group of pesticides. All of these chemicals are derivatives of hexachlorocyclopentadiene and are produced by the Diels-Alder reaction. The discovery and development of these pesticides arose from the synthesis of chlordane by Hyman in 1944 (Shewchuk, 1981). Heptachlor was isolated from technical chlordane and marketed by the Velsicol Corporation for agricultural use in 1948.

In the 1986 spraying programme at Herdsman Lake a 0.5% heptachlor solution containing approximately 9% chlordane was applied (P. Davis, pers. comm.). Heptachlor has been used extensively in agriculture in the United States against soil insects and for fire ant control but its use is now restricted mainly to termite control. The use of heptachlor in Canada has been banned since 1968 due to concern over the occurrence of heptachlor epoxide residues in milk and the possible deleterious effects on birds (McEwen and Stephenson, 1979).

Aldrin and dieldrin were developed in the late 1940s and have been used extensively against agricultural pests, ants and termites. They are more toxic to insects, and mammals, than chlordane or heptachlor. Dieldrin accumulates in animal tissue and has been found in human tissue and in mother's milk (McEwen and Stephenson, 1979). The use of dieldrin in Western Australia is now restricted and, since 1981, the pesticide may only be used for the control of termites, timber and tree borers and African black beetle (Shewchuk, 1981).

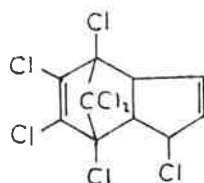
Temephos (Abate) is widely used for the control of mosquito larvae and is the main insecticide used in Western Australia for the control of salt marsh mosquitoes and chironomid midges (Blair, 1979). Temephos was first introduced by the American Cyanamid Company in 1965 under the trademark

Abate. The effects of temephos on target and non-target organisms have been fairly extensively studied because of its widespread use in the aquatic environment. The pesticide is most effective against dipterous insects but small crustacea and microcrustacea and the aquatic larvae of many insects are also susceptible to the effects of Abate. However, many non-target organisms commonly found in aquatic habitats are not destroyed by the concentrations of Abate required to control target species (Blair, 1979). The toxicity of Abate to mammals, birds and fish is low.

Chlorpyrifos was introduced in 1965 by the Dow Chemical Company under the tradenames of Dursban and Lorsban. The pesticide has a broad range of insecticidal activity and is used for the control of mosquitoes, flies, various soil, plant and household pests and for ectoparasites on cattle and sheep (Blair, 1979).

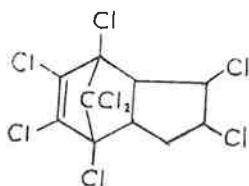
2B. Chemical structure/properties

Heptachlor: (1, 4, 5, 6, 7, 8, 8 - heptachloro - 3a, 4, 7, 7a - tetrahydro - 4, 7 - methaniondene)



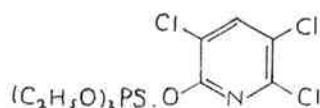
- . crystalline solid; m. p. 95-96°C
- . v. p. 53 mPa at 25°C
- . sol. 56 µg/l water at 25°C

Chlordane: (1, 2, 4, 5, 6, 7, 8, 8 - octachloro - 3a, 4, 7, 7a - tetrahydro - 4, 7 - methyleneidane)



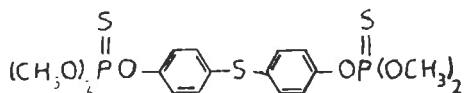
- . technical chlordane is a viscous amber liquid
- . v. p. 61 mPa at 25°C
- . sol. 0.1 mg/l water at 25°C

Chlorpyrifos: (diethyl 3, 5, 6 - trichloro - 2 pyridyl - phosphothionate)



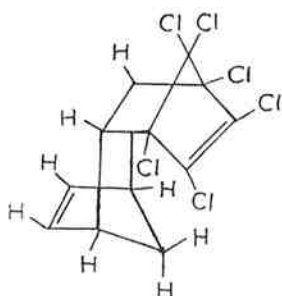
- . forms colourless crystals with mild mercaptan odour
- . m. p. 42-43.5°C
- . v. p. 2.5 mPa at 25°C
- . sol. 2 mg/l water

Temephos: (0,0,0¹,0¹ - tetramethyl 0,0¹ - thiodi-p-phenylene - diphosphor thioate)



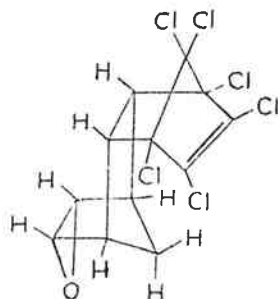
- . Pure temephos is colourless crystalline solid
- . m. p. 30.0-30.5°C
- . insoluble in water

Aldrin: (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-exo-1,4,endo-5,8-dimethanonaphthalene)



- . Aldrin is a tan to dark brown solid
- . m. p. 49-60°C
- . v. p. 700 µPa at 20°C
- . sol. 27 µg/L in water at 27°C

Dieldrin: (1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7-exo-1,4-endo-5,8-dimethanonaphthalene)



- . Technical dieldrin consists of buff to light tan flakes
- . m. p. 175-176°C
- . v. p. 400 µPa at 20°C
- . sol. 0.186 µg/L in water at 20°C

Key: m. p. = melting point, v. p. = vapour pressure, sol. = solubility

Source: Structure and name from Corbett (1974)
Properties from Worthing (1985)

2C. Secondary residual products (and metabolites)

The metabolism of heptachlor results in the formation of an epoxide (heptachlor epoxide), a product as toxic as the parent compound but with the additional characteristic of undergoing bioaccumulation in animal tissues (Brooks, 1974). Conversion to heptachlor epoxide is not the only route by which heptachlor is altered; however, the epoxide is the common residual

product found in the environment (McEwen and Stephenson, 1979). The conversions of heptachlor are shown in Fig. 1.

Aldrin can be epoxidised to form dieldrin. Dieldrin can also be epoxidised to aldrin-trans-diol (Fig. 2), and although its relative persistence is not known, it is suggested that aldrin trans-diol may be the active toxicant in some insects and mammals (Corbett, 1974).

Chlorpyrifos and temephos do not appear to form secondary residual products, although many non-persistent metabolites are formed when chlorpyrifos is applied to aquatic environments (e.g. chlorpyrifos methyl).

3. COMMON USES AND TARGET ORGANISMS

Target organisms, other than Argentine ants, and the method of application of the pesticides are given in Table 1.

Permitted levels of pesticides in drinking water and recommended maximum permissible levels of pesticides in water for the maintenance of aquatic ecosystems are given in Table 2.

4. EFFECTS ON FAUNA

4A. General physiological action

The pesticides under consideration all act on the central nervous system. "Nervous transmission is a suitable target for a pesticide since it is the basis of a co-ordination system which the animal cannot do without even for short periods, but it is unfortunate that the basic molecular events in the nervous systems of all animals, including mammals, seem to be rather similar, so that selective toxicity between animal species is not inherent in the site of action, but most depend on the vagaries of uptake, metabolism and compartmentalisation" (Corbett, 1974).

1. Acetylcholinesterase inhibition

Acetylcholinesterase is the principle enzyme responsible for the hydrolysis of acetylcholine in the insect and vertebrate nervous systems. Its principal role lies in the transmission of nerve impulses. An impulse, upon reaching the synapse, causes the release of a chemical transmitter, usually acetylcholine. The enzyme acetylcholinesterase has the function of destroying the acetylcholine so that stimulation of the receptor stops, and the synapse becomes available for the release of a new transmitter. Organophosphorous pesticides such as chlorpyrifos and Abate inhibit acetylcholinesterase formation (Corbett, 1974). Since organophosphates prevent acetylcholine breakdown, the organ or tissue remains under constant stimulation. Thus, by interfering with normal nervous transmissions, symptoms of overstimulation are produced (e.g. sweating, muscular tremor) (Byrne, 1977).

2. Neuroactive insecticides (mode of action obscure)

It is generally accepted that the cyclodienes (which include heptachlor/chlordane, dieldrin or aldrin) act on the nervous system. However, a detailed mode of action has not been elucidated (Corbett, 1974). Recently, McNulty (1984) merely described the mode of action of dieldrin as "central nervous system stimulant producing convulsions". "Cyclodiene insecticides in general have a characteristically slow effect on the intact insect, possibly because conversion to an active form is required (see Section 2C). Koch (1969) demonstrated that the ATPases of rabbit brain were inhibited by chlorinated hydrocarbons, including chlordane, aldrin and dieldrin (Corbett, 1974). Despite this observed effect, Corbett suggested that inhibition was possibly due to a non-specific effect of the insecticides on membranes, since ATPases are membrane bound.

4B. Effect on aquatic invertebrates

1. Accumulation and toxicity

The specific site of accumulation of both organophosphorous and organochlorine insecticides seems to be largely dependent on the fat content of the particular tissue; most probably as a consequence of the high fat solubility of these pesticides (Matthiessen et al., 1976, Anderson and Fenderson, 1970).

When pesticides reach water, they are rapidly absorbed by the aquatic invertebrates. There are two basic mechanisms for accumulation. Firstly, pesticides are taken up directly from water passing through their bodies, and/or they may accumulate them from their food (Edwards, 1970). The former of the two methods is termed bioconcentration and the latter biomagnification (biological magnification) (Khan, 1977). Biological magnification is of more concern to individuals in higher trophic levels (Bacher, 1967). It is the organochlorine pesticides, due to their high persistence, that are subject to bioconcentration and biological magnification.

Many insecticides are toxic to insects in the 1 to 10 mg/kg range, and thus the likelihood of high residues in their bodies is minimal. Usually, residues of organochlorines found in soil invertebrates are of the same magnitude as that detected in the soil. There are, however, exceptions; in a study of DDT residues in beetle larvae (McEwen and Stephenson, 1979), a bioconcentration factor of about 35 was recorded, that is, the residue in the beetle was 35 times that of the soil. Another study, on earthworms, observed that levels of total organochlorines were nine times greater in the earthworms than that of the soils from which they came (McEwen and Stephenson, 1979).

The degree of magnification appears to be much greater in aquatic environments. A study by Wilson (1965) (cited by Pimental, 1971) on the biological concentration of various organochlorines in seawater systems gives magnification values for heptachlor, dieldrin and chlordane of 17600, 1000 and 7300 times respectively. Table 3 (after McEwen and Stephenson, 1979) gives magnification factors for the organochlorines DDT and aldrin in several species of aquatic invertebrates.

The toxicity of pesticides to aquatic invertebrates is usually given as the concentration (ppb or ppm) required to immobilise or kill 50% (i.e. LC₅₀ or LD₅₀) of the organism for a given period of time (i.e. 24 hr, 48 hr, 96 hr). The toxicity may be confined to a small group, or at the opposite extreme, may affect almost all forms of aquatic life. Usually pesticides differ in their toxicity to different aquatic groups (Khan, 1977). Table 4 gives the toxicities of various pesticides to some common aquatic invertebrates.

2. Development of resistance

A suggested mechanism for resistance was suggested by Matsumura and Hayachi in 1969 from experiments with dieldrin on cockroaches. They found that particular components of the nerve cord of resistant strains bound less dieldrin than the counterparts of susceptible strains. However, Corbett (1974) suggested that resistance to dieldrin (that is, to organochlorines) might be due to reduced sensitivity of the site of action. The latter viewpoint has been generally adopted since there is little evidence that resistant strains of invertebrates either take up less, or detoxify more, dieldrin than susceptible ones (Corbett, 1974).

There is little doubt that genetic changes have taken place in many soil arthropods as a result of insecticides. Resistance to aldrin and dieldrin

in cutworms. several species of root maggots, carrot rust fly and carrot weevil has been recognised for many years. There are also reports of resistance to chlordane by the Japanese beetle (McEwen and Stephenson, 1979).

A reported 225 species of insects and mites have evolved a resistance to cyclodienes (heptachlor, aldrin, dieldrin) and organophosphorous insecticides. The 225 species comprise 121 crop pests, 97 man and animal pests, 6 stored-product pests, and 1 forest pest (Pimental, 1971).

3. Population effects

Edwards (1973) lists four possible effects of pesticides on living organisms in general.

- (1) They may be directly toxic to animal and/or plant life in the soil.
- (2) They may affect these organisms genetically to produce populations resistant to the pesticides.
- (3) They may have sub-lethal effects that result in alterations in behaviour or changes in metabolic or reproductive activity.
- (4) They may be taken into the bodies of soil flora and/or fauna and passed on to other organisms.

The first of these steps is most easily observed. In fact, much of the information now available on the effect of pesticides on aquatic organisms is in terms of acute mortality of individual species (Khan, 1977). Despite this, examples of the other three effects can also be obtained.

As would be expected, the insecticides have been shown to affect invertebrate populations. In many instances this was the intended use of

the insecticides. but because many of the insecticides used are not selective. both beneficial and target species are killed. Pesticides have been shown to be toxic to zooplankton and benthos, the degree of toxicity varying widely among pesticides and among various species and life stages within the animal community (McEwen and Stephenson, 1979).

In the case of chlorpyrifos and temephos, it has been clearly shown that differences in concentration may determine how lethal the impact of these chemicals are on freshwater forms. When Dursban (chlorpyrifos) was applied at 0.005 lb/acre, there was no observed ill-effects on non-target fauna such as corixids and diving beetles. However, when applied at dosages of 0.01 to 0.02 lb/acre there was a noticeable die-off of practically all arthropods. With regard to Abate, its effects on non-target organisms has been widely studied. Abate was applied at 0.03 lb/acre which proved to be an effective larvicide dosage. This treatment also eliminated caddisfly larvae (Limnesphilus indivisus), Cladocera, and early instar libellulid naiads (Odonata) (Muirhead and Thomson, 1971).

Blair (1979) has compiled a table listing the toxicity of Abate (an organophosphate) to species of aquatic invertebrates most commonly found in target habitats. Non target groups such as the Amphipoda (LC₅₀ 1.5 ppm, 48 hr). Decapoda (LC₅₀ ~2.0 ppm, 90 hr) and Copepoda (LC₅₀ ~5.0 ppm, 24 hr) are less susceptible to Abate than target groups, that is, the Chironomidae (LC₅₀ 0.0008-0.06, 24 hr) and the Culicidae (LC₅₀ 0.0008-0.001). Studies on another common organophosphate, Baytex, have revealed the relative insensitivity of the ostracods and copepods. Baytex was shown to be lethal to cladocerans at levels as low as 0.00065 ppm, while it caused little mortality to copepods and ostracods at concentrations up to 0.5 ppm. Similar results have also been obtained with chlorpyrifos and Abate (Muirhead and Thomson, 1971).

General studies have demonstrated that members of the Chironomidae, Ephemeroptera, Trichoptera, Diptera, Hemiptera and the decapod, copepod and cladoceran crustaceans are particularly sensitive to Abate (Matthiessen et al., 1976; Blair, 1979). However, Blair (1979) notes that there is no reported evidence of compounded effects in the food chain through the use of Abate.

An important experiment involving temephos and chlorpyrifos was carried out by Wallace et al. (1973). Temephos and chlorpyrifos were applied at dosages to achieve a 0.1 ppm concentration in a stream for 15 min, for the control of black fly larvae in northern Quebec. Initial results suggested that pesticides, such as temephos, kill many target and non-target insects. However, a population also survived at the post-treatment sample; indicating a potential for insect populations to recover. This ability was also demonstrated in studies on another organophosphate, diazinon, in the Saskatchewan River. Initially there was heavy displacement and/or mortality in Simuliidae, Plecoptera, and Ephemeroptera and less effect on Chironomidae and Trichoptera. However, rapid recolonization occurred, with the exception of Simuliidae and Plecoptera. Chironomidae, Trichoptera and Ephemeroptera had returned to pretreatment levels within fourteen days (Wallace et al., 1973; McEwen and Stephenson, 1979). Yasuno et al. (1985) also showed rapid recovery, after initial depletion, of chironomid and trichopteran (less rapid) populations after application of 5 mg/L of temephos.

The situation with persistent pesticides, such as the organochlorines, heptachlor, chlordane, DDT and dieldrin, is often quite different from that described above for the relatively non-persistent organophosphates (McEwen and Stephenson, 1979). A study conducted by Wallace and Brady (1971) found major differences in invertebrate fauna as a result of a discharge

of dieldrin into a small river. Samples taken from sites only a few meters apart revealed that while colonization of the stream with Ephemeroptera, Trichoptera and Diptera occurred above the discharge, there was no re-colonization below the discharge. In fact, below the discharge the insect fauna consisted of only a few chironomids and simuliids (McEwen and Stephenson, 1979).

It is clear that many aquatic invertebrates concentrate persistent pesticides (organochlorines) in their tissues at levels much in excess of those in the surrounding environment, however, most organophosphates are not found except in a temporary state during or immediately after treatment (McEwen and Stephenson, 1979). Hence the reason for rapid re-colonization when organophosphate pesticides are used and the more drastic long term effects of the persistent organochlorines. "Potential for uptake and bioconcentration into aquatic organisms is an important characteristic in determining how serious the effects of a particular pesticides on an aquatic system can be.....; this is especially a feature of most organochlorine insecticides which often reach concentrations many thousand times greater in the biota than in the water" (Khan, 1977).

Associated with the effect on populations by direct mortality, are the more subtle long-term or indirect effects caused as a result of sub-lethal doses. The implications of findings in terms of long-term effects on aquatic organisms exposed to sub-lethal concentrations of pesticides are open to speculation and will vary with the organism (McEwen and Stephenson, 1979). However, because pesticides act on the central nervous system, sub-lethal amounts may affect the animal's behaviour, which may make it more susceptible to predation (Bacher, 1967). It may also cause changes in an organism's life cycle which could reduce the number of generations per year and put the organism out of

phase with its environment (McEwen and Stephenson, 1979). The criteria that are usually used to assess sub-lethal effects include growth, function of enzyme systems, and behavioural populations of organisms (Khan, 1977).

Morgan (1976), cited by Khan (1977), carried out experiments on the effect of diazinon (a slightly persistent organophosphate) at sub-lethal concentrations. The chironomids exposed at 0.003 ppb diazinon, egg hatching was delayed significantly. The duration of larval life increased and the percent pupation and adult emergence decreased. Amphipods (Gammarus lacustris) exposed to 3ppb diazinon increased their activity significantly.

Of particular concern to this review are previous studies on a non-target invertebrate, the water boatmen or corixids. Blair (1979) cited a study conducted by Hulbert et al. (1970) on the influence of chlorpyrifos on corixids (Corixella sp.). Chlorpyrifos was applied to small ponds at 0.0, 0.011, 0.056, 0.11 and 1.12 kg a.i./ha. Reduction of Corixella populations was variable but approximately proportional to the rate of application. Except in the 1.12 kg a.i./ha. treated ponds the corixid populations recovered well. Another study was conducted on the post-treatment effects of Dimilinon on corixids. Immature corixids were severely affected, with large differences between treatment and control sites. Adult corixids re-colonized well at 80 days after application (Khan, 1977). Rice fields in California treated with chlorpyrifos at 0.0124 and 0.024 lb/acre caused little or no mortality in non-target corixids (Belostoma sp.) (Pimental, 1971).

4C. Effect on fish

Because the effects of pesticides on fish have been very widely investigated, it has not been possible to cover all work within this review. Instead, only general effects and the effects of the relevant pesticides on the mosquito fish (Gambusia affinis) (the most common species of fish recorded from Herdsman Lake) will be considered here.

1. Accumulation and toxicity

Pesticide residues are not distributed equally in all the tissues of fish, but are concentrated in fatty tissues (Edwards, 1970). There are two basic methods of absorption by fish. Firstly, by direct uptake from the water (via the gills) and, secondly, by oral ingestion of contaminated food sources via the food chain (Mattheissen et al., 1976; Edwards, 1970). The relative importance of the two passages is under some degree of dispute. Edwards (1970) suggests that because the concentration factors are similar between invertebrates and fish, direct uptake from the water is a more important route for the pesticides to enter the fish than feeding on invertebrates. Mattheissen (1976), however, indicates that the fish (S. mossambicus) would accumulate moderate residue levels by direct absorption, but possibly larger doses via the food chain.

Table 5 (Edwards, 1970) gives concentration factors recorded for several species of fish. The ability for accumulation of various pesticides in fish are influenced by the polarity and water solubility of the pesticide. There is a qualitative correlation between water solubility and fish bioaccumulation, the higher the solubility the lower the amount of bioaccumulation (Khan, 1977). It follows, therefore, that pesticides like chlordane and heptachlor, both having a "very low" solubility (Faust, 1972), are particularly good bioaccumulators.

Bioaccumulation values for Gambusia affinis vary widely from one pesticide to another. Figure 3 (Khan, 1977) shows the relationship between water solubility of pesticides and the ecological magnification in Gambusia.

The magnification factors for various pesticides are as follows:

| | | |
|----------------------|------|----------------------|
| chlorpyrifos | 314 | Sources: Khan (1977) |
| DDT | 4771 | Pimental (1971) |
| Mirex (o/c) | 2580 | |
| Atrazine (herbicide) | 3-10 | |

Persistence of pesticides in fish is an important factor. Investigations of the persistence of dieldrin and heptachlor have shown that 50% of the chemicals were lost in about one month. Organophosphates, like Dursban and diazinon, have relatively lower persistence, 50% being lost in less than one week (Khan 1977).

The toxicity of pesticides to fish seems to be a cumulative effect of concentration and duration of exposure; much greater toxicity was found with heptachlor, dieldrin, endrin, mevinphos, lindane and methyl parathion at longer exposures (McEwen and Stephenson, 1979).

Measures of fish toxicity consider the dosage required to produce 50% mortality for a given period of time (Muirhead and Thomson, 1971). The toxicity of relevant pesticides to some freshwater species are given in Table 6. Within the organochlorines, chlordane and heptachlor are among the least toxic, having LC₅₀s 10 to 100 times higher than that of endrin. Aldrin and dieldrin are somewhat more toxic, although there is noticeable species variation (Brook, 1974). The acute toxicity of Abate

to fish is comparatively low (Matthiessen et al., 1976; Blair, 1979). Blair (1979) also cites a study by Ferguson et al. (1966), demonstrating that chlorpyrifos is less toxic to fish than most chlorinated hydrocarbons, but generally more toxic than other organosphosphorous insecticides. They concluded that chlorpyrifos is not likely to be harmful to fish at rates of application required for arthropod pest control (Blair, 1979).

2. Development of resistance

The development of actual physiological resistance to particular chemicals on the part of the fish population has now been clearly demonstrated in some areas which have been under heavy treatment with pesticides (Muirhead and Thomson, 1971).

Resistance to pesticides of concern here have been well documented, especially for the mosquito fish, Gambusia affinis. Gambusia populations are of particular concern, as they have long been used as a supplementary method of reducing mosquito larval populations; hence, as part of this concern, the question of development of resistance to insecticides, such as DDT and other organochlorines on the part of the Gambusia populations, receives constant attention (Muirhead and Thomson, 1971).

Several reports that demonstrate the resistance to various pesticides by Gambusia populations have been compiled by Pimental (1971) (see Table 6). Not shown in Table 6 is the development of resistance to chlordane. However, Pimental (1971) states that a natural population of mosquito fish in ditches adjacent to cotton fields was found to be 20 times more resistant to chlordane than normal. Another example of resistance found in cotton growing areas includes one in the Namoi River Valley in New

South Wales, where mosquito fish populations developed a resistance to some of the organochlorines used, including DDT (Mowbray, 1979). In the Mississippi cotton growing areas, the mosquito fish has developed broad-spectrum resistance to many pesticides including DDT, dieldrin and endrin. In some cases the level of resistance developed may be very high, for example, over 300-fold in the case of Strobane (Muirhead and Thomson, 1971).

Resistance has also been observed in other species of fish, including the black bullhead, bluegill, golden shiner and green sunfish (McEwen and Stephenson, 1979). All displayed resistance to dieldrin and aldrin, and the golden shiner and green sunfish also showed resistance to chlorpyrifos (Pimental, 1971).

3. Population effects

As is the case with invertebrates the most easily identifiable effect of pesticides on fish populations is by recording direct kills. It has been calculated that the field application necessary to produce 50% mortality for heptachlor and dieldrin are 0.07 and 0.16 lb/acre respectively (Muirhead and Thomson, 1971). Results of a study by Maye and Luckmann (1964) indicated that a single application of aldrin at 2 lb/acre for insect control killed a large number of fish in a small stream. Also dieldrin applied at 1 lb/acre killed an estimated 20 to 30 tons of fish of 30 species (cited by Pimental, 1971). The former of these two studies also revealed that after a period of seven months there was a rapid recovery in fish population, with the usual diversity of species and size being re-established (Pimental, 1971).

In addition to direct kills of aquatic fauna, more subtle long-term effects also occur (Bacher, 1967). Edwards (1970) discusses reported

effects, including lowered resistance to disease, reduced feeding rates and a degeneration of reproduction. Other effects have included gill membrane thickening, lack of osmoregulation, lower blood counts, brain damage and reduced body weights. Several studies have shown the effect of persistent pesticides on reproduction. Laboratory tests with Gambusia affinis have shown that pregnant females, at almost all stages of pregnancy, may abort when exposed to low concentrations of pesticides. Thus, although no mortality in the adult population occurs, this species may be eradicated in localised areas (Bacher, 1967). Abortion has resulted after surviving exposure to sub-lethal doses of DDT, TDE, methoxychlor, aldrin, endrin, toxaphene, heptachlor and lindane (Pimental, 1971). Further tests on the influence on reproduction have been carried out by Singh (1983). He suggested that both organochlorine and organophosphorous compounds seem to act in the same way by suppressing gonadotrophin secretion.

The effects of the organophosphorous compounds, temephos and chlorpyrifos, seem to be less drastic than those of the more persistent organochlorines. There is some evidence that sub-lethal doses of Abate can affect fish behaviour. Mattheissen (1976) demonstrates that the feeding activity of guppies was reduced by 50% at 2.5 ppm, which is approximately two orders of magnitude lower than the 24 h LC₅₀.

Chlorpyrifos applied at 0.10 lg/acre had no effect on brown bullheads (Pimental, 1971); and a study using mullet and several small native fish, recorded no significant fish mortality at dosages of chlorpyrifos which achieved control of the salt marsh mosquitoes (Muirhead and Thomson, 1971). However, a study cited by Blair (1979) reported mortalities for bluegills and bass of 55 and 46% respectively at an application rate of 0.056 kg a. i. /ha. At a smaller dosage (0.011 kg

a. i. /ha), the mortality for bluegills and bass dropped to 3 and 10% respectively.

In addition to the direct effects of insecticides, there are also indirect effects, which are far more difficult to measure (McEwen and Stephenson, 1979). McEwen and Stephenson (1979) give three main types of indirect effects: changes in physical and/or chemical environment, changes in competition for food supply, and changes in predator-prey relations. All three of these may be disadvantageous or advantageous to fish (and higher vertebrate) populations.

4D. General effects on birdlife

The effect of pesticides residues in birds has been widely documented and only a brief summary is given here.

Biological magnification (i. e. via food chain) of pesticides is especially important in the accumulation of pesticides in fish-eating birds (Khan, 1977). However, it has also been shown that with granular applications, bird toxicity has been caused by direct uptake. This has occurred in rice fields with a number of dabbling ducks (McEwen and Stephenson, 1979). A recent study by Niethammer et al. (1984) looked at the relationship between pesticide accumulation and diet in three species of waterfowl. Levels of organochlorine residues appeared to be closely linked to the birds diets, and specifically to the amount of fish they consumed. The same study observed that Gambusia affinis formed a major part of the heron diet.

The toxicity of the relevant pesticides is shown in Table 7. Sub-acute toxicities indicate that technical chlordane has about the same or a slightly higher toxicity than DDT and that heptachlor is rather more toxic than chlordane (Brooks, 1974). Temephos shows a relatively low toxicity

towards birds. however, chlorpyrifos has been shown to have a severe effect on mallard ducklings (Blair, 1979).

Few bird species appear to have developed a resistance to insecticides. One recorded example states that seed eating birds, like the quail and pheasant, are relatively resistant to the effects of DDE, a metabolite of DDT (Pimental, 1971).

The effect on bird populations of the pesticides of concern in this study has been documented by Pimental (1971). Blair (1979), cited a study by Hulbert et al. (1970) on the effect of chlorpyrifos on mallard ducklings. It was found that at an application rate of 1.12 kg a. i. /ha there was a total mortality of 42% (significant at 5% level). Another organophosphate, diazinon, applied at 5 lb/acre killed nearly 50% of pheasant population. Dieldrin appears to have a severe effect on bird populations. In an experiment with pheasants fed various quantities over a 94 day period, the following results were obtained: 60% mortality and 200 ppm within 28 days, 50% mortality at 200 ppm within 38 days, 40% mortality of females at 50 ppm at the close of the experiment. Dieldrin has been reported to cause significant bird kills where it has been applied. When heptachlor was applied at 2 lb/acre. recorded bird kills included a 61% mortality of quails and a significant reduction in songbird populations (Pimental, 1971).

Sub-lethal effects on birds include changes in reproduction and disease susceptibility (Pimental, 1971). Possibly the most important sub-lethal effect is related to their action on reproduction. Analyses of exposed birds show that organochlorine residues accumulate in the testes and ovaries. Tests with pheasants and quails have demonstrated a decrease in egg production, lowered fertility of eggs, sperm production and high chick mortality (Bacher, 1967). Further studies have shown that eggshell thinning,

embryo mortality (up to 50%) and a doubling of ovulation time are all possibly associated effects of pesticides (Pimental, 1971).

In a recent study by Blus et al. (1984), it was shown that the use of heptachlor had resulted in lowered reproductive success, mortality of adults and a population decline of resident western Canada geese. Another study by Gaines (1969), cited by Pimental (1971), looked at the effect of Abate and chlorpyrifos fed to chickens. In both cases the chickens developed leg weakness, however, the mode of action was unknown. Pimental (1979) also cited a study where the exposure of Arochlor to mallard ducklings increased the susceptibility of ducks to duck hepatitis virus.

4E. General effects on mammals

In all mammals, cumulative pesticides such as chlordane, heptachlor, dieldrin and aldrin, are stored in fat tissues (McNulty, 1984; P. A. N., 1985; Shewchuk, 1981). The absorption route of pesticides is via absorption by the intact skin as well as by inhalation and from the gastrointestinal tract (McNulty, 1984; Shewchuk, 1981). It has also been shown that chlordane/heptachlor are transferred across the placenta from mother to child (P. A. N., 1985).

The organochlorines, chlordane and heptachlor are both excreted in the faeces or in the milk of lactating animals (McNulty, 1984). Dieldrin is excreted largely in the faeces and minor metabolites are also excreted in the urine (Shewchuk, 1981).

The acute toxicities of relevant pesticides to various mammals is given in Table 8. The toxicity of a pesticide to mammals is usually given as the acute oral or acute dermal toxicity in milligrams of active constituent for each kilogram of body weight (mg/kg) (Shewchuk, 1981).

There has been evidence of some resistance in mice populations, both genetic and induced, to two organochlorine pesticides, endrin and DDT. Wild pine mice showed twelve times the normal tolerance to endrin, and after ten generations a colony of mice exhibited an LD₅₀ for DDT of 900 mg/kg compared to a control value of 550 mg/kg (Pimental, 1971).

The usual cause of death in mammals due to organophosphate pesticides is respiratory paralysis (Eto, 1974). In humans, early symptoms of organophosphate poisoning include nausea and vomiting, abdominal discomfort, muscular tremor, sweating, tightness in the chest and pupil contraction (Byrne, 1977).

Symptoms of organochlorine poisoning in man include the following: headache, nausea, vomiting, general malaise and dizziness, possible convulsions followed by coma in severe cases, and hyperexcitability and hyperirritability would also be expected (McNulty, 1984).

Aldrin, dieldrin, chlordane and heptachlor are all suspected human carcinogens (Cawcutt and Watson, 1984; P. A. N. 1985). Experimental studies have shown that chlordane, heptachlor and dieldrin have all caused cancer in test animals. For example, when dieldrin was fed to mice at 10 ppm for two years there was a significant increase in tumours which were morphologically benign (P. A. N. 1985; Shewchuk, 1981). It has also been suggested that chlordane and heptachlor are associated with leukaemia in humans. Despite this, McNulty (1984) claims that heptachlor is not, or should not be considered a chemical known to cause cancer in humans.

Other reported sub-lethal effects of organochlorine pesticides include decreases in litter size, increase in cataracts and increased mortality in rats exposed to heptachlor (McNulty, 1984; Pimental, 1971). A decrease in

rat litter size is also recorded for dieldrin along with reduced lifespan in mice, decrease in number of pregnancies and increased mortality of young rats (Shewchuk, 1981). Dieldrin has also been shown to change sheep behaviour and decrease the growth rate in deers (Pimental, 1971).

There is very little evidence of an effect of organophosphate pesticides on mammals. Abate has a very low mammalian toxicity; based on this and other factors, the World Health Organisation accepts that Abate is suitable for the treatment of potable water at a dosage rate of not greater than 1 ppm (Blair, 1979).

5. PESTICIDES IN SOIL AND WATER

Any chemical that contaminates soil or the atmosphere has the potential for transfer to the hydrosphere and pollution of this medium. Many pesticides are relatively persistent, leaving considerable residues in the soil, and from this media they are rapidly transferred via precipitation, run-off and drainage. Once in aquatic systems, pesticides must either be degraded to simpler compounds, remain there, or move back into the atmosphere by volatilisation (see Fig. 4) (Khan, 1977).

5A. Persistence of pesticides in soil and water

The persistence of pesticides in soil depends upon a number of interactions between the solid, liquid and gaseous phases of soil (Guenzi, 1974). The type of soil treated with an insecticide greatly influences how long residues exist, for example, heavy clays retain insecticides much longer than lighter sandier soils. The content of organic matter in soil seems to be one of the most important single factor influencing the persistence of pesticides in soil; the relationship between organic content and persistence is a curvilinear one. Climatic factors also govern pesticide persistence; increased temperatures accelerate the loss of pesticides. However, dry soil

slows the process down. Despite these exterior influences, the actual chemical structure and resulting intrinsic stability is the most important single factor affecting the time of persistence in soil (Edwards, 1970).

The solubility of a pesticide is a very influential parameter relating pesticide persistence in soil; pesticides that are highly insoluble (e. g. DDT, dieldrin) tend to persist and are not readily leached. The pesticides vapour pressure is also important, as this influences the tendency of the pesticides to volatilize (McEwen and Stephenson, 1979).

The two principal sources of contamination in surface waters are runoff from spraying areas and discharge of industrial water. The runoff from spray sites is a steady source of residues in the aquatic environment (Edwards, 1970).

Solubility of pesticides in water is, again, a very influential factor in determining the persistence of pesticides in water. As a result the chlorinated hydrocarbons are not usually found in solution, instead the insecticides are carried on particulate matter suspended in the water. When insecticides reach the water a large proportion disappears. For example, studies with DDT show that within six hours of application 56% of the insecticide was in the soil, after 24 hours a further 22% had moved into the soil. This phenomenon is termed sedimentation, and is considered a major factor in the removal of persistent pesticides (Edwards, 1970).

Other factors generally considered to affect the movement of pesticides in surface waters are rate of application, slope, vegetation cover of treated area, amount and intensity of rainfall, and texture and moisture content of the soil. Relationships between these factors are complex (Guenzi, 1974).

The average persistence of the relative pesticides in soil is given in Table 9. It has been demonstrated that the persistence of many pesticides is severely altered when the soil is flooded. For example, the persistence of heptachlor in unflooded soils is around nine years, however, in flooded soils this value drops to about 30-90 days (Faust, 1977).

The results listed in Table 9 are highly variable. This is not surprising when the number of complex interactions between the factors are taken into account (Brooks, 1974). Despite this, it is clear that the organochlorine pesticides persist much longer than the organophosphates. This is also true when regarding the persistence of pesticides in water. Khan (1977) shows that after a period of four weeks there was 100% of heptachlor epoxide and dieldrin remaining in river water. The values for chlordane and aldrin were 85 and 40% respectively. This can be compared to the organophosphate Fenthion (Baytex) which only had 10% remaining after four weeks. A study by Szeto (1982) looked at the degradation of chlorpyrifos-methyl in, firstly, flooded sandy loam soil and, secondly, in natural water. He found that when applied to soil at 400 ppb, there was only 10 ppb remaining after 83 days. Over that same period the amount in natural water was reduced from 200 ppb to 0.1 ppb. The relative persistence of pesticides in natural waters is shown in Table 10.

5B. Breakdown in soil and water

The methods by which pesticides are removed from or degraded in soils are: leaching, movement with runoff, movement with eroded soil, volatilization, non-biological degradation and microbial degradation (McEwen and Stephenson, 1979; Guenzi, 1974).

As mentioned previously, leaching is a function of the solubility of the pesticide. Pesticides that have low solubility (e.g. organochlorines) are

less likely to be leached through the soil with rain. Also, leaching is less likely to occur in clay soils than in sandy soils (Guenzi, 1974). Movement with surface water may not only be by leaching, but also may be from lateral movement. Pesticides can be desorbed and moved with this runoff water. Movement may also occur from erosion by either wind or water. When soil particles themselves move, the absorbed pesticide molecules may be transported along with them (McEwen and Stephenson, 1979).

Volatilization has been suggested as a major cause of loss of insecticides from soil. The magnitude of pesticide loss by volatilization can range from a few percent to greater than 50 percent (Brooks, 1974; Guenzi, 1974). High vapour pressure, a low solubility and tendency to be absorbed may contribute to a greater loss of the pesticide by volatilization. Cool, dry conditions normally result in very little loss of even the most volatile pesticides. However, warm, moist conditions bring about greater absorption and greater volatilization losses. In a study on the volatility of pesticides in moist, sandy loam, it was found that little volatilization occurred in chlordane, dieldrin and heptachlor epoxide, but marked evidence of volatility with aldrin, heptachlor and chlorpyrifos (McEwen and Stephenson, 1979).

Non-biological degradation processes play an important role in the dissipation of many pesticides in soil. In particular, the two processes, photochemical degradation and chemical hydrolysis, have received particular attention. Chemical hydrolysis reactions in some cases occur more rapidly in soil than in soil free aqueous systems, due to the catalysis of the reaction by sorption. Sorption catalysed reactions appear particularly important to organophosphate insecticides. Photochemical degradation reactions represent a potentially important pathway for alteration and/or degradation of pesticides applied to soil. Any pesticides which can absorb light above 285 nm are expected to undergo photodecomposition by sunlight. Photochemical

reactions have been recorded for chlorinated cyclocliene insecticides and organophosphorous pesticides (Guenzi, 1974; Liang and Lichtenstein, 1976).

It has become increasingly evident that soil microorganisms play an important role in the degeneration of insecticide residues in soil (Edwards, 1970). With the cyclodiene pesticides (e.g. heptachlor, chlordane, aldrin, dieldrin), epoxidation is the major mechanism of microbial metabolism, although dehalogenation, hydrolysis, reduction, and hydroxylation have also been observed. Since the epoxides of heptachlor and aldrin are insecticidally active, their biological activity in soils is prolonged. Metabolites of dieldrin and aldrin forming as a result of microbial activity have been isolated. Microbial epoxidation and dechlorination of heptachlor have also been shown to occur (Guenzi, 1974). Many microbes are also capable of utilising pesticides as sources of carbon (McEwen and Stephenson, 1979).

The role of microorganisms in the initial degradation of organophosphates is unclear. However, evidence of hydrolysis, reduction and oxidation to the corresponding sulfacide has been provided. Oxidation and hydrolysis are the two major degradation routes (Guenzi, 1974).

Much of what has been said about degradation in soils also applies to water. Chemical hydrolysis and photodegradation also occur in water. In fact, photodecomposition is greatly enhanced in the presence of water (Guenzi, 1974). Microbial degradation is of utmost importance and pesticides also move back into the atmosphere by volatilisation (Khan, 1977). However, the major factors for degradation in water, as previously mentioned, are sedimentation and solubility of the insecticide. Since sedimentation removes large quantities of pesticides, insecticide residues are unlikely to be high in standing water since the persistent (insoluble) pesticides are found on

the particular matter. Solubility is an important factor, the more soluble chemicals taking longer to settle out (Edwards, 1970).

6. PREVIOUS PESTICIDE SPRAYING PROGRAMMES IN THE PERTH REGION

The Argentine ant control programme has been the largest single chemical control programme undertaken in Western Australia (Shewchuk, 1981) and represents the main source of organochlorine pesticides within the Perth region. A dedicated spraying programme under the control of the Argentine Ant Act and the Argentine Ant Control Committee began in Perth in 1954. A new Argentine Ant Act was passed in 1968 and gave responsibility for control to the State Minister for Agriculture (Porter, 1982).

To 30 June 1985 a total of 30,519.5 hectares were sprayed in Western Australia for ant control. Dieldrin was the main pesticide used in the first 14 years of the control programme (1955-1969), and thousands of gallons of dieldrin have been used for ant control in south-western Western Australia. Dieldrin was replaced by heptachlor in 1970 (Shewchuk, 1981). Chlordane was also used between 1955 and 1973. DDT, mirex bait, diazinon, endosulphur and chlorpyrifos have all been tested at various times within the spraying programme (Porter, 1982).

The perimeter of Herdsman Lake has been sprayed for ant control every year since the mid 1950s, except during 1984/85. Spraying was not carried out in 1984/85 due to public concern over the threat to wildlife posed by spraying. However, an infestation of houses adjoining the lake prompted the renewal of spraying operations in 1985/86 (Anon, 1985).

The Argentine ant spraying programme appears to be the only pesticide programme undertaken at Herdsman Lake. The Stirling City Council (the local government authority responsible for management of areas closest to the

lake) does not carry out any spraying at the lake (City of Stirling spokesperson, pers. comm.).

Organochlorine pesticide usage within the Perth region, for control of pest species other than Argentine ants, now mainly involves the use of heptachlor and chlordane. These pesticides fill the role previously played by dieldrin.

In the 1950s and 1960s, dieldrin was the recommended pesticide for a wide range of pest species. However, the Pesticides Advisory Committee placed the first restrictions upon its use in 1971. Further restrictions were applied in 1975 and finally, from July 1981 dieldrin could only be used for the control of termites, timber and tree borers, and the African black beetle in potatoes, and all other uses were prohibited (Shewchuk, 1981).

Organophosphate pesticides are used within the Perth region mainly for the control of mosquitoes and non-biting midges. Abate (temephos) is the most commonly used organophosphate pesticide and spraying programmes are largely under the control of local government authorities. The following shires presently use, or have previously used, Abate for pest control: Armadale (Forrestdale Lake), Melville (North and Bibra Lakes), Rockingham (Lake Richmond), Mandurah, Wanneroo, Cockburn, Perth and Canning (Blair, 1979; N. Bolton, pers. comm.).

7. PREVIOUS PESTICIDE MONITORING IN WESTERN AUSTRALIA

The monitoring of pesticide residues in Western Australia is a joint State and Commonwealth responsibility. The Commonwealth, through the Department of Primary Industry and Australian Government Analytical Laboratories (AGAL), is responsible for the monitoring of a wide range of export products.

Another role the Commonwealth plays, through AGAL and the National Health and Medical Research Council, is the market basket survey. This survey is

conducted regularly to determine residues in various food commodities. Samples from export products rarely exceed the MRL (Maximum Residue Limit) with the majority showing either none detected or less than 20 per cent of the MRL. Results from the market basket survey have revealed an appreciable decrease in the daily intake of DDT, HCB and dieldrin from normal food sources between 1970 and 1980 (Gorman, 1983).

State government monitoring programmes are usually carried out in relation to specific problems or areas. These include monitoring programmes to protect the health of workers involved with the manufacture or use of pesticides and to prevent the consumption of contaminated food. The State is also concerned with the fate and effects of pesticide residues in the environment, including the persistence of residues in soils and water and the effects on wildlife (Gorman, 1983).

A study of dieldrin residues in Western Australia was carried out by the Government Chemical Laboratories in 1981 (Shewchuk, 1981). Levels of dieldrin residues in rivers, lakes, reservoirs, bores, soil, silt, fish and other aquatic species, bovine milk, human milk, human fat, bird eggs, wool grease, cigarettes and exported food products were reported. Levels of dieldrin in the environment were found to be decreasing. With respect to the aquatic environment levels recorded from most rivers between 1974 and 1980 were found to be low. At some locations initially high levels were found to have decreased. Dieldrin levels in the hills catchment dams and metropolitan groundwater sources always remained well below drinking water criteria levels. Levels in several south-western rivers often exceeded the environmental criteria for aquatic freshwater species (0.003 $\mu\text{g/L}$), but no samples exceeded the Australian and American drinking water criteria of 1.0 $\mu\text{g/L}$ (Shewchuk, 1981). Levels of dieldrin in fish and other aquatic species, birds and sediments were low and found to be below the levels reported in

other countries. High levels of dieldrin were found in human milk, but the source or sources were not ascertained (Shewchuk, 1981). Shewchuk (1981) concluded that levels of dieldrin in the environment and foodstuffs in Western Australia were decreasing and that present controls on the use of dieldrin were effective and no additional controls were warranted.

A study of organochlorine residues in the Preston River, Western Australia (Atkins, 1982) found that levels of dieldrin, aldrin, DDT and heptachlor exceeded the criteria for the maintenance and preservation of aquatic ecosystems from time to time but not the limits for human consumption. There was no measurable accumulation of pesticides in the sediments and tissues of fish in Leschenault Inlet.

Extensive monitoring was undertaken in the Ord River area, between 1964-1978, in response to the application of large amounts of pesticides to cotton crops and irrigation water. Residue levels in water, sediment, food, bird and fish tissue, bird eggs and other samples were recorded. The study revealed accumulation of DDT and comphechlor in the various types of samples collected and, in many cases, levels exceeded the Maximum Residue Limit. Pest control ceased after 1974, but an ongoing monitoring programme has continued to obtain information on the persistence of organochlorine residues (Gorman, 1983).

Davis (1985) investigated the degradation of heptachlor and chlordane at Albany and Perth (Lake Badgerup, Wanneroo), and found that an increased effectiveness of heptachlor/chlordane for Argentine ant control in Perth compared with that in Albany may be attributed to a higher decay rate for the compounds in Albany, possibly as a result of wetter conditions in the latter area. A small residue monitoring study was undertaken by Ford (1982) at Loch McNess following the death of a kangaroo which had strayed into an

area sprayed with heptachlor for Argentine ant control. No pesticides were found in any of the samples of soil or grass collected by Ford.

The Water Authority of Western Australia undertakes annual monitoring for pesticides in all major sources of drinking water in Western Australia. Very low levels of dieldrin ($<0.001 \mu\text{g/L}$) and other organochlorines have been detected in some reservoirs and bores. Residues of DDT, heptachlor and dieldrin have also been recorded in Perth rainwater (Gorman, 1983).

Numerous samples of birds and fish have been analysed for pesticide residues. Trace levels of organochlorines are usually present but none at levels that would be of concern. An exception, however, involving organophosphates, is the death of a large number of migratory wading birds at Forrestdale Lake in February, 1984. The deaths were linked to a recent spraying of the lake with Abate. The birds displayed typical signs of organophosphate poisoning and sick birds treated with atropine (a recognised antidote for organophosphate poisoning) recovered rapidly. Tests carried out found levels of organophosphates ranging from 12 mg/kg to 18 mg/kg (Keeling, 1984).

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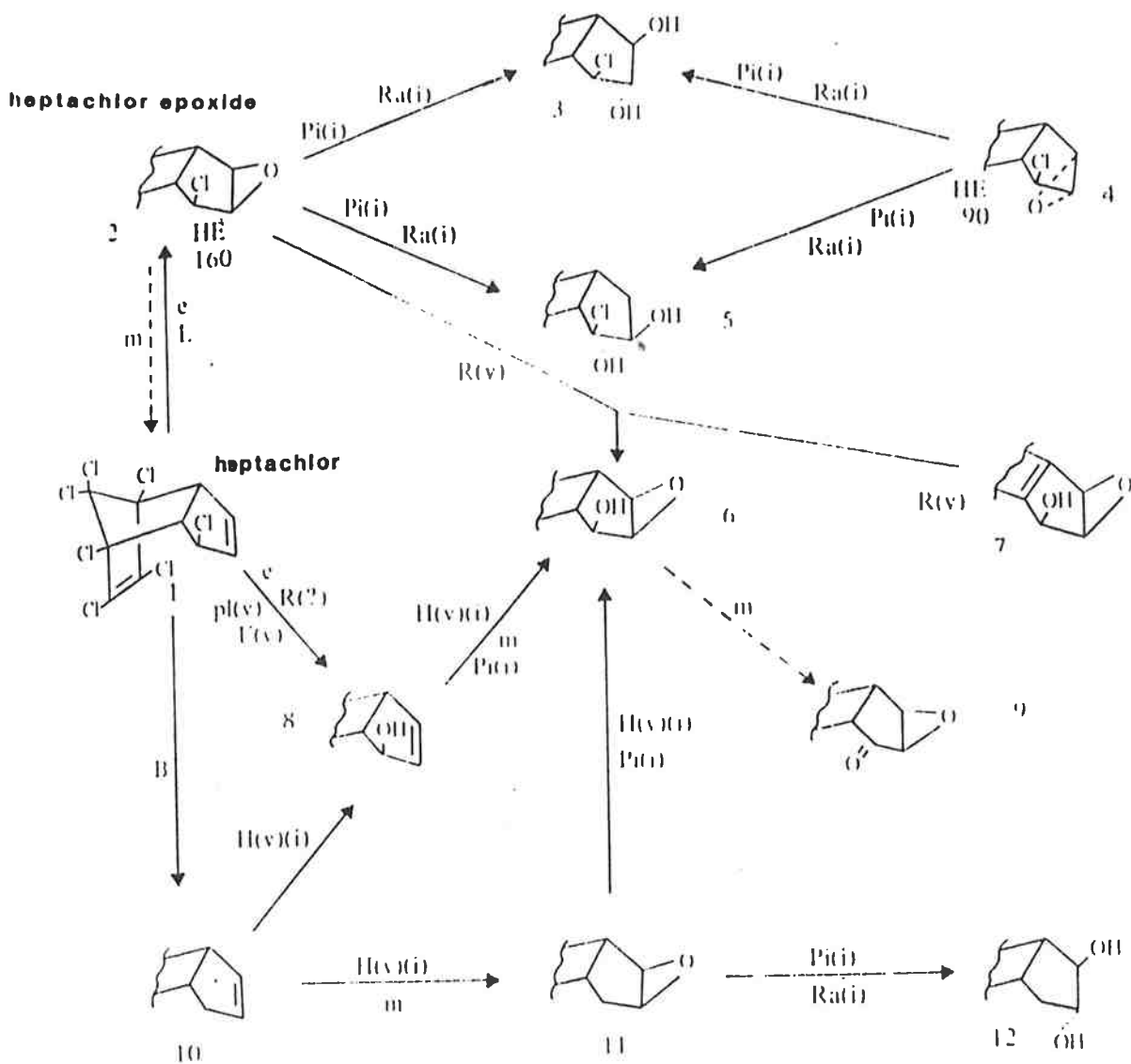
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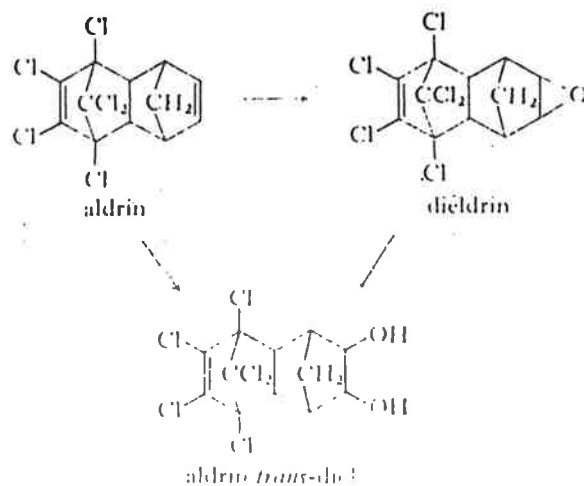
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FIG. 1 Conversions of Heptachlor



From Brooks (1974)

FIG. 2 Epoxidation of Aldrin/Dieldrin



From Corbett (1974)

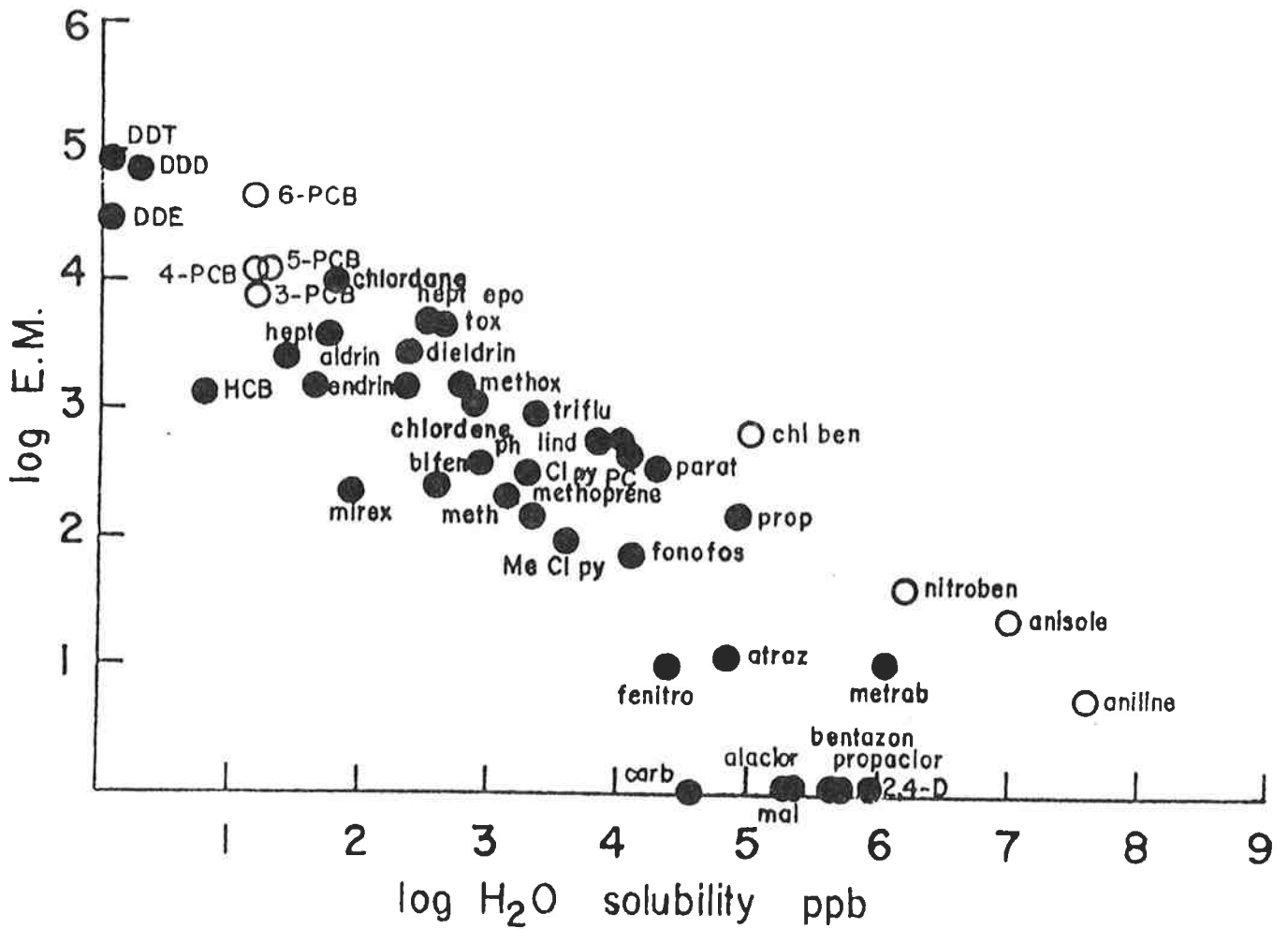


Figure 3. Relationship between water solubility of pesticides and ecological magnification in mosquito fish of terrestrial-aquatic model ecosystem.

From Khan, 1977

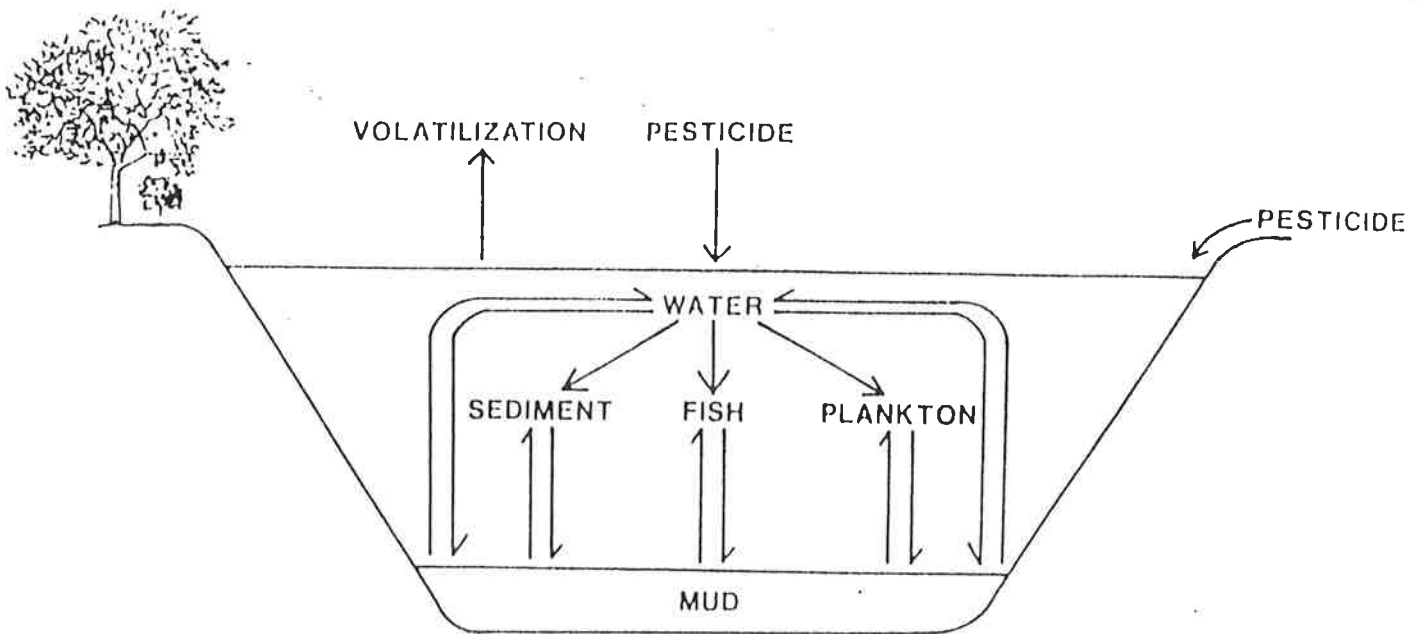


Fig. 4. Movement of pesticides through aquatic systems.

From Khan(1977)

TABLE 1

Target organisms, other than the Argentine ant, and the methods of application for pesticides used in the Argentine ant spraying programme (dieldrin was used prior to 1970).

| <u>Pesticide</u> | <u>Target organism</u> | <u>Treatment method</u> |
|------------------|--|-------------------------------|
| Heptachlor | Fire ant, root maggots, wire worms ¹ | Seed treatment ¹ |
| | <u>Curculio</u> ³ | Butt ³ |
| | Fullers weevil ³ | Foliar ³ |
| | African black beetle, termites ³ | Soil ³ |
| | Cutworms, thrips ⁴ | |
| | Earthworms, cockroaches, wasps ⁵ | |
| | Wheat bulb fly ⁵ | Seed dressing ⁵ |
| Chlorpyrifos | Mosquito larvae ² | Aerial treatment ² |
| | Earthworms ¹ | |
| | Flies ⁴ | |
| | Midge larvae ⁴ | |
| Temephos | Mosquito larvae, biting midge larvae, sandflies | Back pack ⁶ |
| | Chironomid larvae ² | Aerial ⁶ |
| | Moths, fleas, lice ⁴ | |
| | Cutworm, thrips, lygus bugs ⁴ | |
| | | |
| Aldrin/Dieldrin | Termites ⁴ | |
| | Locusts, tropical disease vectors (e.g. <u>Glossina</u> sp.) | |
| | Mosquitoes ⁴ | |
| | Grubs, wireworms, root maggots ¹ | Seed, soil ¹ |
| | Fire ant, Japanese beetle, corn root worms ¹ | Soil ¹ |
| | Coleoptera ¹ | Foliar ¹ |
| | Wheat bulb fly ⁵ | Seed ⁵ |
| | African black beetle ³ | Soil ³ |

- Source of information:
- ¹ McEwen and Stephenson (1979)
 - ² Muirhead and Thomson (1971)
 - ³ Atkins (1982)
 - ⁴ Worthing (1983)
 - ⁵ Advisory Committee on Pesticides (1969)
 - ⁶ Blair (1979)

TABLE 2

Levels of some pesticides permitted in potable water and recommended maximum levels in surface waters for the maintenance of aquatic life. Levels expressed in $\mu\text{g/L}$.

| | Permissible level | Maximum suggested | |
|-----------------|-------------------|--------------------------------|--------------|
| | | Fish | Aquatic life |
| Heptachlor | 0.01 | 0.1 | 0.001 |
| Chlorpyrifos) | 10 | LC ₅₀ not to exceed | |
| Temephos) | | 0.01 of 96 hr | |
| Aldrin/Dieldrin | 0.1 | 0.025 | 0.003-0.005 |
| Chlordane | 0.3 | 0.025 | 0.01 |

Source: McEwen and Stephenson (1979)
EPA (1981)

Table 3. Residues of Two Insecticides in Each of Several Species of Aquatic Invertebrates and Magnification Factor After the Exposure Period Indicated^a

| Pesticide | Period of Exposure | Organism | Concentration | | Magnification Factor |
|-----------|--------------------|---------------------------------------|----------------------------|----------------|----------------------|
| | | | Water (ppb) | Organism (ppm) | |
| DDT | 3 days | <u>Daphnia magna</u> adult | 803 | 9.17 | 114100 |
| | 3 days | <u>Gammarus fasciatus</u> adult | 813 | 1.68 | 20600 |
| | 3 days | <u>Orconectes nais</u> adult | 803 | .233 | 2900 |
| | 3 days | <u>Palaemonetes kadiakensis</u> adult | 1000 | .503 | 5000 |
| | 3 days | <u>Hexagenia bilineata</u> nymph | 521 | 1.68 | 32600 |
| | 3 days | <u>Siphonurus</u> sp. nymph | 470 | 1.08 | 22900 |
| | 2 days | <u>Ischnura verticalis</u> naiad | 1013 | .375 | 3500 |
| | 2 days | <u>Libellula</u> sp. naiad | 793 | .072 | 910 |
| | 3 days | <u>Chironomus</u> sp. larva | 463 | 2.2 | 47800 |
| | 2 days | <u>Culex pipiens</u> larva | 1046 | 13.9 | 133600 |
| | Aldrin | 3 days | <u>Daphnia magna</u> adult | 167 | 2.4 |
| 3 days | | <u>Hexagenia bilineata</u> nymph | 213 | 0.66 | 31400 |
| 3 days | | <u>Chironomus</u> sp. larva | 213 | 0.48 | 22800 |

From McEwen and Stephenson (1979)

TABLE 4

Toxicities (LC₅₀) of various pesticides to aquatic invertebrates - in ppm.

| Pesticide | Heptachlor | Chlordane | Chlorpyrifos | Temephos | Aldrin | Dieldrin |
|---|----------------------|----------------------|------------------------|--------------------------|---------------------------|----------------------|
| STONEFLIES (24 hr) | | | | | | |
| <u>Pteronarcells badia</u> | 0.006 ^a | - | 0.0042 ^a | - | - | 0.003 ^a |
| <u>Pteronarcys californica</u> | 0.008 ^{a,b} | 0.17 ^{a,b} | 0.050 ^{a,b} | 0.10 ^{a,c} (48) | 0.008 ^{a,b} (48) | 0.006 ^{a,b} |
| <u>Claassenia sabulosa</u> | 0.009 ^a | - | 0.0082 ^a | - | - | 0.0045 ^a |
| AMPHIPODS (24 hr) | | | | | | |
| <u>Gammarus lacustris</u> | 0.150 ^{a,b} | 0.160 ^{a,b} | 0.00076 ^{a,b} | 0.96 ^{a,b,c} | 45 ^a | 1.4 ^{a,b} |
| <u>Hyalella azteca</u> | - | - | - | 0.65 | - | - |
| CLADOCERANS (48 hr) | | | | | | |
| <u>Daphnia</u> | 0.042 ^{a,b} | 0.029 ^b | - | - | 0.28 ^{a,b} | 0.25 ^{a,b} |
| MOSQUITOES (24 hr) | | | | | | |
| <u>Culex</u> | 0.054 ^b | | 0.003 ^b | 0.016 ^b | 0.005 ^b | 0.008 ^b |
| MAYFLIES (48 hr) | | | | | | |
| <u>Baetis sp.</u> | 0.032 ^a | | - | - | - | 0.012 |
| COPEPODS (24 hr) | | | | | | |
| <u>Cyclops</u> | - | | - | 5.0 ^c | | |
| <u>Draptomus</u> | - | | - | 0.1 ^c | | |
| <u>Thermocyclops hyalinus</u> | - | | - | 0.20 ^c | | |
| BACKSWIMMERS | | | | | | |
| <u>Notonecta undulata</u> (LC ₅₀ at 48 hrs) | - | | - | 0.01 ^c | - | - |

Source: ^a Pimental (1971)
^b McEwen and Stephenson (1979)
^c Blair (1979)

TABLE 5
CONCENTRATION OF RESIDUES FROM WATER TO FISH

| Organism | Insecticide | Amount of residue | | Concentration factor** | Reference |
|----------------------|-------------------|-------------------------------------|--------------------------------------|------------------------|-----------------------------|
| | | In water (pp 10 ⁻⁹)* | In animal (pp 10 ⁻⁶)† | | |
| Rainbow trout | DDT | 20.0 | 4.15 | 207 | Cope 1966 (46) |
| Black bullhead | DDT | 20.0 | 3.11 | 155 | " |
| Bluegill | Heptachlor | 50.0 | 15.7 | 314 | " |
| Catfish | Aldrin & dieldrin | 0.044 | 0.07 | 1,590 | Sparr et al. 1966 (236) |
| " | " | 0.009 | 0.04 | 4,444 | " |
| " | " | 0.021 | 0.02 | 952 | " |
| " | " | 0.007 | 0.01 | 1,428 | " |
| Buffabfish | " | 0.023 | 0.09 | 3,913 | " |
| " | " | 0.007 | 0.21 | 30,000 | " |
| Scaled sardine | DDT | 0.1 | 0.11 | 1,100 | Butler 1965 (32) |
| Rainbow trout | Toxaphene | 0.41 | 7.72 | 18,829 | Terriere et al. 1965 (250) |
| Fish | DDT | 0.30 | 1.0 - 6.4 | 3,333 - 21,333 | Keith 1964 (151) |
| " | Endrin | 0.10 | 7.0 | 70,000 | Langer 1964 (163) |
| " | Toxaphene | 1.0 - 4.0 | 0.8 - 2.5 | 2,000 - 2,500 | Kallman et al. 1962 (149) |
| " (5 spp.) | DDT | 30 - 40 | 4 - 58 | 130 - 1,450 | Crocker & Wilson 1965 (51) |
| Bullhead trout | DDT | 20 | 2 - 4 | 100 - 200 | Bridges et al. 1963 (24) |
| Fathead minnow | Endrin | 0.015 | 0.15 | 10,000 | Mount & Putnicki 1966 (198) |
| Croakers | DDT | 0.1 | 2.0 | 20,000 | Hansen 1966 (110) |
| Pinfish | DDT | 1.0 | 12.0 | 12,000 | " |
| " | DDT | 0.1 | 4.0 | 40,000 | " |
| Fish | Dieldrin & DDT | 10.0 | 0.1 - 1.0 | 10 - 100 | Holden & Marsden 1966 (131) |
| Trout | Dieldrin | 2.3 | 7.7 | 3,300 | Holden 1966 (130) |
| Chubs | DDT | 5.8 | 0.029 | 5 | Godsil & Johnson 1968 (103) |
| " | Chlordane | 6.6 | 0.008 | 1.2 | " |
| " | Endrin | 10.5 | 0.050 | 4.7 | " |
| Trout | DDT | 20.0 | 4.0 | 200.0 | U.S.D.I. 1963 (262) |
| Bluegills | Heptachlor | 50.0 | 56.8 | 1,130.0 | U.S.D.I. 1964 (263) |
| Fish | DDT | 0.015 | 12.44 | 829,300 | Mack et al. 1964 (181) |
| " | DDT | 0.11 | 3.85 | 35,000 | " |
| White catfish | DDD | 14.0 | 30.4 - 129.0 | 2,172 - 9,214 | Hunt & Bischoff 1960 (135) |
| Largemouth bass | DDD | 14.0 | 19.7 - 25.0 | 1,407 - 1,785 | " |
| Brown bullhead | DDD | 14.0 | 15.5 - 24.8 | 1,107 - 1,771 | " |
| Black crappie | DDD | 14.0 | 5.4 - 115.0 | 386 - 8,214 | " |
| Bluegill | DDD | 14.0 | 6.6 - 10.0 | 471 - 714 | " |
| Sacramento blackfish | DDD | 14.0 | 10.9 - 17.6 | 778 - 1,257 | " |
| Brook trout | DDT | 24.0 | 17.3 | 710.0 | Cole et al. 1967 (44) |

* µg/liter

† mg/kg

** Concentration factor = $\frac{\text{Concentration in animal}}{\text{Concentration in water}}$

From Edwards, (1970)

TABLE 6

Acute toxicities of selected pesticides to some freshwater fish.
(Values are in ppb for 48 hrs unless otherwise indicated.)

| Organism | Pesticide | | | | | |
|--------------------------------------|--------------------|--------------------------------------|---------------------------------------|-----------------------|--|---|
| | Heptachlor | Chlordane | Chlorpyrifos | Temephos | Aldrin | Dieldrin |
| Flathead minnow | | | | 6200 ^{b+} | 28 | 16 ^{d+} |
| Rainbow trout | 9 ^{a,c} | 10.22 ^{a,c} | 20 ^{a,c} | 1900 ^{b+} | 3.0 | 50 ^{c*} 19 ^{a+} |
| Blue gill | 19 ^a | 77 ^{a+} 58 ^{c*} | 53 ^{c*} 3.6 ^{e+} | >200ppm ^{b*} | 96 ^{c*} 13 ^{a,c+} | 8 ^{c,d+} 3.4 ^{a,c} |
| Goldfish | 230 ^a | 81 ^{a,c+} | | | 28 ^{a,c+} | 31-37 ^{a,c,d+} |
| <u>Gambusia affinis</u> ^S | 70 ^{c*} | | 230 ^{c*} | >200ppm ^{b*} | 50 ^{c*,+} | 16 ^{c*} |
| <u>Gambusia affinis</u> ^R | 1300 ^{c*} | | 595 ^{c*} | | 2100 ^{c*} | 500 ^{c*} |
| Striped bass | 3.0 ^a | 11.8 ^a | 0.58 ^a | 1000 ^a | 7.2 | 19.7 ^a |

S = susceptible strain
R = resistant strain
* = 24 hr exposure
+ = 96 hr exposure
= 36 hr exposure

Source: a: McEwen and Stephenson (1979)
b: Blair (1979)
c: Pimental (1971)
d: Shewchuk (1981)
e: Khan (1977)

TABLE 7

LC₅₀ and LD₅₀s for some common bird species in ppm or mg/kg

| Organism | Pesticide | | | | | |
|-----------------|--|---|---|--|--|--|
| | Heptachlor | Chlordane | Chlorpyrifos | Temephos | Aldrin | Dieldrin |
| Mallard duck | 575 ^{ab+} >2000 ^{ab*} | 825 ^{ab+} 1200 ^{ab*} | 75 ^{ab*} | 1500 ^{abd+} 90 ^{ab*} | 160 ^{ab+} 520 ^{ab*} | 200 ^{ac+} 381 ^{acb**} |
| Pheasant | 262 ^{ab+} | 450 ^{ab+} | 35 ^{ab*} | 160 ^{abd+} 31.5 ^{ab*} | 55 ^{ab+} 16.8 ^{ab*} | 52 ^{acb+} 79 ^{acb**} |
| Coturnix | 88 ^{ab+} | 325 ^{ab+} | 282 ^{ab*} 17 ^{ab*} | 250 ^{ad+} 270 ^{ab*} | 35 ^{ab+} | 52 ^{acb+} 69.7 ^{acb*} |
| Bobwhite quail | 95 ^{ab+} | 320 ^{ab+} | | 100 ^{ab*} 96 ^{db+} | 39 ^{ab+} 66 ^{b*} | 39 ^{ac+} |
| House sparrow | | | 21 ^{ab*} | 50.1 ^{ab*} | | 47.6 ^{acb*} |
| Canada geese | | | >80 ^{b*} | | | 50-150 ^{b*} |
| Sandhill cranes | | | 25-50 ^{b*} | | | |

* = LD₅₀ mg/kg
+ = LC₅₀ ppm

Source: a: McEwen and Stephenson (1979)
b: Pimental (1971)
c: Shewchuk (1981)
d: Blair (1979)

TABLE 8

Acute oral and dermal LD₅₀s for some mammals
(in mg/kg unless otherwise stated).

| Organism | Heptachlor | | Chlordane | | Chlorpyrifos | | Temephos | | Dieldrin | | Aldrin | |
|-----------------------|--------------------|----------------------|----------------------|-------------------|------------------------|--------|--------------------|-----------------------|--------------------|---------------------|--------------------|-----------------------|
| | Oral | Dermal | Oral | Dermal | Oral | Dermal | Oral | Dermal | Oral | Dermal | Oral | Dermal |
| Male rats))) | 100 ^{c a} | 195 ^c | | | | | 8600 ^d | 74000 ^d | 46 ^{a b} | 50-120 ^a | | |
| Female rats) | 162 ^{c a} | 250 ^c | 457-590 ^a | 1600 ^a | | | 1300 ^d | | | | 38-60 ^a | 98-200 ^{a c} |
| Rabbit | | >2000 ^a | 100-300 ^c | | 1000-2000 ^a | | | 970-1930 ^d | >150 ^f | 163 ^b | <150 ^f | |
| Human | | 46000 ^{c *} | | | | | 256 ^{d +} | | | | | |
| Dogs | | | | | | | 18 ^{d +} | | 65-95 ^f | | | |

* = Estimated to produce symptoms in single dose

+ = No clinical symptoms or side effects (mg/kg/day)

a: Worthing (1983)

d: Blair (1979)

b: Shewchuk (1981)

e: Cawcutt and Watson (1984)

c: McNulty (1984)

f: Pimental (1971)

TABLE 9

| Pesticide | Heptachlor | Chlordane | Chlorpyrifos | Temephos | Dieldrin | Aldrin |
|-------------|----------------------|-------------------------------------|---|----------|----------------------|----------------------|
| Persistence | 2 ^a yrs | 5 ^a -10 ^b yrs | $\frac{0-12 \text{ weeks}^{**}}{60-120^d \text{ days}}$ | | ~3 ^a yrs | >17 ^b yrs |
| Half life | 2-4 ^c yrs | ~8 ^c yrs | | | 1-7 ^e yrs | 1-4 ^e yrs |

* = Grouped organophosphorus results
 • = In mud

a: Guenzi, 1974
 b: Cawcutt and Watson (1985)
 c: Faust (1972)
 d: Worthing (1983)
 e: Brooks (1974)

Table 10. Relative Persistence of Some Pesticides in Natural Waters

| Non Persistent ^a | Slightly Persistent ^b | Moderately Persistent ^c | Persistent ^d |
|-----------------------------|----------------------------------|------------------------------------|-------------------------|
| azinphosmethyl | aldrin | aldicarb | benomyl |
| captan | amitrole | atrazine | dieldrin |
| carbaryl | CDAA | ametryne | endrin |
| chlorpyrifos | CDEC | bromacil | hexachlorobenzene |
| demeton | chloramben | carbofuran | heptachlor |
| dichlorvos | chlorpropham | carboxin | isodrin |
| dicrotophos | CIPC | chlordan | monocrotophos |
| diquat | dalapon | chlorfenvinphos | |
| DIOC | diazinon | chloroxuron | |
| endosulfan | dicamba | dichlorbenil | |
| endothal | disulfoton | dimethoate | |
| fenitrothion | DNBP | diphenamid | |
| IPC | EPTC | diuron | |
| malathion | fenuron | ethion | |
| methiocarb | MCPA | fensulfothion | |
| methoprene | methoxychlor | fonofos | |
| methyl parathion | monuron | lindane | |
| mevinphos | phorate | linuron | |
| parathion | propham | prometone | |
| naled | Swep | propazine | |
| phosphamidon | TCA | quintozene | |
| propoxur | thionazin | simazine | |
| pyrethrum | vernolate | TBA | |
| rotenone | | terbacil | |
| temephos | | toxaphene | |
| TIM | | trifluralin | |
| 2,4-D | | | |

^aHalf-life less than 2 weeks.

^bHalf-life 2 weeks to 6 weeks.

^cHalf-life 6 weeks to 6 months.

^dHalf-life more than 6 months.