Section 6
ENVIRONMENTAL ASSESSMENT

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1. INTRODUCTION

The organophosphate insecticide chlorpyrifos is included in the second round of chemicals selected for review under the National Registration Authority's Existing Chemicals Review Program. From the environmental perspective, chlorpyrifos was accorded high priority for review because of its toxicity to birds and aquatic organisms.

Chlorpyrifos is an organophosphorous insecticide widely used for urban and domestic pest control, including turf maintenance, and as a termiticidal barrier in, around or under buildings. Agricultural uses include cotton, sugarcane, vegetables, cereals, canola, rice, pome fruit, stone fruit, citrus, tropical fruit and grapes.

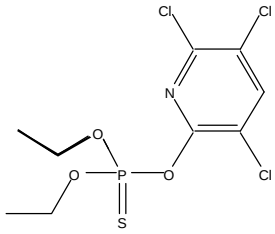
Organophosphorous insecticides exert their effects by inhibiting the activity of an enzyme known as acetylcholinesterase that is important in the transmission of nerve impulses. Chlorpyrifos belongs to a group of organophosphorous compounds known as the phosphorothioates that do not inhibit acetylcholinesterase directly. They rely for their effect on metabolic transformation in target tissue to their oxon form, which is intrinsically less stable and has greater activity, generally by several orders of magnitude.

Chlorpyrifos is widely used around the world and has been very well studied. Recent reviews of the environmental fate and toxicity of chlorpyrifos are available in the scientific literature, but there are at this time no regulatory reviews available from other jurisdictions. A Reregistration Eligibility Decision document is currently being drafted in the United States. Information in this review has mainly been provided by registrants. Some information has been taken from the open scientific literature.

2. CHEMICAL IDENTITY

Name (CAS):	O,O-Diethyl-O-(3,5,6-trichloro-2-pyridinyl)phosphorothioate
Common name:	Chlorpyrifos
CAS number:	2921-88-2
Molecular formula:	$C_9H_{11}Cl_3NO_3PS$
Molecular weight:	350.6

Structural formula:



3. PHYSICO-CHEMICAL PROPERTIES

Melting Point: 42-43.5°C

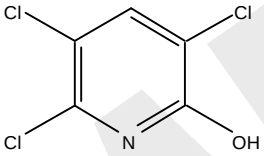
Vapour Pressure: 2.7 mPa at 25°C

Water Solubility: 1.4 mg/L at 25°C

Partition Coefficient: Pow = 50 000; log P = 4.7 (*n*-octanol/water)

Dissociation constant: no readily dissociable functionality

The main degradation product from chlorpyrifos is 3,5,6-trichloro-2-pyridinol (TCP). The following environmentally significant properties have been determined for TCP (Racke, 1993; Meikle and Hamaker, 1981).



TCP

Melting Point: 174-175°C

Vapour Pressure: 3.3 mPa at 25°C

Water Solubility: 117 mg/L at 25°C and pH 2-3
49.1 g/L at 25°C and pH 7

Partition Coefficient: Pow = 1600 at pH 3; log P = 3.2
(*n*-octanol/water) Pow = 22 at pH 7; log P = 1.3

Dissociation constant: pKa = 4.55

4. FORMULATION OF END-USE PRODUCTS

Chlorpyrifos is available in Australia as emulsifiable concentrate (used in agriculture, for turf maintenance and termite protection), wettable powder (favoured for orchard use to avoid phytotoxicity problems with solvents in emulsifiable concentrate formulations), ultra low volume (mainly for cotton), microencapsulate (general urban pest control), seed dressing, granule (home garden use against pests such as ants and beetles), prepared bait (for control of cockroaches in the home; note that user prepared baits are also used to control certain surface feeding soil insects in agriculture) and sustained release (for multi season grub control in sugarcane and ornamentals) formulations. There are also some animal health products (collars and sprays) for use on companion animals.

5. OVERSEAS REGULATORY ACTIVITY

On 27 October 1999, the US EPA released a preliminary ecological risk assessment for chlorpyrifos, together with related documents including a covering note emphasising that the assessment is preliminary in nature and reflects the information available to the US EPA at the time of drafting. The document was released for a 60 day public comment period, with the US EPA cautioning against premature conclusions until the report is further refined, as conclusions may change with availability of new information. An earlier draft (dated 27 November 1998) of the document had been provided to Dow AgroSciences for comment, and the US EPA has posted the registrant's response (dated 15 January 1999) on its website, together with the public release draft of the ecological risk assessment.

The US EPA assessment is very detailed, filling more than 200 pages. In its risk summary, the US EPA concludes that application of chlorpyrifos poses acute and reproductive risks to many non-target aquatic and terrestrial animals for all outdoor uses reviewed. Risks are highest to aquatic fauna, particularly from aerial application, and amphibians appear particularly sensitive. Among terrestrial species, birds appear to be more at risk than most mammals. These predictions, using the standard risk quotient methodology, are supported by the occurrence of wildlife casualties in a range of field studies, and by wildlife incident reports. The US EPA also documents widespread aquatic contamination by chlorpyrifos, including from sewage treatment works, although this specific source of contamination is probably largely historical as Dow AgroSciences voluntarily withdrew companion animal shampoo products from the market two years ago.

The risks of chlorpyrifos were compared with those for other insecticides, using the standard risk quotient approach. Results indicate that chlorpyrifos usually has the second or third highest risk quotient to terrestrial species among the insecticides selected, and the first or second highest risk quotient to aquatic species.

The US EPA suggests a number of application modifications for risk mitigation, including reduced application rates, reduced number of applications, increased time intervals (preferably 2-3 weeks) between treatments, avoidance of aerial application, enforcement of buffer zones for spray drift mitigation, and ensuring that air blast applications are directed away from sensitive areas. Final regulatory outcomes will be developed after the current public comment phase.

6. ENVIRONMENTAL EXPOSURE

6.1 Environmental Release

6.1.1 Volume

According to the available statistics, imports for the 1996-97 financial year approached 1000 tonnes.

6.1.2 Application and use pattern

Dow AgroSciences (formerly DowElanco, referred to as Dow in this report) has provided detailed information on use patterns. According to the available information, termite control, urban/domestic use (including turf maintenance) and agriculture are the main uses.

Chlorpyrifos is used in a wide variety of situations, the more important of which are outlined below.

6.1.2.1 Urban and domestic pest control

Chlorpyrifos is used in and around buildings to control such pests as termites, cockroaches, ants and silverfish. A small proportion is used outside, such as around the perimeter of buildings to control spiders and fleas, or to vegetation for mosquito control. Application rates for mosquito control are 13.5-54 g/ha. Small amounts are also used for lawn and turf maintenance, at rates between 0.35 and 4 kg/ha, the highest rate for African black beetle. Granular products are available for use in the home garden to control pests such as ants and beetles. Chlorpyrifos is also used on companion animals, as slow-release collars, shampoos and sprays. Around 25% of Dow sales into the urban/domestic market are to pest control operators.

6.1.2.2 Termite protection

Pre-construction use entails the installation of vertical and horizontal barriers. Vertical barriers are constructed around the building by trenching, in combination with rodding if necessary. An emulsion of chlorpyrifos (20 g/L in the tropics and 10 g/L in temperate regions) is applied to the backfill at 100 L/m^3 (equivalent to 5 L/m for a trench 150 mm wide and 300 mm deep). Horizontal barriers are applied with a shower nozzle at 5 L/m^2 (equivalent to 500 or 1000 kg/ha chlorpyrifos) to soil loosened to a depth of 80 mm, just before the waterproofing membrane is positioned prior to pouring the concrete slab. Application rates are the same post-construction, but application involves slab drilling and injection unless a reticulation system has been installed.

Power and building poles, fence posts and palings are protected by treating backfill as for vertical barriers. Infested poles can be drilled near ground level and flooded with emulsion.

Termite colonies can be destroyed by breaking open and flooding with a half strength emulsion (5 g/L chlorpyrifos).

Retreatment is recommended after 3-5 years for external barriers and 6-10 years for under floor barriers, with more frequent retreatment needed in tropical regions.

6.1.2.3 Cotton

Dow's Predator 300 Insecticide was re-launched in the 1996-97 season for control of heliothis larvae and mites. An estimated 200 tonnes chlorpyrifos was consumed in that

season. Volumes increased significantly in the 1997-98 season. However, it is expected that introduction of new chemistry and transgenic cottons may limit the commercial life of this product. Relatively high application rates (1.2-1.5 kg/ha chlorpyrifos) are needed for cotton bollworm and native budworm, with most applications made by air. The product can be used as an EC or ULV spray, but the latter is apparently preferred. Up to two treatments per season may be made according to label during stages II and III of the resistance management strategy (commencing in mid-late December, depending on location) with a third treatment authorised by permit for the 1998-99 season. Chlorpyrifos is reportedly preferred over profenofos which has odour problems. Lower application rates are used against pink spotted bollworm (525 g/ha), cotton aphid (150-210 g/ha), cotton flea beetle/red shouldered leaf beetle (450-750 g/ha) and mites (300-750 g/ha). The product is also applied in furrow at planting for control of wireworms and false wireworms in cotton, maize, sunflowers and sorghum, at 240-750 g/ha chlorpyrifos (for a 1 m row spacing).

6.1.2.4 Sugarcane

Dow sold around 19 tonnes chlorpyrifos into this market during 1996, and provided a further 100 tonnes to Crop Care for formulation. Chlorpyrifos is applied at planting as a coarse spray to setts and surrounding soil, at rates of 750 g/ha for sugarcane wireworm and black beetles, and 1 kg/ha for symphylids.

A sustained release formulation, Crop Care's suSCon Blue, is used for control of various cane grubs. Treatment at 21-28 kg/ha (2.9-3.9 kg chlorpyrifos) provides control for 2-3 seasons. Precision granule applicators deliver product granules in furrow and cover with soil in the same operation. Application occurs at planting or after shooting in the early stages of the crop.

No data were presented on release rates of chlorpyrifos from this product, but data for a similar product (see section 5.1.2.5) may be used for indicative purposes.

6.1.2.5 Ornamentals

A sustained release formulation, Crop Care's suSCon Green, has recently been registered for control of a range of soil insects in container grown ornamental plants, and claims to provide effective control for at least two years. The product is expected to gain significant markets.

Crop Care Australasia Pty Ltd presented data on the release rate of chlorpyrifos from this formulation. It is noted in these studies that release rate performance in a given situation will only be able to be reliably determined using field studies, given the effects of different environmental conditions.

Studies in the Netherlands showed cumulative release of 60 and 80%, respectively, after 12 and 24 months at 375 or 750 g/m^3 in potting media, planted with Thuja and watered daily. Pots were apparently maintained in the open. Soil temperatures did not exceed 22^{o}C (May, 1992).

In the USA, levels in the granules declined from an initial 10% to less than 0.2% after 29 months in potting media, planted with Taxus and watered three times per week in a greenhouse. The granules were added to the soil at 1 g/kg as a single layer at mid-depth (May, 1994).

Studies under controlled laboratory conditions found little variation in release rates from sandy loam soil treated at 750, 1000 or 1500 g/m^3 and maintained at 15 or 30^{o}C, except in dry soils where release rates increased markedly at the higher temperature. It is suggested that this probably reflects volatilisation (May, 1993).

In contrast, temperature had a marked influence on release rates from potting media in flooded pots, with complete release within 2 years at 30^{o}C but only 50% release at 15^{o}C from granules that were distributed evenly through the potting medium at 1.2 g/kg (Ahmetagic, 1993).

Release rates in water appear relatively low, although no firm conclusions can be drawn as no temperature is specified in the report submitted. Granules were found to still contain about 90% of the original chlorpyrifos after immersion in static water for 98 days at 1 g/L (nominally 100 mg/L chlorpyrifos). Concentrations in the water initially rose rapidly, probably reflecting dissolution of surface deposits, and then more gradually as chlorpyrifos diffused from the interior of the granule. The maximum concentrations reached was 354 µg/L at day 70, declining to 289 µg/L by day 98. An early peak of 192 µg/L occurred at day 2 (Hanson and Swigert, 1995).

6.1.2.6 Pome fruit

The next major agricultural use pattern after cotton and sugarcane is for control of light brown apple moth (LBAM) and other pests such as woolly aphids in pome fruit orchards. The usual practice in orchard situations is to spray to runoff, normally requiring 1500 to 2000 L/ha of spray solution, but reaching as high as 3000 L/ha to achieve complete wetting of the crop under dry conditions. Chlorpyrifos is applied in high volumes by airblast sprayer at 50 g/100 L, equivalent to 750-1000 g/ha under normal conditions. Higher rates (100 g/100 L) are used for apple dimpling bug, with application at the late pink (balloon) stage. Low volume turbomiser type equipment may also be used. A series of fortnightly sprays commencing after petal fall is usually needed for control of LBAM. Spraying may also occur during the dormant period for control of scale.

Application by boom spray at 250 g/ha may be necessary from time to time in NSW to control wingless grasshopper invasions, usually as a single spray per season if needed.

6.1.2.7 Citrus

Citrus fruits are grown commercially in all states except Tasmania. Around 88% of all Australian citrus is grown in the major irrigated horticultural regions of New South Wales, along the River Murray in Southern New South Wales and northern Victoria (Sunraysia and Mid-Murray) and the Riverland region of South Australia. The Central

Burnett region of Queensland, and production in Western Australia accounts for the majority of the balance.

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

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

In the Waikerie area of South Australia, citrus is grown on deep well drained sand, well away from the river and with no creeks draining the orchards. Underground drainage systems channel any subsurface water away from the river, to a collection site. The watertable needs to be low for successful citrus production. It is common practice in the local industry to limit off-site drift by not spraying the last three downwind rows in the orchard. These conditions are said to be representative of growing conditions along the Murray up to Robinvale. Conditions are different in the Murrumbidgee irrigation area of NSW, where flood irrigation is widely practised, but chlorpyrifos does not appear to be widely used in that area.

Chlorpyrifos may be applied once or twice during summer (November to March) to control citrus red scale, at 50 g per 100 L water or half that rate mixed with summer oil. As biological control of this species is disrupted by ants which feed on excreted honeydew and disturb predators, butt sprays are also used for ant control. A higher rate (200 g per 100 L water) is used as a mixture with yeast autolysate to control Queensland fruit fly, but as strips (bait spraying) rather than a full cover spray. A range of pests including citrus rust thrips, citrus mealybugs and fruiteating weevils may also be controlled using chlorpyrifos, applied in spring or summer at 50 g per 100 L water.

Citrus trees can require large spray volumes for effective coverage because of the dense canopy. Air blast equipment is commonly used, at rates upwards of 3000 L/ha. Some growers use oscillating booms which deliver spray volumes in the order of 10000 L/ha.

Chlorpyrifos is an important chemical for the citrus industry, although not used in large volumes. Alternatives include parathion and methidathion, the latter not favoured by growers because of severe disruption to IPM systems.

6.1.2.8 Cereals and pasture

Chlorpyrifos is applied at 70-150 g/ha as a ground spray to pasture immediately before seedling emergence to control red legged earth mite and blue oat mite, with headlands and surrounding vegetation also sprayed if mite activity is severe. Application to pasture and cereals at 70 g/ha may also occur 3-6 weeks after autumn rains when mites

appear in large numbers, with retreatment as necessary. Seedlings are treated at 350-450 g/ha for cutworm control when infestation is observed. Infestations of common armyworm or southern armyworm in cereals are treated at 350-450 g/ha, the higher rate used when larvae reach 3 cm in length. Pasture webworms are treated at 350 g/ha at the first sign of damage, using ground based equipment (boom or mister) or aircraft. Cereal seed dressings are used at relatively low rates for control of certain scarabs, weevils and wireworms. Other registered uses include control of Australian plague locusts (175-280 g/ha) and spur-throated locusts (625-750 g/ha). Note that the Australian Plague Locust Commission does not use chlorpyrifos. Landholders use a range of chemicals when locusts threaten, and chlorpyrifos is likely to be a common choice. It has a diversity of uses and stocks are therefore likely to be held on farm.

6.1.2.9 Vegetables

The main markets in NSW and Queensland for Dow's Lorsban 500EC are for cutworm control, where the product is said to have excellent efficacy. Efficacy is not as good against heliothis and related pests, but such uses are relatively minor. The main application method is ground-based boom spray, with a minor proportion applied by air.

A wide variety of vegetables are treated at 350 g/ha as soon as cutworm damage to seedlings becomes evident.

Brassica crops may be treated at 750-1000 g/ha at 10-14 day intervals to control cabbage moth, cabbage white butterfly, cabbage aphid, cluster caterpillar and cabbage cluster caterpillar. The label for Lorsban 500EC recommends spraying at 10-14 day intervals, using the higher rate when pest pressure is heavy. Cabbage moth (*Plutella xylostella*) is a highly fecund pest with a short life cycle, and a high potential for resistance development. Resistance to most of the existing insecticide groups is already widespread.

6.1.2.10 Rice

Rice is grown over approximately 133,000 ha in the south west area of NSW. The soil type is predominantly transitional red-brown earths and related clay soils, which are characterised by a shallow sandy clay loam or clay loam A horizon, overlying a deep, heavy clay B horizon. Pre-germinated rice is aerially sown into flooded bays with a water depth of approximately 10-15 cm. The sowing period is September-October, with harvesting occurring in April-May. Water levels are maintained at 10-15 cm for the duration of the crop until close to harvest, with constant topping up of the bays. No release of water from the bays occurs except under circumstances such as prolonged heavy rainfall. In such events, overflow is directed to retention ponds for use in topping up bays.

In NSW, chlorpyrifos is aerially applied at 30 or 75 g/ha for control of rice bloodworm, the higher rate being used where water depth exceeds 15 cm or large amounts of decaying plant material are present. Application occurs 5-7 days after

seeding. Late season applications may be needed occasionally to control armyworm, at the general rate for cereals of 350 or 450 g/ha.

In Queensland, a higher rate (750 g/ha) remains listed on labels for control of brown planthopper. This use can presumably be deleted, as the small rice growing industry established near Townsville ceased production in 1993.

6.1.2.11 Grapes

Application at 250 g/ha may be made just after berry set (early October) for control of LBAM and grapevine moth, with subsequent treatments as required. Dormant sprays (25 or 50 g/100 L) to control scale may be made after pruning (July).

6.1.2.12 Stone fruit

Full cover sprays at 25 g/100 L are used to control LBAM in Tas and WA, at fortnightly intervals commencing after petal fall. Strip or patch sprays as a mixture with yeast hydrolysate may be used in NSW and Queensland to control Queensland fruit fly, as an alternative to cover sprays where integrated mite control is practised. Spray application at 100 g/100 L may occur in spring for control of European earwigs, or baits may be laid (5 kg/ha cracked wheat/sorghum containing 20 g/kg chlorpyrifos). Dormant sprays (50 g/100 L) may also be used to control scale.

6.1.2.13 Canola

Redlegged earth mites and blue oat mites in canola and other oilseeds may be controlled pre-emergence in the same way as for cereals and pasture. Treatment at 250 g/ha may occur for wingless grasshopper infestations. Cutworm infestations may be treated at 350-450 g/ha.

6.1.3 Environmental occurrence

Monitoring studies and incident investigations conducted in Australia and overseas help define the extent of off-target contamination by chlorpyrifos.

Chlorpyrifos is very much an occasional contaminant of surface waters, but can reach high levels on occasion. The use pattern of main concern with respect to high level surface water contamination is termite protection, which involves much higher rates of application than agricultural treatments. Several fish kills have been reported in association with this use pattern in Australia, with levels in water reaching several hundred ppb.

Levels of contamination arising from agricultural uses are much lower, generally below 1 µg/L on the rare occasions that chlorpyrifos is detected in Australian surface waters. Extensive monitoring has been conducted in the cotton areas of northern NSW and the irrigation areas in southern NSW. There are a few high outliers, reaching 26 µg/L in northern rivers and 25 µg/L in irrigation drainage adjacent to rice bays in southern NSW, but these appear to be isolated occurrences which are seldom detected because

of the limited aquatic persistence of chlorpyrifos. In some cases, non-agricultural uses such as termite protection of bridge timbers may contribute.

Monitoring programs provide indicative data on levels of pesticide contamination prevailing in waterways, but not a complete picture, particularly for chemicals such as chlorpyrifos that tend not to persist in the water column. For example, monitoring in the cotton areas of NSW involves the taking of weekly surface water samples during the summer cropping season, mainly from the major rivers in the region but also from smaller waterways. Such sampling is able to detect widespread contaminants such as endosulfan. However, localised contamination events immediately adjacent to areas of production will probably not be detected, although they may cause localised damage to biological communities. The occurrence of such events is supported by exploratory studies in February and March 1997 using solvent filled polyethylene bags to obtain continuous samples from Carole Creek, a site with a history of high level agrochemical detections. Continuous sampling did find chlorpyrifos, but the data could not be verified. Routine weekly samples failed to detect chlorpyrifos at this site in the 1995/96 and 1996/97 seasons, although two low level detections occurred at the end of the 1994/95 season. Continuous samplers found chlorpyrifos at two other sites where grab samples remained consistently negative during the 1997-98 spray season. These detections could reflect accumulation from background levels, or from occasional high pulses entering the river. The latter appears more likely given that such pulses are detected in spot samples from time to time.

Similar results are available from monitoring in other jurisdictions. For example, levels in the San Joaquin River have been reported to reach 0.22 µg/L on occasion. The San Joaquin River drains areas of intensive agriculture where chlorpyrifos is used in high volumes (more than 500 tonnes per annum). Diazinon and methidathion, two more hydrophilic organophosphorous insecticides, are found much more frequently, and at much higher levels. Detections above 1 µg/L in North American surface waters are extremely rare, and the majority of detections are below 0.1 µg/L.

Chlorpyrifos also occurs in surface waters at some distance from agricultural uses, such as Lake Tahoe or Chesapeake Bay, but at very low levels (in the low ppt range). In the former case, atmospheric transport is implicated, as chlorpyrifos has also been found in samples of air, vegetation and precipitation. The more toxic metabolite, chlorpyrifos oxon, can be detected in air samples because of greater atmospheric stability, although both parent and metabolite have low atmospheric persistence (a few hours). Chlorpyrifos can also be found in remote locations, with ppq levels recorded in Arctic seawater.

6.1.3.1 Groundwater contamination from US termite treatments

The estimated rate of suspected well contamination from post-construction treatments in the US was 27.3 for every 100 000 dwellings serviced by a well. Appearance and/or odour were common grounds for suspicion, with complaints arising on average some 1-4 days after treatment where these factors were involved. Most of the incidents occurred east of the Mississipi River, with the highest incidence ($150.6/10^5$) in Pennsylvania. Dug wells were 2.6 times more vulnerable than other construction

types, and rodding (subsurface application under pressure) was implicated in nearly 80% of complaints. Wells were located within 10 m of the dwelling in 70% of cases.

Geology, hydrology and/or particular construction practices may explain the regional variations, but a complete explanation is not possible with available data. However, it seems likely that deep placement via rodding techniques would increase the chance of reaching a subsurface conduit, such as a root channel or pipe, that allows rapid access to the well before sorptive interactions with the soil intervene to immobilise the chemical (Thomas and Chambers, 1997).

6.1.3.2 Surface water contamination from US termite treatments

A fish kill incident resulting from use of chlorpyrifos for termite protection at a house construction site is documented in the literature (Carr *et al*, 1997). Application was followed in the evening by some 100-130 mm rainfall. Within 2 days, local residents noticed large numbers of fish (largemouth bass, bluegill sunfish and golden shiners) floating dead near the shore. Closer investigation revealed all crayfish in the pond to be dead and in an advanced state of decay. However, mosquitofish populations remained unaffected. Another pond populated by the same fish species except golden shiners, located some 100 m away but in a different watershed, remained unaffected.

Ethyl acetate extraction followed by analysis by HPLC revealed chlorpyrifos to be present in the livers of exposed fish, but did not detect the metabolite chlorpyrifos oxon. Survival of the mosquitofish was thought to reflect a lower sensitivity of brain acetylcholinesterase to chlorpyrifos oxon, based on in vivo and in vitro observations.

Dow has provided a retrospective analysis of surface water incidents in the US where chlorpyrifos contamination from termiticides was suspected (Thomas and Chambers, 1996).

Most of the incidents investigated were associated with post-construction applications, particularly where rodding was used to apply large volumes of termiticides beneath basements. It appears that such applications carry an increased risk of injection directly into a conduit such as a sump, drain or root channel. This allows the emulsion to flow rapidly to nearby surface water without breaking and sorbing to soil.

The relevance of this to Australia is unclear. A draft Australian Standard (DR 99131) on termite management in and around existing buildings and structures was released for public comment on 1 April 1999. The draft Standard stipulates that building owners should ensure that the ground levels around the building are maintained so as to minimise water entering under the building, with installation and maintenance of sub-surface drains where necessary to assist with drainage around the building. It is noted that installation of sub-surface or agricultural drains on the uphill side of the building will assist in diverting groundwater away from the building. The draft Standard cautions that rubble and agricultural pipe drains can not be effectively treated, and that such treatment may cause hazardous runoff.

The draft Standard offers protection against incidents such as those described by Thomas and Chambers (1996). However, State authorities need to remain aware of the possibility of aquatic contamination from post-construction treatments if emulsion is introduced into sub-surface drainage channels.

Only a few of the incidents reported by Thomas and Chambers (1996) were associated with pre-construction applications. These incidents occurred when rain fell during or shortly after treatment, washing termiticide into surface waters before it had time to dry and sorb to soil. Overland flow, potentially over relatively long distances, was the route of contamination, rather than movement through sub-surface drainage.

Average peak levels recorded in surface water were 349 g/L, and were highly variable with a range of 1 to 11793 g/L . The majority of sites (73%) had initial residues below 100 g/L, and 38% below 10 g/L. Rapid dissipation occurred from the water column, with an average 42 days elapsed before residues became undetectable. The peak concentration (> 10 mg/L) occurred in a drainage ditch leading to a stream that was successfully stocked with trout 3 months later; stream residues had declined to undetectable levels within 44 days.

6.1.3.3 Australian incidents reported by Dow

Dow has advised of a number of environmental incidents associated with the use of chlorpyrifos. Avian incidents are described under section 6.1.1.14. Aquatic incidents are outlined below.

Minor fish kills in canal areas of the Gold Coast were reported following rainfall on three occasions during summer 1995/96 (1 December, 11 and 24 January). Sampling and analysis found chlorpyrifos in the water column at 0.05-1.2 µg/L. The last of these incidents, at Runaway Bay, was investigated in detail. No new house constructions with drainage to the canal were found, and records of under-slab treatments at the nearest construction site did not coincide with the fish kill. Dow concluded that garden spray runoff was the most likely cause, or washing of containers into storm drains. The possibility of contamination from dirty equipment during a storm event was also mooted. In response, Dow convened a pest control seminar in conjunction with Gold Coast City Council, at which correct washing procedures, equipment cleanliness and avoidance of storm events were stressed.

No further incidents in the Gold Coast area were reported to Dow until a fish kill in Koorong Street drain at Southport in February 1997. Water upstream of the weir contained 1.2 µg/L chlorpyrifos. The most likely cause was thought to be an under slab treatment, where the pouring of the concrete slab was delayed for 6 days by rain. Dow responded by communicating the sequence of events to all under slab applicators in the Gold Coast and Brisbane areas.

A kill of aquatic fauna was reported from Kedron Brook and Sandy Creek, near Brisbane airport, in the intervening period. Inspectors from the Department of the Environment followed the contamination up to a storm water drain at Ennogera, where high concentrations were found close to a pest control operator base. No direct

source could be found, and no prosecution occurred, but officers from the Department of the Environment discussed the incident with the pest controllers. The most likely cause was probably inappropriate washing or disposal.

The other aquatic incident reported by Dow occurred in a small creek downstream from a banana plantation at Mullumbimby NSW in March 1996. Sampling by the NSW EPA found chlorpyrifos in the water and at high concentrations (5 mg/kg) in soil adjacent to a banana processing shed. Deficiencies in the chemical storage area were noted, with the unbunded chemical preparation area sloping steeply to the creek. The most likely cause of the incident was a spill in a poorly designed handling area. Monitoring showed that chlorpyrifos dissipated rapidly from the water, and follow up visits 4 and 6 months later found progressive recoveries of stream fauna.

6.1.3.4 Queensland fish kill incidents

The Queensland Department of the Environment provided the following details of chlorpyrifos related contamination and fish kill incidents, noting that incidents in and around Brisbane are often associated with under slab treatments in the vicinity, particularly after rain. This pattern of contamination suggests that label warnings to prevent runoff from treated areas may not be sufficiently prominent or are being disregarded. Alternatively, the formulation may be leaching. Recent sediment surveys in Brisbane waterways, which contain a legacy of organochlorine contamination originating from termite treatments, has found both bifenthrin and chlorpyrifos at a few µg/kg in some samples.

Location and date	Probable source	Chlorpyrifos in water	Chlorpyrifos in fish tissue
Currumundi Park, Sunshine Coast. January 1995	Stormwater drain	None detected	200 µg/kg
Paradise Point, Gold Coast. February 1995	Unknown	Up to 4.1 µg/L	130 µg/kg
Currumundi Park, Sunshine Coast. March 1995	Stormwater drain	Up to 0.5 µg/L	560 µg/kg
Loders Creek, Gold Coast. May 1995	Unknown	0.1 µg/L	n.a.
Norman Creek, Brisbane. September 1995	Construction site	n.a.	Up to 4500 µg/kg
Loders Creek, Gold Coast. September 1995	Unknown	0.5 µg/L	n.a.
Biggera Creek, Gold Coast. November 1995	Stormwater drain	0.5 µg/L	n.a.
Norman Creek, Brisbane. May-June 1996	Stormwater drain	Up to 525 µg/L	n.a.
Kedron Brook, Brisbane. October 1996	Stormwater drain	Up to 190 µg/L	Present but not quantified
Cooparoo Creek, Brisbane. October 1996	Unknown	Up to 70 µg/L	Up to 14200 µg/kg
Coombabah Creek, Gold Coast. December 1996	Stormwater drain and construction	1.2 µg/L	n.a.

Bribie Island, Sunshine Coast. March 1997	Under slab treatment	5 µg/L (15 µg/kg in sediment)	2835 µg/kg
Biggera Creek, Gold Coast. June 1997	Unknown	Up to 4.7 µg/L	n.a.

Similar incidents have not been formally reported from other States, but anecdotal information indicates that they are occurring.

6.1.3.5 Central and North West Regions Water Quality Program

This program involves comprehensive sampling of surface waters in the Macquarie, Namoi, Gwydir and Border Rivers basins for pesticide residues, in order to monitor the impacts of irrigated agriculture, particularly cotton, on water quality. Most of the sampling sites are located on major rivers in the region, with some on smaller waterways such as Carole Creek, an anabranch of the Gwydir River with a history of high level agrochemical detections. Samples are generally collected from the main flow of the river, from a water depth of 25 cm or from mid depth where water is less than 0.5 m deep. Collection occurs throughout the year, but with more intensive weekly sampling during the summer cropping season. The limit of detection for chlorpyrifos under this program is 0.1 µg/L.

Results for the 1997-98 season have just been released (Muschal, 1998). Cotton production exceeded 300000 ha in NSW, a record year. Conditions were warm to hot and fairly dry, with no unusually high pest pressure in the catchments studied. Pesticide sampling occurred on 15 occasions during the spray season (November to March) at 31 sites. Chlorpyrifos was detected at three locations: Moomin Creek, Iffley (0.2 g/L in January 1998), Thalaba Creek, Merrywinebone (0.13 g/L in Octobe r 1997 and 0.3, 0.6 and 0.2 g/L in January 1998) and Pian Creek, Rossmore (0.1 g/L in December 1997 and February 1998). Passive samplers were deployed in the Gwydir River at Brageen Crossing and the Namoi upstream from Gunnedah between mid December and mid February, and analysed on six occasions. Chlorpyrifos was consistently detected at both sites, even though grab samples were negative. The only other chemical to be consistently detected was endosulfan sulfate, but at lower concentrations. Actual exposure levels in the river are unclear as the bags have not been calibrated, and links between variables such as flow, temperature and turbidity remain unresolved. Samplers may have accumulated chlorpyrifos from low background levels, or from occasional higher pulses that were not detected in grab samples. The latter appears more likely, given that such pulses have occasionally been detected in previous seasons. In general, chlorpyrifos levels in the samplers were higher at Brageen Crossing, within irrigated agriculture, than in the Namoi upstream from irrigation areas. However, higher levels occurred at the upstream site in the initial samples from late December.

For the 1996/97 season (Muschal, 1997) chlorpyrifos was detected at one site only from the 28 sampled for pesticides. Two detections (1.2 and 0.4 µg/L) occurred during January 1997 at Coxs Creek in the upper Namoi catchment. The source of contamination remained unidentified, but widespread uses include turf farms, termite control and insect control in a range of vegetable, oilseed and citrus crops in addition

to cotton. Continuous sampling at two sites in Carole Creek (upstream from Moree in the Gwydir River basin) between February and March 1997 with solvent filled polyethylene bags found chlorpyrifos, but the data could not be verified. Profenofos was found in most bags but it is unclear whether this reflects pulse contamination or continuous accumulation from low background levels. Higher pesticide levels were found downstream, indicating local sources for some of the pollution. Cotton production is the major land use in the area. Results indicate that chlorpyrifos is not a widespread contaminant of surface waters in the region, notwithstanding heavy use. As in the urban situations described above, incidents detected are likely to reflect poor practices.

Monitoring results for chlorpyrifos under this program are also available for the previous two seasons. Three detections occurred during the 1995/96 season, one in early April 1996 at 0.18 µg/L at Brageen Crossing on the Gwydir upstream from Moree, another in early June 1996 at 0.83 µg/L further down the catchment on Thalaba Creek, and a high detection (9.1 µg/L) in early April 1996 on the Lower Namoi at Bugilbone (Cooper, 1996).

Detections were more frequent in the 1994/95 season. High detections occurred in the Boomi River at Kanowna, upstream from Mungindi in the Border River basin (6.5 µg/L on 20 March 1995), at Brageen Crossing on the Gwydir upstream from Moree (8.7 µg/L on 8 March 1995) and in the Mehi River at Bronte, downstream from Moree in the Gwydir River basin (26 µg/L on 8 March 1995). Company representatives have suggested during informal discussions that contamination to such levels probably reflects non-agricultural use such as termite treatment of bridges, but confirmatory evidence is lacking. Lower level detections occurred at Thalaba Creek (0.2 µg/L on 7 March 1995), twice in Carole Creek (0.4 µg/L on 20 February and 0.1 µg/L on 8 March 1995) and in the Namoi River (0.1 µg/L on 7 March 1995) at Bugilbone (Cooper, 1995).

6.1.3.6 Irrigation areas of southwestern NSW

Irrigation farms in this area are located in the Murrumbidgee and Murray Valleys, covering an area of 1.3 million ha in 1994. Irrigation supply water is utilised for a variety of farming enterprises including rice, pasture, horticulture and broad acre crops. Drainage water is stored and re-used on a regional scale but enters a natural waterway (Mirrool Creek) and wetland (Barren Box Swamp) downstream from Griffith and Leeton and may reach large rivers such as the Murrumbidgee, Lachlan and Murray during high rainfall. Surveys in the 1994/95 season indicated that chlorpyrifos was applied to a range of crops in this area, as tabulated below.

Crop	Rate (g/ha)	Frequency	Method	Timing
Rice	50	1-2	Aerial	Oct-Nov/Feb-Mar
Winter cereals	70-150	1	Boom	May-June
Irrigated pasture	50-750	1-2	Aerial/boom	Any time
Canola	70-150	1	Boom	May-July
Maize/sorghum	250-750	1	Boom	Nov-Dec
Grapes	25 g/100 L	2	Air blast	Oct-Mar

Stone fruit	1000	1	Air blast/bait	Oct-Dec
Carrots/parsnips	350	1-2	Boom	Aug-May
Onions	350	1	Boom	Apr-Sep
Tomatoes	750-1000	1-3	Boom	Oct-Mar
Potatoes	350	1-3	Boom	Aug-Sep/Feb-Mar

Surface water monitoring in the Murrumbidgee Irrigation Area (MIA) in the 1994/95 season failed to find chlorpyrifos in monthly samples collected across 18 sites. The limit of detection was 0.01 µg/L. A single detection (0.1 µg/L) occurred from 60 samples taken from large drains in the Colleambally Irrigation Area from 1991 to 1993, including the main outfall drain receiving drainage water from all drainage channels. No detections occurred in the 1994/95 season. Chlorpyrifos was not detected in the supply water entering from the Murrumbidgee River. Sampling in the Murray region from 1990 to 1994 also failed to find chlorpyrifos.

A more detailed study was conducted in a small catchment at Willbriggie, 20 km south of Griffith in the MIA from 16 October to 9 December 1993 and 2-13 March 1994. Supply water for this area contains contaminants from upstream irrigation areas, but chlorpyrifos was found in only 2% of samples, with a maximum of 0.05 µg/L. Daily composite samples of drainage water were taken 1.2 and 3.1 km below the start of the common drain for five rice and maize farms. Chlorpyrifos was detected for short periods at the start of the irrigation season, reaching 0.05 µg/L on 20 October, 25 November and 4-7 December, and 0.07 µg/L on 23 November. Bioassays with *Ceriodaphnia* sp found drainage water to be toxic on 15 occasions at the upstream site and 7 downstream. Contaminants other than chlorpyrifos appeared to be mainly responsible. Chlorpyrifos was only detected at the downstream site towards the end of the first sampling period, reaching 0.05 µg/L on 5 December. The acute toxicity (LC50) of chlorpyrifos was determined to be 0.25 µg/L.

Chlorpyrifos dissipation in rice bays was studied from 11 October to 5 November 1991. Initial concentrations measured near the outlet reached about 5 µg/L a few hours of spraying, well short of the theoretical value of 50 µg/L, and declined to about 0.2 µg/L within 2 weeks after application. The dissipation half life was 2.2 days.

Samples from individual exit drains from rice farms at Willbriggie were taken in 1992 and 1993 (October to December). The maximum chlorpyrifos concentration detected was 25 µg/L. Sampling within the nearest rice bay found 38 µg/L chlorpryifos in October 1992, when the concentration in drained floodwater was 7.1 µg/L. No chlorpyrifos was found in samples taken in March 1994.

Daily sampling (9 October to 29 November 1991) of drainage water from a rice and pasture catchment (15 farms) found chlorpyrifos in discrete pulses against a background of non detection, with a maximum of about 9 µg/L on 20 October. The pattern of contamination suggests aerial overspray of drainage channels near rice bays. Further sampling in 1993 found a similar pattern of contamination pulses, but with all concentrations remaining below 1 µg/L. No chlorpyrifos was detected the following March.

Grab samples taken along Mirrool Creek in November 1991 found high concentrations (14 and 17 µg/L) at two of six sampling locations, with no detection (< 0.05 µg/L) at the remaining four sites. Further work in spring 1994 found chlorpyrifos in daily composite samples (100 mL every 30 mins) of drainage water at levels of 0.01 µg/L or more for extended periods, with nearly all samples taken from late October through November showing such contamination. Peak levels were 0.08 µg/L in Little Mirrool Creek and 0.07 µg/L in Mirrool Creek, occurring as pulses against a general background of low level detection. Chronic bioassays (> 48 hours) with native cladocerans (*Ceriodaphnia* sp) found the drainage water to be toxic on six occasions in Little Mirrool Creek and three occasions in Mirrool Creek. The estimated chemical load leaving the catchment was less than 0.5% of the total applied to rice crops (Bowmer *et al*, 1998).

6.1.3.7 Sydney sewage

Chlorpyrifos is a commonly detected contaminant of sewage in the Sydney region. Peak concentrations in excess of 4 µg/L have been recorded. Anecdotal advice that similar contamination occurs in other parts of Australia, such as southern Queensland, has also been received. Dow has noted that many possibilities exist in a large city like Sydney for improper disposal to sewer, and that it is cooperating with Sydney Water in seeking improved management of this issue.

Sydney Water has identified source control, public education and additional treatment as options for responding to the issue, noting that treatment would not assist in resolving any problems in urban runoff. A sewer survey is being conducted to identify any point sources of contamination. However, diffuse sources are suspected as high concentrations of organophosphates (diazinon and chlorpyrifos) can be found in residential catchments, especially on weekends. Public education would be needed to reduce improper disposal (Sydney Water Corporation, 1999).

Similar exposures have been documented in California. Toxicity identification evaluation studies revealed that chlorpyrifos and diazinon were the main contaminants responsible for toxicity of effluents to *Ceriodaphnia dubia*. Urban uses of these insecticides are generally related to lawn and garden care, indoor pest control, and pet care products.

Mean influent chlorpyrifos concentrations to sewage treatment works in the study area during summer 1996 were 190 ng/L. The study area serves a population of about 400000. Sampling of sewage from residential sources found concentrations up to 1200 ng/L, and daily mean concentrations of 550, 110, 80, 110 and 180 ng/L. Effluents from 9 out of 12 commercial sources (companion animal groomers, kennels and pest control businesses) contained chlorpyrifos, with a maximum concentration of 38 µg/L in the effluent from a companion animal grooming establishment. Respective mean daily loads from residential and commercial sources were 24 and 2.3 g. The authors recommend that any source reduction strategy should focus on reducing loads from residential sources, noting that surveys and sampling of residential areas will be

necessary to determine the specific practices that introduce chlorpyrifos into residential sewage (Singhasemanon *et al*, 1998).

6.1.3.8 North American surface water

Dow has reviewed several published monitoring studies from the US and Canada, 11 in flowing streams and 2 in ponds or reservoirs. Chlorpyrifos residues were infrequently encountered at low concentrations. The maximum concentration found was 4.4 µg/L, but detections above 1 µg/L were extremely rare. Triazine herbicides or more hydrophilic organophosphate insecticides (diazinon and methidathion) were much more frequently encountered, and at higher concentrations (Poletika, 1995).

Two of the studies included in the above analysis are described in more detail below.

6.1.3.9 Surface water contamination in the Lake Erie basin

Sampling from 1983 to 1991 through the pesticide runoff season (15 April to 15 August) at 7 riverine monitoring stations in the Lake Erie basin found chlorpyrifos at 5 locations, with a maximum frequency of detection of 1.06%. The maximum detected was 3.8 µg/L, but 95% of all time-weighted detections were below 0.04 µg/L. Chlorpyrifos was found less frequently and at lower levels than other organophosphates such as terbufos and phorate, and was a minor contaminant compared with the herbicides atrazine, alachlor, metolachlor, metribuzin, cyanazine and linuron (Richards and Baker, 1993).

6.1.3.10 Surface water contamination in California

Monitoring of the Sacramento and San Joaquin Rivers downstream from California's Central Valley in January and February 1993 found residue pulses of diazinon and methidathion, insecticides used on dormant stone fruit orchards, following rain events. Diazinon concentrations reached a peak of 393 ng/L in the Sacramento River on 12 February, accompanied by 212 ng/L methidathion. The peak diazinon concentration in the San Joaquin River of 1070 ng/L occurred on 11 February, and was preceded by a peak of 733 ng/L on 8 February. Methidathion reached 586 ng/L between these two events. In contrast to the widespread detection of these relatively hydrophilic insecticides, and notwithstanding heavier use than methidathion, chlorpyrifos was only found in the San Joaquin River, from 9-18 February with a peak of 42 ng/L on 12 February. The incidence of detection was about 2%. No chlorpyrifos detections occurred downstream in the delta/upper bay region (Kuivila and Foe, 1995).

6.1.3.11 Airborne residues along the Mississippi

Air samples were taken from a moving research vessel during the first ten days of June 1994 by pulling air through a polyurethane plug for up to 24 hours. The collection efficiency was 85%, with oxon formation suggested as a possible reason for the slight shortfall in recovery. Chlorpyrifos was found in all samples, peaking at 1.6 ng/m^3 near the town of St Louis. The median concentration was 0.29 ng/m^3.

Samples were analysed for 42 pesticides and 3 transformation products. Among the pesticides, 15 of 25 herbicides and 7 of 17 insecticides were detected. There was no obvious relationship with such parameters as application rate or vapour pressure. Concentrations were most closely correlated to use on cropland within 40 km of the river, or to local uses in urban areas (Majewski *et al*, 1998).

6.1.3.12 Airborne transport in California

Movement of chlorpyrifos vapours has been studied in California's Central Valley where chlorpyrifos finds widespread use on a range of orchard, vineyard and row crops, and prevailing daytime winds carry contaminated air masses into the adjacent Sierra Nevada mountain range. Chlorpyrifos vapours are diluted as they disperse, with further declines in concentration through such processes as deposition to soil, water and vegetation, partitioning to airborne particles, washout by rain, and degradation. Duplicate high volume air and pine needle samples were taken on at least 8 occasions through summer 1994 at three stations, situated at elevations of 114 m, 533 m and 1920 m, in order to measure the rate of this decline. The lowest site was situated on the eastern edge of the valley and was surrounded by large areas of commercial citrus. The second station was located in Sequoia National Park in the southern Sierras some 22 km east of the nearest agriculture, and the highest station at an exposed rocky outcrop some 10 km to the northeast.

Chlorpyrifos and chlorpyrifos oxon were consistently found on vegetation (pine needles) at the site within the valley, each at concentrations ranging up to about 100 µg/kg. Only occasional detections occurred at the two higher sites, with chlorpyrifos reaching about 30 µg/kg and its oxon 60 µg/kg at 533 m, falling to the 5-15 µg/kg range at 1920 m. Residues were more frequently found in air samples, as summarised in the table below. All results are the mean of duplicate readings. Samples were discarded where duplicates differed by more than 100%.

Sample elevation	Mean concentration (range) ng/m^3	
	Chlorpyrifos	Chlorpyrifos oxon
114 m	63 (3.9-180)	27 (2.4-63)
533 m	0.31 (0-0.49)	1.3 (0.25-3.6)
1920 m	0.19 (0-0.13)	0.33 (0.11-0.65)

Dilution factors between the sites were known from previous work using the stable gas SF_6 as tracer. Estimated levels of chlorpyrifos oxon at the two higher elevation sites, based on residues recorded in the valley, were lower than measured, reflecting transformation of thion to oxon in the atmosphere. Estimated levels of chlorpyrifos were higher than measured, reflecting its atmospheric oxidation. Atmospheric lifetimes for chlorpyrifos and its oxon were estimated at approximately 4.2 and 11 hours, respectively, while transit times from the valley to 533 m were known from the SF_6 work to be about 2 hours. This is long enough to allow substantial degradation of chlorpyrifos and significant production of the oxon, consistent with the observation that the ratio of oxon to thion in air samples increases with increasing elevation. The estimated seasonal deposition to the park of chlorpyrifos and its oxon by dry

deposition to foliage through the spring/summer season was about 16 kg, or 0.01% of the seasonal use in the valley of 160 tonnes. The authors of this study suspect that uptake by nearby vegetation reduces the amounts available for transport to more remote locations (Aston and Seiber, 1997).

6.1.3.13 Wet deposition in California

More recent studies in the same region examined wet deposition (rain and snow) at the same sites in the southern Sierras and at Lake Tahoe (2200 m) in the northern Sierras during the winter/spring season when most precipitation occurs. Estimated use of chlorpyrifos in the San Joaquin Valley (the southern portion of the Central Valley) reached some 675 tonnes in 1995, with heaviest use in summer (300 tonnes during August) and lower but substantial use during the sampling period (December to April).

Chlorpyrifos was a pervasive contaminant of rain and snow samples, being present at 1.3-4.4 ng/L at 533 m, 1.1-13 ng/L at 1920 m and 0.3-3.4 ng/L at 2200 m. Chlorpyrifos was also ubiquitous in water samples taken from various depths to 350 m in Lake Tahoe during June. Level detected (0.18-4.2 ng/L) correspond well with those found in snow, but this is likely to be coincidental as residential and commercial development around the lake provides a number of local sources of chlorpyrifos. Contamination levels in the Sierra Nevada were much lower than had been recorded in Central Valley fogwater (900-14200 ng/L) and rain (<1.3-180 ng/L) or in the San Joaquin River (<10-220 ng/L) which is mainly contaminated through runoff (McConnell *et al*, 1998).

6.1.3.14 Atmospheric deposition to Chesapeake Bay

Regional studies of chlorpyrifos movement have also been reported from Chesapeake Bay. Chlorpyrifos is widely used between April and June in catchments to the bay, being applied to corn (0.56-2.24 kg/ha) and alfalfa as well as being used in urban areas for termite control and turf care. Estimated agricultural use in the region during the 1987 season was 45 tonnes.

The main channel for Chesapeake Bay runs for some 200 km north to south with an average width of about 10 km and numerous sounds and tributaries to either side. The bay is shallow with an average water depth of a little over 8 m. Water and air samples were collected during cruises down the main channel in March, April, June and September of 1993. Water samples (50 L) were collected from 2 m below the surface at eight stations along the channel. Chlorpyrifos residues were extracted onto resin, before Soxhlet extraction and analysis by GLC. Breakthrough in two samples was measured at 1.8 and 6.6%, and differences between three duplicate samples were 1.5, 10 and 24%, being larger at lower concentrations. Three daytime high volume air samples were collected during each cruise, with particulates removed using glass fibre filters and vapours with polyurethane plugs. Recoveries from the glass filters were insignificant, and breakthroughs for the first plug generally below 5%. Chlorpyrifos was analysed by GLC after Soxhlet extraction. There was no attempt to analyse for metabolites such as chlorpyrifos oxon, which may have been present in significant concentrations in some air samples based on results from California (see above).

Highest levels in water samples were generally found in the north near the inflow from the Susquehanna River. Decreasing concentrations north to south correlate with increasing salinity in the bay. Peak concentrations of 1.67 ng/L were recorded in March, and 1.60 ng/L in April, the latter occurring halfway down the bay near the inflow from the Potomac River. Results were unexpected as the March samples were intended as pre-season controls, and are difficult to explain except that riverine flows are highest in March and April. June was expected on the basis of use patterns to provide the highest residues, but peak residues during the month were only 0.55 ng/L, suggesting that warmer temperatures favour more rapid dissipation of chlorpyrifos residues. The highest concentration found in September was lower still at 0.25 ng/L.

Results from air monitoring appear contradictory in that highest levels (0.097 ng/m^3) were recorded in June, with only very low levels found in March. It is thought that this reflects increased volatilisation inputs from local uses. Air concentrations are much lower than observed in the Californian study described above. The intensity of use appears higher in California, and high foliar volatilisation rates from citrus, grown across extensive areas in California's Central Valley, may further account for the differing observations.

A basic model focussing on interactions between the atmosphere and surface water concluded that, notwithstanding the low water temperatures, volatilisation from water prevails during March and April, when most inputs of chlorpyrifos are from rivers. The model estimates that some 145 g/day volatilise from the bay, or about 10% per month. In June and September when concentrations in the water are relatively low and there are higher vapour concentrations from use on crops during the warmer weather, the model predicts deposition of about 85 g/day (McConnell *et al*, 1997).

6.1.3.15 Long range transport

Air, ice, fog, seawater and surface microlayer from the Bering and Chukchi Seas, several thousand kilometres from likely usage areas, have been sampled and analysed using protocols developed for the Chesapeake Bay study. No analyses were conducted for chlorpyrifos oxon. Chlorpyrifos was found at trace levels in six of nine water samples collected from 0.5-1 m depth, with maximum concentrations (46-67 pg/L) in northern and western areas receiving ice melt, and no detectable contamination in the central Bering Sea. Two microlayer samples from the eleven analysed contained chlorpyrifos, at higher levels (> 100 pg/L). Both were from near-shore locations. A single integrated sample from an ice flow contained 170 pg/L chlorpyrifos. Fog appeared to be an efficient scavenger of airborne pesticides, with up to 5 ng/L chlorpyrifos found in fog condensate samples but no detections in air samples (Chernyak *et al*, 1996).

6.2 Environmental Chemistry and Fate

Descriptions follow of the testing that has been conducted to define the environmental fate of chlorpyrifos. Information has mainly been provided by registrants in the form of unpublished reports, with a number of published papers also submitted including a

comprehensive review (Racke, 1993). Except where specifically noted, it would appear that tests have been conducted satisfactorily according to accepted international guidelines such as those of the US EPA (Hitch, 1982a, and subsequent revisions) and OECD.

For radiolabelled studies, chlorpyrifos with ^{14}C at the 2 and 6 positions of the pyridine ring was used.

6.2.1 Hydrolysis

Chlorpyrifos hydrolyses in sterile neutral to acidic solution with a half-life in the order of 1-2 months, forming TCP and desethyl chlorpyrifos (DEC) as main metabolites. The variability in reported half-lives reflects the behaviour of chlorpyrifos, which tends to partition from solution by sorption to glass surfaces or by volatilisation from open systems. Hydrolysis proceeds more rapidly at alkaline pH to form TCP. Hydrolysis in solution is catalysed by cupric ions, and microbial influences also intervene in non-sterile systems to accelerate degradation. The toxic metabolite, chlorpyrifos oxon, hydrolyses much more rapidly than chlorpyrifos.

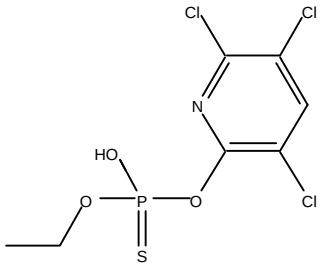
Hydrolysis in sterile soils forms the same metabolites but generally proceeds more slowly than in solution. The exception is air dried soils, where clay catalysed hydrolysis may proceed very rapidly. Half-lives in the range 92-341 days have been recorded in neutral to acid soils, decreasing to 11-200 days in alkaline soils. The faster rates are thought to reflect catalysis by metal ions or soil enzymes. Degradation slows at elevated soil concentrations, apparently because most of the chlorpyrifos remains in the undissolved phase where it is not readily available for hydrolysis.

6.2.1.1 Water

The hydrolysis of radiolabelled chlorpyrifos was studied at a concentration of about 1 µg/L in tap water (pH 7.7) for 112 hours. It is unclear whether solutions were sterile or had light excluded. Radiolabel in solution was determined by scintillation counting, and that ascribable to unchanged chlorpyrifos was determined in the same way after making the solution alkaline and extracting into benzene. The half-life was about 36 hours (Meikle and Youngson, 1971).

Radiolabelled chlorpyrifos was found to be more resistant to hydrolysis when the experiment was repeated in the dark in buffered distilled water at a concentration of about 100 µg/L. Half-lives obtained increased from 23 days at pH 8.1 through 35 days at pH 6.9 to 63 days at pH 4.7. Hydrolysis was accelerated by a factor of 5-10 by chelation in the presence of 0.60-0.85 mg/L cupric ion (Meikle, 1972).

TLC analysis found three products from hydrolysis o radiolabelled chlorpyrifos (0.12 mg/L) in Teflon sealed bottles of phosphate buffer solution, identified as TCP, DEC and didealkyl chlorpyrifos. The presence of the didealkylated metabolite can not be confirmed as radioactivity remained at the origin of the TLC plate Hydrolysis followed pseudo first order kinetics over the pH range studied. Pseudo first order rate constants at pH 8.1 6.9 and 4.7 and 25°C were 0.03, 0.02 and 0.011 per day respectively.



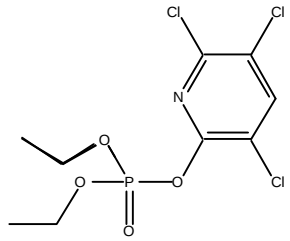
desethyl chlorpyrifos (DEC)

The rate of disappearance from natural canal water (pH 8.0, 173 mg/L total dissolved solids including 0.15 mg/L iron and 0.01 mg/L copper, initial concentration 1.2 µg/L) from California's Central Valley was fifteen times faster at 25°C (rate constant 0.45 per day, half-life 1.5 days) than in buffered solution at the same pH, and in good agreement with earlier studies in pond water where the rate constant at 24°C was 0.49 per day. Separate experiments at 25°C in phosphate buffers found a four to tenfold rate increase (rate constants of 0.277, 0.23 and 0.04 per day) in the presence of 1 mg/L copper (II) ion (Meikle and Youngson, 1977).

More recently, hydrolysis studies have been conducted in sealed tubes using a concentration of 0.6 mg/L in sterilised buffers (pH 5, 7 and 9). Radiolabel was determined at intervals by scintillation counting, and hydrolysis products identified by HPLC. Two products were identified, TCP and DEC. Hydrolysis was found to follow first order kinetics, with half-lives at 25°C of 72-73 days at pH 5 and 7, decreasing to about 16 days at pH 9. TCP was the preferred product at alkaline pH, but both hydrolysis products formed at similar rates at pH 5 and 7. No evidence was found for the didealkylated metabolite, a compound not expected to be stable (McCall, 1986).

A further hydrolysis study with radiolabelled chlorpyrifos at a concentration of 0.5 mg/L in sterile buffered solution with 1% acetonitrile as cosolvent found half-lives at 25°C of 147 days at pH 5, 116 days at pH 7 and 75 days at pH 9, as determined from scintillation counting. Analysis by HPLC revealed TCP as the only product of hydrolysis (Archer and Korsch, 1988).

Half-lives for chlorpyrifos oxon in 50% aqueous methano have been determined as > 85 days at pH 5, 6.3 days at pH 7 and 0.7 days at pH 9. The shorter half-lives are consisten with nucleophilic attack by hydroxide ion at the phosphorous atom, which becomes more electrophilic with the transformation from thion to oxon. Results indicate tha chlorpyrifos oxon is likely to be short lived in the environmen because of rapid hydrolytic degradation (Racke, 1993). This is reflected in monitoring data and field studies where chlorpyrifos oxon is generally not found, except in atmospheric samples, or terrestrial samples contaminated via atmospheric pathways, as described in section 5.1.3.11 above.



chlorpyrifos oxon

6.2.1.2 Soils

Hydrolysis has also been investigated in 37 soils spanning a wide range of types and characteristics. Soils were sterilised with γ-irradiation, fortified to 10 mg/kg with radiolabelled chlorpyrifos, and incubated in the dark at field moisture capacity for up to 4 months. Radiolabel remained readily extractable as chlorpyrifos and TCP using acidified acetone. Scintillation counting of soil extracts found slow degradation in acidic soils (extrapolated half-life 92-341 days, assuming pseudo first order kinetics) and faster but variable degradation in alkaline soils (half-life 11-200 days). The variability is thought to reflect a diversity of mechanisms, including catalysis by metal ions or soil enzymes. Catalysis was also apparent on heterogeneous surfaces, as indicated by a much faster rate of hydrolysis in air dried soils.

Nine soils displaying a wide range of hydrolysis kinetics were also studied under non-sterile conditions to evaluate the relative importance of hydrolytic and microbial degradation pathways. Degradation was more extensive with additional microbial influences, and there was significant release of $^{14}CO_2$ (3.1-34.3%) and formation of unextractable residues (11.4-23.6%) during 45 days of incubation. Unextractable residues were determined by combustion. Microbial degradation predominated in some soils, while rapid abiotic hydrolysis was the main degradation pathway in others.

In general, hydrolysis was slower in soils than in solutions of equivalent pH, reflecting sorptive influences that limit the proportion of chlorpyrifos available for hydrolysis in solution. Rates were comparable with solution hydrolysis in some soils, probably reflecting catalytic influences as noted above. Degradation slowed markedly at higher concentrations (1000 mg/kg), consistent with the low water solubility of chlorpyrifos (Racke *et al*, 1996).

6.2.2 Photolysis

Chlorpyrifos is susceptible to photolytic degradation in aqueous solution, with typical summer half-lives in the order of a month in sunlit surface waters. Photolysis forms TCP which appears generally to be more photolabile than chlorpyrifos, undergoing dechlorination and ring cleavage on further irradiation. Direct and photosensitised reactions are possible, and model studies using acetone found the latter to be faster. However, studies in natural river water found no significant rate increases compared with buffered solution, suggesting that the humic substances generally present in natural surface waters are inefficient photosensitisers for chlorpyrifos. Strong sorptive properties are also likely to reduce the importance of solution photolysis as a breakdown pathway in the environment by removing chlorpyrifos from solution, particularly in the turbid waters characteristic of Australian cropping areas.

Photochemical reactions do not appear to represent a significant mode of degradation for chlorpyrifos on the surface of soils, although the metabolite TCP is photolabile under such conditions.

Photodegradation occurs in the vapour phase, with at least two unidentified reaction products formed in addition to TCP. Chlorpyrifos is photostable in dry air, consistent

with indirect photodegradation through hydroxyl radical attack. Monitoring studies (see section 5.1.3.1) indicate that chlorpyrifos vapours are oxidised to chlorpyrifos oxon as they are transported through the sunlit atmosphere.

6.2.2.1 Water

Early studies found initial half-lives of 29, 25 and 108 days when radiolabelled chlorpyrifos was irradiated using a sunlamp at pH 5, 7 and 9, respectively, in 50% methanolic solution. Similar studies on the pyridinol metabolite produced a variety of products, apparently via dechlorination reactions forming a series of polyhydroxylated pyridine derivatives that oxidised further to coloured products prior to ring cleavage generating smaller fragments. The two compounds were stable as thin films on glass, with less than 2% decomposition during 1200 hours of sunlamp irradiation (Smith, 1968).

Decomposition of radiolabelled chlorpyrifos (300 µg/L) in phosphate buffers exposed in Kimax tubes in a Rayonet reactor followed hydrolytic and photochemical pathways. Scintillation counting was used to determine half-lives for combined hydrolysis-photolysis of about 11, 12 and 8 days, respectively, at pH 5, 6.9 and 8. Corresponding photolytic half-lives were 14, 22 and 13 days. TLC analysis found 30-50% conversion after 13 days irradiation, with traces of DEC and a range of unknown products of greater polarity, the most polar of which was thought to be bicarbonate. TCP was generally not detected, reflecting its photochemical lability. The photochemical half-life as surface deposits on filter paper was about 3 days. Carnuba wax was used to suppress volatilisation. Separate experiments found a volatilisation half-life of about 8 hours from the same substrate under an air flow of 5 m/min (Meikle *et al*, 1982).

Quantum yields determined by actinometry were 0.005 for chlorpyrifos and 0.16 for TCP. These results were used in combination with spectral data to estimate photochemical half-lives in water at 40^{o} latitude in summer and winter. For chlorpyrifos, estimated summer half-lives were 31 days at the surface and 43 days at 1 m depth, and estimated winter half-lives much longer at 1 and 2.7 years. Corresponding estimates for TCP were much faster, with an estimated half-life of 2 hours even in deep water under winter sunlight, reflecting a more efficient quantum yield and much stronger absorbance at 313 nm (Dilling *et al*, 1984).

Sunlamp photolysis of radiolabelled chlorpyrifos (0.35-0.38 mg/L) in sterile phosphate buffers (pH 5) for 743 hours produced two major and several minor degradation products. The hydrolytic pathway was simpler, with one major and one minor product. The estimated hydrolytic half-life was 82 days in dark controls, compared with 52 days under irradiation (Obrist and McCall, 1986). Irradiation of large samples produced at least 7 different photodegradation products that could not be characterised (Obrist and McCall, 1988).

Xenon lamp irradiation for 30 days of a buffered solution (pH 7) of radiolabelled chlorpyrifos (0.7 mg/L) caused exponential decay, with the formation of TCP and a range of unidentified minor products. The half-life of 18.7 days reduced to 5.9 days in

the presence of 1% acetone as photosensitiser, compared with 60-66 days in dark controls (Carpenter, 1989).

Photolysis of radiolabelled chlorpyrifos (0.5-1.0 mg/L) in sterile neutral phosphate buffers used phosphor-coated lamps arrayed in a Rayonet reactor or natural sunlight. Degradation in dark controls formed TCP and DEC with a half-life of 74 days. Neither of these products could be detected in irradiated samples. Rather, up to 29 products formed, none at more than 10% of applied after 21-30 days irradiation. Most of these (~50%) were carboxylic acids derived from dechlorination and fragmentation of the pyridinol ring. A range of chromatographic techniques was used for characterisation. Dichloro analogues of chlorpyrifos were also detected in small amounts. Similar results were obtained in river water (pH 7.6) although the ring fragments were recovered in smaller amounts. Photolytic half-lives were about 30 days in buffer solution, regardless of light source, and about 40 days in sunlit river water at 20.2^{o}C. The hydrolytic half-life in river water with light excluded was 25 days at 25^{o}C, but can not be directly compared with the longer half-life obtained under sunlight because the latter was obtained at lower temperature. Hydrolytic reactions may have been further retarded under sunlight because of the liberation of hydrochloric acid via dechlorination reactions (Batzer *et al*, 1990).

6.2.2.2 Soil

Radiolabelled chlorpyrifos degraded to TCP when added at 33.3 mg/kg as acetonitrile solution to the surface of a thin layer of air-dried silt loam soil and incubated at 24^{o}C, as determined by HPLC and TLC analysis of acetonitrile soil extracts. Degradation half-lives from an initial concentration of 33.3 mg/kg were 28.5 hours in the dark and 30 hours under sunlight. Soil photolysis is unlikely to contribute significantly to the environmental fate of chlorpyrifos (Havens *et al*, 1992).

Exposure of TCP (33 mg/kg) to Californian spring sunlight for 30 days on the surface of a thin layer of silty clay loam soil resulted in rapid degradation to soil bound residues (30%) and carbon dioxide (40%). Analytical recoveries in irradiated samples averaged 97.6%. The first half-life was about 8 hours, followed by a much slower degradation that left 13.6% unchanged TCP at the end of the study, compared with 66.4% in dark controls (Shepler *et al*, 1994).

6.2.2.3 Air

The photochemical stability of chlorpyrifos was investigated in the vapour phase at a concentration of 50 ppb using a sunlamp with intensity equivalent to noon equatorial sunlight. The relative humidity was maintained just below 100%, temperature at 38^{o}C, and the light source was filtered through Pyrex (λ > 300 nm). After 24 hours, approximately 1% each of chlorpyrifos and TCP were recovered, together with about 4% $^{14}CO_2$ and 94% dechlorinated and oxidised products from the pyridinol. At least five such products were detected by TLC, with properties (colour and instability to oxidation) characteristic of polyhydroxylated pyridine derivatives. Chlorpyrifos was photostable when relative humidity was reduced to 5% (Smith and Taylor, 1972).

More recent studies were conducted in sealed 72 L flasks with a borosilicate window through which vapour phase chlorpyrifos was photolysed with a xenon lamp for up to 7 days. Radiolabelled chlorpyrifos was added as hexane solution (0.229 mg/mL) to the flask, which also contained 1 mL water. Reaction progress was monitored by LSC and TLC. The half-life under irradiation was 2.0 days, compared with 10.6 days in the dark. Degradation in the absence of light generated TCP as sole product, while two additional minor products formed under irradiation, one of intermediate polarity and the other more polar than chlorpyrifos or the pyridinol. Attempts to generate larger quantities of these minor products by irradiating a thin film on glass were unsuccessful as chlorpyrifos did not degrade under these presumably anhydrous conditions (Fontaine and Teeter, 1987).

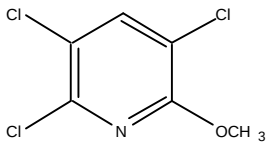
The need for moisture to be present if chlorpyrifos is to undergo vapour phase photodegradation suggests attack by hydroxyl radical as the main degradation pathway. The estimated half-life for reaction of vapour phase chlorpyrifos with photochemically produced hydroxyl radicals is a little over 6 hours (Howard, 1991).

6.2.3 Metabolism

A principal mode of degradation for chlorpyrifos in the environment is metabolism in soils. Chlorpyrifos degrades to TCP in microbially active and sterile soils, but mineralisation only occurs where microbes are active. Based on results from numerous and diverse soils, typical soil half lives for chlorpyrifos at normal agricultural concentrations are in the order of a month, but may range from less than a week to more than 4 months. At elevated concentrations (1000 mg/kg) half lives for chlorpyrifos degradation extend to between 4 and 12 months, and further to more than 4 years in one sandy soil.

The primary metabolite TCP is more resistant to metabolism than chlorpyrifos, with an average half-life at 1 mg/kg of about 2 months but wide variation between soils, from about a week to 9 months. Again, higher concentrations retard metabolism, with a half-life of more than 2 years in one soil spiked at 10 mg/kg.

Degradation of TCP forms trichloromethoxypyridine (TMP) and $^{14}CO_2$. TMP appears persistent in some laboratory soils as it increased in concentration throughout a 300 day study in two soils, but this should not cause problems in the field given the volatility of this metabolite. Degradation of TMP occurs in other soils, forming $^{14}CO_2$ and TCP, and half-lives in the order of 1-2 months have been recorded.



TMP

Chlorpyrifos partitions rapidly from water to sediment following entry to aquatic systems, and also volatilises to the atmosphere, particularly following spray application. Concentrations of chlorpyrifos in the water column decline sharply in the few hours after entry, and then more gradually with dissipation half-lives of a few days generally prevailing in natural surface waters. Dissipation from sediment is slower. Limited data suggest half-lives in the order of a month but possibly extending up to 4 months.

6.2.3.1 Early studies

Radiochromatography of soil extracts obtained during 30 weeks of incubation at 18-35°C indicated rapid hydrolysis of chlorpyrifos (2-5 mg/kg) to TCP followed by a more gradual degradation forming non-extractable residues and small amounts of $^{14}CO_2$. Degradation was slower in steam sterilised soil (Thiegs, 1966).

The mean first half-life of radiolabelled chlorpyrifos following addition to seven soils (see table) at a level of 6.7 mg/kg was 63 days (range 11-141 days). Degradation rates were estimated using a non-linear two compartment model with chlorpyrifos only available for degradation in one compartment. Analytical recoveries were generally 95-100%. The most abundant aerobic metabolite was $^{14}CO_2$ (26.6-88.5% of applied after 360 days at 25°C). TCP was also formed in significant amounts (0.9-32.4% after 360 days) and was accompanied by smaller amounts of TMP. TCP was the main anaerobic metabolite in two soils, where anaerobic half-lives were about 1-2 months (Bidlack, 1979).

Texture	pH	%oc	% sand/silt/clay	Half-life
Loam	7.4	0.68	36/50/14	11 days
Loam	7.1	3.60	42/36/22	22 days
Loamy sand	6.6	0.29	82/10/8	102 days
Silt loam	6.6	1.12	20/52/28	24 days
Silty clay loam	6.1	2.01	10/58/32	34 days
Sandy loam	5.4	1.01	54/34/12	141 days
Clay	5.9	1.15	12/26/62	107 days

6.2.3.2 Concentration effects

Studies were conducted with radiolabelled chlorpyrifos for 12 weeks in urban Iowa soil (loam, pH 7.8, 3% organic carbon) at concentrations of 10, 500 or 1000 mg/kg. Soil moisture tensions were adjusted to 0.3 bar (near field capacity) and an order of magnitude higher or lower, and duplicate studies were conducted at 20 and 27°C. Soil extracts (1% phosphoric acid in acetone) and caustic traps were analysed by scintillation counting, and residual soils by combustion.

Optimum degradation occurred when soil moisture was near field capacity, with drier conditions in particular retarding breakdown. Temperature effects were said to be insignificant, and degradation data are presented as the average from the two temperatures. Concentration was the main rate controlling factor, with marked decreases in the rate of chlorpyrifos degradation and TCP mineralisation apparent after 12 weeks at field capacity at the higher concentrations as indicated in the table. Unextractable residues were also much higher at about 10% in the low dose soil. The authors ascribe these effects to the microbial toxicity of TCP (Cink and Coats, 1993).

Concentration (mg/kg)	10	500	1000
Chlorpyrifos %	3.8	37	58
TCP %	63	59	40
$^{14}CO_2$ %	17	0.7	0.3

6.2.3.3 Overview of chlorpyrifos soil metabolism

Half-lives for chlorpyrifos in a wide variety of soils are reported in a recent review of published and unpublished studies (Racke, 1993). Typical half-lives in 42 soils treated at 0.1-10 mg/kg and maintained at 20-75% field moisture capacity at temperatures between 18 and 35°C are about a month, but there is wide variation. Half-lives of less than a week are reported from some soils, extending to 134 days at 10 mg/kg in a sandy soil from Florida. Calculated rate constants for chlorpyrifos degradation tend to decrease with incubation time.

TCP is the main metabolite identified, accompanied by TMP. Microbes play a key role after the initial breakdown of chlorpyrifos. Both TCP and TMP undergo further degradation in microbially active soils, in contrast to sterile soils where their levels do not decline. Soil moisture levels do not significantly affect rates of chlorpyrifos metabolism, except in air dry soils where degradation is rapid, notwithstanding low microbial activity, because of the catalytic effect of clay surfaces.

Chlorpyrifos is much more persistent at higher concentrations such as used for termite control, with half-lives in four soils at a concentration of 1000 mg/kg ranging between 116 and 335 days, extending to 1575 days in the Florida sand.

6.2.3.4 Degradation of TCP in 15 soils

Metabolism of radiolabelled TCP (1 mg/kg) was studied for up to 300 days at 25°C in 15 soils typical of areas in which chlorpyrifos is used in the US, with total radioactivity determined by combustion and TCP levels quantitated by TLC. Essentially quantitative analytical recoveries were achieved. The major degradation product was $^{14}CO_2$ (14-82%, mean 58%) and the main soil metabolite TMP. The latter metabolite generally remained at less than 15% of applied and was in decline by the end of the study, but increased continuously to as high as 24% in two soils (italicised in table) after 300 days of incubation. TCP degraded according to pseudo first order kinetics with an average half-life of 69 days, but with considerable variation between soils as tabulated below. Only small amounts (usually less than 5% and never more than 10%) of radiolabel remained unextracted from the soil after sequential acid/ether and NaOH extractions (Bidlack, 1977).

Texture	pH	%oc	% sand/silt/clay	$^{14}CO_2$	Half-life
Loam	5.9	0.8	46/32/32	14.3%	279 days
Silty clay loam	5.2	2.2	18/54/28	70.5%	25 days
Clay	6.1	2.9	8/36/56	33.1%	226 days
Loam	6.3	3.1	50/30/20	47.8%	80 days
Clay loam	5.3	2.5	28/44/28	59.4%	9 days
Silty loam	5.5	1.7	16/60/24	46.4%	80 days
Silty loam	6.3	1.0	22/62/16	67.3%	13 days
Silty loam	5.3	0.9	20/62/18	81.6%	9 days
Clay	6.9	1.5	14/22/64	53.3%	81 days
Loam	5.4	1.2	40/42/18	80.6%	8 days
Clay loam	6.6	1.0	28/44/28	55.5%	54 days

Sandy loam	5.9	0.9	70/14/16	78.2%	8 days
Loamy sand	6.0	0.5	82/10/8	71.8%	14 days
Silty loam	6.1	0.8	34/50/16	69.9%	11 days
Sandy loam	6.8	1.4	78/14/8	34.8%	144 days

6.2.3.5 Mineralisation of TCP in 4 soils at 3 different concentrations

Metabolism of radiolabelled TCP was studied at three concentrations (0.005, 0.05 and 1.0 mg/kg, designated L, M and H, respectively, in the table below) in four different soils over a 35 day period, with $^{14}CO_2$ evolution used as a measure of the extent of degradation. The only other significant metabolite, TMP, remained below 15% of applied. Metabolism of the high concentration samples continued through 100 days, during which time around 20% of radiolabel was liberated as $^{14}CO_2$, increasing to around 50% in the clay loam (Bidlack, 1980).

Texture	pH	%oc	% sand/silt/clay	% $^{14}CO_2$ (L, M, H)
Sandy clay loam	6.9	0.6	46/28/26	53.1, 42.8, 9.3
Clay	7.4	3.8	4/32/62	29.6, 15.6, 8.8
Clay loam	7.8	1.0	22/50/28	104.3, 80.2, 23.5
Sandy loam	7.4	1.5	36/52/12	39.3, 32.2, 11.3

6.2.3.6 Metabolism of TCP in soils at elevated concentration

A year long study was conducted in sandy loam (pH 6.5, 0.8% organic matter) spiked with radiolabelled TCP at 10 mg/kg and maintained at 25°C and 75% of field moisture capacity. Extractable radiolabel declined to 73.3%, with a corresponding increase in non-extractable residues to 13.5% and loss of 14.2% to volatilisation (12.7% as $^{14}CO_2$). TCP was still present at 65.2% of applied at the end of the study, and the extrapolated half-life was 752 days (Cranor, 1990).

6.2.3.7 Metabolism of TMP in soils

A recent review (Racke, 1993) reports half-lives of 33 and 72 days in two silt loam soils treated at 1 mg/kg, with $^{14}CO_2$ (57-73%) the main metabolite and some reversion (<10%) to TCP. No further details of the study are specified in the review.

6.2.3.8 Aquatic metabolism

Radiolabelled chlorpyrifos was added as acetone solution to the surface of 6 cm natural surface water overlying 2.5 cm of the corresponding sandy loam (pH 5.7, 2.5% organic carbon) or clay loam (pH 6.3, 3.2% organic carbon) sediment. The estimated initial concentration in the water was 390 µg/L, equivalent to an application of 960 g/ha to 30 cm water. Systems were incubated in the dark at 20°C under gentle air flow for 100 days and sampled periodically, with water and sediment extracted and residual material determined by combustion.

Chlorpyrifos partitioned rapidly from the water column to sediment. Sampling immediately after application found 52% in the sandy loam and 47% in the clay loam. Levels declined with time in both water and sediment. In the sandy loam system, 11%

remained in the sediment after 100 days with 10% in the overlying water, compared with 35 and 12% in sterile units. For the clay loam, recoveries at 100 days were 28 and 8%, compared with 42 and 6% under sterile conditions. Mass balance was good initially but declined after about 2 days, with the shortfall thought to reflect uptake of volatilised material (principally chlorpyrifos) by PVC tubing. Degradation formed TCP and three unknown products, as determined by HPLC, together with small amounts of $^{14}CO_2$. First half-lives were 22 days in the sandy loam system and 51 days for the clay loam (respective DT90s of 72 and 168 days). Corresponding half-lives in the water column were 3 and 6 days, with DT90s of 9 and 21 days (Reeves and Mackie, 1993).

As noted above (section 5.2.1.1) a half-life of 1.5 days has been determined for dissipation of chlorpyrifos from canal water in sealed bottles. Degradation proceeded 15 times faster than in sterile buffers, with copper catalysis apparently playing a significant role.

A half-life of 2.2 days has been determined for dissipation of chlorpyrifos from rice bays (see section 5.1.3.6). The dissipation half-life in a farm pond receiving runoff from a corn plot was a little less than a week (see sections 5.2.5.7 and 5.2.5.8).

Further information on the aquatic dissipation of chlorpyrifos is available from experimental aquatic systems. Half-lives in microcosms were 1-3 days in the initial 24 hours after spray treatment, declining to 4-7 days thereafter (see section 6.1.2.11). Early losses were thought to reflect volatilisation. Studies in littoral enclosure (see section 6.1.2.15) around a Minnesota pond found a similar pattern of rapid initial dissipation after spraying, followed by a more gradual decline from 12 hours after treatment. Volatilisation probably contributes significantly to the early losses. First half-lives of 4-18 hours were determined, with more rapid decline at higher concentrations. Empirically determined sediment half-lives were in the 1-4 month range, and also longer at lower concentrations. The behaviour of chlorpyrifos in experimental ditches (see section 6.1.2.16) was also characterised by a rapid initial decline after spray application through partitioning to sediment and the atmosphere, followed by a more gradual decline with a half-life of 10-18 days, independent of concentration.

6.2.3.9 Biodegradability (closed bottle test)

An aqueous suspension of chlorpyrifos (20 mg/L) was diluted with 10 volumes of nutrient solution and inoculated with one drop of filtered secondary sewage effluent and an aqueous soil extract. Degradation of the test material, as determined by theoretical oxygen demand, reached 8% within 28 days, indicating chlorpyrifos to be poorly degradable under these conditions (Lebertz, 1990).

6.2.4 Mobility

With a mean soil organic carbon sorption coefficient of 8500 from around thirty different soils, chlorpyrifos has a strong tendency to partition from aqueous into organic phases. Sorption is rapid and largely reversible over short timeframes. In contrast to the immobility of the parent, the metabolite TCP is moderately to highly

mobile, with soil organic carbon partition coefficients across 29 different soils ranging from 27 to 389. Mobility of this weakly acidic metabolite tends to increase in alkaline soils. Column leaching studies on four soils confirm that chlorpyrifos is immobile in soils, but significant leaching of TCP from aged samples has been demonstrated in one soil.

Chlorpyrifos is also mobile in the environment by virtue of its volatility. Volatilisation from foliage is particularly pronounced, with around 80% lost within 24-48 hours, compared with up to 25% from soil surfaces. The Henry's law constant is high enough that volatilisation should also occur from water. There is some experimental support for this in that rapid losses have been observed from open or aerated solutions, with unchanged chlorpyrifos recovered from resin plugs in one instance. However, the significance of volatilisation as a dissipation pathway for chlorpyrifos from surface waters remains unclear. Recent modelling studies suggest that mass transfer from the surface microlayer to underlying water is more important than volatilisation.

Spray drift also transports chlorpyrifos into non-target areas. Available data indicate that aerial application generates the highest levels of drift, with buffers of 300 m needed to reduce off-target deposition below 0.5% of the application rate. Nozzle selection is critical. With solid stream nozzles delivering very coarse droplets, aerial applications generate comparable levels of drift to ground based treatments. The other key factor that gives rise to excessive drift is atmospheric stability and associated inversions.

6.2.4.1 Overview of chlorpyrifos soil sorption

Racke (1993) has compiled sorption data for 28 soils, including the four in the study described below, as determined in batch equilibrium studies using soil to water ratios of 1:2 to1:200. Soil organic carbon coefficients vary from 970 to 31000 with a mean of 8500.

6.2.4.2 Adsorption in four soils

Standard batch adsorption studies were conducted on four soils (see table) equilibrated by shaking for 16-20 hours at ambient temperature with 25 volumes of aqueous solution (0.03-1 mg/L) of radiolabelled chlorpyrifos. Range finding studies indicated 16-20 hours to be the optimum shaking time, allowing equilibration but minimising TCP formation. Freundlich exponents (1/n) did not depart significantly from unity, except for a value of 1.41 in the sandy loam where sorption appeared to largely involve mineral surfaces. Similar effects were noted with sorption to glass surfaces, which was more pronounced at higher concentrations, leading the author to suggest that chlorpyrifos in solution has greater affinity for sorbed chlorpyrifos than for glass. Results indicate that chlorpyrifos sorbs strongly to soils (McCall, 1987).

Soil type	pH	Organic carbon (%)	Sand/silt/ clay (%)	Koc
Silt loam	5.9	2.2	16/60/24	3700
Sandy loam	7.5	0.2	64/26/10	31000

Silt loam	7.7	0.7	34/52/14	14000
Clay loam	7.9	5.1	36/32/32	5100

6.2.4.3 Adsorption/desorption in four soils

Soil samples were equilibrated for 48 hours in the dark at 25°C with solutions of radiolabelled chlorpyrifos (0.1, 1.0, 1.5 and 2.0 mg/L), in a ratio of 1:20 for the first two soils and 1:40 for the last two entries in the table below. Radiolabel remaining in solution was determined by LSC, and in the soil by combustion. Degradation during the test was determined by TLC.

Soil type	pH	Organic carbon (%)	Sand/silt/ clay (%)	Koc (ads/des)
Sand	6.5	0.2	93/3/4	15500/20600
Sandy loam	6.5	0.4	54/36/10	6910/8160
Silt loam	7.1	1.2	14/68/18	4690/5990
Clay loam	7.0	1.4	24/48/28	4450/3420

Results indicate chlorpyrifos to be slightly mobile in the second two soils and immobile in the other two, based on the McCall scale (McCall *et al*, 1980). Analytical recoveries remained quantitative but the purity of the test material declined to 87, 86, 76 and 62%, respectively. Sorption appears from the similarity between adsorption and desorption coefficients to be largely reversible over these timeframes (Blasberg and Bowman, 1989).

6.2.4.4 Adsorption/desorption in soils after aging

Radiolabelled chlorpyrifos (10 mg/kg) was aged aerobically for 30 days at 25°C on the same sandy loam as used in the above study. The extrapolated half-life was 107 days, with 79% of the applied dose remaining as unchanged chlorpyrifos (4.4% as unextractable residues) after the aging period, accompanied by 9.4% TCP and about 2% $^{14}CO_2$. Extractable ^{14}C residues were then used for an adsorption/desorption study on the same soil, after sterilisation by autoclaving. The concentrations used were 0.15, 1.0, 1.5 and 2.0 mg/L of ^{14}C-chlorpyrifos equivalents. A soil to water ratio of 1:20 was used, with a 24 hour equilibration period for adsorption and desorption.

Soil organic carbon partition coefficients were 5690 for adsorption and 15100 for desorption, indicative of immobility of aged residues in this soil (Cranor, 1989).

6.2.4.5 Adsorption of TCP in soils

Freundlich soil adsorption coefficients were determined in 25 soils (see table below) equilibrated for 2 hours with 5 volumes of 0.01N $CaCl_2$ solution containing 0.1, 0.5, 1.0 or 10.0 mg/L radiolabelled TCP. Attempts to correlate sorption with the rates of TCP degradation in the same soils were not particularly enlightening, although there

was a significant inverse relationship with pH, consistent with TCP's acidic nature, and a weak positive relationship with organic carbon content. Reliable predictions of TCP persistence were only possible where biodegradation data for similar compounds were available, reflecting the strong influence of specific microbial subpopulations (Racke and Robbins, 1990).

Soil type	pH	Organic carbon (%)	Sand/silt/ clay (%)	Koc
Loam	6.8	3.08	40/38/22	99
Loam	7.5	3.18	34/46/20	62
Loam	7.8	3.20	40/38/22	52
Sandy loam	7.5	1.87	73/18/9	54
Sand	5.4	0.70	90/6/4	389
Loam	4.2	2.35	32/44/24	233
Clay	6.1	1.71	26/30/44	156
Sandy loam	7.3	0.52	58/30/12	71
Loam	7.5	0.45	44/44/12	67
Clay	5.7	1.74	18/38/44	251
Sandy loam	6.1	0.47	79/12/9	245
Sand	7.5	1.92	90/4/6	44
Sandy clay loam	5.7	1.42	56/22/22	256
Loam	8.0	3.06	48/35/17	27
Loam	5.6	2.12	32/43/25	318
Sandy loam	8.3	0.88	60/22/18	40
Silt loam	5.8	2.20	18/66/16	296
Silt loam	5.5	2.00	20/62/18	314
Sandy loam	5.9	0.75	74/12/14	277
Sandy loam	7.6	2.43	64/20/16	55
Sandy loam	6.5	1.10	68/22/10	152
Sandy loam	5.6	0.59	70/14/16	290
Clay loam	7.9	0.89	26/44/30	33
Sandy loam	5.7	5.90	76/15/9	344
Clay loam	8.0	1.20	32/38/30	67

Racke and Robbins (1991) report the average Koc as 168 over 25 different soils and that the sorption is related to pH and organic carbon. The Koc for the neutral and anionic forms is 3344 and 54 respectively.

6.2.4.6 Adsorption/desorption of TCP in soils

Standard batch adsorption studies were conducted on four soils (see table) equilibrated by shaking overnight at 24^{o}C in the dark with 5 volumes of aqueous solution (0.01-10 mg/L) of radiolabelled TCP. Range finding studies indicated that equilibration required 3-7 hours. Freundlich exponents (1/n) were about 0.8, indicating proportionally less sorption at higher concentrations. Sorption coefficients indicate moderate to high mobility of this weakly acidic compound (pKa 4.55). Desorption coefficients were some 30-100% higher (Racke and Lubinski, 1992).

Soil type	pH	Organic carbon (%)	Sand/silt/ clay (%)	Koc
Sand	7.0	0.22	94/2/4	242
Clay loam	7.8	2.52	39/30/31	77
Sandy loam	7.1	0.31	71/12/17	194
Silt loam	6.9	2.08	20/58/22	81

6.2.4.7 Column leaching

Radiolabelled chlorpyrifos was added as acetone solution to the surface of soil columns (17 mm x 25 cm) at a rate equivalent to 0.5 kg/ha and eluted with 50 cm artificial rain at 1 mL/hour. Soils used were the two silt loams used in the sorption study by the same author, and a sandy loam, pH 6.2, 1.1% organic carbon. The most leaching occurred in soil with least organic matter, with 5% of applied found below 5 cm and 1.3% eluted through the column. For the other two soils, less than 1% was found below 5 cm, with 0.3% in leachate. Soil organic carbon distribution coefficients following overnight equilibration with 3.75 volumes of aqueous chlorpyrifos solution (1 mg/L) were about 6000, confirming that chlorpyrifos is immobile in soils (McCall, 1985a).

6.2.4.8 Leaching of aged samples of chlorpyrifos

Chlorpyrifos (1.2 mg/kg) was incubated for 10 days in sandy loam soil (pH 7.5, 1.9% organic carbon) during which it degraded with a half-life of 14.5 days, from 80% unchanged chlorpyrifos at zero time to 43.5% after 10 days, accompanied by 28.1% TCP. A 2 cm layer was placed on top of a 30 cm column of fresh soil and eluted with 50 cm artificial rain. Chlorpyrifos remained in the surface 5 cm of the column, accompanied by 11.1% of the added TCP. The remainder of the added TCP was found at 3-5% in each of the deeper segments and at 6.2% in the leachate (McCall, 1985b).

A more recent study on sandy soil (Speyer 2.1, pH 5.9, 0.6% organic carbon) involved aging for 58 days (the half-life) at a concentration of 0.96 mg/kg before leaching through a 28 x 5 cm column with 393 mL water over 48 hours. The initial mixture contained 67% chlorpyrifos, 9% TCP, 7% unknown metabolites (3 components) and 16% unextractables. Some 5% of radiolabel appeared in the leachate, comprising $^{14}CO_2$, unextractables, and an unknown polar metabolite, in roughly equal proportions. Most of the radiolabel (74%) remained within the surface 5 cm, with less than 4% dispersed through the column (Reeves, 1994a). When the study was conducted with fresh chlorpyrifos, the majority of the radioactivity remained in the surface 6 cm, with less than 1% in each of the deeper segments and 0.7% in the leachate (Reeves, 1994b).

6.2.4.9 Volatilisation from soil

Volatilisation studies were conducted in Erlenmeyer flasks containing 50 g soil (sand, pH 6.4, 0.65% organic matter and silt loam, pH 5.4, 2.5% organic matter) which were foil wrapped to exclude light, equipped with polyurethane plugs and caustic traps to intercept volatiles, and maintained at 75% field moisture capacity and 25^{o}C.

Chlorpyrifos test solutions were added as droplets to the soil surface, with the equivalent of 6.8 kg/ha added to the sand and 1.12 kg/ha to the silt loam. The latter soil was studied as sterile and non-sterile samples. Pre-moistened air was drawn through the flasks at 150 mL/min for 30 days. Soil and polyurethane extracts were analysed by HPLC to determine the fate of chlorpyrifos under these conditions.

Volatilised chlorpyrifos recovered from plugs amounted to 9.3% in the sand, 3.9% in the sterile silt loam and 2.6% in the non-sterile silt loam. These emissions were accompanied by 1.1, 2.0 and 17.3%, respectively, of $^{14}CO_2$. Soil extracts were primarily unchanged chlorpyrifos, with some TCP (<5%) also detected in the sand and sterile silt loam. Based on these results, measurable amounts of chlorpyrifos would be lost to volatilisation in the field, but volatilisation would only provide a minor dissipation pathway as degradative processes are faster (Racke *et al*, 1991).

6.2.4.10 Volatilisation from soil and corn

Volatilisation studies were conducted under a moist airflow of 1 km/hour on three soils (loam, pH 6.7, 0.68% organic carbon; sandy loam, pH 6.2, 2.63% organic carbon; sandy clay loam, pH 6.4, 1.46% organic carbon) maintained at field moisture capacity and 25°C in volatilisation chambers equipped with polyurethane plugs. Radiolabelled chlorpyrifos was added as acetone solution to the soil surface at a rate equivalent to 1.12 kg/ha. Studies were also conducted with corn plants, to which an emulsified aqueous solution of chlorpyrifos was added as 1 µL droplets, maintained at 30°C under an airflow of 0.8 km/hour. Periodic methanol extraction quantified remaining radiolabel, and analysis of foam plugs allowed estimation of the portion that had volatilised.

The most retention occurred on the sandy loam, where residues declined with a half-life of 163 hours, equivalent to losses of 80.4 g/ha/day. Losses from the sandy clay loam and loam were 292 and 264 g/ha/day, respectively, the former equivalent to an estimated half-life of 45 hours. Volatilisation was more pronounced from corn foliage, which lost 80% of applied radiolabel within 48 hours, equivalent to daily losses over the first 3 days of 400, 60 and 20 g/ha, assuming 50% interception and an application rate of 1.12 kg/ha. Residues recovered from the leaf after 4 days were essentially unchanged chlorpyrifos (McCall *et al*, 1985).

6.2.4.11 Volatilisation from soil and beans

Samples of silty sand soil or garden beans (*Phaseolus vulgaris*) were sprayed with chlorpyrifos at 0.96 kg/ha and maintained under an airflow of 1.1 m/second for 24 hours in a wind tunnel. Volatile material collected on polyurethane plugs amounted to 80% of applied from foliage and 24% from soil. Mass balance was confirmed by extraction of the substrate (Day and Rudel, 1992).

6.2.4.12 Volatilisation from water

Volatilisation may be a significant dissipation pathway in aquatic systems, particularly for spray applications which leave high concentrations of chlorpyrifos at the water

surface. This phenomenon has not been specifically demonstrated, but supporting evidence has been compiled by Racke (1993). The Henry's Law constant of 0.7 $Pa.m^3$/mole is high enough that volatilisation from water should occur. Early laboratory half-lives of 8-24 hours in open beakers of distilled water are too short for hydrolysis and thought to reflect volatilisation. Aeration of 10 L of a 50 ppb solution at 80 mL/minute left less than 15% of the applied dose after 24 hours. The most compelling evidence is the recovery of 63% of applied chlorpyrifos from resin traps attached to jars holding aerated seawater solutions.

Rapid volatilisation from surface films left on water following spray application has been invoked for a number of hydrophobic pesticides. A laboratory study that compared dissipation rates from beakers of natural water in the laboratory, with light excluded, found much faster losses following surface spraying than after subsurface injection. Losses followed pseudo first order kinetics for about 3 half-lives, but at very divergent rates. The half-life for disappearance of fenitrothion sprayed at a nominal 275 g/ha was about 0.5 hours, with an average 65% recovery on air filters. Following sub-surface injection, the half-life was 58 days, with 51% recovery on filters. Similarly, the half-life of surface applied deltamethrin was about 2 hours (71% recovery) compared with 5 days following sub-surface injection (limited recovery on filters because losses appear to occur through hydrolysis). The short half-lives following surface application compare well with earlier field-derived values of 0.3 hours for fenitrothion and 0.1 hours for deltamethrin (Maguire, 1991). Similar behaviour would be expected for chlorpyrifos, which is of intermediate volatility compared with fenitrothion and deltamethrin.

However, recent modelling studies have failed to confirm the importance of volatilisation losses from the surface microlayer. A fugacity based model with four bulk compartments (air, water, sediment and the organic rich microlayer) was formulated and applied to five case studies from the UK and Canada of pesticide dissipation in surface microlayers. The model was calibrated by adjusting input parameters through an iterative fitting process, with improvements shown by reductions in the root mean square error. Model results were very sensitive to changes in the film-to-water mass transfer coefficient and film/water partition coefficient. In order to fit model results to the available data, upward scaling of the transfer coefficient was necessary for most chemicals, indicating that transfer to the water column tends to be a rapid process. Mixing due to wave action and currents would be expected to favour such dissolution, but information to quantify this was not available. The partition coefficient between film and water was found to be much lower than for octanol/water, and was considered likely to be quite site-specific. Mass transfer from film to water appeared to be a dominant process for removal of pesticides from the film in all five studies, and more important than volatilisation in three. However, it was acknowledged that field measurements of additional environmental parameters, such as surface film volume and film/water partitioning, would be necessary to provide more accurate mathematical characterisations (Southwood *et al*, 1999).

6.2.4.13 Spray drift

Spray drift studies (Valcore, 1995) were conducted in the hot dry climate of Texas over rank cotton (mean height 68 cm, 59% ground cover) with mowed stubble downwind. The small, moderate density canopy was expected to be less efficient than typical cotton foliage in intercepting fine droplets. An emulsifiable formulation was aerially applied at 188-1472 g/ha in 3 swaths, or as 3 passes over the same swath, as a diluted spray containing 2.1% chlorpyrifos. Application used a boom equipped with solid stream nozzles, producing a VMD of 435 µm with 5.5% below 164 µm, or a flat fan nozzle producing a VMD of 226.5 µm with 24.5% below 164 µm. Release heights were between 2.5 and 5 m, wind speeds between 5.9 and 18.6 km/hour. Atmospheric conditions varied from near neutral to relatively unstable, with temperature 27-34^{o}C and 48-69% humidity. Downwind deposition to 600 m was monitored using horizontal alpha-cellulose squares.

Data are tabulated below. Large droplets (VMD 435.5 µm) were applied in treatments 1, 2, 3, 5 and 8. The remainder used smaller droplets with a VMD of 226.5 µm. Treatments 1 and 7 involved 3 passes over the same swath. Treatments 3, 8 and 9 were made over mowed stubble rather than the cotton canopy. Deposition within the target area ranged from 33 to 109% of applied. At 50 m downwind, deposition reduced to between 1.3 and 8.3%, with further declines to 0.08-0.49% at 300 m and generally nondetectable residues at 600 m. Considerable variability was found, even for treatment replicates with similar meteorology. This variability makes any conclusion hard to draw with the limited number of field replicates. A small reduction in deposition at 300 m downwind is evident on moving to larger droplets.

	Deposition (% of applied) at the following distances (in metres) downwind of application:												
Treatment	**7.6**	**15.2**	**22.8**	**30.4**	**38.0**	**45.6**	**53.2**	**60.8**	**76.0**	**91.2**	**137**	**182**	**304**
1/1	54.6	121	52.7	28.0	18.3	8.3	7.7	5.4	5.0	2.7	3.0	0.90	0.49
1/2	80.6	61.4	30.8	25.0	12.6	8.0	4.7	3.6	3.1	1.5	1.7	0.69	0.42
2/2	60.9	29.6	22.5	10.3	6.7	4.3	3.7	3.5	3.2	1.8	1.6	0.73	0.38
2/3	75.5	17.2	6.4	4.4	5.0	1.3	2.1	1.4	0.63	0.66	0.41	0.28	0.16
3/1	109	17.9	12.7	9.5	5.8	4.6	2.3	2.6	1.6	0.78	0.63	0.24	0.19
3/2	91.8	27.5	12.9	5.8	4.5	4.1	2.1	1.6	0.88	0.50	0.63	0.26	0.12
4/1	59.2	58.4	21.1	9.9	5.7	6.0	4.9	4.1	3.5	0.73	2.2	1.0	0.27
4/2	59.8	19.0	17.6	7.6	4.5	3.9	3.3	5.1	4.3	2.0	2.2	0.79	0.34
5/1	74.6	34.6	15.8	9.4	4.9	3.1	3.9	2.8	3.4	2.1	1.7	1.1	0.29
5/2	47.6	19.6	7.4	4.7	4.5	3.5	2.3	2.3	1.9	0.77	0.41	0.24	0.19
5/3	84.7	18.7	12.5	8.3	6.2	3.0	2.0	2.0	1.9	0.97	1.18	0.35	0.18
7/1	33.2	45.1	23.0	11.4	9.1	7.2	5.0	3.5	3.5	2.7	1.4	0.64	0.38
7/2	67.1	52.7	26.6	15.4	14.2	5.5	3.9	3.0	2.1	1.6	1.8	0.51	0.28
8/1	94.0	32.5	13.6	7.0	4.9	1.6	1.4	1.8	1.1	0.61	0.59	0.35	0.08
8/2	65.3	27.6	15.2	5.6	4.6	3.9	4.9	2.3	2.0	0.68	0.71	0.30	0.11
9/1	87.2	45.5	19.5	9.3	11.3	6.8	5.1	5.1	3.9	1.0	1.6	0.58	0.39
9/2	49.3	58.7	26.4	10.8	8.5	6.5	3.2	4.2	2.3	1.3	1.1	0.68	0.25

Higher rates of drift may be expected from aerial application to Australian cotton because of the use of ULV formulations generating fine spray droplets with a VMD typically in the order of 100-150 µm.

A recent paper on aerial spray drift examined the results of 36 applications under standard conditions (side by side applications) which allowed a statistical approach to the amount of spray drift that occurs (Bird *et al*, 1996). The field was sprayed with four parallel swaths, 13.7 m apart using a fixed-wing aircraft, with unstable air and wind speed from 2-20 kph. This is likely to underestimate the spray drift from typical paddocks due to the limited number of swaths sprayed. The results, tabulated below, show that even under the best conditions, with the best application techniques, considerable spray drift occurs, ie 25% of applications resulted in spray drift of >0.22% of the application rate 300 metres downwind.

Distance down wind, metres	**Cumulative percentage probability**			
	25%	**50%**	**75%**	**95%**
91	0.9%	1.2%	1.8%	3.0%
152	0.33%	0.5%	0.6%	1.0%
305	0.1%	0.15%	0.22%	0.35%

Also included in the paper is a summary of 45 previous studies reported in the scientific literature, with results as average cumulative probability. Most of this previous literature work (60% of studies) reviewed was conducted under stable to very stable atmospheric conditions (inversion layers). This review showed that while the spray drift for the 50 percentile (mean) is only 0.22% of application rate at 305 m from the spray area, the 95 percentile has 1% of the application rate as spray drift. The amount of spray drift is dependent on the atmospheric conditions and the tabulated data should be considered to be for "recommended conditions" only.

The paper concludes that altering nozzle type to change droplet size distribution is the only change to application variables that significantly alters drift from low-flight, fixed-wing applications. ULV applications with their fine droplet size (VMD < 200 µm) have a higher drift potential, by some 5- to 10-fold, than conventional application techniques. Solid stream nozzles delivering coarse droplets (VMD > 500 µm) reduce aerial drift to levels comparable with conventional ground spraying. Other drift control measures such as reduction of boom length, use of additives or reduction in flying speed have relatively minor effects on off-target drift. Where fine sprays are used, increased release heights will give rise to significant increases in off-target deposition. Apart from nozzle type, the main factor influencing off-target drift is meteorology. Atmospheric stability appears to be the most critical factor, with dead calm conditions potentially increasing long range drift (> 800 m) by a factor of 13 relative to unstable atmospheric conditions. Control of droplet size and restrictions to application during low inversions are considered the most effective approach to maintaining off-site drift at low levels.

6.2.5 Field Dissipation

Chlorpyrifos would not be expected to persist in the field based on the laboratory results, and this prediction is supported by results from field trials.

Three separate studies on turfgrass plots indicated a rapid initial degradation with half-lives of about a week, followed after a month by a more gradual decline with half-lives

in the order of a month. Residues remained at the site of application because of good retention by the organic rich thatch layer, with less than 0.1% lost with runoff water.

Studies in citrus orchards found a rapid dissipation of surface soil residues, which declined by at least an order of magnitude in the month after application.

Studies in cotton found that as much as 4.5% can be lost in runoff water when heavy rains occur. Studies were conducted on heavy clay and lighter silt loam soils, with chlorpyrifos applied at 0.56 or 1.12 kg/ha. Most of the chlorpyrifos leaving the field in runoff was in the dissolved phase, suggesting foliar wash off as the main source. Losses were lower after canopy closure, notwithstanding increased foliage, because the larger plants depleted soil moisture under the prevailing dry conditions and allowed greater infiltration before runoff occurred. The main factor determining the magnitude of runoff losses was the time between application and precipitation, during which foliar deposits are lost to volatilisation.

Pond studies indicate that volatilisation also occurs from water, particularly soon after spray contact while the bulk remains near the surface. Volatilisation is the main process for dissipation of chlorpyrifos from water, with a half-life of 3.5 days estimated by modelling. The half-life in sediment was 200 days.

Studies on corn receiving various treatments in consecutive seasons found seasonal losses to an adjacent pond of about 0.2-0.4% of applied. In contrast to the cotton study where a mature crop was treated, most losses occurred in runoff as sorbed residues. Foliar washoff provided minor dissolved contributions as foliar interception was generally low due to small plant size, and delays between application and runoff events allowed volatilisation to occur. Peak concentrations in an adjacent receiving pond approached 10 µg/L in the second year when heavy rains fell, with peak residues approaching 1 mg/kg in sediment. Simulated storms soon after application at the time of planting when soil was bare removed some 2-3% of applied chlorpyrifos from the field in runoff. The half-life of chlorpyrifos in the soil appeared to be about 3 weeks. No residues were detected below 25 cm in the soil, or in tile drainage.

Bare soil studies in Germany found half-lives in the order of 2 months. Similar persistence was recorded after application at 3.4 kg/ha to bare soil in Illinois, Michigan and California, with no residues of chlorpyrifos or metabolites (TCP/TMP) found below 30 cm in the year following treatment. Canadian studies found half-lives of 2 weeks in a sandy soil and 2 months in a muck soil seeded with carrots and radish.

6.2.5.1 Turfgrass runoff study, Kentucky

Chlorpyrifos (emulsifiable concentrate) was applied at 2.24 kg/ha to small turf plots (300 m^2) situated on the Arlington golf course in Kentucky. Four plots of Kentucky bluegrass had slopes of 8-12.6%, and two of Bermudagrass had slopes of 5.8-6%. Soil was a silty clay loam with slow water infiltration, with 4.0-5.8% organic carbon in the surface 15 cm. The insecticide was watered in with 2.5 cm irrigation roughly 90 minutes after application, meaning that soils were close to field capacity and prone to runoff in the ensuing week.

Core samples of grass/thatch/soil were frozen and ground for storage. Extraction used acidified acetone, assisted by sonication, with analysis by HPLC after partitioning into hexane. Post application residues were 11.9-15.9 µg/cm^2 (53-71% of theoretical) with volatilisation possibly accounting for some of the shortfall as applications were made at midday. Residues on four plots at 1 day post application were 11.8-12.8 µg/cm^2 (53-57% of theoretical), declining to 8.8-8.9 µg/cm^2 (39-40% of theoretical) on the remaining two plots at 7 days post application. Residues were mainly (71-79%) in the foliage in the 1 day samples, but dispersed fairly equally between foliage and soil/thatch in the 1 week samples.

Meaningful conclusions regarding runoff potential were only possible from the bluegrass plots as the two Bermudagrass plots appeared to have been hydrologically compromised given that runoff differed greatly between them. Runoff was induced 1 or 7 days after application, with the earlier simulation delivering about 6 cm over 2 hours, and the later about 9 cm over 3 hours (storm frequencies of 1-in-10 and 1-in-50 years, respectively). Runoff was produced in yields of 9.2-15.3% of applied precipitation but contained few suspended solids (3-35 mg/L, or less than 5 kg/ha). Chlorpyrifos concentrations were also low (6.2-13.5 µg/L, equivalent to losses of 0.56-1.56 g/ha, or 0.02-0.07% of applied) with no obvious differences between the two irrigation events. The low runoff potential for chlorpyrifos reflects retention by the organic rich thatch layer. Distribution coefficients (Kd) determined in the laboratory for thatch and underlying soil (160 µg/g chlorpyrifos equilibrated for 17 hours with 20 volumes 0.01 M $CaCl_2$) were 679 and 136-175, respectively, the latter range being consistent with previously published soil distribution coefficients. Chlorpyrifos residues in runoff water are rapidly retained by thatch, with similar sorption coefficients obtained from 1 and 17 hour equilibrations (Racke *et al*, 1994).

6.2.5.2 Turfgrass dissipation study, Indiana

Chlorpyrifos was applied at 4.5 kg/ha to Kentucky bluegrass and fallow plots underlain by clay loam soil. Samples were taken at intervals to 119 days, during which rainfall and supplementary irrigation provided 133% of the long term average rainfall. Degradation was biphasic, with a rapid initial half-life of 9.3 days in turfgrass and fallow soil, declining to 37.4 and 28.4 days, respectively, from 4 weeks after application. Initial mean surface levels were 1.9 mg/kg in turfgrass and 1.66 mg/kg in fallow soil. Peak metabolite levels in turfgrass plots occurred between days 5 and 14 for TCP (0.09 mg/kg) and on day 56 for TMP (0.01 mg/kg). Levels of metabolites were higher in fallow soil, with TCP reaching 1.01 mg/kg on day 5 and TMP 0.06 mg/kg between days 28 and 56. No residues were detected at depths below 30 cm (Racke and Robb, 1993a).

6.2.5.3 Turfgrass dissipation study, Florida

Chlorpyrifos was applied at 4.5 kg/ha to St Augustinegrass (*Stenotaphrum secundatum*) and fallow plots underlain by sandy soil. Samples were taken at intervals to 119 days, during which rainfall and supplementary irrigation provided 132% of the long term average rainfall. Degradation was biphasic, with a rapid initial half-life of

6.5 days in turfgrass and 11.4 days in fallow soil, declining to 23.8 and 38.3 days, respectively, from 4 weeks after application. Initial mean surface levels were 2.46 mg/kg in turfgrass and 1.67 mg/kg in fallow soil. Peak metabolite levels in turfgrass plots occurred between days 7 and 14 for TCP (0.10 mg/kg) but remained low for TMP (maximum 0.01 mg/kg). Levels of metabolites were slightly higher in fallow soil, with TCP reaching 0.14 mg/kg on day 5 and TMP 0.02 mg/kg on day 28. No residues were detected at depths below 15 cm (Racke and Robb, 1993b).

6.2.5.4 Florida citrus

Chlorpyrifos dissipated rapidly following boom spray application between the rows of a citrus grove situated on gently rolling country underlain by sandy soil with low organic matter. A total of three applications were made within 41 days, each at 1.12 kg/ha. Residues in the order of 1-2 mg/kg in the surface 2.5 cm were typical soon after application, with occasional detections above 4 mg/kg, but had declined below the detection limit of 0.1 mg/kg by 32 days after the final application (Oliver *et al*, 1986).

6.2.5.5 Cotton runoff study

Chlorpyrifos (emulsifiable concentrate) was applied at 0.56 or 1.12 kg/ha to small cotton plots (650 m^2) situated in Mississippi. Two plots on heavier soil received a single application at 50% canopy closure, and a further two plots on lighter soil received three applications, the first at 80% canopy closure and repeat sprays to full canopy cotton. The slope on all plots was less than 0.5%. The heavier soil was slightly acidic and predominantly clay, with about 1.5% organic carbon, and the lighter soil was a silt loam with neutral pH and less than 1% organic carbon. Runoff events were induced after application using simulated rainfall, generally with a delay of about 2 hours but increasing to 28 hours for the later treatments. The objective of delivering a 1-in-10 year storm event of about 8 cm within 3 hours was not achieved for the second event at the latter site because the rainfall simulator failed after about 2 hours. Water storage capacity increased and runoff potential decreased through the season as the larger cotton plants depleted soil moisture and relatively little rain fell for replenishment.

The importance of canopy closure in reducing soil erosion is evident from the much lower losses later in the season. Thus the first simulated runoff event when canopy cover was 80% removed about 80 kg from the experimental plot, but this declined to about 13 kg for the final simulation after the canopy had closed. These losses are also due in part to the lower runoff volumes that are generated from drier soil later in the season (35% of applied, compared with 60% for the initial simulation).

Losses of chlorpyrifos were also significantly heavier early in the season, in part reflecting the higher rates of production for surface runoff water and sediment. The main factor responsible for reducing losses was found to be time between application and rainfall. Losses following the first application were 1.1-1.6% of applied from the site with 50% canopy closure, and 4.4-4.5% from the site with 80% canopy closure. Chlorpyrifos in runoff was mostly in solution rather than sorbed to sediment,

supporting its derivation from foliar washoff. Chlorpyrifos losses from the final irrigation for the season, incorporating a 28 hour delay before simulated rainfall, were about 0.2% of applied. Chlorpyrifos dissipates rapidly from foliage, largely through volatilisation, and the delay between treatment and rainfall reduces dislodgeable foliar residues that would otherwise wash off to soil (Poletika and Robb, 1994).

6.2.5.6 Early pond studies

The runoff potential and environmental fate of chlorpyrifos have been evaluated in a typical terrestrial-aquatic watershed in Illinois, containing a 0.3 ha pond with a mean depth of 2 m. Pond samples were taken at weekly intervals from four sites in the pond, two near the surface and two near the bottom, and composited. Chlorpyrifos was applied to corn preplant incorporated at 4.48 kg/ha followed by two broadcast sprays at 1.68 kg/ha each, the first at the 2-4 leaf stage and the second when the corn plants were approaching a metre in height.

Concentrations detected in the pond were low. The highest level of 0.31 µg/L occurred on the day of the first treatment and is said to reflect a drift incident. Concentrations in the order of 0.1 µg/L were detected around 2 weeks after each of the lower rate treatments. Chlorpyrifos dissipated rapidly from the water column with a half-life of about 3 days.

A model was developed to predict the behaviour of chlorpyrifos in the pond. The rate of loss from the water column was related to rate constants for hydrolysis, photolysis, volatilisation and microbial degradation, together with rate constants for sorption to and desorption from sediment. Sediment concentrations were dependent on the degradation rate in the sediment and on the rates of sorption and desorption.

Degradation in sediment was a slow process, with a half-life of about 200 days. Microbial degradation in the water column was assumed on this basis to be negligible. The model assumed 60 day hydrolytic and 30 day photolytic half-lives, and fairly rapid sorption to sediment (half-life 3.5 days). Based on these assumptions, the estimated half-life for volatilisation is 3.5 days. The main factors influencing dissipation of chlorpyrifos from the water column are volatilisation, which is particularly important while the bulk of applied chlorpyrifos remains near the surface, and sorption to bottom sediment (McCall *et al*, 1984).

6.2.5.7 Corn runoff study - year one

Chlorpyrifos (granular formulation) was applied 3 times at monthly intervals to a 7 ha corn plot (silt loam, pH 5.7, 1.8% organic carbon in surface layers, 2.6-5.1% slope) draining through 3 monitoring stations to a pond of approximately 0.24 ha containing 4740 m^3 of water at commencement of the study. The first was a T-band incorporated at planting, the second a surface band over the developing corn whorls, and the third an aerial broadcast application near canopy closure, at respective rates of 1.46, 1.52 and 1.05 kg/ha. Corn was planted along the contour, from immediately up-slope of the pond's runoff collection walls. Prior to planting, vegetation around the pond was mowed. A single drain tile entering the pond was monitored as another potential

source of chlorpyrifos to the pond, as was drift from the final application. Evaporation and seepage losses were estimated. Exports from the pond were monitored at its single outlet, and concentrations within the pond were measured in water and sediment samples in an attempt to complete water and chemical balances. Dissipation from soil and foliage were also investigated.

Little rain fell until 3 weeks after the second treatment, but conditions then became very wet with runoff occurring on 6 of the next 23 days. Significant volumes of surface runoff were produced, amounting to nearly 20% of total rainfall and culminating in pond overflow through an emergency spillway, confounding any further measurement of water balance.

More water entered the pond than could be accounted for by rainfall and runoff, with subsurface flow (including tile drains) thought to have delivered the balance. Monitoring of tile drain flow found no chlorpyrifos, apart from a single detection below the limit of quantitation, and the low mobility in soil was further illustrated by the absence of residues at depths below 25 cm.

Most of the chlorpyrifos transported from the plot in runoff was sorbed to suspended sediment, reflecting losses of foliar residues to volatilisation rather than wash off under the dry conditions, and relatively low foliar interception by the small corn plants. Monitoring at the flumes over a 12 day period commencing just before the final treatment indicated a total of 20.4 g chlorpyrifos was transported in the sediment phase and 9.34 g as dissolved residues (total 29.7 g or 0.106% of the total seasonal application to the plot). Sampling in the pond over the same period indicated slightly higher amounts, 33.6 g and 11.46 g, respectively, for a total 45.1 g (0.161% of the seasonal application). Drift to the pond from the third application, as monitored using acetone-filled pans, delivered 0.29 g chlorpyrifos. The study abstract and summary indicate that total chlorpyrifos transport in the 73 days from planting was 71.1 g (0.25% of the seasonal application) as quantified by flumes and pond monitoring. The report concludes that a total of 68.6 g chlorpyrifos was quantified as leaving the site in edge of field runoff in the 68 days following planting.

The half-life of chlorpyrifos in soil was estimated as 21 days. This would be an overestimate given additional inputs to soil over the study period. A dissipation half-life of 6.7 days was estimated in the pond over the 10 day period preceding the final treatment.

Peak concentrations in the pond were a little over 2 µg/L, and the maximum mean concentration across a 96 hour period was also marginally above 2 µg/L. In sediment, the highest mean concentration found was 397 µg/kg.

Runoff from small plots (0.06 ha) was also investigated using simulated rainfall (1-in-5 year storm) on the day following application of granular or emulsifiable concentrate formulations. Runoff losses were 2.93% of applied when the granular formulation was incorporated as a T-band at planting, and 2.02% when the emulsifiable formulation was applied to bare soil and incorporated. At least 95% of transported residues were sorbed to sediment. Application 6 weeks after planting, as broadcast or band

treatments respectively, generated lower runoff losses of 0.69 and 0.47% (Cryer and Robb, 1995).

6.2.5.8 Corn runoff study - year two

The second year of the study at the same site involved two applications at 2.37 and 1.13 kg/ha, the first a T-band at planting (granular formulation) and the second a broadcast treatment (emulsifiable formulation) 6 weeks later. Heavy rains began one day before the second treatment, delivering 18.7 cm over a 1 week period. Some 22.5% of precipitation during this rainy week and the preceding 10 days was lost to surface runoff.

Monitoring at the flumes found a total of 93.4 g chlorpyrifos (0.38% of total seasonal application to the plot) to be transported off-site in runoff over the 17 day period during which runoff was monitored, mostly in the sediment phase (88.9-99.5%). In contrast to the first year of the study, runoff losses are consistently reported in the study abstract, report proper (including conclusions) and attached tables. Pond residue data again provided a slightly higher estimate of chlorpyrifos loading (65.8 g in sediment and 52.4 g in the water column, total 118 g) but span a longer interval (Julian days 154-182, compared with 169-185 for flume monitoring). Drift to the pond as determined by blotter cards was practically non-existent. The maximum amount transported in a single event, based on flume monitoring, was 37 g.

Peak concentrations in the pond reached 9.86 µg/L, with the mean over 96 hours remaining high at 8.74 µg/L. An aquatic dissipation half-life of 5.1 days was determined for the ensuing 17 day period, during which two runoff events delivered more chlorpyrifos to the pond. Sediment concentrations reached 0.97 mg/kg. The authors state that these data may be interpreted as actual environmental concentrations for chlorpyrifos in a farm pond adjacent to a commercial watershed. Five dead catfish (mean weight 0.96 kg) were recovered from the pond during this period and found to contain an average 16.7 mg/kg chlorpyrifos on a whole fish basis. A bioconcentration factor of 1700 can be estimated. The fish did not appear to be exposed to lethal concentrations of chlorpyrifos, based on the LC50 of 280 µg/L for channel catfish, but additional stressors such as increased turbidity and decreased dissolved oxygen may have contributed to their demise.

Two nested small plots (0.06 ha each) within the upper reaches of the main watershed were also studied under the same regime of natural rainfall. Runoff losses of 3.25 and 1.82 g chlorpyrifos were recorded for three runoff events between Julian days 169 and 185, with mean sediment fractions of 66 and 75%, respectively. Losses equate to 1.43 and 0.80% of seasonal application, respectively. The bulk of the residues were transported in the first event at one plot, but in the second at the other, notwithstanding that the two plots appeared to be similarly situated across the contour. The authors argue that small plots can not be directly scaled to the watershed as this would greatly overestimate transport, particularly of dissolved residues but also of sorbed residues. Scaling from small plots to the field scale would require a model that specifically and accurately addresses the underlying mechanisms responsible for soil erosion over different spatial scales (Cryer and Dixon-White, 1995).

6.2.5.9 Persistence in sand and muck soils

Chlorpyrifos (EC formulation) was applied at 3.4 kg/ha (in 455 L water) in late spring to small field plots in Ontario where the surface 20 cm had been replaced by pesticide free sand (0.52% organic matter) and muck (64.6% organic matter) soils. The insecticide was immediately raked in, and duplicate control and treatment plots were seeded with radish and carrots. Plots were spaded and replanted after 1 year of the 2 year study.

Soils were extracted with acetone. The extract was diluted with benzene and treated with aqueous sodium carbonate, leaving chlorpyrifos in the organic layer. After acidification, TCP was extracted from the aqueous layer with benzene. Analysis used GLC, with results for TCP corrected for 60% recovery.

Chlorpyrifos declined by 50% over the first 2 weeks in the sandy soil, and further to 5% of applied by 24 weeks after application. Immediate post-treatment TCP levels were 2% of applied chlorpyrifos, increasing to 13% during the first week before declining to 1% by 24 weeks. Chlorpyrifos remained at 4% of applied after a year, accompanied by small amounts (< 1%) of TCP, and was still present at 2% of applied after 2 years, by which time TCP could no longer be detected.

The first half-life in muck soil was longer at 8 weeks, and 13% remained unchanged after 24 weeks. Residues of TCP peaked at 39% 8 weeks after treatment. Chlorpyrifos and TCP accounted for 9 and 3%, respectively, after 1 year, declining to 3 and 0% after 2 years. Crop residues were found in the first year only, at low levels but higher in the sandy soil (Chapman and Harris, 1980).

6.2.5.10 US leaching studies

Chlorpyrifos was applied at 3.4 kg/ha in late spring to gently sloping (0-2%) plots in Illinois, Michigan and California and incorporated into the soil by cultivation. Soils were silt loam, sandy loam and loam, respectively, with organic matter contents at the surface of 3.1, 1-1.6 and 1%. Samples were taken at intervals to 365 days and analysed by GLC for total radiolabel after acetone extraction. Caustic extraction allowed determination of TCP by subtraction.

Chlorpyrifos residues dissipated according to pseudo first order kinetics with respective half-lives of 56, 33 and 46 days. Cumulative rainfall at the three sites over the duration of the study reached 95, 83 and 50 cm, respectively. No residues of chlorpyrifos or metabolites (TCP and TMP) were found below 30 cm (Fontaine *et al*, 1987).

6.2.5.11 German bare soil dissipation studies - year one

Chlorpyrifos was applied at 0.72 kg/ha to bare soil plots of sandy loam (pH 6.2) and sandy silt loam (pH 5.3), with samples taken at intervals to 210 days. Results obtained

indicate pseudo first order kinetics and respective half-lives of 55 and 68 days (Khoshab *et al*, 1993).

6.2.5.12 German bare soil dissipation studies - year two

Chlorpyrifos was applied at 0.72 kg/ha to bare soil plots of loamy silt (pH 5.7) and loamy silt (pH 6.0-6.2), with samples taken at intervals to about a year. Results obtained indicate pseudo first order kinetics and respective half-lives of 51 and 40 days (Khoshab, 1994).

6.2.6 Bioaccumulation

Chlorpyrifos bioconcentrates to moderate to high levels in fish and other aquatic life. A bioconcentration factor of about 1400 has been recorded in rainbow trout, and 745 in oysters. Steady state is soon achieved, and residues depurate rapidly in clean water, with typical half-lives of about 2 days. Bioconcentration of TCP in mosquito fish is insignificant.

6.2.6.1 European eels

River mud (100 kg) contaminated by chlorpyrifos (60 µg/kg) was equilibrated with 1000 L dechlorinated water in a polypropylene lined tank for 21 days at 14°C.
Chlorpyrifos desorbed to the water column, producing an equilibrium concentration of 3 µg/L within 24 hours. Eels (*Anguilla anguilla*) collected from the wild and held for a week were then added to the tank. Around 40 eels, mean weight 63 g, were used. Fish were sampled at intervals during a 28 day exposure phase for determination of chlorpyrifos uptake after removal of the head and alimentary tract, and further during a 14 day depuration phase in clean water. Residues in fish tissue increased to 0.5-1 mg/kg within 2 weeks, with a concomitant decline in concentrations measured in the water column, to a mean of 1.8 µg/L. Wide variations between specimens after about a week of exposure were thought to reflect behavioural characteristics such as burial in the mud. Residues reduced to about 0.1 ppm during the depuration phase. A tentative bioconcentration factor of about 400 was determined (Douglas and Pell, 1985a).

6.2.6.2 Rainbow trout

Rainbow trout (mean weight 0.6-0.7 g) were exposed for 30 days under flow-through conditions to an average 0.3 µg/L radiolabelled chlorpyrifos, followed by a 16 day clearance period. Levels of chlorpyrifos in fish increased for about 10 days before equilibrium was reached. The bioconcentration factor in whole fish was 1374, and the half-life for depuration during the clearance phase was between 2 and 3 days. The main component of the radioactivity absorbed by the fish was unchanged chlorpyrifos, accompanied by TCP and two polar metabolites, shown by enzyme treatment to be β-glucuronide conjugates of TCP (Murphy and Lutenske, 1986).

6.2.6.3 Catfish

Levels of chlorpyrifos in catfish administered chlorpyrifos at 500 µg/kg in the feed reached steady state in 7-12 days, with a biomagnification factor of 0.045. Residues were eliminated from whole fish with a half-life of 3.5 days when clean feed was restored (Woodburn *et al*, 1995).

The half-life for oral absorption following intravascular administration as a bolus injection via cannula to the dorsal aorta was about 4 hours, and the terminal elimination half-life 4.6 days. A two compartment pharmacokinetic model (metabolism and storage) was developed and used to predict that catfish consuming 0.2-0.5 mg/kg chlorpyrifos in the diet would accumulate body residues equal to about 60% of the residue level in the food. Residues were almost entirely unchanged chlorpyrifos, indicating rapid excretion of metabolites. The major metabolite excreted in urine and bile was the glucuronic acid conjugate of TCP, with urine the primary route of excretion (18.5% in 32 hours). Unconjugated TCP was the primary metabolite in blood (Barron and Wilga, 1990).

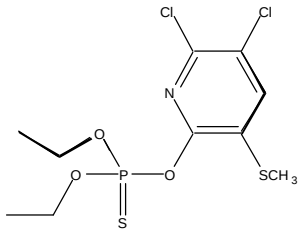
Similar patterns were seen following waterborne exposure for 24 hours to an initial concentration of about 12 µg/L radiolabelled chlorpyrifos, which declined to below 0.5 µg/L by the end of the exposure period. Intravascular administration via the caudal vein allowed evaluation of the excretion of parent chlorpyrifos. Chlorpyrifos was rapidly absorbed into blood, with peak levels after 1-2 hours, and distributed more slowly to peripheral tissues. Residues in whole fish were predominantly chlorpyrifos (> 92%) and were concentrated in excretory tissues and especially in fat. The major biliary and urinary metabolite was TCP glucuronide (Barron *et al*, 1990, 1993).

A bioconcentration factor of 1700 has been estimated for catfish exposed during a field study (see section 5.2.5.8).

6.2.6.4 Eastern oysters

Eastern oysters (*Crassostrea virginica*) rapidly accumulated chlorpyrifos when exposed for 28 days under continuous flow conditions to an average concentration of 0.7 µg/L. The estimated average steady-state bioconcentration factor was 745 in whole oysters. Observed bioconcentration factors were much higher in the oyster tissue fraction (1650) than in the shell liquor fraction (30-54). Depuration proceeded rapidly in clean water, with half-lives of 1.6 days in whole oysters and 2.2 days in oyster tissue (Thacker *et al*, 1992).

A second study was conducted under the same conditions of exposure to investigate the metabolism of radiolabelled chlorpyrifos in eastern oysters. A single metabolite dominated the residue profile, as tabulated below. The metabolite was identified as a methylthio derivative of chlorpyrifos (see structure) by GC/MS and comparison with an authentic sample.



	Concentration µg/kg (percentage)			
Day	**Metabolite**	**Chlorpyrifos**	**Unidentified**	**Total**

14	189 (59%)	114 (36%)	15 (5%)	318
21	160 (52%)	139 (46%)	6 (2%)	305
28	130 (54%)	99 (41%)	13 (5%)	242
28 + 1	137 (72%)	36 (19%)	16 (9%)	190
28 + 3	111 (81%)	18 (13%)	7 (5%)	136

Bioconcentration factors of chlorpyrifos and total radiolabel were 180 and 430, respectively, in whole oysters. Residues levels in oysters reached 90% of steady state within 2 days. Half-lives for depuration were 1 day for chlorpyrifos and 2 days for its methylthio metabolite. Total residues had declined to 37 µg/kg after 7 days of depuration (Hansen *et al*, 1992).

6.2.6.5 TCP in mosquito fish

Mosquito fish (*Gambusia* sp) were exposed for 6 days under flow-through conditions to 1.1 µg/L radiolabelled TCP. Equilibration required 3 days, by which time residues in the fish were about 3.4 µg/kg. A polar metabolite was detected in the fish after 12 hours of exposure, and in the water after 24 hours. This metabolite accounted for some 30-40% of radiolabel in the fish during the exposure phase. Residues depurated rapidly in clean water, with none remaining in the fish after 3 days (Hedlund, 1972).

6.3 Summary of Environmental Exposure

6.3.1 Release

Chlorpyrifos is widely used in Australia, with current annual consumption of about 1000 tonnes. It is sold as emulsifiable concentrate (used in agriculture, for turf maintenance and termite protection), wettable powder (favoured for orchard use to avoid phytotoxicity problems with solvents in emulsifiable concentrate formulations), ultra low volume (mainly for cotton), microencapsulate (termite protection and general urban pest control), seed dressing, granule (home garden use against pests such as ants and beetles), prepared bait (for control of cockroaches in the home; note that user prepared baits are also used to control certain surface feeding soil insects in agriculture) and sustained release (for multi season grub control in sugarcane) formulations. There are also some animal health products (collars, shampoos, sprays) for use on companion animals.

6.3.2 Occurrence

Chlorpyrifos is very much an occasional contaminant of surface waters, but can reach high levels on occasion. The use pattern of main concern with respect to high level surface water contamination is termite protection, which involves much higher rates of application than agricultural treatments. Several fish kills have been reported in association with this use pattern in Australia, with levels in water reaching several hundred ppb.

Levels of contamination arising from agricultural uses are much lower, generally below 1 µg/L on the rare occasions that chlorpyrifos is detected in Australian surface waters.

Extensive monitoring has been conducted in the cotton areas of northern NSW and the irrigation areas in southern NSW. There are a few high outliers, reaching 26 µg/L in northern rivers and 25 µg/L in irrigation drainage adjacent to rice bays in southern NSW, but these appear to be isolated occurrences which are seldom detected because of the limited aquatic persistence of chlorpyrifos. In some cases, non-agricultural uses such as termite protection of bridges may contribute.

Monitoring programs provide indicative data on levels of pesticide contamination prevailing in waterways, but not a complete picture, particularly for chemicals such as chlorpyrifos that tend not to persist in the water column. For example, monitoring in the cotton areas of NSW involves the taking of weekly surface water samples during the summer cropping season, mainly from the major rivers in the region but also from smaller waterways. Such sampling is able to detect widespread contaminants such as endosulfan. However, localised contamination events immediately adjacent to areas of production will probably not be detected, although they may cause localised damage to biological communities. The occurrence of such events is supported by exploratory studies in February and March 1997 using solvent filled polyethylene bags to obtain continuous samples from Carole Creek, a site with a history of high level agrochemical detections. Continuous sampling did find chlorpyrifos, but the data could not be verified. Routine weekly samples failed to detect chlorpyrifos at this site in the 1995/96 and 1996/97 seasons, although two low level detections occurred at the end of the 1994/95 season. Continuous samplers found chlorpyrifos at two other sites where grab samples remained consistently negative during the 1997-98 spray season.

Similar results are available from monitoring in other jurisdictions. For example, levels in the San Joaquin River have been reported to reach 0.22 µg/L on occasion. The San Joaquin River drains areas of intensive agriculture where chlorpyrifos is used in high volumes (more than 500 tonnes per annum). Diazinon and methidathion, two more hydrophilic organophosphorous insecticides, are found much more frequently, and at much higher levels. Detections above 1 µg/L in North American surface waters are extremely rare, and the majority of detections are below 0.1 µg/L.

Chlorpyrifos also occurs in surface waters at some distance from agricultural uses, such as Lake Tahoe or Chesapeake Bay, but at very low levels (in the low ppt range). In the former case, atmospheric transport is implicated, as chlorpyrifos has also been found in samples of air, vegetation and precipitation. The more toxic metabolite, chlorpyrifos oxon, can be detected in air samples because of greater atmospheric stability, although both parent and metabolite have low atmospheric persistence (a few hours). Chlorpyrifos can also be found in remote locations, with ppq levels recorded in Arctic seawater.

6.3.3 Chemistry and fate

Chlorpyrifos partitions to soil or disperses to the atmosphere following application. Limited quantities may enter aquatic environments with runoff, and will mainly partition to sediment where slow to moderate degradation occurs. Atmospheric persistence appears limited, while residues in soil are degraded at a moderate rate by the following processes.

6.3.3.1 Hydrolysis

Chlorpyrifos hydrolyses in sterile neutral to acidic solution with a half-life in the order of 1-2 months, forming TCP and desethyl chlorpyrifos (DEC) as main metabolites. The variability in reported half-lives reflects the behaviour of chlorpyrifos, which tends to partition from solution by sorption to glass surfaces or by volatilisation from open systems. Hydrolysis proceeds more rapidly at alkaline pH to form TCP. Hydrolysis in solution is catalysed by cupric ions, and microbial influences also intervene in non-sterile systems to accelerate degradation. The toxic metabolite, chlorpyrifos oxon, hydrolyses much more rapidly than chlorpyrifos.

Hydrolysis in sterile soils forms the same metabolites but generally proceeds more slowly than in solution. The exception is air dried soils, where clay catalysed hydrolysis may proceed very rapidly. Half-lives in the range 92-341 days have been recorded in neutral to acid soils, decreasing to 11-200 days in alkaline soils. The faster rates are thought to reflect catalysis by metal ions or soil enzymes. Degradation slows at elevated soil concentrations, apparently because most of the chlorpyrifos remains in the undissolved phase where it is not readily available for hydrolysis.

6.3.3.2 Photolysis

Chlorpyrifos is susceptible to photolytic degradation in aqueous solution, with typical summer half-lives in the order of a month in sunlit surface waters. Photolysis forms TCP which appears generally to be more photolabile than chlorpyrifos, undergoing dechlorination and ring cleavage on further irradiation. Direct and photosensitised reactions are possible, and model studies using acetone found the latter to be faster. However, studies in natural river water found no significant rate increases compared with buffered solution, suggesting that the humic substances generally present in natural surface waters are inefficient photosensitisers for chlorpyrifos. Strong sorptive properties are also likely to reduce the importance of solution photolysis as a breakdown pathway in the environment by removing chlorpyrifos from solution, particularly in the turbid waters characteristic of Australian cropping areas.

Photochemical reactions do not appear to represent a significant mode of degradation for chlorpyrifos on the surface of soils, although the metabolite TCP is photolabile under such conditions.

Photodegradation occurs in the vapour phase, with at least two unidentified reaction products formed in addition to TCP. Chlorpyrifos is photostable in dry air, consistent with indirect photodegradation through hydroxyl radical attack. Monitoring studies indicate that chlorpyrifos vapours are oxidised to chlorpyrifos oxon as they are transported through the sunlit atmosphere.

6.3.3.3 Metabolism

A principal mode of degradation for chlorpyrifos in the environment is metabolism in soils. Chlorpyrifos degrades to TCP in microbially active and sterile soils, but mineralisation only occurs where microbes are active. Based on results from numerous and diverse soils, typical soil half lives for chlorpyrifos at normal agricultural concentrations are in the order of a month, but may range from less than a week to more than 4 months. At elevated concentrations (1000 mg/kg) half lives for chlorpyrifos degradation extend to between 4 and 12 months, and further to more than 4 years in one sandy soil.

The primary metabolite TCP is more resistant to metabolism than chlorpyrifos, with an average half-life at 1 mg/kg of about 2 months but wide variation between soils, from about a week to 9 months. Again, higher concentrations retard metabolism, with a half-life of more than 2 years in one soil spiked at 10 mg/kg.

Degradation of TCP forms trichloromethoxypyridine and $^{14}CO_2$. TMP appears persistent in some laboratory soils as it increased in concentration throughout a 300 day study in two soils, but this should not cause problems in the field given the volatility of this metabolite. Degradation of TMP occurs in other soils, forming $^{14}CO_2$ and TCP, and half-lives in the order of 1-2 months have been recorded.

Chlorpyrifos partitions rapidly from water to sediment following entry to aquatic systems, and also volatilises to the atmosphere, particularly following spray application. Concentrations of chlorpyrifos in the water column decline sharply in the few hours after entry, and then more gradually with dissipation half-lives of a few days generally prevailing in natural surface waters. Dissipation from sediment is slower. Limited data suggest half-lives in the order of a month but possibly extending up to 4 months.

6.3.3.4 Mobility

With a mean soil organic carbon sorption coefficient of 8500 from around thirty different soils, chlorpyrifos has a strong tendency to partition from aqueous into organic phases. Sorption is rapid and largely reversible over short timeframes. In contrast to the immobility of the parent, the metabolite TCP is moderately to highly mobile, with soil organic carbon partition coefficients across 29 different soils ranging from 27 to 389. Mobility of this weakly acidic metabolite tends to increase in alkaline soils. Column leaching studies on four soils confirm that chlorpyrifos is immobile in soils, but significant leaching of TCP from aged samples has been demonstrated in one soil.

Chlorpyrifos is also mobile in the environment by virtue of its volatility. Volatilisation from foliage is particularly pronounced, with around 80% lost within 24-48 hours, compared with up to 25% from soil surfaces. The Henry's law constant is high enough that volatilisation should also occur from water. There is some experimental support for this in that rapid losses have been observed from open or aerated solutions, with unchanged chlorpyrifos recovered from resin plugs in one instance. However, the significance of volatilisation as a dissipation pathway for chlorpyrifos from surface

waters remains unclear. Recent modelling studies suggest that mass transfer from the surface microlayer to underlying water is more important than volatilisation.

Spray drift also transports chlorpyrifos into non-target areas. Available data indicate that aerial application generates the highest levels of drift, with buffers of 300 m needed to reduce off-target deposition below 0.5% of the application rate. Nozzle selection is critical. With solid stream nozzles delivering very coarse droplets, aerial applications generate comparable levels of drift to ground based treatments. The other key factor that gives rise to excessive drift is atmospheric stability and associated inversions.

6.3.3.5 Field dissipation

Chlorpyrifos would not be expected to persist in the field based on the laboratory results, and this prediction is supported by results from field trials.

Three separate studies on turfgrass plots indicated a rapid initial degradation with half-lives of about a week, followed after a month by a more gradual decline with half-lives in the order of a month. Residues remained at the site of application because of good retention by the organic rich thatch layer, with less than 0.1% lost with runoff water.

Studies in citrus orchards found a rapid dissipation of surface soil residues, which declined by at least an order of magnitude in the month after application.

Studies in cotton found that as much as 4.5% can be lost in runoff water when heavy rains occur. Studies were conducted on heavy clay and lighter silt loam soils, with chlorpyrifos applied at 0.56 or 1.12 kg/ha. Most of the chlorpyrifos leaving the field in runoff was in the dissolved phase, suggesting foliar wash off as the main source. Losses were lower after canopy closure, notwithstanding increased foliage, because the larger plants depleted soil moisture under the prevailing dry conditions and allowed greater infiltration before runoff occurred. The main factor determining the magnitude of runoff losses was the time between application and precipitation, during which foliar deposits are lost to volatilisation.

Pond studies indicate that volatilisation also occurs from water, particularly soon after spray contact while the bulk remains near the surface. Volatilisation is the main process for dissipation of chlorpyrifos from water, with a half-life of 3.5 days estimated by modelling. The half-life in sediment was 200 days.

Studies on corn receiving various treatments in consecutive seasons found seasonal losses to an adjacent pond of about 0.2-0.4% of applied. In contrast to the cotton study where a mature crop was treated, most losses occurred in runoff as sorbed residues. Foliar washoff provided minor dissolved contributions as foliar interception was generally low due to small plant size, and delays between application and runoff events allowed volatilisation to occur. Peak concentrations in an adjacent receiving pond approached 10 µg/L in the second year when heavy rains fell, with peak residues approaching 1 mg/kg in sediment. Simulated storms soon after application at the time of planting when soil was bare removed some 2-3% of applied chlorpyrifos from the

field in runoff. The half-life of chlorpyrifos in the soil appeared to be about 3 weeks. No residues were detected below 25 cm in the soil, or in tile drainage.

Bare soil studies in Germany found half-lives in the order of 2 months. Similar persistence was recorded after application at 3.4 kg/ha to bare soil in Illinois, Michigan and California, with no residues of chlorpyrifos or metabolites (TCP/TMP) found below 30 cm in the year following treatment. Canadian studies found half-lives of 2 weeks in a sandy soil and 2 months in a muck soil seeded with carrots and radish.

6.3.3.6 Bioaccumulation

Chlorpyrifos bioconcentrates to moderate to high levels in fish and other aquatic life. A bioconcentration factor of about 1400 has been recorded in rainbow trout, and 745 in oysters. Steady state is soon achieved, and residues depurate rapidly in clean water, with typical half-lives of about 2 days. Bioconcentration of TCP in mosquito fish is insignificant.

7. ENVIRONMENTAL EFFECTS

This assessment of the environmental effects of chlorpyrifos relies heavily on a recently published, comprehensive review (Barron and Woodburn, 1995). A large number of individual study reports presented by registrants are also evaluated. Except where specifically noted, it would appear that these tests have been conducted satisfactorily according to accepted international guidelines such as those of the US EPA (Hitch, 1982b, and subsequent revisions) and OECD.

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

7.1.1 Avian Toxicity

Detailed test reports on acute oral toxicity were submitted for the standard test organisms, bobwhite quail and mallard duck. A comprehensive literature review including data for a much wider variety of species was also submitted. Chlorpyrifos has been shown to be highly to very highly toxic (LD50s below 20 mg/kg) to several species (house sparrow, red-winged blackbird, Japanese quail, ring-necked pheasant, common pigeon and mallard duck) when administered as an acute oral dose, although there are other results available for some species indicating lower toxicity. Acute oral testing is compromised by the tendency of some birds, notably mallards, to regurgitate the test material. Testing with quail indicated the metabolite TCP to be practically nontoxic by the acute oral route.

Detailed dietary toxicity test reports were submitted for bobwhite quail and mallards. Dietary toxicity is moderate to high, with mallards becoming anorexic when dietary concentrations exceed 100 ppm. Choice tests with young mallards offered the option

of food contaminated with 112-1124 mg/kg chlorpyrifos revealed an ability to discriminate in favour of clean feed. Earlier studies indicated that some other birds share this ability, with the onset of repellency between 1000 and 10000 mg/kg chlorpyrifos. However, pheasants, which are highly sensitive to chlorpyrifos, suffered mortality following consumption of food contaminated with 10000 mg/kg chlorpyrifos, with no sign of any repellency. The metabolite TCP was found to be practically nontoxic to mallards.

Chlorpyrifos does not appear to have significant reproductive toxicity based on testing in bobwhite quail and mallards. Reproductive performance was compromised in mallards at elevated dietary concentrations (above 100 ppm) as the birds stopped eating and lost condition, but this appears to reflect nutritional deficiencies rather than true reproductive toxicity. Reproductive parameters remained unaffected in bobwhite quail fed at 125 ppm.

Overseas studies have found little evidence for avian impact. Geese grazing on pasture sprayed at 0.72 kg/ha were clearly exposed to chlorpyrifos as residues were found in excreta, but suffered no ill effect. No dead birds were found when golf courses in Florida were closely monitored after treatment at relatively high rates (4.5 kg/ha) for grubs and crickets. Studies in Iowa corn at lower rates (1.1-3.4 kg/ha) found only two American robins as possible chlorpyrifos casualties, despite abundant bird life and significant residues in vegetation and insects. Similar studies in California citrus found some changes in abundance following a high rate treatment (6.7 kg/ha) but these were thought to reflect avoidance rather than mortality. Field studies in Senegal found a few avian casualties following application of chlorpyrifos at 280 or 387 g/ha for grasshopper control. Post-treatment reductions in avian populations appeared to reflect reduced food resources. In general, field studies in which birds were abundant provided little indication of chlorpyrifos related effects on birds. The notable exception is a study in freshwater ponds in California in which significant mortality of mallard ducklings was recorded following application of chlorpyrifos to the water at rates of 11-1120 g/ha. Birds apparently died as a result of consuming contaminated water boatmen, but the study is old and causal factors can not be firmly established.

There are some reports of adverse avian impact from use of chlorpyrifos in Australia. Again, these appear to involve the consumption of contaminated invertebrates. Occasional bird kills (scavenging species such as crows and butcher birds) have been reported in association with the use of chlorpyrifos baits to control surface feeding insects in cotton, sorghum, sunflowers and maize. There is a report of dead magpies that were found following treatment of power poles to treat termites, with contaminated worms apparently responsible. A granular ant control product was recently reported to have killed a number of pigeons at a Darwin residence. Chlorpyrifos may have been the cause of a major incident at an ibis rookery in the Macquarie Marshes in early 1995 in which large numbers of nestlings died, apparently from consumption of contaminated invertebrates brought back to the nest by parents.

Isolated avian incidents have also been reported from overseas, with chlorpyrifos specifically identified as the causal factor in some. Abnormally high levels of

chlorpyrifos and other organophosphates were found in dead shorebirds following relatively large incidents in Florida in 1997.

Reported avian incidents, while relatively few, appear inconsistent with the generally favourable outcomes from field studies. One explanation may be the much higher toxicity of chlorpyrifos oxon, which may reach significant levels in contaminated invertebrates. This does not appear to have been specifically investigated, and may have been overlooked. Chlorpyrifos oxon would probably remain undetected using standard analytical procedures because of its instability.

7.1.1.1 Acute oral

Acute oral toxicity data for 17 species are included in the review by Barron and Woodburn (1995). Chlorpyrifos has been shown to be highly to very highly toxic (LD50s below 20 mg/kg) to several species (house sparrow, red-winged blackbird, Japanese quail, ring-necked pheasant, common pigeon and mallard duck) when administered as an acute oral dose, although there are other results available for some species indicating lower toxicity. For example, reported LD50s for mallard ducks range from 14.5 mg/kg in 1.5 day old ducklings to 167 mg/kg in 17 day old birds, the latter result probably reflecting regurgitation as described below. The most sensitive species is the ring-necked pheasant (LD50 = 8.4 mg/kg) and nearly all results are below 100 mg/kg. Chlorpyrifos is highly toxic to most birds by the acute oral route, with very high toxicity to some species and moderate toxicity to others.

Test	Species	Result	Reference
Acute oral	Bobwhite quail	LD50 = 25 mg/kg	Lloyd *et al*, 1989a
Acute oral	Bobwhite quail	LD50 = 128 mg/kg	Lloyd *et al*, 1989b
Acute oral	Bobwhite quail	LD50 = 38 mg/kg	Rodgers, 1996
Acute oral	Mallard duck	LD50 = 490 mg/kg	Roberts, 1988a
Acute oral	Mallard duck	LD50 > 6 mg/kg	Campbell, 1994

Five avian acute oral toxicity test reports that would meet contemporary reporting standards were submitted, as tabulated above. Only the quail studies are considered robust enough for use in risk assessment, because regurgitation by mallards means that dosing levels are uncertain. However, given the broad range of acute oral toxicity data available from published sources, and the consistency of those data, further detailed test reports are not considered necessary.

The first of the three bobwhite studies listed used a 14% granular formulation, administered by capsule to 24 week old birds. Typical symptoms of chlorpyrifos intoxication were lethargy, wing droop, depression, a ruffled appearance, reduced reaction to external stimuli, loss of coordination, convulsions, salivation, shallow and rapid respiration, lower leg weakness and stiff legged ataxia. Food consumption was reduced. The LD50 cited above refers to active ingredient, and has 95% confidence limits of 17-140 mg/kg.

The second study listed used suSCon Blue granules, administered by capsule to 24 week old bobwhites weighing 196-260 g. Symptoms of toxicity were as reported

above, and occurred intermittently for about 10 days after dosing at 100 or 200 mg/kg. A no effect concentration could not be determined because early symptoms of toxicity were observed even at the lowest dose of 12.5 mg/kg, and feed consumption was reduced with adverse consequences for body weight gain. Endpoints are expressed as active ingredient, and the LD50 has 95% confidence limits of 89-231 mg/kg.

The most recent bobwhite study used a 480 g/L EC formulation (45.4% by weight). Range finding studies found mallards to be an unsuitable species as vomiting occurred within 30 minutes of dosing at 60 mg/kg formulation, with death following soon after. Bobwhite quail used in the definitive test were 21 weeks old and weighed 172-218 g. Birds were subdued and unsteady prior to death, with salivation in some individuals that had received a higher dose The LD50 cited above refers to active ingredient, and has 95% confidence limits of 30-48 mg/kg.

The earlier mallard study used technical chlorpyrifos administered in corn oil by oral gavage to adult birds, approximately 14 months old. Birds became subdued and unsteady between 1 and 2 days after dosing, and food consumption was depressed. Results are not considered sufficiently robust for use in risk assessment. The protocol requirement that mortality occur over at least three dosage levels was fulfilled, but only because of two deaths in the medium dose group (162 mg/kg) that occurred 12 and 14 days after dosing and are probably not dose related. A single mortality occurred the day after dosing at 292 mg/kg, and six in the three days following dosing at 525 mg/kg. The calculated LD50 has very wide 95% confidence limits (327-1781 mg/kg).

A precise LD50 could not be determined in the more recent mallard study, in which suSCon granules were administered by capsule. The lower limit tabulated above, expressed in terms of active ingredient, reflects the lowest dose at which regurgitation did not occur. Birds were not actually seen to regurgitate, but adequate evidence was seen on the day of dosing in the dropping pans, tinted with blood or bile in some cases. A single mortality, preceded by wing droop and lower limb weakness, occurred at the intermediate dose of 81 mg/kg. Apart from the immediate symptoms of regurgitation, all other birds remained normal in appearance and behaviour.

Reports were also submitted for the following tests, but results should be treated with caution because insufficient detail was provided to confirm that reliable protocols were followed. However, the brief reports provided do contain some useful observations, such as tendencies for some birds to regurgitate the test material.

Test	**Species**	**Result**	**Reference**
Acute oral	Mallard duck	LD50 = 167 mg/kg	Tucker, 1967
Acute oral	Ring-necked	LD50 = 8.4 mg/kg (.)	Tucker, 1966
Acute oral	pheasant	LD50 = 17.7 mg/kg (.)	Tucker, 1966

Toxicity testing in 17 day old mallard ducklings (168-304 g) dosed with a 40% aqueous gum acacia solution of chlorpyrifos was compromised by the tendency of some ducklings to regurgitate part of the test material, even at doses as low as 23 mg/kg.

Ring-necked pheasants were tested in four groups, each containing four birds which had been fasted overnight. Male birds ranged in age from 5 months to a year and weighed 819-1822 g. Females were 3-5 months old and weighed 701-860 g. Few details are provided, and some anomalous observations are included, such as a stated absence of mortality in females treated at 25 mg/kg (well above the LD50). Symptoms of intoxication, such as excessive blinking, salivation, tachypnea and convulsions, occurred some 15-60 minutes after treatment and persisted for 2-3 days unless death intervened. Death typically occurred between 1 and 2 days after administration of an LD50, but were spread dose-dependently over a period from 55 minutes to 5 days. Different citations for male and female birds (the former from 1971 and the latter from 1984) are provided in Barron and Woodburn (1995), where the birds are reported to have been younger in age than stated above.

7.1.1.2 Acute oral - TCP

A study with bobwhite quail found no mortality at the highest dose tested (2000 mg/kg) but some signs of toxicity with birds lethargic and losing body weight at and above doses of 250 mg/kg (Campbell *et al*, 1990).

7.1.1.3 Acute dietary

Acute dietary toxicity (5 days feeding followed by 3 days observation) of chlorpyrifos to waterfowl, quail and pheasants falls generally in the 200-600 ppm range, indicative of moderate to high toxicity (Barron and Woodburn, 1995).

Test	Species	Result	Reference
8 day dietary	Mallard duck	LC50 = 591 ppm	Beavers, 1978a
16 day dietary	Mallard duck	LC50 = 357 ppm	Beavers, 1978b
8 day dietary	Mallard duck	LC50 = 203 ppm	Roberts, 1987
8 day dietary	Bobwhite quail	LC50 = 423 ppm	Beavers, 1978c
8 day dietary	Bobwhite quail	LC50 = 506 ppm	Roberts, 1988b

The above studies were reported in sufficient detail to confirm that they had been conducted to modern protocols.

The older 8 day mallard study used 14 day old birds. Sub-lethal doses produced lethargy as the only symptom, progressing to depression, reduced reaction to external stimuli, loss of coordination and lower limb weakness at higher doses. Dietary toxicity increased when the feeding period was extended to 11 days, with a 5 day observation period. Increased dietary toxicity is also apparent, however, from a subsequent 8 day study conducted elsewhere. Food consumption almost ceased at higher doses, and dead birds were found at necropsy to have partially to completely empty intestinal tracts.

The bobwhite quail studies also used 14 day old birds. Sub-lethal doses produced lethargy as the only symptom. At lethal doses, death was preceded by lethargy, wing droop, loss of coordination, lower limb weakness, depression, reduced reaction to

external stimuli, a ruffled appearance, prostrate posture, lower limb rigidity, and shallow and rapid respiration terminating in a comatose state. No abnormal lesions were found at necropsy in survivors of lethal doses, but these birds were notably smaller in size. The result from the more recent study should be treated with some caution as the protocol requirement that at least 3 doses produce partial mortality was not fulfilled.

Reports were also submitted for the following tests, but results should be treated with caution because insufficient detail was provided to confirm that reliable protocols were followed.

Test	Species	Result	Reference
8 day dietary	Mallard duck	LC50 = 361 ppm	Stevenson, 1965a
8 day dietary	Mallard duck	LC50 = 180 ppm	Shellenberger, 1970
8 day dietary	Bobwhite quail	LC50 = 721 ppm	Stevenson, 1965b

Dietary levels above about 100 ppm produced marked effects on feed consumption and body weight gains in mallard ducklings and bobwhite quail.

7.1.1.4 Acute dietary - TCP

Acute dietary exposure of TCP to mallards found no mortalities at the highest concentration of 5620 ppm. Two mortalities at lower dietary concentrations (3160 ppm) were possibly related to TCP exposure as birds exhibited symptoms of intoxication such as lethargy and incoordination. A reduction in body weight gain was noted at all concentrations tested, becoming more pronounced at and above 1780 ppm (Long *et al*, 1990).

7.1.1.5 Food avoidance

Mallard ducklings were found to have the ability to discriminate between clean and contaminated (112-1124 ppm) food in choice tests. Birds "tasted" the contaminated food but consumed very little and suffered no ill effect. The 16 day LC50 in the absence of clean food was 357 ppm. When the diet was adjusted by reducing concentrations to reflect a 5 day half-life of chlorpyrifos in the feed, the LC50 based on initial concentration was 644 ppm, indicating that testing procedures that offer a constant concentration to test birds are likely to overestimate field toxicity (Fink and Beavers, 1978).

Earlier studies did not follow any standard protocol, but involved caging individual birds with 25 treated seeds for 16-18 hours. Birds were considered to have been repelled when 13 or more seeds remained uneaten. Complete consumption occurred in controls. Repellency to the common grackle, starling, redwing blackbird and house sparrow occurred at concentrations between 0.1 and 1%. Ring-necked pheasants were not repelled, and suffered mortality following consumption of seeds dressed at 10000 ppm (Kenaga, 1969).

7.1.1.6 Sub-acute dietary

Groups of mature mallard ducks were exposed for 8 weeks to dietary concentrations of 46-1000 ppm, with diets refreshed weekly. No symptoms of intoxication or behavioural abnormalities were noted at doses to 100 ppm, apart from a slight reduction in egg production and food consumption at 100 ppm. These effects became more marked at 215 ppm and were accompanied by symptoms such as lethargy and incoordination, but surviving birds (2/10) maintained normal body weights. At the 464 ppm dose level, no eggs were laid and all birds lost weight prior to mortality, which was complete by day 23. The experimental diet was almost completely rejected at 1000 ppm and all birds died within 21 days. Dead birds were found at necropsy to have exhausted their fat reserves, consistent with death by starvation (Fink, 1977).

Similar testing in Japanese quail found severe reductions in egg production resulting from dietary exposure for 4 weeks to 70-100 ppm chlorpyrifos, and virtual termination at higher exposures (300-500 ppm). Mortality only occurred at the highest dose of 500 ppm, reaching 20%. Typical symptoms of anorexia were noted. The test report (Anon, 1965) is too synoptic to enable confirmation that procedures followed met contemporary protocols.

7.1.1.7 Reproduction

Groups of mallards (2 drakes and 5 hens per pen) were exposed for 17 weeks to chlorpyrifos contaminated food (25 or 125 ppm) with egg collection during the last 8 weeks. Locomotor disfunction was observed in the high dose group in the fifth week of exposure, with birds showing signs of anorexia in preceding weeks. A total of 8 birds (23%) died between weeks 5 and 15 of the study, and were found at autopsy to have depleted fat reserves and muscle mass. Neither symptoms nor reproductive impairment were observed in the low dose group, but statistically significant impairment was found in the following parameters in the high dose group: eggs laid, viable embryos, normal hatchlings, 14 day old survivors, egg weight, eggshell thickness and body weights in representative hatchlings and 14 day old survivors (Beavers, 1978d).

Similar testing with bobwhite quail found no symptoms of intoxication and no reproductive impairment. Occasional mortalities did not appear to be dose related, and a high incidence of eggshell cracks was attributed to behaviour as the birds were not debeaked before the study (Beavers, 1978e)

7.1.1.8 Field study on English pasture

No changes were observed in numbers or behaviours of brent geese and Canada geese grazing during January on English pastures that had been treated with chlorpyrifos at 0.72 kg/ha. Treatment left residues of about 20 ppm on grass 2 days after application, declining by 80-90% over the subsequent 2 days. The geese were exposed to chlorpyrifos as residues were found in faeces, reaching 4-10 ppm soon after treatment (Clements and Murray, undated).

7.1.1.9 Field study on Florida golf courses

Studies on golf course plots (1.9-2.9 ha) on Florida's gulf coast in late summer through early autumn investigated effects from two applications for mole cricket and grub control, each at 4.5 kg/ha and separated by 21 days. Granular product and liquid formulation were each applied to four plots, with a further four plots used as controls. Avian populations were monitored in the early morning by observation using a fixed circular plot census technique, and carcase searches were conducted along 2.4 km of transects along the perimeter of each plot and in adjacent habitat. Samples of soil (10 cm depth) and water (from 10 cm below surface) were taken periodically for analysis, and carcases were similarly analysed where conditions allowed.

Chlorpyrifos was consistently found in samples of soil, grass and thatch, with peak levels in the order of 4.3-4.4 ppm. Half-lives were a few days to a week. Aquatic residues were found on one occasion only, at 0.91 µg/L following granular treatment.

Avian census and general observations identified a total of 112 bird species, 16 mammals, 20 reptiles and 3 amphibians, with about half these species observed on the turf. Carcase searching found 4 specimens for each treatment regime before application and 11 after, compared with 0 and 4, respectively, on control plots. The search efficiency was estimated to be 71% based on recovery of placed carcases, which were also removed by scavenging or predation with a half-life in the order of 1-2 days. Only two of the recovered carcases were possibly treatment related based on the presence of residues, with 1.1 mg/kg found in a Florida soft-shelled turtle after spray application, and 15.1 mg/kg in a ribbon snake recovered after granular treatment (Worley *et al*, 1994).

7.1.1.10 Field study on and around Iowa cornfields

Chlorpyrifos was applied preplant as spray emulsion at 3.36 kg/ha, with further treatments at 1.68 kg/ha at emergence, whorl and tassel stage. Alternatively, granular chlorpyrifos was applied at 2.9 kg/ha and incorporated at planting, followed by two broadcast treatments at 1.1 kg/ha at whorl and tassel stage.

Carcase searching in and around treated corn plots found similar numbers of casualties in treated plots (spray or granules) and controls. Only a minor proportion were possibly linked to chlorpyrifos, and only after applications at the tassel stage. Two American robins and a mouse were found on spray treated plots (four replicates) with symptoms or residues suggestive of possible chlorpyrifos intoxication, and a northern short-tailed shrew on plots treated with granules. A second northern short-tailed shrew found dead on the granular blocks was considered a likely chlorpyrifos casualty based on internal residues of 2.1 ppm. Birds were abundant and diverse, with 135 species observed in the area, 69 within the crop.

Invertebrates were collected from within the crop using pitfall traps, but limited numbers precluded residue analyses in most instances. Residues of 11.5 ppm were recorded in one composite sample collected 4 days after the emergence treatment. Highest daily mean residues from spray and granule treatments at the tassel stage were

about 5 ppm in invertebrates collected 7 days after application. Residues on corn foliage were highest on the day of spray application, reaching 358 ppm at emergence, 193 ppm at whorl and 104 ppm at tassel stage (Frey *et al*, 1994).

Statistical analysis of avian census data collected in the above study found persistent differences between plots, with some birds consistently present or absent on certain fields. It was possible to detect increased abundance of house wrens and eastern bluebirds following provision of nesting boxes. Total mean abundance and mean abundances of 16 different species showed changes over time, but there were no indications of chlorpyrifos related effects on avian abundance (Fontaine, 1994).

7.1.1.11 Field study on and around California citrus

Carcass searches in and around California citrus found no clear differences between treated and control plots. Chlorpyrifos was applied as spray emulsion by airblast at 1.68 kg/ha post bloom and 6.73 kg/ha post petal fall, or 3.92 and 4.49 kg/ha on the same schedule. Only three casualties (one bird, two mammals) under the former treatment regime were considered possible chlorpyrifos casualties based on external residues, and a western rattlesnake was considered a likely casualty based on internal residues. All were recovered after the second, high rate treatment. Under the latter regime, two casualties were possibly chlorpyrifos related being a house mouse recovered after the first treatment and an unidentified passerine nestling collected after the second. These specimens represented less than 10% of total carcasses recovered.

Invertebrates were collected from within the orchard using pitfall traps, but limited numbers precluded residue analyses in most instances. Mean residues peaked on the day of treatment at 5.5 and 4.2 ppm, respectively, for the initial treatment, declining to non detectable levels within 14 days. The final treatment left residues of 14.2 and 5.15 ppm, respectively, with 1.28 ppm still remaining 14 days later in the former case. Residues on citrus foliage were highest on the day of spray application, reaching 30 and 110 ppm, respectively, after the initial treatment, and 166 and 117 ppm after the final. Half-lives for foliar dissipation were about 4 days (Gallagher *et al*, 1994).

Statistical analysis of avian census data for species observed more than 40 times found no indications of treatment effects under the latter treatment regime. Under the former regime, the mean abundances of three species (California quail, western kingbird and ash-throated flycatcher) were reduced following the high rate treatment (6.7 kg/ha) just after petal-fall. It was considered unlikely that mortality was the cause for this decline, and the author speculates that birds avoided the area after the heavy treatment (Fontaine, 1995).

7.1.1.12 California freshwater ponds

This study used fenced experimental ponds (9 x 18 m) with a water depth of 25-33 cm. Chlorpyrifos was applied to the water surface and surrounding vegetation four times at fortnightly intervals as spray emulsion, at rates of 11, 56, 112 and 1120 g/ha. Water samples taken 4 hours after treatment contained 223 g/L, well short of the estimated 340-450 g/L. Residues declined to 97 g/L at 1 day, and further to 68 g /L at

2 days after treatment. Sharkskin filtration indicated that roughly half the residues were associated with suspended particulates.

Five mallard ducklings (3-4 weeks old) were placed on each of the ponds 3 weeks before treatment and provided with chicken starter mash to supplement the natural vegetation present. Mash was removed after the first and third treatments to encourage feeding on contaminated material.

Mallards rapidly gained weight while food was available, from an initial average of 350 g to 800 g two days before treatment. Withdrawal of supplementary feeding caused weight losses of 21-31%. Individual bird weights were too variable to allow detection of any treatment related effects. No birds died in control ponds, but mortality in treated ponds reached about 40%, albeit with no clear dose-response, with most mortality occurring after the initial spray when supplementary feeding was withdrawn. The authors conclude that chlorpyrifos caused marked mortality of young mallard ducks. No deaths occurred after the third spray, although birds lost weight with the withdrawal of food. The authors suggest that timing of treatment in relation to the age of the birds or seasonal availability of food resources may have an important bearing on the outcome. Alternatively, the initial treatment may have killed all the sensitive ducks.

Ducks were observed to feed on water boatmen, which came to the surface and started to swim erratically soon after treatment. The authors suggest that residues on these dying insects may have been an important contributor to the mortalities observed, and that the absence of a clear dose-response may be explained if ducks began feeding as soon as the insects surfaced, which in turn may reflect a common threshold concentration of chlorpyrifos oxon required to elicit toxic effects in the insects. Residues on the insects were not measured, but moderate residues (26 mg/kg) were found on vegetation 4 hours after treatment, declining to 1.1 mg/kg after 7 days. The authors presume that chlorpyrifos analogues would break down rapidly into compounds not detectable with the analytical methods used. This presumption would appear valid for the unstable toxic metabolite, chlorpyrifos oxon (Hurlburt *et al*, 1970).

7.1.1.13 Field studies in Senegal

Pilot studies on unreplicated 2 x 3 km study plots in Senegal where chlorpyrifos was aerially applied at 270 and 387 g/ha across areas of semi-arid thornbush savannah with high grasshopper populations found a reduction in total bird numbers. Weekly bird counts along 1 km parallel transects on a 250 m spacing between 7 and 10 am provided a relative index of bird abundance, and were supplemented by bird counts between 10 am and 1 pm in shallow topographical depressions that supported a greater diversity and biomass of vegetation. Carcass searches were conducted 24 and 48 hours after treatment, with searching efficiency and disappearance rate evaluated by placement of dead birds. Dead or debilitated birds were collected for analysis, as well as healthy specimens by netting or shooting.

A total of 131 bird species was observed on the study plots between June and October. Removal of rare and incidental species, and of golden sparrows that were sufficiently

numerous to mask effects on other species, left 71 species for consideration, 21 being common. Total numbers of birds and the sum of the 21 most common species declined by some 26-28% on treated plots, with little difference between treatments. In contrast, depression counts increased on treated plots.

Carcass searching found one dead or debilitated button quail on the lower dose plot and three birds (white-throated bee-eater, Abyssinian roller and singing bush lark) on the higher dose plot. No dead birds were found on the control plot. After correction for searching efficiency (40-70% for larger birds but only 12% for smaller birds) it was estimated that some 2-3% of birds on the high dose plot suffered mortality.

When corrected for variations in controls, bird numbers on chlorpyrifos treated plots declined by 8-10%, a greater reduction than estimated to be due to mortality. A general decrease occurred with all bird species monitored. Population reductions appeared to mainly reflect bird movement in response to a reduction in grasshopper prey (Mullié and Keith, 1993).

7.1.1.14 Australian incidents

Avian exposure to chlorpyrifos is described on the National Toxics Network's website (http://www.spirit.com.au). Chlorpyrifos was isolated in currawong autopsies from the Sydney region, and detected in 1990 sampling of three eggs of little terns (0.06-0.36 ppm), one liver sample from little terns (0.02 ppm) and one pelican egg (0.5 ppm) from the Wallace Lake Colony, central coast of NSW.

The Queensland Department of Primary Industries advised the NRA in March 1994 of occasional bird kills associated with the use of chlorpyrifos baits to control surface feeding insects in cotton, sorghum, sunflowers and maize. Birds affected are scavenging species such as crows and butcher birds, and incidents appear to be associated with high populations of large insects (cockroaches, false wireworms) that die on the surface. The baits are often prepared by landholders by treating grain with chlorpyrifos. A number of Beetle Bait products (O'Briens, Monsan and Hygrain) including pelleted formulations are specifically registered for this purpose.

A major incident occurred at an ibis rookery in the Macquarie Marshes in March 1995, with the following details reported to the NRA's Registration Liaison Committee in August 1995. Ibis were breeding in response to heavy rain in January, and had a ready food source as local grasshopper populations had also become plentiful in response to the rain. On 24 March, a field officer of the NSW National Parks and Wildlife Service found two groups of dead nestlings among apparently healthy straw-necked ibis nestlings. Further fresh casualties were discovered on 29 March, and bodies that had been dead for about a week on 18 April. Altogether, about 400-500 nestlings were affected, and about half a dozen adults were found dead. Nestlings were found lying on their backs, and appeared to have full stomachs. Chlorpyrifos was found at low

levels (0.026 and 0.167 mg/kg, respectively) in liver and intestinal tissues from two dead nestlings sampled on 24 and 29 March.

While chlorpyrifos was considered a possible cause of ibis mortality, investigations were limited and evidence of causation remained weak. No adults were analysed because their carcases had been dismembered by scavengers. Food in the crops of dead nestlings remained unidentified, and no pathology tests were conducted to discount disease. Analysis for chemicals other than chlorpyrifos did not occur. There was no obvious local source of chlorpyrifos contamination. A cotton crop some 30 km distant was sprayed with chlorpyrifos in early March, but this was considered an unlikely source because the maturing crop, with its closing canopy, does not represent ibis foraging habitat. Unidentified grasshopper control operations are clearly a possibility, and the source need not necessarily have been local as ibis will fly long distances to feed.

The NSW Environment Minister issued a media release on the above incident in May 1995, reporting that "tests have confirmed that the deaths were due to high levels of chlorpyrifos, a chemical found in pesticides registered for use in cotton farming". It was also reported that "goannas, normally found at the rookery site, have not been seen for several weeks and fears are also held that they may have been killed by secondary poisoning" (Allan, 1995).

Dow advised of an incident in southern Queensland in June 1996 in which eight dead magpies were found following treatment of power poles to treat termites. Soil at the base of the power pole was removed to enable treatment of the pole and then replaced. Magpies had been feeding on worms in the loose soil, and were assumed to have died of chlorpyrifos poisoning because of the high rates used.

A Darwin householder reported in June 1998 that use of a 30 g/kg granular chlorpyrifos product to control ants led to the death of all his pigeons as a result of granule consumption. This incident was reported at the 15th meeting of the NRA's Registration Liaison Committee. Mortality of domesticated birds is of concern, but its significance to wild populations which are likely to behave differently is uncertain. Domesticated birds may be more likely to consume insecticide granules, particularly if they are accustomed to consuming food dispensed by hand. Alternatively, avian consumption of granules may be a more widespread occurrence, but mortalities may go unnoticed except where domesticated birds are involved. Further investigation of these possibilities would appear warranted if this use pattern is to continue.

Advice has recently been received from residents of Uraidla SA that Lorsban EC is used illegally by some growers in the area to protect crops from bird damage, and that dogs and cats become very ill after eating birds that have been poisoned. These concerns have been brought to the attention of State authorities.

Avian incidents reported above, while relatively few, appear inconsistent with the generally favourable outcomes from field studies. One explanation may be the much higher toxicity of chlorpyrifos oxon, which may reach significant levels in contaminated invertebrates. This does not appear to have been specifically investigated, and may

have been overlooked. Chlorpyrifos oxon would probably remain undetected using standard analytical procedures because of its instability.

7.1.1.15 Overseas incidents

The US National Wildlife Health Centre posts quarterly mortality reports on the Internet. The report for for October-December 1997 contains the following information. Two mortality events involving approximately 150 western sandpipers, black skimmers, and a few other shorebirds occurred in July and again in October on Marco Island, Collier County, Florida. The cause of death in these events was poisoning by an organophosphorus compound. Subsequent contaminant analysis of birds from the July event confirmed an unusual combination of very high levels of phorate, diazinon, dimethoate, dursban (chlorpyrifos) and malathion in one bird and dursban in another. Western sandpipers are migratory while the black skimmers are resident birds in Florida. Biologists are baffled as to the route of exposure. To date there has been no analysis of stomach contents on birds collected during the second event to confirm these findings.

Chlorpyrifos toxicosis was specifically identified as the causal factor in the deaths of 4 American robins at Fort Walton Beach, Florida in February 1997, and of 7 common grackles at North Charleston, North Carolina in October/November 1997. Numerous other incidents in recent years were ascribed to other, often unidentified organophosphorous insecticides.

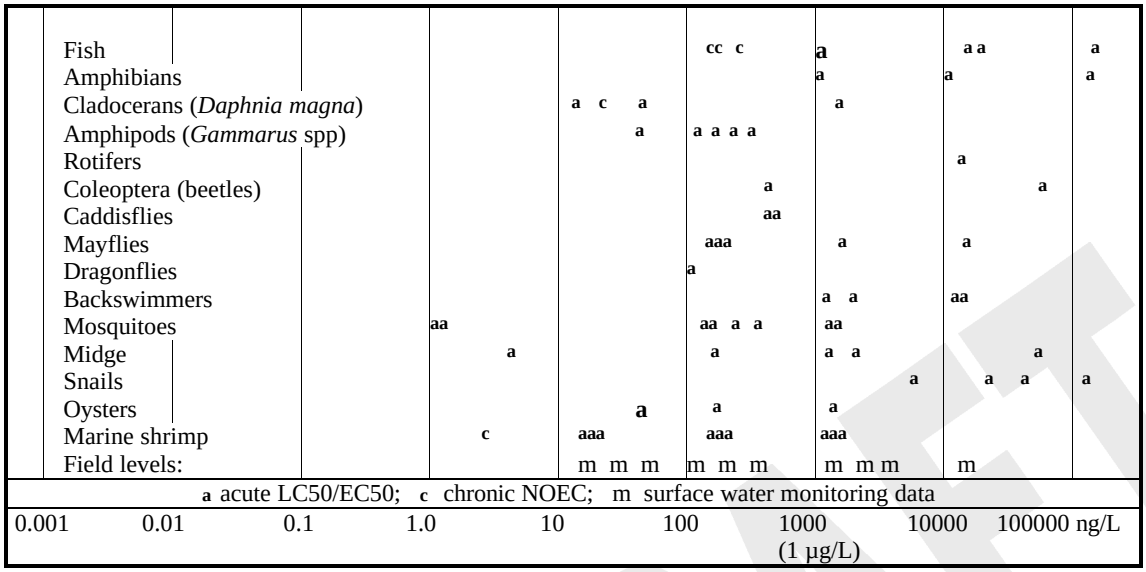
7.1.2 Aquatic Toxicity

Extensive testing shows chlorpyrifos to be highly to very highly toxic to fish, aquatic arthropods, oysters and algae. Limited data suggest that some amphibians may share similar sensitivity. Acute LC50s for freshwater and marine fish are typically below 100 µg/L, with bluegill sunfish sensitive at around 2 µg/L. For invertebrates, acute LC50s are typically in the 0.1-10 µg/L range. Algal endpoints are typically above 100 µg/L, but with one well reported result of 64 µg/L for the sensitive freshwater species, *Selenastrum capricornutum*. Testing with fish and invertebrates shows the metabolite TCP to be slightly to moderately toxic, consistent with its hydrophilic character.

Chronic exposure of rainbow trout resulted in complete mortality at low concentrations (2-3 µg/L). The NOEC was 0.5 µg/L. Life-cycle testing with fathead minnows returned a similar NOEC, with larval mortality observed at concentrations in the order of 1 µg/L. Semi-static reproductive testing with *Daphnia magna* found a no effect concentration of 0.056 µg/L. Complete mortality occurred within 21 days at the next highest test concentration, nominally 0.1 µg/L. Reproductive testing with mysid shrimp, a sensitive marine invertebrate, found mortality and growth impairment at concentrations above 10 ng/L, with a NOEC of 4.6 ng/L.

Aquatic toxicity data for chlorpyrifos are summarised below. Available Australian surface water monitoring data are included for comparison. It should be noted that most water samples test negative for chlorpyrifos, and would therefore contain less

than the detection limit of 0.01 or 0.1 µg/L, but that any detections will be toxic to sensitive species.



Differences in toxicity to fish, invertebrates and vegetation are readily apparent from multi-species testing in microcosms and ponds. As a general rule, aquatic arthropods suffer dose-responsive impacts following acute (pulse) exposure at 0.1-1 µg/L, while only minor fish impacts occur at such doses, consistent with the summary depiction above. Algae are not affected directly by such exposures, but indirect effects of increased algal and periphyton growth may arise due to suppression of planktonic grazers. Some gastropods may also increase in number with increased food resources. The threshold for acute effects at species and community levels in such studies appears to be about 0.1 µg/L. Invertebrate communities generally recover from acute exposures within 6 months, depending on the magnitude of the disturbance and the responses of less sensitive species, which may occupy ecological niches vacated by sensitive organisms before they can recover.

A static microcosm study in fibreglass tanks examined spray drift and runoff simulations delivering target concentrations between 0.03 and 3 µg/L. Nominal concentrations were achieved soon after drift simulation and declined with a half life of about 3 days. Aquatic concentrations after slurry application reached about half of nominal but remained fairly constant for some days as further material desorbed. Rotifers remained unaffected by treatment, but arthropod populations suffered sharp reductions at target concentrations of 0.3-3 µg/L and needed 2-4 weeks to recover. Bluegill sunfish were reduced by about a third by drift simulation at the highest rate, and almost eliminated by the corresponding slurry treatment, repeated three times at fortnightly intervals. Drift simulation at 10 µg/L eradicated bluegill populations. Various alternating spray and slurry sequences were also investigated. Measured concentrations suggested biphasic dissipation kinetics, with rapid losses (half-lives of a day or two) in the initial 24 hours after spray treatment followed by a more gradual decline (half-life about a week). Initial losses were thought to reflect volatilisation. Sorption to sediment was a relatively minor dissipation pathway, with levels recorded in sediment remaining generally below 10% of applied. Results indicate that repeat

exposure to concentrations in the order of 1 µg/L should not affect bluegill survival or growth, and will cause only temporary reductions in invertebrate populations, provided that chronic exposures remain below 1 µg/L.

The maximum concentration of 4.7 µg/L detected in samples taken from 15-20 cm below the surface of shallow Minnesota ponds following spray application was about 25% of nominal. All other recordings were below 1.5 µg/L, or 10% of nominal. Effects seen in the pond were consistent with laboratory data. Substantial numbers of bluegill sunfish, for which laboratory LC50s in the order of 2 µg/L are typical, were killed. Arthropod populations, particularly water fleas, were reduced.

Similar trends were evident in deeper Minnesota ponds sprayed at three different rates. Bluegill mortality at target concentrations of 5 and 20 µg/L reached 38 and 99%, respectively. Minimal mortality occurred at a target concentration of 0.5 µg/L. Arthropod populations were reduced, and cladocerans were again most sensitive with major reductions at all treatment levels. Analyses of water samples indicated that nominal concentrations at mid-depth were exceeded 1 hour after treatment. However, some doubt is attached to this observation because of contradictory results from vertical mixing studies, which found less than 10% of applied chlorpyrifos at mid-depth during the initial 2 hours after treatment. An initial rapid drop in chlorpyrifos concentrations in the water column (half-life 4-18 hours, with greater persistence at higher dose) was followed after about 12 hours by a more gradual decline.

Actual concentrations in artificial drainage ditches containing standing water were estimated by measuring the stratification and by taking depth-integrated water samples. Nominal target concentrations exceeded actual concentrations by a factor of about two following surface spray treatment. Stratification was evident for about a day in open water and 2-4 days where aquatic vegetation was present. The nominal NOEC at species and community levels was 0.1 µg/L under this acute dosing regime.

Australian studies in flowing water dosed continuously for 6 hours at a nominal 0.1 µg/L found no effect on artificial stream communities. Significant reductions in invertebrate density occurred at higher dose (nominally 5 µg/L). Continuous dosing over 21 days reduced numbers of chironomids, copepods and cladocerans at low and high doses. Periphyton density increased with reduced grazing pressure, as did one species of gastropod mollusc.

Artificial stream studies in Minnesota examined continuous dosing for 100 days at nominal concentrations of 0.2-1.01 µg/L, or 24 hour pulses at a nominal 3.1-11.5 µg/L every fortnight. The number of invertebrate taxa and number of organisms sampled declined under pulse dosing. Amphipod bioassays found no effect under continuous dosing but 50% mortality under pulse dosing. Symptoms of intoxication were seen in caged bluegills, but only under pulse dosing. Unstocked white suckers were found dead or dying following pulse dosing.

7.1.2.1 Fish acute toxicity

Acute toxicity data for some 20 freshwater species are included in the review by Barron and Woodburn (1995). Chlorpyrifos is highly to very highly toxic to freshwater and saltwater fish. Bluegills are the most sensitive species, with 96 h LC50s only a little above 1 µg/L, while catfish are relatively insensitive with 96 h LC50s of a few hundred ppb for fingerlings weighing less than a gram, increasing to about 800 µg/L as weight increases to 7.9 g. Toxicity is higher under flow-through conditions because of sorptive interferences in static systems. Numerous saltwater species have 96 h LC50s in the low ppb range, with the sheepshead minnow a relatively insensitive exception among the dozen or so species for which data are reported.

The submissions of data contained a number of original study reports. The following studies were reported in sufficient detail to confirm that they had been conducted to modern protocols, with some variations as noted in the text below.

Test	Species	Result	Reference
Flow-through	Rainbow trout	96 h LC50 = 25 µg/L	Bowman, 1988
Flow-through	Rainbow trout	96 h LC50 = 68 µg/L	Douglas, 1993a
Flow-through	Rainbow trout	96 h LC50 = 22 µg/L	McMinn, 1995
Semi-static	Rainbow trout	96 h LC50 = 110 mg/L	Sewell, 1993
Flow-through	Sheepshead	96 h LC50 > 76 µg/L	Surprenant, 1989a
Flow-through	Fathead	96 h LC50 = 140 µg/L	Jarvinen, undated
Semi-static	Roach	96 h LC50 = 250 µg/L	Douglas, 1985b
Semi-static	Ide	96 h LC50 = 10 µg/L	Douglas, 1985c

The 1988 trout test used nominal concentrations of 5, 10, 20, 40 and 80 µg/L technical chlorpyrifos (mean measured concentrations of 4.2, 8.1, 16, 37 and 72 µg/L). Control fish had a mean weight of 0.72 g at the end of the study, which was conducted at 13^{o}C. Symptoms of intoxication such as quiescence, loss of equilibrium and dark discolouration were noted at all test concentrations.

Trout in the 1993 flow-through test had mean length 4.9 cm and mean weight 1.56 g and were tested at 14^{o}C, using a 480 g/L EC formulation. Symptoms of intoxication included increased pigmentation, loss of equilibrium, muscle spasms on stimulation, and lethargy. Results are expressed as nominal concentrations of chlorpyrifos. The NOEC was 4.5 µg/L.

The 1995 trout test was conducted at 12^{o}C on fish with a mean weight of 0.6 g, using a 480 g/L EC formulation. Fish were exposed to nominal concentrations of 16, 26, 43, 72, 120 and 200 µg/L formulation (mean measured concentrations 3.2, 15, 28, 43, 93 and 140 µg/L). Results are expressed here as mean measured concentrations of chlorpyrifos. Intoxication was characterised by partial loss of equilibrium and lethargy. The NOEC was 1.5 µg/L.

The semi-static test was conducted using a 24% microencapsulated formulation dispersed in water. The result is expressed as nominal concentration of the formulation. Based on this single test, microencapsulated formulations of chlorpyrifos have low toxicity to fish.

The saltwater fish sheepshead minnow (mean weight 0.24 g) was tested at nominal concentrations of 89, 140, 210, 330 and 500 µg/L technical chlorpyrifos. Mean measured concentrations were well below nominal at 19, 23, 38, 55 and 76 µg/L, but there were no visible signs of undissolved material. The highest measurement is thought to approximate the solubility of chlorpyrifos in seawater. No toxicant related adverse effects were noted at any test concentration.

The fathead minnow test exposed newly hatched larvae to technical chlorpyrifos. Static endpoints, apparently based on nominal concentrations, were only marginally higher, reflecting the stability of chlorpyrifos (half-life 41 days) in the test water.

Roach and ide are not standard test species, and the specimens used were rather large (respective mean weights of 8.3 and 5.9 g). Recrystallised chlorpyrifos was the toxicant. Concentrations used in the semi-static tests (daily renewal of test solution) were not confirmed by analysis. However, a good dose-response was achieved. Intoxication was characterised by torpor and loss of equilibrium.

Reports were also submitted for the following tests, but results should be treated with caution because insufficient detail was provided to confirm that reliable protocols were followed.

Test	Species	Result	Reference
Static	Rainbow trout	96 h LC50 = 10.5 µg/L	Cope, 1965
Static	Bluegill sunfish	96 h LC50 = 2.1 µg/L	Cope, 1965
Static	Bluegill sunfish	96 h LC50 = 1.7 µg/L	McCann, 1970a
Static	Bluegill sunfish	96 h LC50 = 1.5 µg/L	McCann, 1970b
Static	Rainbow trout	96 h LC50 = 3.0 µg/L	Alexander, 1965
Static	Bluegill sunfish	96 h LC50 = 3.3 µg/L	Alexander, 1965
Static	Channel catfish	96 h LC50 = 13.4 µg/L	Alexander, 1965
	Spot	48 h LC50 = 7 µg/L	Lowe, 1967
	Longnose killifish	48 h LC50 = 3.2 µg/L	Lowe, 1967

In respect of the first two entries, rainbow trout were tested at 13^{o}C, and bluegills at 24^{o}C, both apparently under static conditions. The two subsequent bluegill tests used fish with a mean weight of 0.97 g and were conducted at 19^{o}C. Fish were exposed to a 25% formulation, and results are expressed in terms of active ingredient. The three later entries for trout, bluegill and catfish, used fish with a mean weight of 1.8-1.9 g, and 100 mg/L acetone to aid solubility. Trout were tested at 16^{o}C, and bluegills and catfish at 27^{o}C.

The marine species spot (*Leiostomus xanthurus*) was tested at 30^{o}C, and the marine species longnose killifish (*Fundulus similis*) at 11^{o}C. Another marine species, sheepshead minnow (*Cyprinodon variegatus*) was much less sensitive, with only 10% mortality following 48 h exposure to 1 mg/L. No details of this testing were provided, and it is unclear whether controls were used.

Early studies (Ferguson *et al*, 1966) investigated differences in sensitivity between fish

taken from clean and contaminated environments. Golden shiners (6-10 cm), mosquito fish (2.5-6 cm) and green sunfish (2.5-9 cm) were taken from two Mississippi farm ponds, believed to be uncontaminated, and from a location on the Mississippi delta known to be contaminated by cotton pesticides. Results from 36 hour static tests, tabulated below, indicate fish from the two clean environments to be at least 3 times more sensitive than those that have already been challenged by toxic chemicals. There was a more gradual dose-response relationship in fish from the delta. Intoxicated fish became quiescent, with sunfish moving to the bottom and shiners and mosquito fish surfacing before death. Spontaneous abortions were seen in gravid mosquito fish in the terminal stages of gestation.

Species	**36 h median tolerable limit (µg/L)**	
	Farm pond	**Delta**
Golden shiner	45/35	125
Mosquito fish	215/230	595
Green sunfish	22.5/37.5	125

7.1.2.2 Fish acute toxicity - TCP

Early static testing with rainbow trout (mean weight 3.5 g), bluegill sunfish (mean weight 2.3 g) and goldfish (mean weight 2.5 g) returned 96 hour LC50s of 0.75, 4.25 and 4.85 mg/L, respectively (Duddles, 1968).

More recent static testing at 12°C with rainbow trout (mean weight 0.81 g) returned a 96 hour LC50 of 12.6 mg/L, based on measured concentrations that did not depart significantly from nominal. The NOEC was 7.6 mg/L. TCP is slightly toxic to rainbow trout (Gorzinski *et al*, 1991a).

More recent static testing at 22°C with bluegill sunfish (mean weight 0.69 g) returned a 96 hour LC50 of 12.5 mg/L, based on measured concentrations that did not depart significantly from nominal. The NOEC was 4.4 mg/L. TCP is slightly toxic to bluegill sunfish (Gorzinski *et al*, 1991b).

Flow-through testing at 22°C with Atlantic silverside (mean weight 0.14 g) returned a 96 hour LC50 of 58.4 mg/L, based on measured concentrations that did not depart significantly from nominal. No effects were seen at 44.5 mg/L, but death was complete within 24 hours at 76.7 mg/L. TCP is slightly toxic to Atlantic silverside (Graves and Smith, 1991).

7.1.2.3 Fish chronic toxicity

Rainbow trout (mean weight about 10 g) were exposed at 14-16°C for 21 days under flow-through conditions to nominal concentrations of 0.56, 1, 1.8, 3.2 and 5.6 µg/L technical chlorpyrifos. Mean measured concentrations during the exposure phase were 53% of nominal, the shortfall thought to reflect sorptive interactions with fish, food and excreta. All fish died during the last 3 days at the highest concentration. The NOEC based on growth was 0.93 µg/L, assuming the true concentration to be 53% of

nominal. Based on symptoms (discolouration, loss of equilibrium, anorexia and lethargy) the NOEC was 0.51 µg/L (Adema, 1990).

7.1.2.4 Fish life-cycle toxicity

Fathead minnows were continuously exposed under flow-through conditions for 34 weeks to chlorpyrifos (83, 144, 300, 568 and 1093 ng/L) from the embryonic stage (< 24 hours old) through 32 days of the F1 generation. Mortality was the most consistently sensitive end-point, with larvae less than 25 days old the most sensitive life stage. Statistically significant effects on reproductive end-points were not observed. The NOEC was 568 ng/L (Mayes *et al*, 1993).

7.1.2.5 Amphibian acute toxicity

Early studies (Whitney, 1965) found toad tadpoles (species not identified) with hind legs to be highly sensitive to Dursban, with an approximate LC50 of 1 µg/L over an unspecified timeframe. Leopard frog tadpoles at a similar stage of development were much less sensitive, with an LC50 of about 3 mg/L, while the LC50 in adult leopard frogs was 30 mg/L.

Adult bull frogs inhabiting a Mississippi pond appeared to remain unaffected by chlorpyrifos treatment (see section 6.1.2.13). Tadpoles would be expected to be more sensitive than adults, and this expectation finds support in the review by Barron and Woodburn (1995). The 1 day and 6 day LC50s for tadpoles of the Indian bull frog (*Rana tigrina*) were 177 and 10 µg/L, respectively.

7.1.2.6 Aquatic invertebrate acute toxicity

Acute toxicity data for a broad range of freshwater and marine invertebrates are reported in Barron and Woodburn (1995). The majority of species are sensitive in the 0.1-10 µg/L range. Mosquito larvae are most sensitive, with LC50s ranging down to about 1 ng/L, while endpoints for rotifers exceed 10 mg/L. Molluscs are also relatively insensitive, with the exception of oysters which are highly sensitive. Available data are summarised above (see section 6.1.2).

The submissions of data contained a number of original study reports. The following studies were reported in sufficient detail to confirm that they had been conducted to modern protocols, with some variations as noted in the text below.

Test	Species	Result	Reference
Flow-through	*Daphnia magna*	48 h EC50 = 100 ng/L	Burgess, 1988
Static	*Daphnia magna*	48 h EC50 = 15 ng/L	Douglas, 1993b
Semi-static	*Daphnia magna*	48 h EC50 = 1.2 µg/L	van der Kolk, 1995a
Flow-through	Mysid shrimp	96 h EC50 = 45 ng/L	Surprenant, 1989b

The flow-through *Daphnia magna* test exposed 1st instars less than 24 hours old to technical chlorpyrifos. The nominal NOEC of 24 ng/L could not be confirmed as the analytical method lacked sufficient sensitivity.

The static *Daphnia magna* test exposed 1st instars less than 24 hours old to an emulsifiable concentrate containing 480 g/L chlorpyrifos. Nominal concentrations of total formulation were 1, 1.8, 3.2, 5.6, 10, 18, 32, 56 and 100 ng/L. Initial concentrations at the upper end of this range were confirmed by analysis, but no such confirmation was possible for lower concentrations. Results are expressed in terms of active ingredient. The nominal NOEC was 2.5 ng/L. The increased sensitivity compared with other tests may reflect increased bioavailability of the emulsifiable formulation, or hypersensitivity in the particular laboratory strain used for testing.

The semi-static *Daphnia magna* test exposed 1st instars less than 24 hours old to an emulsifiable concentrate containing 480 g/L chlorpyrifos, with renewal of the test medium after 24 hours. Nominal concentrations of total formulation were 0.16, 0.31, 0.63, 1.3, 2.5, and 5 µg/L, and mean measured concentrations were 0.11, 0.22, 0.42, 1.1, 2.0 and 3.9 µg/L. Results are expressed in terms of active ingredient. The NOEC was 100 ng/L.

The mysid test used mean measured concentrations of 31, 38, 70, 110 and 200 ng/L (nominally 43, 66, 100, 160, 240 ng/L). Complete mortality occurred within 96 hours at the three highest concentrations. The NOEC was 31 ng/L.

Original reports were also submitted for the following tests, but results should be treated with caution because insufficient detail was provided to confirm that reliable protocols were followed.

Test	Species	Result	Reference
Static	Scud	96 h LC50 = 0.11 µg/L	Cope, 1965
Static	Stonefly	96 h LC50 = 0.56 µg/L	Cope, 1965
	Brown shrimp	48 h LC50 = 0.2 µg/L	Lowe, 1967
	Pink shrimp	48 h LC50 = 2.4 µg/L	Lowe, 1967
	Grass shrimp	48 h LC50 = 1.5 µg/L	Lowe, 1967

Scud (*Gammarus lacustris*) were tested at 21°C, and stonefly nymphs (*Claassenia* sp) at 15°C, both apparently under static conditions. No details were provided of testing with the three marine shrimp species apart from temperatures used, being 29°C for brown shrimp (*Penaeus aztecus*) and 12°C for pink shrimp (*P duororum*) and grass shrimp (*Palaemonetes pugio*).

7.1.2.7 Aquatic invertebrate acute toxicity - TCP

Static testing at 20°C with *Daphnia magna* neonates returned a 48 hour LC50 of 10.4 mg/L, based on measured concentrations that did not depart significantly from nominal. The NOEC was 4.9 mg/L. TCP is slightly toxic to *Daphnia magna* (Gorzinski *et al*, 1991c).

Earlier studies had returned a nominal 48 hour LC50 of 3.13 mg/L (Rhinehart and Bailey, 1978).

7.1.2.8 Aquatic invertebrate reproduction

Semi-static testing with *Daphnia magna*, with thrice weekly renewal of test medium, found complete mortality within 21 days at nominal concentrations of 0.10, 0.18 and 0.32 µg/L, but no significant mortality at 0.056 µg/L. Mortality reached 20% in blank controls and 15% in solvent (DMSO) controls. Similarly, no reproductive impairment was observed at 0.056 µg/L, but reproduction was almost completely reduced at 0.10 µg/L. Separate stability testing indicated true concentrations to be about 71% of nominal (Adema and de Ruiter, 1990).

A 35 day test was conducted at 27^{o}C under flow-through conditions with mysid shrimp neonates (< 24 h old) separated into pairs after 14 days of exposure to technical chlorpyrifos containing radiolabelled tracer. Mean measured concentrations (4.6, 10, 20, 43, 73 ng/L) were in close agreement with nominal test concentrations (5, 10, 20, 40, 80 ng/L). Concentration dependent mortality was observed at concentrations of 10 ng/L and above, both before and after pairing, with erratic swimming and surfacing noted at concentrations of 20 ng/L and above. Growth was affected at similar concentrations, with a small but significant weight depression in males exposed at 10 ng/L. The NOEC based on growth and survival was 4.6 ng/L. Reproductive capacity appeared a slightly less sensitive endpoint, but this is difficult to evaluate in the face of strong solvent effects. Reproduction in negative controls was 0.477 young per reproduction day, compared with 0.0717 in solvent controls containing 0.04 mL/L acetone. Reproduction was comparable with the solvent control at the two lowest test concentrations, but no reproduction occurred at the three highest test concentrations (Sved *et al*, 1993).

7.1.2.9 Oyster acute toxicity

Eastern oysters were exposed under flow-through conditions to mean measured concentrations of 17, 41, 85, 150 and 180 µg/L (nominal concentrations of 50, 83, 140, 230 and 380 µg/L) chlorpyrifos technical. Shell growth was significantly reduced at the three highest concentrations. The 96 hour EC50 was 84 µg/L, indicative of very high toxicity (Surprenant, 1989c).

7.1.2.10 Algal toxicity

Green algae (*Scenedesmus subspicatus*) were cultured under continuous illumination on an orbital shaker for 96 hours in the presence of chlorpyrifos (nominal concentrations of 62.5, 125, 250, 500 and 1000 µg/L). Absorbance at 665 nm was measured in samples taken at 24 hour intervals. Mean measured concentrations declined from 73% of nominal at initiation to 6-20% at termination of exposure. The 96 h EC50, based on biomass and expressed as nominal concentrations, was 660 µg/L, indicative of high algal toxicity (Douglas *et al*, 1990).

A more recent test has been conducted with the freshwater green alga *Selenastrum capricornutum* under a similar dosing regime but with an emulsifiable formulation of chlorpyrifos. Mean measured concentrations were 56-67% of nominal and remained fairly constant throughout the exposure period. The 72 h EC50, based on biomass and

expressed as mean measured concentration of chlorpyrifos, was 64 µg/L, indicative of high toxicity (van der Kolk, 1995b).

The ecotoxicological review by Barron and Woodburn (1995) reports that toxicity to freshwater and saltwater algae generally occurs at concentrations above 100 µg/L, with differences between species spanning at least two orders of magnitude.

7.1.2.11 Microcosm studies

Outdoor microcosm studies were conducted during summer 1991 in Kansas, in fibreglass tanks holding 11.2 m^3 pond water, depth 1.4 m, arrayed in a water filled basin. Pond sediment (pH 7.4, 3.2% organic matter) as a 10 cm layer in plastic trays covered about a third of the total tank area, and introduced native macroinvertebrate and macrophyte communities to the microcosms. Juvenile bluegill sunfish (40 per tank) were also added. Simulated spray drift (emulsifiable formulation) treatments were applied on 8 July to achieve nominal aquatic concentrations of 0.03, 0.1, 0.3, 1 and 3 µg/L chlorpyrifos. An emulsifiable concentrate formulation was first dissolved in acetone. Appropriate (but unspecified) volumes of the acetone stock were diluted in water and applied to the microcosms as an aqueous spray. The same target concentrations were used for each of three runoff (clay slurry) simulations, introduced to the microcosms at 14 day intervals. Each exposure regime was replicated three times. One additional microcosm was spray treated at 10 µg/L.

Water samples were taken from four locations for each microcosm and composited. The sampler was a PVC tube, open at the top and fitted with a check valve and drain at the lower end, with a 15 cm feeler to prevent contamination by mud from the bottom of the microcosms. Collection involved lowering the check valve end of the vertical tube to the bottom of the tank, retrieval, and discharge through the drain. Water pressure as the tube was slowly lowered opened the valve and allowed the tube to fill until contact with the bottom, whereupon the valve closed, capturing a column of water as a depth-integrated sample.

Analysis revealed that spray treatment produced measured residues 2 hours after treatment of 0.030, 0.088, 0.25, 0.83 and 2.7 µg/L, which declined over the next 14 days with a mean half-life of 3.6 days, as estimated by linear regression after omission of anomalously low 12 hour samples. Data for the two low dose microcosms (estimated half-lives of 2.2 and 4.9 days, respectively) were poorly correlated, perhaps reflecting analytical error at low concentrations. Occasional detections of chlorpyrifos in the low ppb range occurred in sediment cores sampled from the three low dose microcosms, increasing in frequency at higher doses. An average 9.2 µg/kg was found 10 days after the highest replicated treatment, declining to 3.9 µg/kg at 21 days and 3.6 µg/kg at 42 days.

Possible reasons for the anomalously low residues in 12 hour samples are not discussed in the report. One explanation would be sorption to suspended solids, but any such residues should have been picked up by the analytical method, which involved solid phase partitioning followed by elution with acetonitrile. Volatilisation is another possibility, and would merit closer investigation.

Mean concentrations in slurry treated systems were only slightly above 50% of nominal at 2 hours after the initial treatment, and remained fairly constant over the next 1-3 days as chlorpyrifos gradually desorbed from the slurry. Sediment concentrations were mostly undetectable in the two lowest dose microcosms and varied irregularly with time at higher doses, but were in decline by 84 days after treatment (mean residues of 3.3 and 10.6 µg/kg at the two highest doses, after peaking at an average 8.6 and 42.6 µg/kg, respectively).

There were no obvious chlorpyrifos related effects on phytoplankton or aquatic macrophytes.

Tube sampling (35 µm mesh) revealed that rotifers, the dominant zooplankton, remained largely unaffected by spray treatments, but arthropods were much more sensitive, with effects seen at the three highest replicated doses. Sharp reductions in arthropod abundance occurred after treatment, and numbers remained depressed for about a month apart from the lowest of these three doses where population recovery was evident by two weeks after treatment. Populations remained lower than controls for a further 4 weeks, but the differences were not statistically significant. Zooplankton taxonomic richness was significantly reduced for 2-4 weeks at the three highest replicated doses.

Similar responses were seen following slurry treatment, except that the first introduction reduced arthropod abundance at all treatment levels, and reduced taxonomic richness at all but the lowest dose. Cladocerans were particularly affected, with abundance reduced for 3 weeks after the first treatment at the two highest doses.

Diptera and Ephemeroptera were the main macroinvertebrates colonising artificial benthic substrates. Among the Diptera, chironomids were particularly sensitive, with significant reductions following the three highest spray treatments, reductions being strongest at the highest dose but with recovery within 6 weeks. Total insect abundance was significantly reduced at most treatment levels, with a clear and consistent dose-response at the three highest treatments. Simulated runoff events induced similar responses. Counts of insect emergence found similar reductions following spray or slurry treatment to those observed using artificial substrates. Greatly increased emergence of Ephemeroptera was observed during the treatment period at the highest slurry treatment, reflecting reduced bluegill predation.

Bluegill sunfish populations were reduced by about a third in the highest replicated spray treatment, and eradicated in the single microcosm treated at 10 µg/L. Bluegill biomass was significantly reduced in the two highest replicated spray treatments. Slurry treatments had greater impact, with a single fish surviving from the highest treatment. Again, total biomass was significantly reduced in the two highest replicated treatments (Giddings, 1993a).

Some of the results from the above studies have now been published (Giddings *et al*, 1997). Reanalysis of the kinetics revealed a biphasic dissipation, with half-lives in the order of 1-3 days during the initial 24 hours after spray treatment, declining to 4-

7 days thereafter. Rapid early losses were attributed to volatilisation. After the initial 24 hour period, dissipation half-lives were comparable to those determined for slurry treatment (6-8 days) after the initial desorption.

Results were also reported from combined treatments in which weekly or fortnightly spray applications were alternated with slurry treatments 4 days later. Half-lives in the initial 24 hours after spraying were 1.75 days, compared with 6.98 days for the following three days. Except for the lowest dose, the mass of chlorpyrifos in the sediment never exceeded 10% of applied, indicating that sorption to sediment plays an insignificant role in removing chlorpyrifos from the water column.

The new results confirm the high sensitivity of bluegill sunfish to chlorpyrifos. A single exposure above 1 µg/L can cause direct effects, notwithstanding rapid dissipation. Chronic exposure to concentrations below this threshold appears much less damaging. The IC25 concentrations for survival, based on mean measured concentrations, ranged from 1.20 µg/L (slurry) to 1.89 µg/L (spray). Corresponding values for biomass ranged from 0.632 µg/L (slurry) to 1.76 µg/L (spray).

The original study report for the alternating spray and slurry treatments (Giddings, 1993b) indicates that alternating spray and slurry treatments respectively delivering a nominal 1 and 0.6 µg/L over a 6 week period had no significant effect provided that sufficient time elapsed between each exposure. The overall pattern of chlorpyrifos concentrations in the water consisted of pulses after each addition, with declines between additions. Spray treatments delivered target concentrations to the water, but addition of slurry increased water concentrations by about two-thirds of nominal. Spray treatment at fortnightly intervals produced a mean maximum pulse concentration across 3 tanks of 1.17 µg/L (mean 1.06 µg/L for three spray pulses) based on analysis of depth integrated samples. This exposure regime had no discernible effect on bluegills. Significant but temporary reductions occurred in populations of zooplankton crustacea and emergent insects. Cladocerans were most severely affected, being virtually eliminated almost immediately and showing signs of recovery only 6 weeks after the final treatment. When the frequency of treatment was doubled, bluegills suffered major reductions in survival and total biomass, and invertebrate impacts were longer lasting, with several taxa not recovering to control levels. Maximum and mean spray pulse concentrations increased to 1.86 and 1.48 µg/L, respectively. Results indicate that repeat exposure to concentrations in the order of 1 µg/L should not affect bluegill survival or growth, and will cause only temporary reductions in invertebrate populations, provided that chronic exposures remain below 1 µg/L.

7.1.2.12 Artificial ponds

Polyethylene lined pits (2 x 2 x 1 m) containing 3000 L water and leaf litter from dried woodland ponds were treated with Dursban (41.2% chlorpyrifos) at 10 µg/L by surface application followed by gentle mixing. A single natural pond received the same treatment. Concentrations declined rapidly from the water column soon after application through partitioning processes, including sorption to the polyethylene liner. Chlorpyrifos appeared more persistent in artificial than in natural ponds because of gradual release of chlorpyrifos back to the water column from the polyethylene liner.

Cladocerans were almost eliminated by the treatment and showed no signs of recovery over the next 40 days. In contrast, mean densities of calanoid copepods showed no significant change. A consistent relationship was found between treatment and the development after about 30 days of algal blooms because of reduced grazing by a suppressed zooplankton population (Hughes *et al*, 1980).

7.1.2.13 Mississippi pond studies

A small Mississippi pond with an average depth of about 0.8 m and emergent aquatic plants covering 25-40% of the surface was sprayed with chlorpyrifos at 280 g/ha during summer 1966, simulating an aerial treatment. Observations were restricted to biological effects, with no analyses to determine chlorpryrifos levels. Caged bluegill sunfish suffered complete mortality within 24 hours. Signs of damage were visible within half an hour in the form of dead flea beetles and distressed mayfly nymphs. Distressed small green sunfish were seen 3 hours after treatment. Bottom sampling 24 hours after treatment revealed a complete kill of aquatic insects and heavy kills of green sunfish, bluegill sunfish and mosquito fish. A few bullhead catfish were surfacing. Mortality in this more resistant species was apparent by 48 hours, but flea beetles had begun to repopulate from elsewhere. Two months after application, a diverse invertebrate fauna had returned to the pond, but immature aquatic forms were present in unusually high number, suggesting little predation by fish. Bull frogs could also be seen, and one adult green sunfish was caught.

A larger pond with an average depth of 2.7 m was treated at 28 g/ha with the same formulation. Caged bluegills measuring 12-15 cm did not suffer significant mortality, although large numbers of smaller bluegills (2-5 cm) were found dead 24 hours after treatment. Smaller bluegills (< 2.5 cm) appeared healthy in deeper water (2 m), and other organisms such as dragonfly nymphs, water striders, mayfly nymphs and tadpoles remained unaffected. Sport fishing in deeper waters for adult bluegills remained productive but largemouth black bass known to be present were inactive, perhaps because of heavy feeding on smaller dead and dying bluegills. Bottom samples at 48 hours found a healthy insect fauna. The pond appeared to have largely returned to its pre-treatment condition by 2 weeks after treatment. Fish samples netted 2 months after treatment revealed a healthy population, although intermediate bluegills were greatly reduced in number (Miller, undated; Byrd *et al*, 1966).

The observed biological effects are consistent with prediction. The higher rate treatment would have left residues of 35 g/L if dispersed evenly through the po nd. Such high concentrations would be expected to impact on fish, particularly sensitive species such as bluegills, and invertebrates. The lower rate treatment would have left residues of about 1 g/L. Toxic effects would be expected in more sensitive f ish such as young bluegills, particularly in shallower water where concentrations would be expected to be higher. Effects would also be expected in sensitive invertebrates, but may have been overlooked.

7.1.2.14 Minnesota pond studies

A small pond (0.72 ha, mean depth 32 cm) was aerially treated with 56 g/ha chlorpyrifos on 3 occasions during summer 1983 at intervals of about 3 weeks, the first two treatments using a sand granule slow-release formulation and the final application as an emulsion. Shoreline vegetation was dominated by reed canary grass and cattails. Submergent vegetation, mainly coontail, began to appear in early June soon after the first treatment, and the surface of the pond became largely covered with star duckweed and greater duckweed by mid-July.

Wooden walkways were constructed to allow collection of water samples, which were taken daily from 15-20 cm below the surface. More intensive sampling (1, 2, 4 and 8 hours after treatment) occurred on the days of application. The highest concentration recorded following granular treatment was 0.31 µg/L, well short of the expected 4 µg/L. Concentrations rose sharply to 4.7 µg/L at one location immediately after the final emulsion treatment, declining to 3.0 µg/L at 2 hours post-treatment and 1.2 µg/L at 4 hours. All other concentrations remained below 1.5 µg/L, well below the theoretical concentration of 17.5 µg/L that would result from immediate distribution through the water column. The authors attribute this shortfall to sorption to suspended solids and sediment, dilution from rain, and/or hydrolysis. Volatilisation may also be expected to contribute. The outlier occurred along the northern walkway, consistent with movement of spray droplets or the expected surface slick of chlorpyrifos under the influence of a prevailing southerly breeze. Water samples along all walkways shared a common pattern of rapid decline in the first three days after treatment. This was followed by a more gradual decline, with concentrations remaining below 0.4 µg/L from four to fourteen days post treatment and generally below 0.3 µg/L for the next six weeks. Sediment residues ranged up to 8.2 mg/kg (mean 0.42 mg/kg) with no clear trends apparent.

Bioassays used laboratory reared bluegills (mean weight 2.6 g) tethered in cages near the surface in 30 or 60 cm water. The two granular treatments produced only minimal effects on bluegill survival, which was not unexpected as the peak residue recorded in the water column (0.31 µg/L) was below toxic levels. In contrast, the spray application produced substantial bluegill mortality, particularly in deeper water, although differences with water depth were not statistically significant. Complete mortality occurred in freshly caged fish, which may be less resistant because of handling stresses and toxicological naivete. Control survival was 63%, but can not be directly compared with the treatment pond because the spray treatment was characterised by a pronounced sag in dissolved oxygen levels which would have further stressed the fish.

Horizontal zooplankton tows (80 µm net) found rapidly increasing total zooplankton numbers in late May and early June in the treatment pond but a marked decline with the 2nd treatment on 20 June. The reference pond developed differently, with lower zooplankton density until rotifers (*Keratella* sp) increased dramatically in late June. Rotifers in the treatment pond increased from 27% of the zooplankton population to 46% after the 20 June application, with corresponding declines in cladocerans (2.2 to 0.6%) and immature copepods (65.1 to 29.3%, part of the decline reflecting development to adults). Cladocerans recovered to represent 13.5% in September/October, and rotifers increased their dominance to represent 67%. The

reference pond had a different zooplankton community, with rotifers dominant early but declining to 0.2% in September/October, at which time cladocerans represented 58% of the population.

Funnel trap sampling in littoral areas to catch upward migrating zooplankton at sundown was used in July because heavy vegetation precluded use of the nets. Some cladoceran species were preferentially collected using this technique. A general patchiness of distribution was noted, even in small areas. Catches declined after the July treatment but populations then appeared fairly steady through to September. Reference pond populations remained steady until a dramatic increase in cladoceran numbers in September.

The cladoceran *Daphnia catawba* was particularly sensitive, with declining populations following the first treatment and eradication by the second, but limited repopulation in October, apparently from a recent ephippial hatching. Declining populations were also evident in the reference pond in early June, perhaps because of predation by chaoborid (phantom midge) larvae, but populations increased dramatically later in the month, probably reflecting reduced predation by chaoborid larvae as adults emerge. Other daphnid species (*Daphnia pulex*, *Chydorus sphaericus*, *Ceriodaphnia pulchella*) were also eradicated by the 20 June treatment.

Rotifer and cyclopoid copepod populations were less clearly affected than cladocerans and benthic invertebrates. On-site bioassays found lethal effects in *Daphnia*, the amphipod *Hyalella azteca* (which was virtually eliminated by the 2nd treatment), the backswimmer *Plea striola* (which also suffered severe population reductions by the end of June) and mosquito larvae (*Aedes* sp). Laboratory bioassays confirmed these findings, with levels of 0.1-0.4 µg/L toxic within 24 hours to cladocerans, anostracans, chironomids and mosquito larvae. The laboratory sensitivity of other species varied between 0.33 and 3.17 µg/L (Siefert, 1984).

7.1.2.15 Minnesota pond studies in littoral enclosures

Studies in summer 1986 were conducted in a different pond using littoral enclosures (average maximum depth 1.1 m) extending some 10 m into the pond from 5 m sections of natural shoreline. The pH of the pond water varied between 7.92 and 8.45. Chlorpyrifos was applied as an EC spray on 16 June at rates of 2.6, 28 and 123 g/ha to achieve target concentrations of 0.5, 5 and 20 µg/L. The two higher doses were replicated 4 times, and low dose and control enclosures replicated twice. Four 1 L water samples per enclosure were collected from approximately mid-depth at intervals to 128 days, with more detailed sampling on the day of application including the collection of samples at 20 minute intervals from various depths in one of the high dose enclosures to determine rates of vertical mixing immediately after treatment. Sediment samples were taken to 420 days, using in-situ vessels deployed in one enclosure for each concentration, and core samples from one high dose enclosure. Invertebrates were monitored using funnel traps and artificial substrate samplers, and in-situ bioassays were conducted with fish and invertebrates.

Mean maximum concentrations in water samples of 0.51, 6.29 and 32 µg/L were found 1 hour after treatment, declining by half in 12-18, 8-10 and 4-6 hours, respectively. A more gradual dissipation prevailed from 12 hours after treatment. Concentrations and degradation curves were consistent between replicates. Vertical mixing studies in one of the high dose enclosures found no chlorpyrifos below 7.6 cm 20 minutes after application, with no detections near the bottom for an hour and 55% remaining in this surface layer 2 hours after treatment, with 3.6% near the bottom. Less than 10% could be found at mid-depth during this initial 2 hour period of intensive sampling.

It is difficult to reconcile the initial slow rates of mixing with the detection of high concentrations (32 µg/L) in water samples taken from mid-depth in the high dose enclosures at 1 hour after application. There appears to be some bias in the results from samples collected at mid-depth. The samples appear to represent near surface rather than mid-depth concentrations as intended. Overestimation of initial concentrations would help explain the steep loss curve recorded soon after application.

Adsorption studies in the laboratory involving equilibration in inverted scintillation flasks of aqueous chlorpyrifos solutions with discs of the polyolefin used, as a liner on the flask caps, found 75% partitioning to the plastic at equilibration after 200 hours. The degree of adsorption was found to be directly proportional to the initial concentration. Data obtained allowed the prediction, based on the unrealistic worst case assumptions of constant chlorpyrifos concentrations in the water column for 200 hours and no biological fouling of the plastic, that less than 4% of the chlorpyrifos added to the pond would partition to the plastic enclosure walls.

Results from analyses of water and sediment samples are tabulated below as percentages of the original application, with aquatic residues at later sampling times when concentrations had declined below detectable levels determined by linear regression (see italicised entries). Chlorpyrifos quickly dissipates from water, but with relatively minor amounts partitioning to sediment. Residues dissipate slowly from the sediment phase with an empirically determined half-life of 32 days at high dose, extending to 64-128 days at low dose. Rapid initial declines from water are likely to reflect high rates of volatilisation soon after treatment, as the method of application would be expected to leave a surface slick of chlorpyrifos which would be prone to volatilisation. Further losses would occur through degradation, uptake and metabolism by biota, and sorptive interactions with aquatic vegetation and the walls of the enclosures, but appear insufficient to account for the initial dramatic declines in aqueous concentrations.

The significance of volatilisation as a dissipation pathway is difficult to assess quantitatively as dispersion of the surface film into bulk water will greatly reduce the rate of volatilisation, and the rate of dispersion of the applied emulsion through the water column is not known but could be rapid. However, several lines of evidence support the occurrence of volatilisation, including the observation that the initial half-life varies inversely with concentration dosed to the microcosms. This inverse relationship is consistent with a slower dispersion into the water column at higher doses, which in turn is consistent with a higher concentration of chlorpyrifos in the spray emulsion used to treat the higher dose microcosms. All microcosms received the

same volume of spray emulsion, with concentrations ranging from around 1.3 mg/L (approximately the water solubility) for the low dose, up to about 80 mg/L (well above aqueous solubility) for the high dose microcosms.

Time since treatment	High dose		Medium dose		Low dose	
	Water	Sediment	Water	Sediment	Water	Sediment
12 hours	68.4%	n/a	83.6%	n/a	65.6%	n/a
1 day	22.5%	3.2%	22.6%	3.8%	44%	3.3%
64 days	0.17%	0.95%	0.3%	0.8%	*0.7%*	1.5%
420 days	*0.04%*	0.5%	*0.08%*	0.3%	*0.1%*	0.6%

Microinvertebrate species abundance as determined from funnel traps was similar across enclosures before treatment, but changed markedly after chlorpyrifos application. Cladocerans were most sensitive, with major reductions in the 5 species collected at all treatment levels. Ostracods were also heavily impacted at all treatment levels. Copepods appeared less sensitive, although 3 species were significantly reduced in at least one treatment level, as were 5 species of rotifer. Some signs of recovery were apparent by day 64, and species richness returned to normal by day 350. Abundances remained depressed, even in controls, suggesting seasonal or enclosure effects. Indirect impacts were also evident at 350 days after treatment, with copepod abundances in medium and high treatments some 3-4 times higher than in controls. Significant increases in phytoplankton chlorophyll a were observed 8 days after treatment, reflecting the depleted numbers of grazing zooplankton. Significant increases in periphyton dry weight also occurred at this time.

Macroinvertebrate species richness as determined from artificial substrates was reduced relative to controls on days 4, 16 and 64, but had largely recovered to be only slightly below control levels by a year after treatment. Total insect abundance was markedly affected, being 75, 4 and 0% of controls at 16 days after treatment. Recovery occurred in low dose enclosures, with insects (especially chironomids) more abundant by day 64, but numbers in medium and high dose enclosures remained below 25% of controls at this time, and were still below 37% a year after treatment. However, some insects were more abundant in the open pond than controls at this time, suggesting interference from enclosure effects. No toxicity was observed in snails, clams, flatworms and leeches, with one snail species (*Helisoma anceps*) increasing in number, presumably because there was more vegetation to forage on in treated enclosures.

Fish bioassays were conducted in situ in stainless steel cages (30 cm deep, 60 cm diameter) tethered at the water surface. Fathead minnows (2-3 months old) survived 96 hours of exposure, but were sluggish and anorexic for 48 hours in the high dose enclosures, with 3 fish found dead after 144 hours. Longer term studies with larvae of this species found reductions in growth rate at higher exposures, apparently caused in part by reduced invertebrate food resources. Bluegill sunfish (3 months old) survived low dose and control exposures, but suffered 38 and 99% mortality, respectively, after 96 hours in medium and high dose enclosures. Symptoms such as erratic swimming and body spasms were observed during the early stages of exposure, but with 90% remission in survivors at 144 hours. The estimated field 96 hour LC50 for this more

sensitive species, based on 24 hour weighted average concentrations, was 2.67 µg/L, in good agreement with laboratory data (Siefert, 1988; Knuth and Heinis, 1992).

7.1.2.16 Artificial drainage ditches

PVC lined mesocosms (40 m long, 3.4 m wide at water surface, volume 60 m^3) containing 50 cm standing water underlain by 25 cm sandy loam sediment, almost completely covered by vegetation two years after establishment, were treated along their entire lengths by boom with chlorpyrifos spray emulsion. Target concentrations were 0.1, 0.9, 6 and 44 µg/L. Actual concentrations were estimated by measuring the stratification and by taking depth-integrated water samples.

Highest concentrations of chlorpyrifos were initially found near the water surface. Complete mixing occurred within a day in open water but was delayed for 2-4 days where macrophytes were abundant. Mean concentrations declined from 40-50% of nominal a day after treatment to 1-3% after 28 days. After the initial brief period of partitioning, chlorpyrifos declined from the water column with half-lives of 10-18 days.

Acute effects became apparent within 24 hours of treatment. The lowest dose appeared to approximate the NOEC for the mesocosm as skimming yielded similar numbers in controls. Acute effects at this low dose were restricted to insects (van Wijngaarden *et al*, 1996).

Redundancy analysis of macroinvertebrate and zooplankton samples collected for 55 weeks after treatment revealed direct effects on Crustacea and Insecta, with rapid, dose-responsive decreases in numbers after treatment. Indirect effects were also apparent, with gastropods and Oligochaeta increasing in number. The lowest concentration (nominally 0.1 µg/L) under this acute dosing regime was found to approximate the NOEC at both species and community level. Invertebrate communities recovered by 24 weeks after treatment (van den Brink *et al*, 1996).

7.1.2.17 Artificial stream studies in Queensland

Outdoor artificial stream systems (40 m long, 40 cm wide) were dosed continuously for 21 days with chlorpyrifos at nominal concentrations of 0.1 or 5 µg/L. Chironomids, the dominant colonisers of the streams, were significantly reduced by treatment, with some species eliminated, but had recovered by 70 days after treatment. Reduced abundance was also seen in copepods and cladocerans. Total invertebrate abundance and Shannon-Weaver diversity were reduced by both high and low doses. Evenness increased in high dose streams, as expected given reduced diversity, number of taxa and abundance.

Periphyton density increased with decreased grazing pressure, and one species of gastropod mollusc also increased in number. Periphyton biomass was found to be higher in the high dose stream 21 days after dosing ceased, apparently reflecting slow recovery of planktonic grazers (Ward *et al*, 1995).

Earlier studies at the same nominal concentrations used an acute exposure period of 6 hours. Gas chromatographic analysis of upstream water samples from the high dose streams at the end of the dosing period revealed concentrations of 2.70 and 3.18 µg/L, declining to 2.43 and 1.97 µg/L, respectively, in downstream samples. For the low dose stream, mean concentrations were 0.06 µg/L with small decreases (0.01 µg/L) downstream. Only minor shortfalls from target concentrations are apparent as analytical recoveries from standard samples were 60-70%.

No significant reductions were found in numbers of taxa, but there were significant reductions in invertebrate density at the higher dose. These effects were apparent for at least the first 10 days after dosing, but in-treatment variability between samples reduced statistical power to detect them. Reduced invertebrate density in the lower reaches was a general characteristic of the streams, but density in the high dose streams was fairly uniform for the first 38 days after dosing. Chironomids were the dominant stream fauna, and reduced invertebrate densities were mainly due to chironomid impacts. Four chironomid taxa were reduced at the high dose, but no extinctions were apparent, and indices of diversity could not distinguish between the two treatments. However, reductions in dominant species would be expected to increase rather than decrease diversity. The major effect was disruption of the normal pattern of community succession in the high dose stream, with rapid recovery within 2 weeks of the disturbance. Recovery was rapid because of colonisation by chironomids, organisms with short generation times that tend to predominate in artificial streams. In natural environments inhabited by species with longer generation times, recovery may take longer.

The study shows that pulse dosing with chlorpyrifos at 0.1 µg/L has no effect on artificial stream communities, but that higher concentrations (5 µg/L) exert marked effects (Pusey *et al*, 1994).

7.1.2.18 Artificial stream studies in Minnesota

The effects of chlorpyrifos under different dosing regimes have been studied in Minnesota in outdoor artificial streams (520 m long with surface area 0.14 ha) each containing 9 mud-bottomed pools (30.5 m long, 3.6 m wide, 76-86 cm deep) alternated with 8 gravel riffles (typically 30.5 m long, 2.4 m wide, 10-20 cm deep). Water was continually pumped from the nearby Mississippi River to provide a flow of about 4.5 L/minute. Chlorpyrifos (emulsion concentrate) was continuously introduced over a 100 day period in summer 1981 at a concentration of 0.22 µg/L, or fortnightly for 24 hour periods at 3.1 µg/L. Concentrations were increased after 22 days to compensate for a 40% shortfall in measured concentrations, and further after 41 days to nominal concentrations of 1.01 and 11.5 µg/L in order to obtain the desired level of biological effect.

Concentrations measured at the upstream ends increased through the study from 1.9 through 2.8 to 7.0 µg/L for the stream receiving pulse dosing, and declined by about half by the time they reached the downstream sections. The half-life of chlorpyrifos in a 4 L water sample set aside beside the stream was about 11 days.

The biological study area of each stream (245 m near the upstream end) contained a naturally colonising plant and invertebrate assemblage, and was stocked with bluegills and fathead minnows. Screens were used to isolate different species in different sections, with fathead minnows in the upper reaches, bluegills in the middle sections and wild suckers at the downstream end.

Unfiltered water samples were taken from midstream several cm below the surface, on roughly a daily basis in the three sections of the biological study area for continuous dosing, with more intensive sampling surrounding the pulse events.

Benthic samplers were used to determine riffle benthos abundance and diversity, and organism drift to the downstream end of the second riffle was determined with nets. Sampling revealed that considerable differences in relative abundance of dominant species and total numbers of macroinvertebrates existed between streams before treatment. The two streams receiving chlorpyrifos rapidly became dominated by isopods while riffle benthos in the control stream evolved less rapidly, with amphipods displacing isopods to become dominant. Daytime samples found relatively high numbers of drifting amphipods in continuously treated streams, whereas this was mainly a nocturnal phenomenon in the undosed control. Pulse dosing gave rise to a statistically significant drop in the mean number of invertebrate taxa sampled and a corresponding drop in the number of organisms collected. Amphipod bioassays in floating baskets found about 50% immobilisation or death during pulse dosing, when mean measured concentrations were in the range of 1.7-2.5 µg/L, but no effects during continuous dosing at an estimated 0.15 µg/L. Laboratory bioassays showed similar responses.

Fathead minnows sampled in August towards the end of the dosing period had a roughly 20% incidence or deformities such as scoliosis under pulse dosing, but deformities reduced to about 2% under continuous dosing. No other effects were noted on survival, growth or reproduction of stocked fish, but behaviour of caged bluegills was affected under pulse dosing, with symptoms of lethargy and some fish exhibiting tetanic spasms. Unstocked fish (white suckers) were found dead or dying in downstream sections following pulse dosing (Eaton *et al*, undated).

7.1.2.19 Fish kills in agricultural areas

Aquatic exposure to chlorpyrifos in agricultural areas occurs as pulses against a background of low or non-detection. Concentrations that would be lethal to some fish are recorded from time to time, but chlorpyrifos has not been identified as the definite causal factor for any fish kills in these areas. However, causal factors are frequently not identified, particularly if pesticides such as chlorpyrifos with relatively low aquatic persistence are involved. It is often too late to diagnose causal factors by the time such incidents are detected.

Fish kills in cotton growing areas have been compiled by Bowmer *et al* (1996). Chlorpyrifos was present in the water of Wee Waa Lagoon in October 1989, following a kill incident involving more than 600 fish (golden perch, Murray cod, bony bream

and European carp). A number of other incidents are attributed to unidentified cotton pesticides in suspected tailwater releases or spray drift.

An older review (Whyte and Conlon, 1990) concluded that chlorpyrifos presented low aquatic risk in NSW cotton areas because of the insignificant amounts used, estimated at the time to be below 0.01 kg/ha, or just 3% of all organophosphate sprays. The low historical incidence of chlorpyrifos related fish kill incidents reflects low exposure rather than low toxicity. Recent sharp increases in the volume of chlorpyrifos used on cotton would significantly increase the risk of such incidents occurring.

Fish kills are more common in and around urban areas, where chlorpyrifos is applied at high rates to bare soil for termite protection. It appears that these incidents, which are documented in sections 5.1.3.3 and 5.1.3.4, reflect careless use.

7.1.3 Non-target Terrestrial Invertebrates

Acute oral and contact testing using technical material and an emulsifiable concentrate found chlorpyrifos to be highly to very highly toxic to honey bees. Semi-field studies using a microencapsulated formulation applied at 800 g/ha to flowering ground cover confirmed that chlorpyrifos is harmful to bees, with peak mortality after a few days, presumably reflecting delayed release from the microcapsules.

Artificial soil tests in three laboratories found chlorpyrifos to be slightly toxic to the earthworm *Eisenia foetida*, but with weight loss at sub-lethal concentrations. Reviews indicate other species to have similar acute sensitivity, and to suffer reproductive impairment at concentrations above 100 ppm.

Testing with short-winged beetles found chlorpyrifos (1 kg/ha) to be very harmful to their parasitisation capacity. Sevenspotted lady beetles were completely killed by chlorpyrifos at relatively low rates (180-400 g/ha) with mortality remaining above 50% at 7 days after treatment. Testing in an apple orchard found chlorpyrifos (1 kg/ha) to be highly toxic to all beneficial arthropod groups, but limited residual activity meant that impacts were relatively short-lived with recovery apparent after 10 days. Impacts to beetles, spiders and collembola were also evident in pasture sprayed at 750 g/ha, with some weeks needed for recovery.

Chlorpyrifos residues appear to impair microbial processes in some soils, even at normal application rates, but to exert no adverse influences in other soils, even at elevated rates (5-8 kg/ha). Some microbial species, particularly fungi, appear to be highly susceptible, and the metabolite TCP is reported to have some microbial toxicity.

7.1.3.1 Bees

Oral and contact administration to honey bees (*Apis mellifera*) of an emulsifiable concentrate formulation of chlorpyrifos revealed high to very high toxicity. Contact testing involved administration of the test substance in 1 µL acetone to the ventral thorax of anaesthetised bees. Oral testing on groups of 10 bees involved provision of 20 µL spiked sucrose solution per bee, an amount consumed in about 3 hours. The

48 hour contact and oral LD50s, expressed as nominal concentrations of chlorpyrifos, were 0.10 and 0.15 µg/bee, respectively. Toxicity was similar whether determined 24 or 48 hours after dosing (Bell, 1993).

Analogous testing with technical chlorpyrifos returned 48 hour LD50s of 0.027 µg/bee (contact) and 0.040 µg/bee (oral), indicative of very high toxicity. Similar sensitivity was again observed over 24 hour timeframes (Bell, 1994).

Semi-field studies were conducted in Germany on small honey bee hives in screening tents with flowering phacelia, treated with a 250 g/L microencapsulated formulation as a 0.4% spray mix at 800 L/ha (equivalent to 800 g/ha chlorpyrifos). A slight decrease in flight intensity occurred immediately after treatment in one of two replicates, but with return to pre-application intensity after 1 hour, indicating that the test substance does not repel bees. The toxic standard (triazophos) caused a clear decrease in flight activity. Mortality in bee traps at the hive entrance and on linen sheets around the cage wall was markedly higher than controls following treatment, by an order of magnitude in one replicate, and slightly higher than for the toxic standard. Peak mortality was delayed for 5 days in one replicate and 2 days in the other, presumably reflecting delayed release from the microcapsules. The toxic standard caused maximum mortality the day after treatment. Chlorpyrifos is harmful to bees under these conditions (Tornier, 1995).

7.1.3.2 Earthworms

Chlorpyrifos (emulsion concentrate) was slightly toxic (14 day LC50 = 142 ppm) to the earthworm *Eisenia foetida* in an artificial soil test. The NOEC was 57 ppm, based on mortality and weight loss at 114 ppm. All deaths occurred during the first 7 days of the study (Johnson, 1993).

The 14 day LC50 to this species was 210 ppm when the test was repeated using technical chlorpyrifos. The LC50 after 7 days was 298 ppm (Rodgers, 1994).

Further testing with a 45.4% emulsifiable concentrate (31.25-1000 ppm) returned a 14 day LC50 of 163 ppm, based on nominal concentrations of chlorpyrifos. Burrowing times, being the time from placement of ten worms at test initiation to complete burial, varied dose responsively from 8 to 45 minutes, compared with 6.8 minutes in controls, suggesting some repellency. Mortality in the three highest treatments (113, 227, and 454 ppm chlorpyrifos) reached 15, 85 and 100%, with some of the survivors being lethargic. Control earthworms lost an average 3.25 mg, as expected given a lack of feeding through the exposure phase. Weight loss in worms that survived chlorpyrifos exposure varied dose responsively from 16.9 to 178 mg (Candolfi, 1995).

Data for six earthworm species are reported in the review by Barron and Woodburn (1995). Acute LC50s range from 104-262 ppm in *Lumbricus rubellus* to 1174 ppm in *Eisenia vereta*. The EC50 based on reproduction in *Lumbricus rubellus* was 121 ppm, with a NOEC of 4.6 ppm, and in *Eisenia vereta* 121 ppm, with a NOEC of 49 ppm.

7.1.3.3 Short-winged beetles

The effects of chlorpyrifos on fertility/parasitisation capacity of the short-winged beetle (*Aleochara bilineata*) was examined in laboratory bioassays. Adult short-winged beetles predate on eggs and young larvae of various insects, and larval beetles develop parasitically in the puparia of various diptera.

Bioassays involved placement of 10 beetle pairs (3 days old) beneath layers of moist sand followed by spray application of chlorpyrifos (480 g/L emulsion concentrate at 2 L/ha in 600 L/ha water). Beetles were fed five times a week on frozen midge larvae, and provided with onion fly (*Delia antiqua*) puparia (500 per beetle) on days 8, 16 and 22 after treatment. Covers were removed to allow sand to dry on day 29, and a week later puparia were removed by sieving. The sand was allowed to dry out further until hatching was complete some 6-8 weeks later. Opened puparia were counted, and compared with numbers obtained in controls. Closed puparia were microscopically examined to determine whether they had been parasitised.

The effects of chlorpyrifos on parasitisation capacity of short-winged beetles was very harmful, with no beetles hatching after treatment, compared with 40.7% in controls, and no puparia parasitised, compared with 51.7% in controls (Moreth, 1992).

7.1.3.4 Sevenspotted lady beetles

Residual toxicity of chlorpyrifos to the sevenspotted lady beetle (*Coccinella septempunctata*) has been investigated following two applications to rape, separated by 20 days. This beneficial predator is a voracious consumer of aphids. Chlorpyrifos was applied as spray emulsions (180 and 240, or 300 and 400 g/ha) or dusts (250 and 375 g/ha). Beetles (5 grubs and 10 adults) were exposed in petri dishes to leaf discs collected from the crop at various intervals after treatment.

Mortality of small grubs (8±1 mm) was complete for samples collected immediately after treatment and the following day, and remained above 50% at 7 days after treatment. Dust treatment left the most residual activity. Late instars (16±1 mm) and adults were only slightly less sensitive. The reference toxicants quinalphos and oxydemeton-methyl exhibited less residual toxicity (Thomas and Phadke, 1991).

7.1.3.5 Beneficial arthropods in apple orchards

A semi-abandoned apple orchard in Southern France was marked into a block design with two replicates and four treatments, each containing about 100 trees. Plots were treated in June 1991 with Reldan 50EC (chlorpyrifos methyl), Dursban 4EC (chlorpyrifos), Gusathion M (azinphos methyl) or water (control), applied in two passes by mist blower in 1000 L/ha water. The application rate for chlorpyrifos was 960 g/ha.

Three different sampling methods were used throughout the study. Visual observation for spider mites (*Panochus ulmi*) and aphids (*Aphis pomi*) was done on 50 leaves per replicate. Invertebrate fauna were sampled by inventory spraying (3 trees per

replicate) using the volatile dichlorvos to penetrate niches in bark and foliage, and by beating ten branches per replicate. Spray date collections were also made on 3 trees per replicate. All sampling methods relied on mylar collecting sheets.

Chlorpyrifos was found to be highly toxic to all beneficial arthropod groups, but also killed the largest numbers of spider mites, aphids and other phytophagous groups. Effects on predator and parasite populations within the treated area were relatively short-lived. For example, ladybird beetles (*Chilocorus bipustulatus*) were not found at 4 days after treatment, but recovered quickly as adults emerged from pupae, reaching similar populations to control plots by 10 days after treatment. Juvenile earwigs (*Forficula auricularia*) also showed signs of recovery at this time, after suffering heavy casualties. Large numbers of spiders were killed by treatment, but populations were apparently unaffected. Chlorpyrifos has limited residual activity on foliage, allowing repopulation by beneficial species through immigration or development from protected juvenile stages (Brown, 1991).

7.1.3.6 Beneficial arthropods in pasture

Chlorpyrifos (Dursban 4EC) was applied at 750 g/ha in spring 1992 by boom in 200 L/ha water to triplicate 1.5 ha plots of Devon pasture with a history of low pesticide inputs. Good populations of the major predatory arthropod groups (carabid beetles, staphylinid beetles and spiders) were present. Pitfall trapping was used to determine initial acute effects, recovery through summer and autumn, and arthropod abundance and diversity the following spring. Residual toxicity to 28 days was determined using bioassays on soil cores with the noctuid moth *Agrotis segetum*, a target cutworm species readily cultured in the laboratory, placed as larvae on the grass surface.

Carabid beetles declined sharply following treatment but recovered to about 50% of control levels after 3 weeks, and reached control levels by the end of summer. A marked reduction in staphylinid beetles was also evident, with some recovery after about 2 weeks but generally lower populations through summer. The sub family Aleocharinae appeared particularly sensitive and were found in significantly lower numbers relative to controls in the following spring. The spring population of linyphiid spiders was affected by treatment, with numbers remaining low for about 7 weeks until the mid summer increase, which occurred a week later than in controls. Treatment was also harmful to Collembola, reducing numbers to very low levels for 5 weeks.

Mortality of *Agrotis segetum* on soil cores declined from about 100% immediately after treatment through 59% on day 9 to 45% on day 14. No residual toxicity remained at 28 days after treatment. Bioassay and trapping results indicate that chlorpyrifos delivers residual activity for about 3 weeks after application (Brown, 1993).

7.1.3.7 Soil microorganisms

Treatment of soils at label rates (3 L ha Dursban 4 EC containing 480 g/L chlorpyrifos) and a fivefold overdose inhibited soil respiration, as indicated by reduced

dehydrogenase activity. Inhibition in a sandy soil reached 20% at the higher dose after 28 days before returning to normal. Inhibition was delayed in a silt loam, reaching 30% after 56 days and 50% after 84 days at the higher dose, and 18% after 84 days at the normal field rate. Nitrogen mineralisation was affected in both soils, but there were no long-term inhibitory effects (McGibbon *et al*, 1989).

Dehydrogenase activity was reduced in one of two sandy loam soils treated with Dursban 4EC at 10 L/ha, but the result is not considered reliable because dehydrogenase activity had fallen to a low level in all samples. There was also a slight retardation of the rate of nitrification in this soil, but nitrification was complete within 3 weeks (Baloch and Todt, 1990).

No significant effects on respiration and nitrification were noted in two sandy loams treated with Dursban 4EC at 2 and 10 L/ha (Baloch and Hund, 1990).

No ecologically significant effects on soil dehydrogenase activity were noted in 3 soils treated at normal application rates (3.1 mg/kg). Inhibition was more pronounced at higher doses, but only exceeded 50% in one soil (Speyer 2.1) where microorganisms were stressed by low organic matter content (Greaves and Shales, 1991).

While results are favourable, it needs to be noted that respiration, ammonification and denitrification are not good indicators of microbial toxicity. These soil processes can be maintained in the face of significant toxic impacts as resistant microbes increase their populations at the expense of sensitive species (van Beelen and Doelman, 1997).

A more recent study examined the impacts of chlorpyrifos on soil microbial populations by determining total viable cell numbers on nutrient media. The LC50 for bacteria was 660 ppm on the first day after treatment and 300 ppm on the third. Fungi were more sensitive, being totally inhibited even at 1 ppm (Desai, 1996).

As noted in section 5.2.3.2, the metabolite TCP appears to exert toxic effects on soil microbes.

7.1.4 Reptiles

As noted in section 6.1.1.9, two reptiles (a turtle and a snake) were suspected casualties of high rate (4.5 kg/ha) chlorpyrifos treatment of golf courses in Florida.

Information is also available from sub-Saharan Africa where chlorpyrifos is one of a number of pesticides used to control locusts. Widespread mortality (> 100/ha) of two lizard species (*Acanthodactylus boskianus* and *A dumerili*) was observed 8 hours after application of chlorpyrifos at 240 g/ha to control immature desert and mature tree locusts in Mauritania. A large monitor (*Varanus albigularis*) was found moribund from acute poisoning 24 hours after treatment at 387 g/ha to control acridid nymphs and adults in Senegal. Its stomach was filled with contaminated beetles, grasshoppers and other invertebrates (Lambert, 1997).

7.1.5 Mammals

Reported oral LD50 values (62-2000 mg/kg body weight) indicate that chlorpyrifos has slight to moderate acute mammalian toxicity. Mammals appear to be less acutely sensitive than birds. Mammals and birds appear to have comparable chronic sensitivity to chlorpyrifos (Barron and Woodburn, 1995).

7.1.6 Phytotoxicity

Absorption and translocation of foliar deposits of chlorpyrifos is very low, with the bulk dissipating through volatilisation. Absorption by roots from the soil is also poor, although uptake of TCP can be extensive, depending on pH.

Phytotoxicity testing was conducted in standard potting medium with foliage and woody landscape plants. There was a reduction in nonroot biomass in African violets, two varieties of Azalea and one of Ilex exposed to 75.6 mg/kg chlorpyrifos, applied as granules to the soil. No other phytotoxicity was apparent in the 39 cultivars tested. For surface sprays with chlorpyrifos emulsions, reductions in root biomass were noted in most of the 11 cultivars tested at 25.6 or 75.6 mg/kg. Germination and emergence were reduced in mustard at soil concentrations of 26-75 mg/kg (Barron and Woodburn, 1995).

Some phytotoxicity is also evident from field use, as noted in the agricultural assessment. Turf may be affected if its nutritional status is low. Phytotoxic reactions have been reported in the floriculture industry in such species as azaleas, camellias, poinsettias and roses. A high rate off-label use caused damage to potatoes in Western Australia. High volume sprays of chlorpyrifos emulsion are phytotoxic to immature banana fruit.

7.1.7 Summary of Environmental Toxicity

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

7.1.7.1 Birds

Detailed test reports on acute oral toxicity were submitted for the standard test organisms, bobwhite quail and mallard duck. A comprehensive literature review including data for a much wider variety of species was also submitted. Chlorpyrifos has been shown to be highly to very highly toxic (LD50s below 20 mg/kg) to several species (house sparrow, red-winged blackbird, Japanese quail, ring-necked pheasant, common pigeon and mallard duck) when administered as an acute oral dose, although there are other results available for some species indicating lower toxicity. Acute oral testing is compromised by the tendency of some birds, notably mallards, to regurgitate the test material. Testing with quail indicated the metabolite TCP to be practically nontoxic by the acute oral route.

Detailed dietary toxicity test reports were submitted for bobwhite quail and mallards. Dietary toxicity is moderate to high, with mallards becoming anorexic when dietary concentrations exceed 100 ppm. Choice tests with young mallards offered the option

of food contaminated with 112-1124 mg/kg chlorpyrifos revealed an ability to discriminate in favour of clean feed. Earlier studies indicated that some other birds share this ability, with the onset of repellency between 1000 and 10000 mg/kg chlorpyrifos. However, pheasants, which are highly sensitive to chlorpyrifos, suffered mortality following consumption of food contaminated with 10000 mg/kg chlorpyrifos, with no sign of any repellency. The metabolite TCP was found to be practically nontoxic to mallards.

Chlorpyrifos does not appear to have significant reproductive toxicity based on testing in bobwhite quail and mallards. Reproductive performance was compromised in mallards at elevated dietary concentrations (above 100 ppm) as the birds stopped eating and lost condition, but this appears to reflect nutritional deficiencies rather than true reproductive toxicity. Reproductive parameters remained unaffected in bobwhite quail fed at 125 ppm.

Overseas studies have found little evidence for avian impact. Geese grazing on pasture sprayed at 0.72 kg/ha were clearly exposed to chlorpyrifos as residues were found in excreta, but suffered no ill effect. No dead birds were found when golf courses in Florida were closely monitored after treatment at relatively high rates (4.5 kg/ha) for grubs and crickets. Studies in Iowa corn at lower rates (1.1-3.4 kg/ha) found only two American robins as possible chlorpyrifos casualties, despite abundant bird life and significant residues in vegetation and insects. Similar studies in California citrus found some changes in abundance following a high rate treatment (6.7 kg/ha) but these were thought to reflect avoidance rather than mortality. Field studies in Senegal found a few avian casualties following application of chlorpyrifos at 280 or 387 g/ha for grasshopper control. Post-treatment reductions in avian populations appeared to reflect reduced food resources. In general, field studies in which birds were abundant provided little indication of chlorpyrifos related effects on birds. The notable exception is a study in freshwater ponds in California in which significant mortality of mallard ducklings was recorded following application of chlorpyrifos to the water at rates of 11-1120 g/ha. Birds apparently died as a result of consuming contaminated water boatmen, but the study is old and causal factors can not be firmly established.

There are some reports of adverse avian impact from use of chlorpyrifos in Australia. Again, these appear to involve the consumption of contaminated invertebrates. Occasional bird kills (scavenging species such as crows and butcher birds) have been reported in association with the use of chlorpyrifos baits to control surface feeding insects in cotton, sorghum, sunflowers and maize. There is a report of dead magpies that were found following treatment of power poles to treat termites, with contaminated worms apparently responsible. A granular ant control product was recently reported to have killed a number of pigeons at a Darwin residence. Chlorpyrifos may have been the cause of a major incident at an ibis rookery in the Macquarie Marshes in early 1995 in which large numbers of nestlings died, apparently from consumption of contaminated invertebrates brought back to the nest by parents.

Isolated avian incidents have also been reported from overseas, with chlorpyrifos specifically identified as the causal factor in some. Abnormally high levels of

chlorpyrifos and other organophosphates were found in dead shorebirds following relatively large incidents in Florida in 1997.

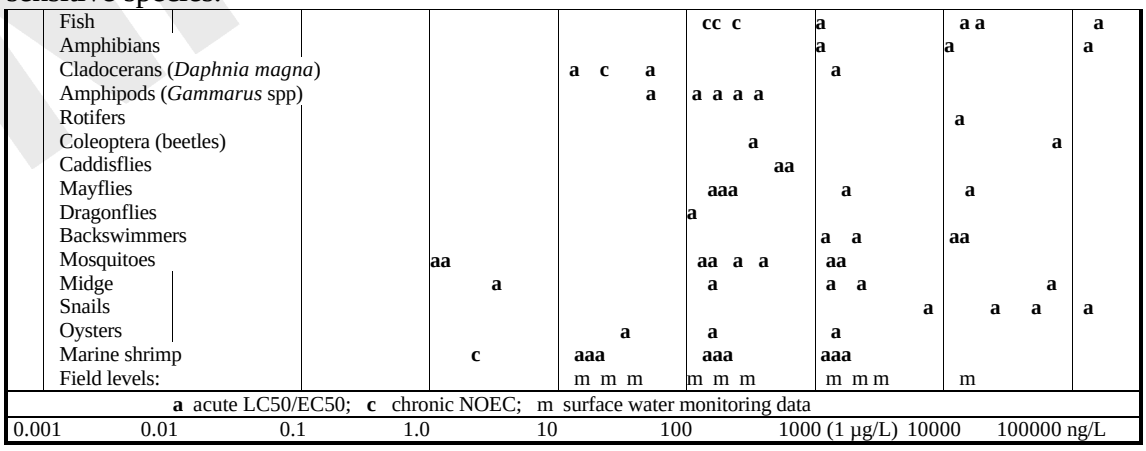
Reported avian incidents, while relatively few, appear inconsistent with the generally favourable outcomes from field studies. One explanation may be the much higher toxicity of chlorpyrifos oxon, which may reach significant levels in contaminated invertebrates. This does not appear to have been specifically investigated, and may have been overlooked. Chlorpyrifos oxon would probably remain undetected using standard analytical procedures because of its instability.

7.1.7.2 Aquatic organisms

Extensive testing shows chlorpyrifos to be highly to very highly toxic to fish, aquatic arthropods, oysters and algae. Limited data suggest that some amphibians may share similar sensitivity. Acute LC50s for freshwater and marine fish are typically below 100 µg/L, with bluegill sunfish sensitive at around 2 µg/L. For invertebrates, acute LC50s are typically in the 0.1-10 µg/L range. Algal endpoints are typically above 100 µg/L, but with one well reported result of 64 µg/L for the sensitive freshwater species, *Selenastrum capricornutum*. Testing with fish and invertebrates shows the metabolite TCP to be slightly to moderately toxic, consistent with its hydrophilic character.

Chronic exposure of rainbow trout resulted in complete mortality at low concentrations (2-3 µg/L). The NOEC was 0.5 µg/L. Life-cycle testing with fathead minnows returned a similar NOEC, with larval mortality observed at concentrations in the order of 1 µg/L. Semi-static reproductive testing with *Daphnia magna* found a no effect concentration of 0.056 µg/L. Complete mortality occurred within 21 days at the next highest test concentration, nominally 0.1 µg/L. Reproductive testing with mysid shrimp, a sensitive marine invertebrate, found mortality and growth impairment at concentrations above 10 ng/L, with a NOEC of 4.6 ng/L.

Aquatic toxicity data for chlorpyrifos are summarised below. Available Australian surface water monitoring data are included for comparison. It should be noted that most water samples test negative for chlorpyrifos, and would therefore contain less than the detection limit of 0.01 or 0.1 µg/L, but that any detections will be toxic to sensitive species.



Differences in toxicity to fish, invertebrates and vegetation are readily apparent from multi-species testing in microcosms and ponds. As a general rule, aquatic arthropods suffer dose-responsive impacts following acute (pulse) exposure at 0.1-1 µg/L, while only minor fish impacts occur at such doses, consistent with the summary depiction above. Algae are not affected directly by such exposures, but indirect effects of increased algal and periphyton growth may arise due to suppression of planktonic grazers. Some gastropods may also increase in number with increased food resources. The threshold for acute effects at species and community levels in such studies appears to be about 0.1 µg/L. Invertebrate communities generally recover from acute exposures within 6 months, depending on the magnitude of the disturbance and the responses of less sensitive species, which may occupy ecological niches vacated by sensitive organisms before they can recover.

A static microcosm study in fibreglass tanks examined spray drift and runoff simulations delivering target concentrations between 0.03 and 3 µg/L. Nominal concentrations were achieved soon after drift simulation and declined with a half life of about 3 days. Aquatic concentrations after slurry application reached about half of nominal but remained fairly constant for some days as further material desorbed. Rotifers remained unaffected by treatment, but arthropod populations suffered sharp reductions at target concentrations of 0.3-3 µg/L and needed 2-4 weeks to recover. Bluegill sunfish were reduced by about a third by drift simulation at the highest rate, and almost eliminated by the corresponding slurry treatment, repeated three times at fortnightly intervals. Drift simulation at 10 µg/L eradicated bluegill populations. Various alternating spray and slurry sequences were also investigated. Measured concentrations suggested biphasic dissipation kinetics, with rapid losses (half-lives of a day or two) in the initial 24 hours after spray treatment followed by a more gradual decline (half-life about a week). Initial losses were thought to reflect volatilisation. Sorption to sediment was a relatively minor dissipation pathway, with levels recorded in sediment remaining generally below 10% of applied. Results indicate that repeat exposure to concentrations in the order of 1 µg/L should not affect bluegill survival or growth, and will cause only temporary reductions in invertebrate populations, provided that chronic exposures remain below 1 µg/L.

The maximum concentration of 4.7 µg/L detected in samples taken from 15-20 cm below the surface of shallow Minnesota ponds following spray application was about 25% of nominal. All other recordings were below 1.5 µg/L, or 10% of nominal. Effects seen in the pond were consistent with laboratory data. Substantial numbers of bluegill sunfish, for which laboratory LC50s in the order of 2 µg/L are typical, were killed. Arthropod populations, particularly water fleas, were reduced.

Similar trends were evident in deeper Minnesota ponds sprayed at three different rates. Bluegill mortality at target concentrations of 5 and 20 µg/L reached 38 and 99%, respectively. Minimal mortality occurred at a target concentration of 0.5 µg/L. Arthropod populations were reduced, and cladocerans were again most sensitive with major reductions at all treatment levels. Analyses of water samples indicated that nominal concentrations at mid-depth were exceeded 1 hour after treatment. However, some doubt is attached to this observation because of contradictory results from

vertical mixing studies, which found less than 10% of applied chlorpyrifos at mid-depth during the initial 2 hours after treatment. An initial rapid drop in chlorpyrifos concentrations in the water column (half-life 4-18 hours, with greater persistence at higher dose) was followed after about 12 hours by a more gradual decline.

Actual concentrations in artificial drainage ditches containing standing water were estimated by measuring the stratification and by taking depth-integrated water samples. Nominal target concentrations exceeded actual concentrations by a factor of about two following surface spray treatment. Stratification was evident for about a day in open water and 2-4 days where aquatic vegetation was present. The nominal NOEC at species and community levels was 0.1 µg/L under this acute dosing regime.

Australian studies in flowing water dosed continuously for 6 hours at a nominal 0.1 µg/L found no effect on artificial stream communities. Significant reductions in invertebrate density occurred at higher dose (nominally 5 µg/L). Continuous dosing over 21 days reduced numbers of chironomids, copepods and cladocerans at low and high doses. Periphyton density increased with reduced grazing pressure, as did one species of gastropod mollusc.

Artificial stream studies in Minnesota examined continuous dosing for 100 days at nominal concentrations of 0.2-1.01 µg/L, or 24 hour pulses at a nominal 3.1-11.5 µg/L every fortnight. The number of invertebrate taxa and number of organisms sampled declined under pulse dosing. Amphipod bioassays found no effect under continuous dosing but 50% mortality under pulse dosing. Symptoms of intoxication were seen in caged bluegills, but only under pulse dosing. Unstocked white suckers were found dead or dying following pulse dosing.

7.1.7.3 Non-target terrestrial invertebrates

Acute oral and contact testing using technical material and an emulsifiable concentrate found chlorpyrifos to be highly to very highly toxic to honey bees. Semi-field studies using a microencapsulated formulation applied at 800 g/ha to flowering ground cover confirmed that chlorpyrifos is harmful to bees, with peak mortality after a few days, presumably reflecting delayed release from the microcapsules.

Artificial soil tests in three laboratories found chlorpyrifos to be slightly toxic to the earthworm *Eisenia foetida*, but with weight loss at sub-lethal concentrations. Reviews indicate other species to have similar acute sensitivity, and to suffer reproductive impairment at concentrations above 100 ppm.

Testing with short-winged beetles found chlorpyrifos (1 kg/ha) to be very harmful to their parasitisation capacity. Sevenspotted lady beetles were completely killed by chlorpyrifos at relatively low rates (180-400 g/ha) with mortality remaining above 50% at 7 days after treatment. Testing in an apple orchard found chlorpyrifos (1 kg/ha) to be highly toxic to all beneficial arthropod groups, but limited residual activity meant that impacts were relatively short-lived with recovery apparent after 10 days. Impacts to beetles, spiders and collembola were also evident in pasture sprayed at 750 g/ha, with some weeks needed for recovery.

Chlorpyrifos residues appear to impair microbial processes in some soils, even at normal application rates, but to exert no adverse influences in other soils, even at elevated rates (5-8 kg/ha). Some microbial species, particularly fungi, appear to be highly susceptible, and the metabolite TCP is reported to have some microbial toxicity.

7.1.7.4 Plants

Laboratory tests indicate that chlorpyrifos can be phytotoxic to some sensitive plants at elevated doses, and this has been confirmed by field reports of phytotoxicity, particularly in the floriculture industry. There are no reports of off-target damage to native vegetation.

7.1.7.5 Reptiles

Widespread mortality (> 100/ha) of two lizard species was observed 8 hours after application of chlorpyrifos at 240 g/ha to control immature desert and mature tree locusts in Mauritania. A large monitor was found moribund from acute poisoning 24 hours after treatment at 387 g/ha to control acridid nymphs and adults in Senegal. Its stomach was filled with contaminated beetles, grasshoppers and other invertebrates.

7.1.7.6 Overview

As a broad spectrum insecticide, chlorpyrifos is very highly toxic to a broad range of insects, including beneficial species. Very high toxicity is also evident to aquatic arthropods, in both laboratory and field situations. Chlorpyrifos is also very highly toxic to fish, but less so than to aquatic invertebrates. Fish kills have been reported where aquatic contamination is high, with termiticide treatments a common cause, particularly if followed by heavy rain. Fish kills from agricultural uses are also possible in misuse situations such as direct overspray, but none appear to have been reported in Australia. Kills of aquatic fauna in the field appear to be infrequent, notwithstanding very high laboratory toxicity, because of the limited persistence of chlorpyrifos in the water column. Toxicity profiles observed during prolonged, constant concentration exposure in the laboratory may not accurately reflect toxicological responses to pulsed and rapidly declining concentrations in water under field conditions.

Chlorpyrifos is slightly to moderately toxic to mammals under conditions of acute exposure, and has relatively low mammalian toxicity compared with other organophosphorous insecticides. Birds are more sensitive, with high to very high toxicity recorded in the laboratory. Chlorpyrifos has been implicated in a number of bird kills in Australia, most notably a major die off at an ibis rookery in the Macquarie Marshes in 1995. While conclusive proof of causation is lacking for most of these incidents, the weight of evidence indicates that chlorpyrifos will give rise to occasional bird kills, particularly in predatory and scavenging species feeding on contaminated invertebrates. Abnormally high levels of chlorpyrifos and other organophosphates were found in dead shorebirds following a recent incident in Florida, but the route of exposure remains unclear. Overseas evidence suggests that similar impacts may occur with reptiles.

8. PREDICTION OF ENVIRONMENTAL HAZARD

Chlorpyrifos is used in many diverse situations. The major use is for termite protection of homes, with very high rates applied using manual application methods with a low potential for off-site spray drift but much higher potential for runoff, particularly if heavy rain falls soon after application. Lower rates are also applied in urban areas for control of household pests such as ants and cockroaches, and garden pests such as scarabs. Chlorpyrifos is also used on companion animals, a use pattern that seems to be associated with contamination of sewage in the Sydney region.

The next major use, which has increased substantially in recent years, is for control of lepidopteran pests in cotton, using aerially applied ULV formulations at fairly high rates (up to 1.5 kg/ha). Aerial application is also common in rice for control of rice bloodworm, but rates are much lower (30-75 g/ha).

Sugar is a significant consumer of chlorpyrifos, with the main use pattern being use of slow release formulations for multi-season control of canegrubs in the soil. A similar formulation has recently been registered for control of soil insects in container grown ornamentals, and is expected to find significant markets.

Use in orchards (citrus, pome and stone fruit) and vineyards mainly uses ground based equipment such as air blast sprayers. Application rates (50-100 g/100 L) may be fairly high (similar to cotton) where large spray volumes are required for coverage.

The other major use pattern involves mostly ground based application, typically by tractor mounted boom spray, in crops such as canola, cereals, pasture and vegetables. In general, rates are relatively low (less than 0.5 kg/ha) but repetitive treatments may reach 1 kg/ha for control of lepidopteran pests in brassicas.

Hazard assessment involves integrating the level of environmental exposure to a chemical with its intrinsic toxicity in order to determine whether toxic effects may arise in exposed organisms. The approach used is essentially that of the US EPA and involves determining the ratio of concentration to toxicity, a parameter generally referred to as the risk quotient (Q). The shortcomings of this approach, in particular that it represents a deterministic method rather than a true probabilistic assessment of the likelihood and scale of adverse effects, have attracted criticism in recent years. A number of conservative assumptions make the process cautious and protective in terms of adverse environmental effects, such that the approach best serves as a screen with very little information provided on the likelihood or extent of damage. The parameter Q is more correctly described as a hazard quotient, and that term will be used in this report.

According to methodology used by the US EPA for its reregistration program (US EPA, 1994) a Q of less than 0.2 (for terrestrial species) or 0.1 (for aquatic species) indicates that acute risk is minimal and no further assessment is needed. A potential acute risk is indicated where Q falls above this threshold but below 0.5, but may be mitigated by restricted use classification. Higher Q values indicate high acute

risk and possible regulatory action. The hazard quotient is an essentially qualitative parameter rather than a highly quantitative measure of ecological risk, particularly as exposure and environmental fate are currently excluded from its derivation. Environmental concentrations used to derive the hazard quotient are simply estimated from the application rate.

This report will adopt the same levels of concern as used by the US EPA, but will use them as indicators of hazard rather than risk. Hazard is defined as a potential source of harm, while risk is the probability that harm will occur. Adverse effects are possible where levels of concern are exceeded. However, there is too much scientific uncertainty to allow accurate estimation of the probability that harm will occur, given the limitations of this deterministic approach and the varied environments where exposure may arise.

The US EPA has yet to update its methods but is currently working with stakeholders to develop more refined approaches to risk assessment. Where supporting data are available, this assessment of chlorpyrifos will also refine the initial prediction of hazard derived using deterministic methods by considering aspects such as the dissipation of chlorpyrifos from the environment. Actual measurements of environmental exposure levels will be used in preference to simple estimates where available.

8.1.1 Terrestrial hazard

Birds, mammals and non-target invertebrates are sensitive to chlorpyrifos. Hazard to these organisms is evaluated below.

8.1.1.1 Birds

Maximum residues following spraying may be estimated using the updated Kenaga nomogram (Fletcher *et al*, 1994) as tabulated below for representative agricultural uses. Note that insects are included, as in Urban and Cook (1986). Estimated residues for insects should be treated with caution given the additional uncertainties such as accumulation of higher residues through inhalation or ingestion.

Crop	Rate (g/ha)	Estimated environmental concentration, µg/kg			
		Short grass	Tall grass	Broadleaf plants, small insects	Fruits, pods, seeds, large insects
Pasture	150	40	18	23	3
Cereals	450	121	55	68	8
Orchard	1000	269	123	151	17
Cotton	1500	403	185	227	25

Estimated residue levels are in reasonable agreement with measured values. Application at 1.68 kg/ha to corn (see section 6.1.1.10) left residues of 358 µg/kg at emergence and 193 µg/kg at the whorl stage (comparable to short and long grass, respectively). Residues on invertebrates reached only 11.5 µg/kg, some 4 days after treatment, highlighting the additional uncertainties in estimating residues for insects.

Acute dietary LC50s for birds may fall as low as 200 ppm. Residues of 40-100 ppm therefore represent a potential acute hazard to sensitive birds, and residues above 100 ppm indicate high acute hazard.

This deterministic approach leads to the conclusion that birds may suffer adverse effects if they feed on vegetation or small insects in areas treated with chlorpyrifos at 1000 g/ha or more. A number of current higher rate uses would provide such exposure, although few birds feed on foliage. Adverse effects may also occur if birds feed exclusively on short grass in areas treated at 450 g/ha, but this scenario would probably only involve species such as wood ducks which graze on treated turf. This deterministic analysis probably overestimates hazard as it rests on a number of conservative assumptions. Hazard would decline rapidly in the field as chlorpyrifos dissipates rapidly from foliage through volatilisation. Acute hazard from consumption of large insects appears minimal, even using this conservative approach.

Overseas field studies generally indicate a relatively low hazard to birds, with only one avian casualty possibly related to chlorpyrifos recovered from field trials in Iowa cornfields, California citrus orchards and Florida golf courses. Some reptile and mammal casualties were also recovered. A study on UK pasture found no adverse impacts on grazing geese, notwithstanding significant residues in their faeces. The exception is an older study in California freshwater ponds in which ducks died, apparently as a result of consuming contaminated water boatmen. A contributing factor may have been metabolic conversion in the water boatmen to chlorpyrifos oxon, which is expected to be much more toxic than chlorpyrifos to birds.

Australian incident reports tend to confirm that the hazard quotient approach is conservative. At the lower residue levels characteristic of agricultural applications, incidents are only rarely reported, consistent with the relatively low hazard quotients and the rapid dissipation of chlorpyrifos from foliage. Incidents are mainly anecdotal rather than formally reported, occurring where populations of larger insects are present and feeding on baits containing chlorpyrifos that are laid to control surface feeding insects in cotton, sorghum, sunflowers and maize (see section 6.1.1.14). However, this situation is probably not amenable to the quotient approach, because it involves ingestion of chlorpyrifos by the insect rather than contact exposure as assumed with the Kenaga nomogram. There would be some metabolic activation to chlorpyrifos oxon and perhaps some accumulation of this more toxic metabolite in the insect. Overall, it appears that use of chlorpyrifos in agriculture presents a less serious hazard to birds than may be indicated by deterministic hazard presumptions, consistent with the conservative nature of those presumptions.

At higher application rates such as used for termite control, hazard would clearly be much higher than for agricultural uses. Reported deaths of magpies following termite protection of power poles, apparently through consumption of contaminated earthworms, substantiate predictions that treatment at the higher rates used for termite protection represents an acute hazard to birds and is likely to give rise to occasional incidents such as the one reported. Similarly, the reported deaths of pigeons after feeding on granules containing 30000 mg/kg chlorpyrifos are not unexpected given the high doses that would be delivered.

The home garden granular ant control products appear problematic as they are likely to be used at high rates and contain sufficient toxicant to kill birds that ingest them. Labels do not state specific rates and frequencies of application, but simply instruct users to sprinkle granules lightly around nests and trails whenever ants are active. Similar products used for control of grubs in lawns are applied at 8 g/m^2 (0.4 g/m^2 chlorpyrifos). For an LD50 of 20 mg/kg, this application rate would deliver an LD50 to a thousand small (20 g) birds over each square metre treated. This exceeds the US EPA's level of concern for granular insecticides by two orders of magnitude. Use of the ant control products in home garden situations is likely to occur on hard surfaces such as concrete, rather than on vegetated areas. Avian exposure is more pronounced with such use patterns, as granules are easily seen by birds and may be blown around and accumulate in certain areas. In such situations, granules will not be concealed by vegetation or turf thatch, or irrigated into the soil.

It is not possible to determine the frequency at which chlorpyrifos related avian incidents may occur with any accuracy. The hazard quotient approach leads only to the conclusion that toxic levels can be exceeded, and incident reports are an unreliable basis for making quantitative determinations of risk, even on a comparative basis against other chemicals. However, given the intensity of use and limited number of incident reports, it seems reasonable to conclude that impacts will be isolated rather than commonplace, and avian populations should remain unaffected. Field studies support this conclusion, with very few avian casualties reported from most studies.

Even if populations remain unaffected, avian impacts are undesirable. Restrictions such as label warnings can help reduce the risk of such incidents occurring, and need to be considered, particularly for the high rate termite protection products and the home garden granular products.

However, the Macquarie Marshes ibis kill (see section 6.1.1.14) and the recent shorebird incidents in Florida (see section 6.1.1.15) suggest that chlorpyrifos may present more substantial risks to birds in certain circumstances. Problems seem to be just emerging, and remain poorly understood at the present time. A watching brief needs to be kept on this issue. The granular ant control products appear to warrant special attention as they are likely to kill any birds that eat them. Their suitability for home garden use is questioned.

8.1.1.2 Mammals

Few data are available for estimating the hazard that chlorpyrifos presents to mammals. However, given that mammals appear less acutely sensitive than birds to chlorpyrifos, mammalian hazard is probably low to moderate, and any adverse impacts that may occur should be isolated and infrequent. This is supported by the results from US field trials in which only very few mammalian casualties were recovered.

8.1.1.3 Reptiles

Little information is available, but incident reports from North Africa and the discovery in US field studies of a few reptile carcases suspected to be linked with chlorpyrifos indicate that impacts on reptiles may occur in or around sprayed areas. Again a watching brief needs to be kept on this issue. Label warnings of avian hazard could be extended to include reptiles.

8.1.1.4 Arthropods

Testing indicates chlorpyrifos to be harmful to honey bees and a range of beneficial invertebrates, but with populations recovering fairly quickly, typically in a few weeks, through immigration or emergence from pupae. Laboratory testing indicates that chlorpyrifos is very harmful to beneficial beetle species. Field studies found chlorpyrifos to be highly toxic to all beneficial arthropod groups, but with fairly rapid recovery. Similarly, populations of beetles, spiders and Collembola declined sharply following pasture treatment but recovered in a few weeks.

In contrast to the harmful effects documented in laboratory and field studies, local anecdotal reports indicate that chlorpyrifos is relatively soft on beneficial arthropods. A number of respondents to the review commented on the compatibility of chlorpyrifos in integrated pest management programs, particularly in apples. Chlorpyrifos is regarded as relatively soft on beneficial insects and mites, presumably because of its limited persistence on foliage. Use of chlorpyrifos to control ants in orchards was highlighted as another example of integrated pest management. Trees are not sprayed directly, allowing beneficial species to predate on pests such as mealybugs or aphids which would otherwise be protected by ants.

In summary, use of chlorpyrifos represents an obvious acute hazard to non-target arthropods, but the hazard does not persist and it appears that populations can recover relatively quickly.

8.1.2 Aquatic hazard

Pesticides that present minimal aquatic hazard can be identified using a simple screening method in which the concentration that would result from direct overspray to 15 cm standing water is compared with toxic endpoints. Chlorpyrifos clearly would not meet these screening criteria as it is very highly toxic to a broad range of aquatic organisms, with invertebrates in particular sensitive in the low and sub-ppb range. Even at the low rate of 150 g/ha, overspray would leave residues of 100 µg/L.

8.1.2.1 Hazard to fish – initial considerations

In its simplest form, the hazard assessment process incorporates generic worst-case exposure assumptions and standard aquatic toxicity endpoints. No consideration is given to mitigating factors that may operate in natural environments to moderate the toxic responses seen in laboratory bioassays, or to management practices that reduce exposure.

Following the initial calculation based on direct overspray, consideration is given to the more realistic exposure scenario of spray drift. The US EPA adopts a standard assumption of 5% drift, but assumes that as much as 20% may be deposited in a body of water from ULV applications, which produce a fine spray that remains airborne for longer than the larger droplets from standard spray applications.

Freshwater fish are sensitive to chlorpyrifos, with acute LC50s of 10-250 µg/L reported from reliable studies. Lower endpoints are reported from other studies, but without the level of experimental detail necessary for validation. However, consistency between results indicates that the warmwater species, bluegill sunfish, is likely to be sensitive to chlorpyrifos at lower concentrations (in the order of 2 µg/L). It is not known whether any Australian species would share this sensitivity.

In order to conclude that chlorpyrifos presents minimal acute hazard to fish, hazard quotients must remain below 0.1. Estimated environmental concentrations (EECs) therefore need to remain below 0.2 µg/L to protect sensitive species such as bluegill sunfish. This criterion is clearly not met, as indicated in the table below. Hazard quotients remain well above 0.5 in 15 cm water, regardless of the use pattern. In 2 m water, application to cotton, cereals and pomefruit represents a high acute hazard, while application at pasture rates represents a potential acute hazard to fish, extending to high acute hazard if drift reaches 10%. However, given that endpoints for most fish species exceed 10 g/L, the acute hazard to most fish in this pasture situation would be minimal.

Crop	Rate (g/ha)	Drift (%)	EEC (hazard quotient)	
			15 cm water	2 m water
Pasture	150	5	5 µg/L (2.5)	0.4 µg/L (0.2)
		10	10 µg/L (5)	0.8 µg/L (0.4)
Cereals	450	5	15 µg/L (7.5)	1.1 µg/L (0.55)
		10	30 µg/L (15)	2.2 µg/L (1.1)
Orchard	1000	5	34 µg/L (17)	5 µg/L (2.5)
		10	67 µg/L (33)	10 µg/L (5)
Cotton	1500	10	100 µg/L (50)	8 µg/L (4)
		20	200 µg/L (100)	15 µg/L (7.5)

8.1.2.2 Hazard to fish – mitigating factors

The foregoing analysis indicates that the possibility exists of adverse effects to fish, particularly at higher application rates. However, it includes a number of conservative assumptions, such as instantaneous distribution of chlorpyrifos through the water column and no dissipation. The need for such assumptions can be overcome by using more realistic data, such as obtained from microcosms and natural ponds.

Volatilisation appears to be a significant mitigating factor, particularly for spray drift incidents, but is not well understood. A theoretical model applied to five case studies in temperate environments (Canada and the UK) suggests that transfer to the water column can be more important than volatilisation for dissipation from the surface microlayer. However, volatilisation was dominant in two of the examples studies, and there is further experimental evidence to suggest that volatilisation of chlorpyrifos and

other hydrophobic insecticides from water can be significant, or even the dominant removal process (see section 5.2.4.12). The company has noted that it is plausible that the model would identify volatilisation as the dominant dissipation process in Australian cotton areas because of the relatively high ambient temperatures. Spray drift exposures of surface waters are a particular problem in cotton growing areas because of the widespread use of aircraft to deliver ultra low volume formulations as fine droplets.

Another significant mitigating factor is sorption to sediment, but again the evidence appears conflicting. Metabolism studies found that around half the chlorpyrifos added as acetone solution to achieve a nominal 400 g/L partitioned immediately from water to sediment (see section 5.2.3.8). In contrast, sediment fractions did not exceed 10% of the chlorpyrifos added at 3.5 g/L to microcosms (see section 6.1.2.11). High target concentrations in the former case may have caused some precipitation, but two other distinctions are evident between these situations, namely water depth (6 cm versus 1.4 m) and formulation (acetone solution versus EC spray). Where chlorpyrifos comes in contact with sediment, rapid sorption can be expected. However, slow vertical mixing means that surface emulsions deposited on deeper water dissipate through other mechanisms, among which volatilisation probably predominates, before sorption to bottom sediments can occur. Pond studies in littoral enclosures (see section 6.1.2.15) also found only limited sorption to sediment beneath an average 1.1 m water. Sorption to suspended particulates may also moderate toxicity in Australia's characteristically turbid surface waters, but this has not been investigated.

Regardless of dissipation mechanisms, it appears likely that concentrations to which fish would actually be exposed are likely to be much lower than estimated based simply on the application rate. Some supporting evidence is available from studies conducted in microcosms or in artificial or natural water bodies. Unfortunately, most of these studies do not report analytical data. The most useful data are probably those from the Minnesota pond studies (see section 6.1.2.14). Overspray of shallow ponds produced measured concentrations at 15-20 cm below the water surface that generally did not exceed 10% of applied. A single high reading represented about 25% of the theoretical concentration that would arise if all the spray contacting the water immediately distributed through the water column, and appears to reflect movement of surface deposits by wind. Residues dissipated from the water column with typical half-lives of a few days. The most rapid dissipation occurred immediately after application, apparently as a result of volatilisation from the surface microlayer. Similar results were obtained in shallow California ponds (see section 6.1.1.12) although details of sampling are sketchy. Concentrations measured 4 hours after treatment at 1.12 kg/ha were about half of predicted levels, declining further over the next 2 days with a half life of about a day. Roughly half the measured residues were sorbed to suspended particulates and may be presumed to have reduced bioavailability.

Available analytical data suggest that, at least in deeper water, the hazard quotient method overstates aquatic exposure at 15-20 cm below the water surface by a factor of about ten. In shallower water, deterministic predictions appear to exceed measured concentrations by a factor of about two initially. Further dissipation appears likely to reduce concentrations to around 10% of nominal within 2 days of treatment. Shallow

water will provide much less opportunity for fish to avoid the high concentrations arising from surface deposits, but sorption to sediment should provide some mitigation, based on the results from metabolism studies (see section 5.2.3.8) in which there was an immediate loss of 50% to sediment.

This conclusion is contradicted by other evidence, however. Target concentrations were confirmed by analysis in microcosms (section 6.1.2.11) but only limited details were provided as to how the microcosms were dosed. Target concentrations at mid-depth were exceeded soon after application to littoral enclosures constructed in a Minnesota pond, but appear to be biased towards near-surface concentrations. Stratified samples collected at similar sampling times found much lower concentrations except near the surface and lend support to the contention that exposure at mid-depth will not exceed 10% of the estimated environmental concentration (see section 6.1.2.15).

Limited data suggest that biological responses in flowing water are likely to be less pronounced than would be predicted from laboratory data. Thus bluegill sunfish survived 24 hours of exposure to nominal concentrations of 3.1 to 11.5 µg/L, although fish became lethargic and some exhibited tetanic spasms. Corresponding measured concentrations were 1.9-7.0 µg/L upstream, declining by about half in the lower reaches where fish were bioassayed (see section 6.1.2.18). The analytical and biological response data suggest an amelioration of hazard compared with simple deterministic predictions based on nominal concentrations. The shortfall from nominal concentrations is less marked than for still water, perhaps reflecting more efficient mixing in flowing water.

The weight of evidence allows the assumption that mitigating factors reduce fish exposure through the initial days after exposure by a factor of 5 relative to deterministic predictions. A fivefold mitigation would reduce most hazard quotients in deeper water below the threshold of 0.5, as tabulated below. In shallow water, acute hazard remains generally high, even from low rate pasture treatments. However, most fish, being at least five times less sensitive than bluegills, would face minimal hazard from pasture uses, even in shallow water.

			Hazard quotient	
Crop	**Rate (g/ha)**	**Drift (%)**	**15 cm water**	**2 m water**
Pasture	150	5	0.5	0.04
		10	1.0	0.08
Cereals	450	5	1.5	0.11
		10	3.0	0.22
Orchard	1000	5	3.4	0.5
		10	6.6	1.0
Cotton	1500	10	10	0.8
		20	20	1.5

The above table indicates that fish populations in deeper waters should not in general suffer adverse impact from spray drift events, except for sensitive species such as bluegill sunfish exposed to high levels of drift from high rate applications to orchards and cotton. For fish inhabiting shallow water, all uses of chlorpyrifos appear to pose

high acute hazard. Further refinement is needed to reduce the hazard quotients below the high acute hazard presumption level of 0.5, particularly in orchard and cotton treatments.

8.1.2.3 Hazard to fish – regional exposure modelling studies

The foregoing presumptions of 5 or 10% drift do not account for the location of spray operations in relation to surface water, and probably overestimate exposure in many situations. More refined estimates of environmental exposure may be obtained using computer models. Modelling of environmental exposure is best suited to comparative assessments at the present time as it does not give reliable information on actual levels likely to occur in the environment. However, the likely success of proposed mitigation options can readily be predicted using such modelling techniques. Particular high risk areas can also be identified, provided that sufficient input data are available for geographic and climatic variables.

Dow has conducted regional exposure modelling for use on cotton in the lower Mississippi delta region. Typical soils in the area have high clay content and poor drainage. Two low volume aerial applications were included in the model, an early season spray treatment at 370 g/ha with 27% plant cover and a later treatment at 1.12 kg/ha when maturing plants intercepted 85% of the spray. The models assumed half-lives in pond water, sediment, soil and on foliage of 28, 45, 10.4 and 0.17 days, respectively.

Surface runoff was modelled using GLEAMS 2.10. Mitigation with an "empirical buffer strip" that intercepted 85% of dissolved and 76% of sorbed residues was also studied. Spray drift was modelled with input data from the US Spray Drift Task Force. Fate in the pond was studied with EXAMS.

Predicted peak concentrations in an adjacent water body were above 20 µg/L, predominantly due to spray drift. Use of vegetative filter strips to intercept runoff improved the outcome only marginally as surface runoff was a minor contributor under this scenario. Drift setback (buffer) zones were much more effective in mitigating exposure. A buffer of 150 m reduced the estimated concentrations in the pond by an order of magnitude, with a further twofold improvement possible by extending the buffer to 300 m. Vegetated filter strips were also a worthwhile option when used in conjunction with buffer zones, reducing the majority of predicted concentrations from combined spray drift and surface runoff below 1 µg/L with the 300 m buffer. Changing from a low to medium volume spray also improved the predicted outcome, reducing concentrations by around 20-30%.

The study also examined application to peanuts, which receive high rate granular applications (2.24 kg/ha) as a surface band without incorporation when peanuts are at the pegging growth stage. Peak concentrations without mitigation reached 56 µg/L, although timed release from the granules would probably mitigate the outcome in the field. Use of vegetated filter strips reduced peak predictions to 9 µg/L, with a 90%ile between 2 and 3 µg/L. US peanut production is limited to localised areas of Georgia,

Alabama and Florida. Parts of Alabama showed very high potential for impact (Havens and Peacock, 1995).

A separate study examined use on corn, the market for more than half the chlorpyrifos sold in the USA. The main use involves granular application in furrow at planting (1.38 kg/ha) or pre-plant incorporated application at 2.24 kg/ha. Predictions were based on 90%ile weather records.

Estimated environmental concentrations from granular treatments without mitigation reached as high as 41 µg/L, although only 5% of the study area exceeded 12 µg/L. Mitigation with an empirical buffer strip reduced peak concentrations to 7 µg/L, with 80% of the study area below 1 µg/L. For pre-plant treatments, more than 98% of the study area remained below 1 µg/L with mitigation. Unmitigated predictions reached as high as 17 µg/L. Moving from conventional to conservation tillage practices also reduced maximum estimated environmental concentrations, and shifted the overall distribution towards lower values (Havens *et al*, 1994).

Simulations of uses on alfalfa and wheat returned similar results, with drift again the main contributor to aquatic contamination. Simulated buffer strips were effective in reducing runoff impact, but runoff was a minor pathway for contamination. The simulations assumed a single aerial application to wheat at 0.56 kg/ha and one to three aerial treatments at 1.12 kg/ha for alfalfa. Maximum predicted residues in water were 1.7 µg/L for wheat and 8.7 µg/L for alfalfa receiving three treatments. Buffer zones were effective in reducing contamination. For example, estimated environmental concentrations for alfalfa in California's Imperial Valley, treated three times at monthly intervals through summer, reduced from 3.2 µg/L with no buffer to 0.65 µg/L at 80 m and 0.27 µg/L at 160 m (Havens, 1995).

The modelling results indicate that drift can be reduced by an order of magnitude if a 150 m buffer is observed upwind of water bodies, and by a factor of 20 with a 300 m buffer. A threefold reduction would probably require a buffer of about 50 m. These predictions are supported by the spray drift data submitted (see section 5.2.4.13) which found that levels of drift from application of emulsifiable formulations to cotton could be quite high (1.3-8.3%) at a distance of 50 m but reduced to 0.08-0.49% at 300 m. Note that drift of chlorpyrifos from Australian cotton could be higher because of the use of ULV formulations, perhaps reaching levels in the order of 1% at 300 m. However, this still affords a scaling factor of 0.05 relative to the initial presumption of 20% drift.

The scaling factor of 0.05 provided by a 300 m buffer would reduce the hazard quotient for cotton, based on an assumption of 10% drift, to 0.5. The hazard quotient for 20% drift, reflecting fine droplet ULV application, can not be mitigated to this level, even with a 300 m buffer. Buffers also appear essential in orchards, but there are no regional modelling data for orchard situations. Spray drift models can offer guidance regarding buffers in orchards, as outlined below.

8.1.2.4 Hazard to fish – AgDRIFT™ model

As noted above, spray drift is the exposure route of principal concern for aquatic organisms. Exposure can be estimated using the AgDRIFT™ model being developed for possible regulatory use by the US EPA (Teske *et al*, 1997). The estimates are for a pond or stream 60 m (208 feet) wide with an average depth of 2 m (6 feet) situated with the near edge 30 m (100 feet) downwind from the site of application, or for a wetland with the same dimensions apart from shallow water depth of 15 cm (6 inches). Accordingly, buffers of 0 m in the tables below are equivalent to a distance of 30 m between the edge of the crop and the edge of the water body. Deposition is integrated across the water body to provide an estimated average concentration.

Note that the concentrations are estimated directly from deposition data with no recognition of the losses that would be expected to occur through volatilisation or sorption. Therefore, a prediction that aquatic exposures will exceed toxic levels does not infer that biological consequences will inevitably follow. As outlined in section 7.1.2.2, aquatic concentrations appear unlikely to exceed around 20% of nominal.

Studies in microcosms (see section 6.1.2.11) indicate that exposures below 1 g/L do not adversely affect bluegill sunfish, the most sensitive species in laboratory testing with an acute LC50 in the order of 2 g/L. Reliable laboratory testing (see sectio n 6.1.2.1) shows most fish to be at least an order of magnitude less sensitive than bluegills. Therefore, no adverse effects on fish would be expected where predicted concentrations remain below 5 g/L, likely to correspond to measured concentrations below 1 g/L. For most species, predicted concentrations below 50 g/L, corresponding to likely concentrations below 10 g/ L, should not elicit adverse effects. Predicted concentrations exceeding the 5 and 50 g/L thresholds are shaded in the tables below.

Predictions for aerial application to cotton at 1.5 kg/ha are tabulated below for low, medium and high volume sprays (vmd 119, 226 and 353 m). The estimates represent the 90th percentile of the deposition data on which the model is based. All predictions in the pond exceed the 10 g/ L endpoint unless buffers are observed. Similarly, predicted concentrations in shallow wetlands are problematic except with a 150-300 m buffer and large droplet sprays. Wetland predictions are marginal with respect to fish safety for medium droplets, even with a 300 m buffer. It would therefore appear essential to observe at least a 300 m buffer to protect fish from excessive spray drift, and to avoid the use of low volume sprays.

Buffer	**Pond**			**Wetland**		
	119 m	**226 m**	**353 m**	**119 m**	**226 m**	**353 m**
0 m	18 g/L	11 g/L	11 g/L	243 g/L	150 g/L	150 g/ L
150 m	5 g/L	1.8 g/L	0.52 g/L	71 g/L	24 g/L	6.9 g/L
300 m	3.5 g/L	1.2 g/L	0.29 g/L	46 g/L	16 g/L	3.8 g/L

For boom spray treatment of pastures (150 g/ha) and canola (450 g/L) the following estimates are obtained. All remain below the 5 g/ L threshold. Buffer zones to protect fish do not appear necessary for conventional ground based application at these relatively low rates, provided that shallow water does not occur within 30 m.

Buffer	Pond		Wetland	
	150 g/ha	450 g/ha	150 g/ha	450 g/ha
0 m	80 ng/L	242 ng/L	1074 ng/L	3223 ng/L
50 m	21 ng/L	63 ng/L	280 ng/L	850 ng/L
150 m	10 ng/L	30 ng/L	134 ng/L	403 ng/L
300 m	5.4 ng/L	16 ng/L	72 ng/L	216 ng/L

Higher rate treatment (1 kg/ha) of vegetables using ground rigs or medium volume aerial sprays gives rise to the following estimated aquatic concentrations. Again, there does not appear to be a strong need to observe buffer zones for ground based application. However, for aerial treatments a minimum buffer of 100 m would seem essential. This precaution would protect most fish in shallow wetlands from the majority of drift exposures. In order to protect sensitive species, a buffer in excess of 300 m would be needed.

Buffer	Pond		Wetland	
	Ground	Aerial	Ground	Aerial
0 m	0.5 g/L	7 g/L	7 g/L	100 g/L
50 m	0.14 g/L	2.5 g/L	1.9 g/L	33 g/L
100 m	0.09 g/L	1.6 g/L	1.2 g/L	21 g/L
150 m	0.07 g/L	1.2 g/L	0.9 g/L	16 g/L
300 m	0.04 g/L	0.8 g/L	0.5 g/L	10 g/L

Orchard applications can also be modelled, but in this case a more conservative approach is warranted as supporting data are limited and the model output represents the mean rather than the 90th percentile prediction. The following estimates are obtained for airblast treatment at 1 kg/ha of sparse foliage (dormant sprays), normal orchards (vineyards, stone and pome fruit) and dense foliage (citrus or taller trees such as mature pears).

Note that rates in citrus may reach 5 kg/ha where oscillating booms are used to deliver spray volumes of 10 kL/ha. The predictions tabulated below should be scaled upwards accordingly. Conversely, lower spray volumes in dormant orchards should allow some downward scaling of predicted concentrations. With these considerations and the mitigating factors of sorption and exposure in mind, a buffer of 50 m would appear to offer adequate protection of fish in shallow wetlands exposed to drift from spray operations in dormant and densely foliated orchards. Protection becomes marginal, however, when application rates in citrus exceed 2 kg/ha, suggesting that the buffer should be increased to 100 m if application rates exceed 2 kg/ha chlorpyrifos. Buffers do not appear necessary for normal orchard spraying.

Buffer	Pond			Wetland		
	Sparse	Normal	Dense	Sparse	Normal	Dense
0 m	2810 ng/L	90 ng/L	930 ng/L	37.5 g/L	1270 ng/L	12 g/L
50 m	340 ng/L	7 ng/L	166 ng/L	4.5 g/L	98 ng/L	2.2 g/L
150 m	73 ng/L	1.5 ng/L	39 ng/L	970 ng/L	20 ng/L	520 ng/L
300 m	23 ng/L	0.45 ng/ L	13 ng/L	300 ng/L	6 ng/L	170 ng/L

In summary, the AgDRIFT™ model provides the following predictions.

- **High rate aerial application to cotton**

Based on the assumption that measured residues in water do not exceeed 20% of nominal, the model predicts that 90% of shallow water exposures from aerial application to cotton at 1.5 kg/ha will remain below 1 g/L, provided that coarse droplets (vmd 353 m) are used and a 300 m buffer is observed. Use of medium droplets (vmd 226 m) roughly triples drift, and raises concerns for sensitive fish in shallow wetlands. However, adequate protection remains for less sensitive fish species. Environmental hazard from this use pattern appears acceptable provided that coarse droplets are used and a 300 m buffer is observed.

- **Low rate ground based treatment**

The model predicts that ground based and medium volume aerial treatments at rates below 0.5 kg/ha do not present an unreasonable environmental hazard. Buffer zones do not appear necessary.

- **High rate ground based and aerial treatments**

Again, the model predicts that ground based treatment at higher rates (1 kg/ha) does not present an unreasonable hazard to fish, even without buffer zones, although some hazard remains for sensitive species in shallow wetlands. For aerial treaments, a buffer of 100 m appears essential. Even this precaution may not adequately protect the most sensitive fish species, and the model suggests that some impacts may occur unless buffers are increased to at least 300 m. This may not be practical.

- **Orchards**

For orchard spraying, a 50 m buffer appears adequate for protection of sensitive fish in shallow water from treatment of dormant and densely foliated orchards. The buffer should be increased to 100 m if rates rise above 2 kg/ha chlorpyrifos, as may occur in citrus. It is common practice in the South Australian citrus industry to limit off-site drift by not spraying the last three downwind rows in the orchard. Buffer zones do not appear necessary for normal orchard spraying.

8.1.2.5 Hazard to fish – European approaches

Drift depositions from ground based applications made according to good agricultural practice have been determined by German authorities for a range of situations (Ganzelmeier *et al*, 1995). The 95%ile results have been used to derive basic spray drift values as tabulated below. Where drift is expressed as a range, this reflects the difference between early and late season treatments. Early season treatments to apples are more drift prone than later applications because of a reduced catching surface to intercept the air assisted droplets. In contrast, early season treatments to grapevines according to good agricultural practice dispense with air assistance as there is no foliar canopy to penetrate, and are therefore less drift prone than later treatments.

Distance	Cereals	Grapevines	Apples
5 m	0.6%	1.6-5.0%	20.0-10.0%
10 m	0.4%	0.4-1.5%	11.0-4.5%
15 m	0.2%	0.2-0.8%	6.0-2.5%
20 m	0.1%	0.1-0.4%	4.0-1.5%
30 m	0.1%	0.1-0.2%	2.0-0.6%
40 m		0.1-0.2%	0.4%
50 m		0.1-0.2%	0.2%

The basic drift values have been used to derive buffer distances such that 95% of aquatic exposures will remain below levels likely to impact irreversibly on aquatic ecosystems. The threshold for ecosystem effects is 1 g/L, which for spray drift incidents equates to a theoretical exposure of 5 g/L given the tendency for chlorpyrifos to volatilise from surface films on water. The cereals category was used to derive buffer distances for ground based application to cereals (450 g/ha) and vegetables (1000 g/ha) and the apples category for general tree crops (1000 g/ha). Note that only the lower drift value was used for orchard applications at 1000 g/ha. The higher drift values for early season treatments are balanced by reduced rate requirements.

For a water depth of 15 cm, the basic drift values can be used to justify a buffer distance of 5 m for cereals and vegetables, increasing to 30 m for orchards. Orchard buffers would need to increase to 40 m where application rates exceed 2000 g/ha, and to 50 m where rates exceed 4000 g/ha, as may occur in citrus. There is probably no need to stipulate a 5 m buffer on labels as cereals and vegetables would not normally be grown this close to water.

The authors note that the basic drift values represent the basis for a scientific approach to setting buffer distances such that negative effects on aquatic organisms would not be expected, and contrast this with less flexible approaches used in other jurisdictions. For example, Dutch authorities assume a standard amount of drift that does not vary with distance (1% for short field crops, 5% for taller field crops such as canola and cereals, and 10% for tall crops where spray nozzles have a lateral or upward orientation). In contrast, Canadian and British authorities prescribe a standard buffer distance (15 and 6 m, respectively). Note that the UK Pesticides Safety Directorate has since revised its requirements, with effect from March 1999 (details are posted on its website). The standard buffer zone has been reduced to 5 m, but is now measured from the top of the bank rather than the water's edge. Scope exists to reduce the buffer distance based on local factors such as size of watercourse and use of low drift equipment, but this is not an option for organophosphate insecticides because any such reduction may lead to an unacceptable risk.

The German and US approaches show different level of drift and generate different buffer requirements. For example, lower rate orchard treatments require a 50 m buffer (as well as the 30 m distance from the water's edge that is assumed in the model) according to AgDRIFT, but only 30 m using the Ganzelmeier approach. It is

considered that this could be due to the different trial conditions and the different nozzles used, as the AgDRIFT data reflect use of hollow cone nozzles (fine spray, high drift) while the German studies used flat fan nozzles (medium spray, reduced drift) under favourable meteorological conditions (wind speed < 5 m/s, temperature < 25^{o}C). This emphasises the importance of using equipment that reduces the drift potential in situations where drift could be an environmental problem. AgDRIFT results represent a worst case based on conservative assumptions while the Ganzelmeier results are based on real world data and may better approximate the spray drift that would be typical where basic precautions, including the use of less drift prone nozzles, are taken to minimise the spray drift hazard. The AgDRIFT predictions indicate that, for those areas close to natural waterways, low drift nozzles should be used.

8.1.2.6 Hazard to fish – Australian field data

Environmental monitoring generally does not find chlorpyrifos, even in irrigation drainage waters with a detection limit of 0.01 µg/L. Samples taken from drains in the Murrumbidgee Irrigation Area found occasional occurrences, generally at concentrations below 0.1 µg/L, with a few samples taken near the exit point from rice bays approaching 10 µg/L. Persistent contamination occurs in certain areas during spring, notably Mirrool Creek (used as a drain) where concentrations between 0.01 and 0.1 µg/L prevail through September and October with occasional high detections (approaching 20 µg/L) in grab samples.

Detections are less frequent in riverine environments than in irrigation drainage, particularly in areas such as northern NSW where tailwater returns to the river are tightly controlled. The Central and North West Regions Water Quality Program finds chlorpyrifos in a very small number of samples (well below 1%) at concentrations generally between 0.1 and 1 µg/L. However, chlorpyrifos accumulated to quite high levels in passive samplers deployed during 1998. This could reflect accumulation from background levels, or from occasional high pulses entering the river, with the latter appearing more likely given that such pulses are detected from time to time. Such detections, generally below 10 µg/L but reaching as high as 26 µg/L in one sample from the Gwydir, may reflect non-agricultural uses such as termite protection of bridges. However, predicted concentrations of this magnitude may also occur in shallow water contaminated through excessive spray drift from higher rate uses, such as for cotton. It seems likely that higher concentrations would occur in minor tributaries where pesticide residues first enter the riverine system.

Analysis of available data indicate that the high dose pulse exposures that occur occasionally in Australian rivers and irrigation channels may kill sensitive fish species in localised areas, but that background exposures do not appear to reach levels that could be damaging to fish.

The high dose exposures may reflect spray drift events or non-agricultural uses such as termite protection of bridges. There is clearly a need to improve current agricultural practices in order to further reduce off-target movement of pesticides, with particular attention to matters such as spray drift that can give rise to elevated pulse exposures. Simple calculations indicate that excessive spray drift can give rise to levels of

contamination in shallow water that will kill fish. A lack of documented fish kill incidents does not discount their occurrence, given the limited aquatic persistence of chlorpyrifos.

8.1.2.7 Hazard to fish from surface runoff

Surface runoff may also deliver high concentrations of chlorpyrifos to riverine systems if localised summer storms that are hard to predict occur soon after treatment. This is likely to be a particular problem in cotton areas where chlorpyrifos is used in high volumes at a time when summer storms may occur. Turf applications appear to present much lower hazard because residues are well retained by the thatch layer (see section 5.2.5.1).

Based on the Californian experience, surface runoff may also be a particular problem during winter where dormant orchards are sprayed. Large volumes of organophosphate dormant sprays are used in the San Joaquin watershed, with pesticide levels peaking in local rivers during and shortly after winter storms (see section 5.1.3.10). In an effort to reduce toxicity in surface waters, Californian authorities are encouraging growers to adopt voluntary practices such as avoiding mixing and loading near streams, reducing application rates, shutting off spray rigs at the ends of rows near streams, and using alternatives.

Fish kills associated with construction work indicate that high rate non-agricultural uses need to be tightened. Runoff is clearly the main risk factor to be controlled in these scenarios.

Note that hazard quotients for termiticide applications would be extremely high because of the high application rates (500 or 1000 kg/ha in treated areas, depending on geography). Termiticide treatments represent a serious hazard to fish if appropriate measures are not taken to prevent runoff from the site of application, as exemplified by Australian incidents (see sections 5.1.3.3 and 5.1.3.4). Queensland has reported numerous incidents, probably because of the higher application rates and more intense rainfall in tropical and sub-tropical climates. With modern construction trends, high rate chlorpyrifos treatments in new housing estates may cover more than half the estate, representing an application rate of at least 500 kg/ha. If exposure in an adjacent 1 m water body reaches 1% of this treatment rate, the estimated concentration is 500 g/L and a heavy fish kill would be predicted. Such predictions are clearly realistic, as demonstrated by the incidents tabulated in section 5.1.3.4, and indicate the importance of action being taken in this area.

8.1.2.8 Hazard to invertebrates – the quotient approach

Acute laboratory data indicate that sensitive invertebrates may be affected at very low concentrations of chlorpyrifos, between 0.01 and 0.1 µg/L. The most sensitive acute endpoint is the EC50 of 15 ng/L for *Daphnia magna* (see section 6.1.2.6). In order to have confidence that adverse impacts to these organisms will not occur, chlorpyrifos concentrations in aquatic environments should not exceed 0.001 µg/L, which is the current ANZECC guideline for protection of aquatic ecosystems.

The quotient approach to hazard assessment provides the following initial results based on the acute endpoint of 15 ng/L for *Daphnia magna*. Note that, while quotients are large, this endpoint is something of an outlier, and therefore a conservative criterion.

Crop	Rate (g/ha)	Drift (%)	Hazard quotients	
			15 cm water	2 m water
Pasture	150	5	333	27
		10	667	53
Cereals	450	5	1000	73
		10	2000	147
Pomefruit	1000	5	2267	333
		10	4467	667
Cotton	1500	10	6667	533
		20	13333	1000

The calculated hazard quotients indicate that chlorpyrifos poses a very high acute hazard to aquatic invertebrates. As for fish, it can be argued that the actual levels occurring in water are likely to be considerably lower than those estimated. Further reductions are possible if appropriate buffer zones are observed upwind of water bodies in order to reduce drift. However, nearly all hazard quotients would remain above 0.5, even with these mitigating factors.

These simple deterministic predictions indicate that there is a likelihood of adverse impacts to sensitive aquatic invertebrates from the use of chlorpyrifos. It is not possible to predict the frequency with which impacts may occur, or their magnitude, using the quotient approach. More refined approaches, including consideration of actual levels of exposure and the ecology of invertebrate populations, is necessary to any more refined assessment of risk.

8.1.2.9 Hazard to invertebrate populations

Because of relatively rapid regeneration times, a certain level of invertebrate impact can occur without adversely affecting populations. Even in undisturbed environments, aquatic invertebrate populations tend to undergo wide swings in population density as conditions change.

The resilience of invertebrate populations in the face of brief toxic exposures is exemplified by the results from the microcosm study (section 6.1.2.11). Zooplankton in the microcosms would be expected, based on laboratory data, to have acute LC50s between 0.1 and 1 µg/L. Impacts were seen following exposures to 0.3-3 µg/L chlorpyrifos, but a significant proportion of the population survived even the highest exposure. Chlorpyifos dissipated rapidly from the microcosms, and populations recovered by 2-4 weeks after treatment. Lower populations in treated microcosms were apparent for a further 4 weeks, but the differences were not statistically significant. Pulse exposures to chlorpyrifos at concentrations up to 1 µg/L appear to cause no lasting ecological damage, although short term impacts on sensitive invertebrates may occur at lower concentrations. If the 1 g/L criterion is used, the assessment endpoint for invertebrates is lower than for fish by a factor of two, and

measures that avoid acute fish impacts should also be fairly protective of invertebrate populations.

8.1.2.10 Hazard to invertebrate populations – model predictions

The AgDRIFT™ model predictions for fish (see section 7.1.2.4) require little modification for assessment of hazard to invertebrates. Microcosm studies (see section 6.1.2.11) indicate that exposures below 1 g/L will cause only temporary invertebrate reductions. Hazard to individual invertebrates is higher than to fish, but populations can recover provided that chronic exposure remains below 1 g/L. Acute exposures above 1 g/L may be more damaging to invertebrates as a wider range of species is sensitive at such levels, compared with fish where most species can tolerate concentrations to 10 g/L.

The buffer zone recommendations for fish arising from the AgDRIFT™ model predictions do not require major revision for invertebrates. For cotton, it is clearly essential to observe a 300 m buffer, and highly desirable to use coarse droplets rather than medium. Fine droplets are too hazardous to aquatic life unless very large buffer zones are observed. Aerial applications to vegetable crops should also observe a 300 m buffer, although it is acknowledged that this may be impractical. Buffer zones of 50 m should be observed when spraying dormant orchards or more densely foliated trees such as citrus and tall pears, increasing to 100 m when application rates exceed 2 kg/ha chlorpyrifos.

European approaches predict less onerous buffer requirements, apparently because of the use of less drift prone nozzles. For a water depth of 15 cm, the basic drift values derived by Ganzelmeier *et al* (1995) can be used to justify a buffer distance of 5 m for cereals and vegetables, increasing to 30 m for orchards. Orchard buffers would need to increase to 40 m where application rates exceed 2000 g/ha, and to 50 m where rates exceed 4000 g/ha, as may occur in citrus. These buffer requirements are more pragmatic than the AgDRIFT predictions, but need to be combined with other measures, particularly the use of lower drift nozzles, when spraying chlorpyrifos near sensitive areas such as waterways.

8.1.2.11 Hazard to invertebrate populations – Australian field data

Artificial stream studies in Queensland and elsewhere indicate that a pulse exposure to 0.1 µg/L chlorpyrifos should have no effect on invertebrates at species or community level, but that chronic exposures to such concentrations is likely to lead to reduced diversity, number of taxa and abundance. Even a pulse of 5 g/L had no effect, but this finding should be treated with caution as fauna inhabiting artificial streams tend to be resilient species, and natural environments are likely to be more sensitive to chlorpyrifos exposures.

As noted above, most chlorpyrifos detections in Australian surface waters are below the threshold of 1 g/L. Such exposures are not expected to give rise to lasting damage to invertebrate communities. However, occasional higher detections, generally below 10 µg/L but reaching as high as 26 µg/L in one sample from the

Gwydir, are more likely to cause damage. These higher detections may reflect non-agricultural uses such as termite protection of bridges, but may also occur in shallow water contaminated through excessive spray drift from higher rate uses, such as for cotton.

Analysis of available data indicate that the high dose pulse exposures that occur occasionally in Australian rivers and irrigation channels are likely to cause significant damage to invertebrate populations in localised areas, but that background exposures do not appear to reach levels that could be damaging in the longer term. Damaging levels of chlorpyrifos are only found occasionally, for example in less than 1% of samples taken in cotton areas of NSW. Invertebrate populations have the ability to reestablish from surrounding unaffected areas when impacts are sporadic and localised, as appears to be the case with chlorpyrifos.

The high dose exposures may reflect spray drift events or non-agricultural uses such as termite protection of bridge timbers, whereas background exposures probably reflect diffuse agricultural inputs. There is clearly a need to improve current agricultural practices in order to further reduce off-target movement of pesticides, with particular attention to matters such as spray drift that can give rise to elevated pulse exposures. Simple calculations indicate that spray drift can give rise to levels of contamination in waterways that would be harmful to aquatic life. A failure to detect any incidents does not discount their occurrence, given the limited aquatic persistence of chlorpyrifos. Surface runoff is probably the main contributor to the background exposures, but may also deliver high concentrations to riverine systems if localised summer storms that are hard to predict occur soon after treatment.

8.1.2.12 Probabilistic approaches to water quality

As noted above, the deterministic quotient approach to assessing aquatic hazard is conservative. It aims to protect the most sensitive species, and to do so with a high degree of certainty by the application of safety factors to the lowest concentrations found to be toxic in testing. In recognition that efforts to assure absolute safety can impose excessive costs, regulatory authorities are beginning to consider probabilistic approaches that aim to protect a certain proportion of species (typically 90-95%) with a high level of confidence (typically 90-95%). Methods that aim to protect 100% of species tend to deliver exceedingly small exposure concentrations that are impractical to implement as standards.

The US EPA has mandated probabilistic techniques for derivation of water quality standards for the Great Lakes System. Available toxicity data are first grouped by species, and species mean acute values (the geometric mean of the data) are determined. A similar exercise generates genus mean acute values where data are available for more than one species in a genus. The final acute value is the calculated concentration such that 95% of genera have higher genus mean acute values (unless important/critical species with greater sensitivity are present, in which case the final acute value defaults to the species mean acute value). The criterion maximum concentration is about half this final acute value, and represents the highest

concentration to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

A final acute value of 148 ng/L has been determined for chlorpyrifos, based on 35 acute studies that met conservative selection criteria (Giesy *et al*, 1999). The same authors have also calculated a 10%ile of 102 ng/L for all 48 hour normalised species mean acute values for freshwater aquatic organisms. This reduced to 55 ng/L when only freshwater arthropods were considered. For freshwater vertebrates, the 10%ile was 5.4 g/L. The authors note that the 10%ile of 102 ng/L approximates the no observed effect concentration in microcosms. Responses to toxicants are more sensitive in laboratory test systems than in natural environments (or simulations such as microcosms) where sorptive interactions reduce bioavailability. The use of laboratory data therefore represents a conservative approach to hazard assessment.

The above authors use US surface water monitoring data to determine the likelihood of exceeding the above criteria. Deterministic assessments based on risk quotients had found unacceptable levels of concern from use of chlorpyrifos in corn, but this outcome was considered over-protective given the lack of widespread aquatic impact. While the probabilistic approach is less protective, it is important to recognise that exceeding the 10 centile of laboratory toxicity values does not infer the permanent removal of 10% of species from an ecosystem, or that such an outcome would be acceptable. Species with short regeneration times, such as the arthropods that are particularly sensitive to chlorpyrifos, can readily recover from such insults by repopulating from unexposed refugia or from less sensitive resting stages. Functional substitution means that temporary reductions in some species can have a short term effect on ecosystem structure without compromising ecosystem function. In the case of chlorpyrifos, phytoplankton are relatively insensitive, and some zooplankton species are much more tolerant than others.

For the Lake Erie basin, the analysis found only low probabilities (<10%) that the above criteria would be exceeded. In California, some 30% of results from drains exceeded the 10 centile of 102 ng/L for all 48 hour normalised species mean acute values, but less than 10% of monitoring data from larger rivers violated the criteria. Overall, the available data did not suggest ecologically significant risks, except possibly in a few locations. Site specific risk assessments and mitigation measures would be warranted where such risks are identified.

8.1.2.13 Chronic and multiple exposures

Australian and overseas exposure data indicate that aquatic exposures are primarily acute, occurring as relatively short-term pulses. Chlorpyrifos dissipates rapidly from the water column, and inputs are discrete rather than continuous. Chlorpyrifos volatilises rapidly from foliage, but has limited atmospheric persistence and does not appear to contaminate water significantly through the vapour route. The possibility remains of chronic low level exposure, at concentrations below analytical detection. Multiple sequential acute exposures are probably of more concern than chronic background exposures.

The effects of sequential exposures to chlorpyrifos are likely to be more significant, and it would appear essential to avoid repeat applications for an appropriate period where there is a likelihood of aquatic exposure. An interval of 3 weeks can be suggested, based on the recovery period of 2-4 weeks for arthropods in microcosms (see section 6.1.2.11), but is probably conservative as opportunities for repopulation from refugia are limited in microcosms. In addition, a second exposure within this timeframe may only delay rather than preclude recovery, as indicated by the alternating spray/slurry treatments in microcosms. These experiments showed that invertebrate populations could recover from repeated pulse exposures to about 1 g/L chlorpyrifos, provided that the exposures were not too frequent. Populations, particularly of cladocerans, did not recover from six consecutive weekly spray treatments but were able to recover within 6 weeks after three consecutive fortnightly treatments. This implies a minimum repeat interval of 10 days, as each spray treatment was followed 4 days later by a slurry treatment.

Furthermore, monitoring indicates that chlorpyrifos contamination events occur with low frequency. The probability of two such events occurring in rapid succession at a specific location is therefore very low. The principal registrant has argued that significant adverse ecological effects are unlikely to result from sequential applications at 7-14 day intervals. Environment Australia agrees with this analysis and notes that it is consistent with the microcosm data showing recovery from consecutive fortnightly spray treatments, but not from weekly treatments.

There is also the question of simultaneous exposures to other toxic chemicals, particularly where chemicals are used heavily, as in cotton production. It is unrealistic to consider the ecological effects of chlorpyrifos in isolation. Heavy use of other toxic insecticides in crops such as cotton may compromise the ability of populations to recover from acute chlorpyrifos impacts, just as chlorpyrifos exposures will delay recovery from other chemical insults.

8.1.2.14 Summary of aquatic hazard

Simple deterministic predictions indicate that essentially all uses of chlorpyrifos present high hazard to fish and aquatic invertebrates. Spray drift appears to be the main risk factor, but runoff can also be problematic, particularly if rain falls soon after treatment. Some uses can be considered of low hazard, however. Use of soil incorporated sustained release formulations in sugar and ornamentals is not expected to lead to significant non-target exposure because of low release rates.

Calculations using the AgDRIFT model indicate that substantial reductions in drift can be achieved by observing buffer zones upwind of water bodies. In order to protect aquatic life from most non-target exposures, a minimum buffer of 300 m should be observed for aerial application to cotton, and fine droplets should be avoided (a vmd of at least 226 m is preferred). Aerial applications to vegetable crops should observe a buffer of 100 m. For orchard treatments, a buffer of 50 m should be observed during the dormant period or when treating densely foliated trees such as citrus and tall pears, increasing to 100 m where rates exceed 2 kg/ha chlorpyrifos.

Smaller buffer distances can be determined using other approaches, such as that of Ganzelmeier *et al* (see section 7.1.2.5). The different outcomes appear to reflect different operating conditions, with hollow cone nozzles used for the AgDRIFT approach and flat fan nozzles by Ganzelmeier *et al*.

Note that, from an individual organism perspective, the above restrictions would only offer acceptable safety margins for fish. Essentially, the buffer distances aim to restrict peak concentrations in the water below 1 g/L. Aquatic inver tebrates are much more sensitive, and can be expected to suffer sporadic and localised acute impacts from spray drift or runoff events. Single species laboratory studies show adverse effects well below 1 g/L, including one EC50 of 15 ng/L for *Daphnia magna*. In microcosms, adverse effects in invertebrates occur at concentrations down to about 0.1 g/L, but populations can recover from acute exposure to 1 g/L. In natural environments, adverse impacts on invertebrate populations are not expected at current exposure levels because of rapid regeneration times. Invertebrates can repopulate from surrounding areas that have not been impacted by chlorpyrifos, or from less sensitive resting stages.

The preceding hazard assessment is mainly based on single acute exposures only, as there is little evidence for significant chronic exposure to chlorpyrifos in Australian waters. However, heavy use of other toxic insecticides in crops such as cotton may compromise the ability of populations to recover from acute chlorpyrifos impacts, particularly as microcosm and pond studies show that this recovery may require several weeks. The effects of sequential exposures to chlorpyrifos are likely to be more significant, and it would appear essential to avoid repeat applications for an appropriate period. An interval of 10 days is suggested, based on population recovery following forthnightly but not weekly exposures of arthropods in microcosms (see section 6.1.2.11). There is also the question of simultaneous exposures to other toxic chemicals, particularly where chemicals are used heavily, as in cotton production. Chlorpyrifos may be tank mixed with a broad range of compatible insecticides. Such exposures are likely to increase the susceptibility of non-target organisms to chlorpyrifos intoxication. Few data are available on the toxicity of chlorpyrifos when mixed with other chemicals, and a well designed study would help shed light on this area.

Linking invertebrate impacts with chlorpyrifos exposure, or disproving such connections, would be a difficult undertaking in non-laboratory situations where other contaminants exert simultaneous impacts. Natural fluctuations in environmental variables such as temperature, turbidity and water flow would also affect invertebrate populations, making effects from anthropogenic contaminants difficult to demonstrate. The ANZECC Water Quality Guideline for protection of aquatic life (1 ng/L) is well below the usual detection limits (10-100 ng/L) for chlorpyrifos in surface waters. It will only be possible to have confidence that residues of toxic insecticides such as chlorpyrifos are not impacting on aquatic life by using less toxic alternatives instead. While this may not be feasible at the present time, it should remain a medium to longer term objective.

At the present time, a range of options can be used to minimise aquatic contamination through spray drift and runoff. To minimise spray drift, application should only occur under suitable meteorological conditions, avoiding application during periods of atmospheric instability, high winds or dead calm. Placement spraying using larger droplets is greatly preferred over ULV treatment when applying pesticides near sensitive areas. It is strongly recommended that consideration be given to encouraging such options for use of chlorpyrifos in cotton.

Avoidance of application when heavy rains or storms are expected is crucial if surface runoff is to be minimised. This is particularly important for chlorpyrifos as volatilisation from foliage greatly reduces the contribution of foliar washoff to aquatic contamination. On-farm retention of at least the first flush of stormwater is another important technique for reducing off-site contamination.

The cotton industry has taken the lead in developing best management practices for avoiding off-site contamination by pesticides and other pollutants. The first edition of the Australian Cotton Industry's Best Management Practices Manual, released in November 1997, contains detailed guidance for minimising off-site impacts. The manual is an important resource that should be consulted by other agricultural industries with a view to reducing the environmental impacts of their production methods.

9. CONCLUSIONS

Chlorpyrifos is widely used as an agricultural insecticide and for general urban pest control, including lawn maintenance and termite protection. A large volume of environmental data is available for this substance. The data show that chlorpyrifos will tend to become associated with the soil beneath the treated crop, where it is slightly to moderately persistent. However, aerial transport will occur through spray drift and volatilisation (although only the former will lead to significant off-target deposition). Surface runoff represents a significant waterborne transport pathway. Chlorpyrifos is highly to very highly toxic to birds and aquatic fauna.

9.1.1.1 Avian issues

Simple screening methods identify a high acute hazard to birds from use of chlorpyrifos. Incident reports confirm the existence of avian impacts, which have been reported to attend the use of chlorpyrifos granules in the home garden and chlorpyrifos termiticides in urban situations. Use of baits to control surface feeding soil insects in agricultural situations also reportedly gives rise to avian mortality on occasion when pest pressure from larger invertebrates is heavy. Recent significant but unexplained avian incidents in the Macquarie Marshes and in Florida suggest that chlorpyrifos can present particular hazards to birds in some circumstances. Use of chlorpyrifos does not appear to incur widespread avian impacts, but isolated incidents are likely to be occurring where birds ingest granules or invertebrates containing significant levels of chlorpyrifos. Limited observations suggest the occurrence of similar and possibly more widespread incidents in reptiles that feed on contaminated invertebrates. A watching brief needs to be maintained on these issues. Specific monitoring of some

products (home garden ant control granules and baits for surface feeding insects in agriculture) appears warranted. Registrants should keep the NRA informed of any further incidents that may occur in Australia or overseas. Label warnings appear warranted.

9.1.1.2 Aquatic issues

Chlorpyrifos dissipates from water through hydrophobic mechanisms such as volatilisation and sorption to sediment. Environmental monitoring finds only occasional detections, nowithstanding widespread use. When detected, chlorpyrifos generally occurs at concentrations in the order of 0.1 µg/L, a concentration likely to be lethal to sensitive aquatic invertebrates although it should not impact on populations. Occasional higher detections in agricultural areas, at concentrations between 1 and 30 µg/L, may reflect spray drift incidents or high rate non-agricultural uses such as termite protection of bridges. Aquatic contamination may extend into the hundreds of µg/L in urban areas, apparently as a result of high rate underslab treatments for termite protection, with insufficient precautions taken to avoid surface runoff from the treated area. Overseas evidence indicates that such problems may also occur with post-construction treatments if termiticide emulsion is injected into sub-surface drainage channels. State authorities need to be mindful of such possibilities when investigating fish kills associated with use of chlorpyrifos in urban areas.

Artificial stream studies indicate that chronic exposure to 0.1 µg/L is likely to lead to reduced diversity, number of taxa and abundance or aquatic arthropods, but that pulse exposures of this magnitude should have no effect on invertebrates at species or community level. Fish are less sensitive, but may suffer impacts from some of the higher pulse exposures that have been documented to occur, as would some invertebrates.

Current environmental exposures to chlorpyrifos in Australian surface waters appear unlikely to exert broadscale environmental impact, but isolated incidents of fish and invertebrate mortality are likely to be occurring.

Modelling studies suggest that aquatic hazards from spray drift can be mitigated to acceptable levels by observing appropriate buffers upwind from aquatic areas, depending on application method and rate. For aerial application to cotton, a buffer of at least 300 m is recommended, together with use of coarse droplets. Buffers do not appear necessary for lower rate ground based treatments or the use of soil incorporated slow release formulations such as used in sugar.

The modelling studies also suggest that surface runoff may give rise to aquatic hazard, particularly if application rates are high, as for cotton. Vegetated filter strips are one option for mitigating this hazard. Field studies show that concentrations in surface runoff decline markedly in the 24-48 hours after treatment, largely because of foliar volatilisation. Avoidance of treatment when heavy rains are expected would be expected to significantly reduce risks from surface runoff. On-farm retention of at least the first flush of stormwater will also significantly reduce aquatic contamination from surface runoff.

9.1.1.3 Labelling issues

Risks from use of chlorpyrifos can be reduced by modifying labels to alert users to the hazards and ways of minimising them. Hazards are particularly acute for the high rate termiticide products. Warning statements could be expressed as follows:

> VERY HIGHLY TOXIC TO FISH AND AQUATIC LIFE. Rinse waters, and runoff from treated areas, MUST NOT enter drains or waterways. For underslab treatments, the moisture membrane MUST be installed immediately after treatment. Do NOT apply to waterlogged soils. Do NOT apply if heavy rains are expected to occur within 48 hours of application. Users may be liable to prosecution under State legislation if surface waters become contaminated through use of this product.
>
> HIGHLY TOXIC TO BIRDS. Birds may be killed if they consume food such as grubs and worms from treated areas. Any treated backfill MUST be replaced immediately.

For general agricultural uses, risks could be reduced by upgrading labels to warn users to avoid runoff and drift after application. Warnings could be expressed as follows:

> HIGHLY TOXIC TO BIRDS AND REPTILES. VERY HIGHLY TOXIC TO AQUATIC LIFE.
>
> Allow maximum time interval (preferably at least 10 days) between repeat applications when applying sprays to, or near, sensitive areas.
>
> Do NOT apply under meteorological conditions or from spraying equipment which could be expected to cause spray to drift onto wetlands, natural surface waters, neighbouring properties or other sensitive areas.
>
> Do NOT apply if heavy rains or storms that are likely to cause surface runoff are forecast within two days of application.
>
> DO NOT apply when irrigating or for at least two days after irrigation, or to waterlogged soil, or while water remains in furrows unless tailwater can be captured.
>
> DO NOT apply near sensitive areas (such as natural streams, rivers or waterways and human dwellings) without applying measures to limit the spray drift on these areas. A spray drift management strategy such as those in the 'Best Management Practices Manual for Cotton Growers' or the 'Pilots and Operators Manual' should be applied.
>
> A minimum buffer of 100 m should be observed upwind of sensitive areas where chlorpyrifos is applied by air using medium volume sprays to crops other than cotton.

A minimum buffer of 300 m should be observed upwind of sensitive areas for aerial treatment of cotton. Coarse droplets (vmd greater than 250 m) should be used.

A 30 m buffer should be observed upwind of sensitive areas when spraying dormant orchards, dense foliage (such as citrus) or large trees (such as mature pears). The buffer should be increased to 40 m when application rates exceed 2 kg/ha chlorpyrifos, and to 50 m where application rates exceed 4 kg/ha chlorpyrifos.

Do NOT allow water from treated paddocks to enter adjacent pastures, crops or water unless irrigation tailwater and up to 25 mm of rainfall can be captured on farm.

The grain bait products used to control surface feeding insects in agricultural situations warrant specific statements in view of their avian hazard and the avian incidents reported, for example: "Birds may be killed if they feed in areas where granules have been laid".

Label upgrades also appear warranted for household products. Several products are registered for lawn maintenance by the homeowner. In general, users are advised to dispose of empty containers by wrapping in paper and placing in the garbage, but it appears that at least one product (David Grays Lawn Beetle Spray) may carry instructions to wash out the container thoroughly before disposal. Such advice is likely to introduce chlorpyrifos residues into sewers, and should be replaced by the standard statement: "Dispose of empty container by wrapping in paper, placing in plastic bag and putting in garbage". Similar attention should be given to household insecticide and companion animal products, to ensure that rinsing does not form part of the container disposal instructions.

The home garden ant control products are of particular concern with respect to avian toxicity. Label statements need to be included to warn of the risk to birds, for example as follows: "DO NOT heap granules. Birds may be killed if they eat granules. DO NOT feed granules or otherwise expose to wild or domestic birds".

9.1.1.4 Continuation of certain use patterns

Discontinued use patterns, such as for rice in Queensland, should be deleted from labels.

Use in cotton raises particular concerns as the application rate is high and the preferred ULV method of application is especially prone to aerial drift. Application to cotton using large droplet placement spraying needs to be actively encouraged.

The home garden granular ant control products appear problematic as they are likely to be used at high rates and contain sufficient toxicant to kill birds that ingest them. Mortality of pigeons that ingested granules has recently been reported from the

Northern Teritory. Environment Australia is unable to support continued registration of granular home garden products for ant control, given the hazard identified and the evidence that bird kills can occur. Provision of further information, such as obtained from careful monitoring to better determine the likelihood of avian consumption, may allow reconsideration of this position. Such monitoring would aim in the first instance to determine through careful observation whether birds consume granules in the home garden situation. If such exposure occurs, further work will be necessary to determine whether adverse impacts occur. Protocols should be agreed between registrants, the NRA and Environment Australia before monitoring occurs.

Registrants of the bait products used to control surface feeding insects in agriculture should also address the issues of whether birds are attracted to the baits or to baited areas, and whether such attraction leads to adverse effects. If no such information is currently available, it will need to be generated by monitoring, as outlined above.

9.1.1.5 Education of users

Particular concerns arise in urban areas. High application rates mean that the termiticide use, particularly pre-construction across new housing estates, presents a high hazard to aquatic life if surface runoff occurs. Use of household products appears to give rise to excessive concentrations in sewage effluent in the Sydney region and probably in other cities. This illustrates the importance of following label warnings. Responsible registrants will educate users regarding these hazards, and ensure that labels contain appropriate warnings, so that risks can be minimised.

9.1.1.6 Conclusion

Responses to this draft report will be taken into consideration in formulating a final regulatory position on chlorpyrifos.

Environment Australia
Environment Protection Group

September 1999.

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