Australian Government

Australian Pesticides and Veterinary Medicines Authority

# Reconsideration of chlorpyrifos:

Supplementary environment assessment report

Part 1—Home garden, domestic and certain non-agricultural uses

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# EXECUTIVE SUMMARY

Chlorpyrifos is a broad spectrum, non-systemic organophosphorus insecticide with contact, stomach and respiratory action. It acts by cholinesterase inhibition, which disrupts nerve impulse transmission. Since the chlorpyrifos review includes consideration of environmental risks its potential adverse impacts on non-target organisms such as birds, aquatic organisms, terrestrial invertebrates, reptiles, mammals and vegetation have been assessed.

The interim environmental assessment report for chlorpyrifos published in September 2000 identified potential unacceptable risks to birds and aquatic organisms, particularly fish (APVMA 2000). Therefore this supplementary report considers updated environmental data which have resulted in revised avian and aquatic toxicological end-points and revised risk assessment. The key revisions to environmental toxicological end-points are as follows:

- there are data available warranting a revision of avian toxicological end-points, which are as follows:
  - the acute avian oral lethal dose ($LD_{50}$) has been amended to 28.9 mg/kg bw, compared to 20 mg/kg bw used in the interim environmental assessment (APVMA 2000). This was based on a geometric mean approach. A species sensitivity distribution resulted in a HD5 ($5^{th}$ percentile of the distribution) of 9.5 mg/kg bw, which was applied in a higher tier avian assessment
  - the chronic avian dietary no observed effect concentration (NOEC) 25 mg/kg diet was affirmed as the most appropriate end-point. This relates to a daily dose of 2.88 mg/kg bw/d, which is applied in the risk assessment.
- the consideration of additional aquatic higher tier data has resulted in a 10-fold reduction of the aquatic toxicity end-point, the aquatic NOEC to 0.1 µg/L.

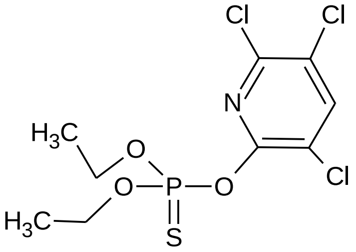
Risks to birds and native mammals have been assessed. It was demonstrated that the highest risk was through acute exposure to birds, and mitigation measures in this area were considered protective to native mammals and to birds through chronic exposure. Based on a screening assessment, rates exceeding 38 g ac/ha were identified as potentially resulting in an acute risk to birds. Analysis of toxicity data, higher tier avian assessment and a range of field data demonstrated that single application rates below 850 g ac/ha are within acceptable limits and the possibility of avian field mortality is unlikely.

The aquatic runoff assessment was performed applying Australian specific real world data since the screening approach identified an unacceptable risk at most surface application rates. Applying a refined method that allowed the use of slope in different growing areas and incorporating data for soil organic carbon, soil profiles, rainfall and stream flow in different geographic regions, both temporal and spatial scale runoff assessments were undertaken. These were variable in their outcomes as the results depended on several factors such as application rates and methods (foliar-applied, bare soil, soil-incorporated), numbers of applications and time interval between applications.

Where unacceptable environmental risks are identified as an outcome of the risk assessment, consideration is given to whether risk management measures, such as reduced application rates, label restraints or environmental protection statements, would reduce the risk to an acceptable level.

# 1 CHEMICAL IDENTITY

Table 1 Summary of chemical identity

| | |
|---|---|
| Common name | Chlorpyrifos |
| Chemical name—CAS | O,O-Diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate |
| CAS registry number | 2921-88-2 |
| Molecular formula | $C_9H_{11}Cl_3NO_3PS$ |
| Molecular mass | 350.6 g/mol |
| Structural formula |  |

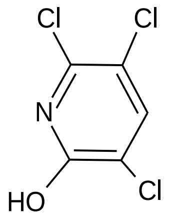
# 2 PHYSICO-CHEMICAL PROPERTIES

### Table 2: Summary of physico-chemical properties

| | |
|---|---|
| **Melting point** | 42–43.5°C |
| **pKa** | No readily dissociable functionality |
| **Vapour pressure** | 2.7 mPa at 25°C |
| **Solubility in water** | 1.4 mg/L at 25°C |
| **Log Kow (n-octanol/water)** | 4.7 |

### Table 3: Degradation Product: TCP

The main degradation product from chlorpyrifos is 3,5,6-trichloro-2-pyridinol (TCP). The following environmentally significant properties have been determined for TCP.

| | |
|---|---|
| **Structural formula** |  |
| **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<br>49.1 mg/L at 25°C and pH 7 |
| **Log Kow (n-octanol/water)** | 3.2 at pH 3<br>1.3 at pH 7 |

# 3 INTERNATIONAL REGULATORY STATUS

## 3.1 European commission

Chlorpyrifos is registered in Europe but not in all countries. In 2002, home uses of chlorpyrifos were phased out. Chlorpyrifos is registered in the UK for use on cole crops (broccoli, Brussel sprouts, cabbage and cauliflower) in protected situations (HSE 2017). Currently, authorisation of chlorpyrifos is being re-evaluated which is expected to complete in January 2020.

## 3.2 United States of America

The US Environment Protection Agency (US EPA) completed its re-evaluation in 2000 that led to the phasing out of home, landscape and lawn uses of chlorpyrifos (except insect baits) because of exposure risks to children. Over the years the US EPA has also mandated spray drift restrictions to minimise the risks to aquatic habitats and residential areas and schools.

In 2006, the US EPA completed a Reregistration Eligibility Decision (US EPA 2006), which found that the registration of chlorpyrifos products should continue, provided certain risk mitigation measures were implemented. To mitigate ecological risks, mandatory label amendments were required including the establishment of no-spray buffer zones around water bodies, reductions in application rates and frequency and increased treatment intervals.

US EPA also incorporated information from a 2012 assessment of spray drift exposure and new restrictions were put into place to limit spray drift. Currently, US EPA is continuing to evaluate the potential risks posed by chlorpyrifos as part of the ongoing registration review and intend to complete the assessment by October 2022.

## 3.3 Canada

Chlorpyrifos is currently being re-evaluated by PMRA (Pest Management Regulatory Agency, Health Canada). Chlorpyrifos was re-evaluated in two phases based on use patterns.

The phase 1 mainly covered the non-agricultural uses (eg, indoor and outdoor residential uses). The regulatory actions announced on September 28, 2000, phased out use of chlorpyrifos in and around homes and residential areas such as parks and school yards. As part of the PMRA’s re-evaluation of chlorpyrifos, an update note was published in 2007 requiring the implementation of interim environmental risk mitigation measures including the establishment of buffer zones to protect aquatic ecosystems and precautionary label statements for the protection of bees (PMRA 2007). The phase 2 covered the agricultural and forestry uses and the final regulatory decision is scheduled for release in 2020.

# 4 ENVIRONMENTAL EXPOSURE

## 4.1 Application and use patterns

Chlorpyrifos products are used in domestic, veterinary, commercial pest control and agricultural situations. There are uses registered in turf and pastures. Domestic uses involve foliar and bait application in gardens (including use by householders or the general public) and crack/crevice treatment in buildings (eg for cockroaches).

Table 4: Summary of chlorpyrifos domestic and certain non-agricultural use-patterns

| Situation | Pests | Maximum application rate |
|---|---|---|
| Home garden, lawns, domestic premises | Ants, beetles, cockroach, crickets, earwig, grubs, millipedes, slaters, spiders, worms | Granular 40 g ac/100 $m^2$<br>Spray 20 g ac/50 $m^2$ |
| Turf | Ants, beetles, crickets, earwigs, millipedes, slaters | Spray 3000 g ac/ha |
| Domestic and public places<br>Commercial and industrial areas | Ants, cockroaches, fleas, silverfish, spiders | Spray 50 g ac/10 L water (apply as required) |
| Ornamental | Beetles, flies, scarabs, weevils | Spray 20 g ac/100 L water<br>Granular 40 g ac/100 $m^2$ |
| Vegetation, polluted water impoundment | Mosquitoes | Spray 50 g ac/ha (vegetation)<br>Spray 1 g ac/10,000 L water (polluted water impoundment) |

### Urban/domestic use patterns

Chlorpyrifos products are registered for home garden use and include granular and spray formulations for control of insects in lawns and home gardens. Granular formulations are also registered for use in other public areas such as bowling greens, golf greens and tennis courts.

### Products not considered for this assessment

Uses that were not considered in this assessment include agricultural uses, termite control uses and uses exclusive for commercial nursery. Several registered chlorpyrifos products were considered to be of low environmental risk and were not considered as part of this report such as banana bags, banana ribbon strips and cattle ear tags.

## 4.2 Environmental monitoring

There are several state and territory based monitoring programs reporting the occurrence of pesticides including chlorpyrifos in the environment. The Tasmanian Pesticide Water Monitoring Program involves routine monitoring of water catchments for a range of pesticides, including chlorpyrifos. Launched in 2005, the program includes baseline monitoring of rivers and streams across Tasmania on a quarterly basis as well as flood monitoring collected during flood events at sites on the George and Duck Rivers. Chlorpyrifos has not been detected (method reporting limit 0.1 µg/L) in any samples at any sites over the course of the monitoring program (Tasmanian DPIPWE 2016).

Australian water monitoring data are collected and reported by several irrigation companies as part of ongoing licence commitments with the State government departments. Reports published by Murrumbidgee Irrigation provide monthly data from 14 different surface water areas sampled within the Murrumbidgee Irrigation Area. Drought conditions for many years have meant limited flows, so many samples were unable to be taken (in times of 'no flow'). Licence Compliance Reports from 2006 onwards indicate that chlorpyrifos is consistently found at levels above the limit of detection, but most samples are below the aquatic NOEC of 0.1 µg/L, with the exception of one sample in 2007 (0.1 µg/L) and two samples from 2013 (0.138 and 0.250 µg/L) (Murrumbidgee Irrigation, Annual Compliance Reports[1]).

Similar reporting is available from Colleambally Irrigation, which has published annual reports since 2001 summarising testing results for chlorpyrifos concentration in water from various sites within the Colleambally Irrigation Area. Since 2001, chlorpyrifos has been reported above the limit of detection on two occasions with water concentrations of <0.20 (2015) and 30 µg/L (2006) (Colleambally Irrigation, Annual Compliance Reports[2]).

[1]mirrigation.com.au/Environment/Annual-Compliance-Report

[2]new.colyirr.com.au/?TabId=107

# 5 ENVIRONMENTAL EFFECTS

The ecotoxicological data that were available during the year 2000 were reported in the chlorpyrifos interim review report (APVMA 2000). This supplementary report considers only the new data available since completion of the interim report that may result in amendment of ecotoxicity end-points used previously in the risk assessment.

After considering the post 2000 interim environmental assessment report outcomes and all available contemporary literature, the APVMA's environmental concerns are focused on potential risks to avian and aquatic organisms.

## 5.1 Birds and mammals

Chlorpyrifos was nominated for review in Australia because of concerns about its human toxicity, its acute toxicity to birds and its water pollution potential. Risks to mammals were not assessed in the interim review. In their conclusion on the peer review of chlorpyrifos, the European Food Safety Authority (EFSA) could not exclude a high acute risk to birds and small herbivorous mammals with available data; and a high long term risk to mammals was identified (EFSA 2011). In their assessment, the US EPA identified risks to small mammals and birds for nearly all registered outdoor uses (US EPA 2002). Similarly, the APVMA's interim assessment report in 2000 identified a potentially high acute risk to birds from use of chlorpyrifos.

Birds have been reported to consume both the chlorpyrifos granules directly in the home garden as well as insects poisoned by chlorpyrifos uses in urban situations resulting in adverse effects. Use of baits to control surface feeding soil insects in agricultural situations also reportedly gives rise to avian mortality on occasions when pest availability for bird predation (particularly larger invertebrates) is high. As reported in the interim report, significant but unexplained avian incidents in the Macquarie Marshes (1995) and in Florida, United States (1997) 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. Consequently, the interim review recommended a watching brief be maintained on these issues with specific monitoring of some products (home garden ant control granules and baits for surface feeding insects in agriculture). These products have been re-evaluated in this assessment.

### Avian acute oral

The interim environmental assessment (APVMA 2000) reported several acute $LD_{50}$ results of less than 20 mg/kg, but because of limitations including lack of study details, the results were not used for the risk assessment. A review of literature since the interim review revealed further non-standard bird toxicity data, however, they did not meet contemporary study guidelines and were not considered.

The US EPA report for chlorpyrifos, used in the interim reregistration eligibility decision (IRED), has been obtained in part (US EPA 1999). This document contains a large amount of avian toxicity data that have been considered in this assessment, but were not available for comparison during APVMA's interim review in 2000.

Table 5 below summarises the acute oral avian toxicity results reported by US EPA (1999) and Solomon et al (2001), that were considered in this report.

**Table 5: Acute avian oral toxicity results**

| Species | $LD_{50}$ (mg/kg) | References cited in US EPA (1999) |
|---|---|---|
| Ring-necked pheasant (male) (*Phasianus colchicus*) | 8.41 | Hudson et al (1984) |
| Ring-necked pheasant (female) (*Phasianus colchicus*) | 17.7 | Hudson et al (1984) |
| Northern bobwhite (*Colinus virginianus*) | 32 | Smith (1987) |
| Mallard duck (female) (*Anas platyrhynchos*) | 75.6 | Hudson et al (1984) |
| Mallard duck (*Anas platyrhynchos*) | 476 | Roberts and Phillips (1987) |
| Mallard duck (duckling; male and female) (*Anas platyrhynchos*) | 112 | Hudson et al (1984) |
| Common crackle (*Quiscalus quiscula*) | 5.62 | Schafer and Brunton (1979) |
| Common pigeon (*Columba livia*) | 10.0 | Schafer and Brunton (1979) |
| House sparrow (*Passer domesticus*) | 10.0 | Schafer and Brunton (1979) |
| | 122 | Gallagher et al (1996) |
| House sparrow (male) (*Passer domesticus*) | 21 | Hudson et al (1984) |
| Red-winged blackbird (*Agelaius phoeniceus*) | 13.1 | Schafer and Brunton (1979) |
| Coturnix quail (*Coturnix japonica*) | 13.3 | Schafer and Brunton (1979) |
| Coturnix quail (male) (*C. japonica*) | 15.9 | Hudson et al (1984) |
| Coturnix quail (female) (C. japonica) | 17.8 | Hudson et al (1984) |
| Sandhill crane (male) (*Grus Canadensis*) | 25–50 | Hudson et al (1984) |

| Species | $LD_{50}$ (mg/kg) | References cited in US EPA (1999) |
|---|---|---|
| Rock dove (*Columba livia*) | 26.9 | Hudson et al (1984) |
| White leghorn cockerel (*Gallus domesticus*) | 34.8 | Miyazaki and Hodgson (1972) |
| Canada goose (*Brania Canadensis*) | 40–80 | Hudson et al (1984) |
| Chuckar (male) (*Alectoris chukar*) | 61.1 | Hudson et al (1984) |
| Chuckar (female) (*Alectoris chukar*) | 60.7 | Hudson et al (1984) |
| California quail (female) (*Callipepla californica*) | 68.3 | Hudson et al (1984) |
| Starling (*Sturnus vulgaris*) | 75 | Schafer and Brunton (1979) |

| Species | $LD_{50}$ (mg/kg) | References cited in Solomon et al (2001) |
|---|---|---|
| Mallard duck (*Anas plathynchos*) | 145 | Hudson et al (1972) |
| | 29.4 | Hudson et al (1972) |
| | 50.4 | Hudson et al (1972) |
| | 83.3 | Hudson et al (1972) |
| Common grackle (*Quiscalus quiscula*) | 13 | Schafer and Brunton (1971) |
| Red-winged blackbird (*Agelaius phoeniceus*) | 13.3 | Schafer and Brunton (1979) |
| Japanese quail (*Coturnix japonica*) | 13.3 | Schafer and Brunton (1979) |
| Ring-neck pheasant | 8.41 | Hudson et al (1984) |
| | 17.7 | Hudson et al (1984) |
| Leghorn cockerel (*Gailus gallus*) | 25.4 | Sherman et al (1967) |
| | 31.6 | Stevenson (1963) |

### *Acute toxicity end-point based on geometric mean approach*

Traditionally in Australian assessments, the lowest available $LD_{50}$ is adopted in the first instance for assessing risk as recommended by the Standing Council on Environment and Water (SCEW 2009). One issue with undertaking additional ecotoxicity testing on a substance, and applying the lowest available end-point is that, as more species are tested, the risk assessment is based on increasingly sensitive species. This has been considered by the European Union (EU) Joint Working Group for the European Food Safety Authority and the following approach was therefore adopted and is currently applied in EFSA assessments:

> “The geometric mean should be used for the acute assessment, except when the end-point for the most sensitive species is more than a factor of 10 below the geometric mean of all the tested species. Where this is the case, the most sensitive species will be used for the risk assessment but generally without any assessment factor (unless there are specific reasons to believe that this is not appropriate).”

This approach is adopted here and considered scientifically valid. However, it is considered important to include the ‘supplementary’ data and additional results in Table 5 above to allow the full range of data. If only those considered to fulfil EPA requirements were used, the geometric mean $LD_{50}$ is larger than applying the full range of data. The following end values were applied in the establishment of the geometric mean $LD_{50}$ and subsequent species sensitivity distribution:

**Table 6: Final avian acute $LD_{50}$ values used for geomean and SSD**

| Species | $LD_{50}$ (mg/kg) | Comment |
|---|---|---|
| Ring necked pheasant (*Phasianus colchicus*) | 12.2 | Species geomean value |
| Northern bobwhite (*Colinus virginianus*) | 32.0 | |
| Mallard duck (*Anas platyhynchos*) | 95.4 | Species geomean value |
| Common grackle (*Quiscalus quiscula*) | 8.5 | Species geomean value |
| Rock dove (*Columba livia*) | 16.4 | Species geomean value |
| House sparrow (*Passer domesticus*) | 29.5 | Species geomean value |
| Red-winged blackbird (*Agelaius phoeniceus*) | 13.2 | Species geomean value |
| Coturnix quail (*Coturnix japonica*) | 15.6 | Species geomean value |

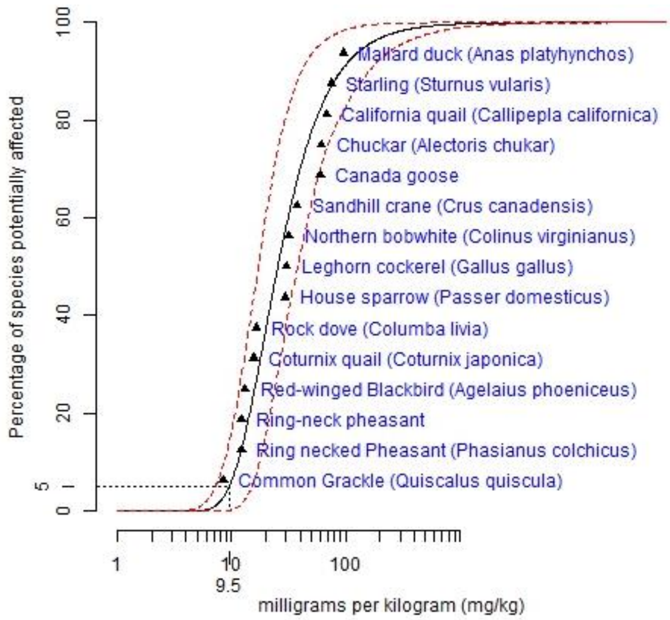
| Species | $LD_{50}$ (mg/kg) | Comment |
|---|---|---|
| Leghorn cockerel (*Gallus gallus*) | 30.3 | Species geomean value |
| Chuckar (*Alectoris chukar*) | 60.9 | |
| California quail (*Callipepla californica*) | 68.3 | |
| Starling (*Sturnus vularis*) | 75.0 | |
| Sandhill crane (*Crus canadensis*) | 37.5 | Mean of upper and lower value |
| Canada goose | 60.0 | Mean of upper and lower value |

The geometric mean avian $LD_{50}$ = 28.9 mg/kg bw. This is within an order of magnitude of the most sensitive end-point of 8.5 mg/kg (geomean) to the common grackle, so will be applied as the acute avian end-point in the risk assessment.

### *Species sensitivity distribution approach*

The species sensitivity distribution (SSD) has been generated using the BurlliOz V2.0 software. In distributing these results, geometric mean values were used for multiple results for a single species. When a range of results were reported (Canada goose and sandhill crane), the arithmetic mean of the lowest and highest values was used. The following distribution was obtained as indicated in Figure 1 below:

**Figure 1: Species sensitivity distribution results for acute avian toxicity**




The HD5 (protection of 95 per cent of species) from this distribution was calculated to be 9.50 mg/kg bw (95 per cent confidence interval 7.40–14.70 mg/kg bw).

## Avian chronic/reproduction

The APVMA interim review only considered two reproduction studies. The interim assessment did not identify an NOEC, or perform a chronic avian risk assessment. The following chronic/reproduction avian toxicity data have been reported in US EPA (1999) which are reviewed and used in the current assessment.

**Table 7: Avian chronic/reproduction toxicity results**

| Species | NOEC/LOEC (ppm) | Author |
|---|---|---|
| Mallard duck, 8 wk preliminary study (*Anas platyrhynchos*) | 46/100 | Fink (1977) |
| Mallard duck (*Anas platyrhynchos*) | 30/60 | Hakin (1990a) |
| | 25/125 | Fink et al (1978a) |
| Bobwhite quail (*Colinus virginianus*) | 40/130 | Hakin (1990b) |
| | 125/> 125 | Fink et al (1978b) |

Both the European Union (EC 2005) and US EPA used a NOEC of 25 mg/kg diet as their chronic avian end-point. There is no detail provided in the EU report. However, the US EPA provides the following discussion:

> "The avian reproductive studies on mallard ducks indicate that chlorpyrifos reduces the number of eggs laid and the adult body weights at 60 ppm. The dietary concentration was reduced from 90 ppm to 60 ppm at

> the beginning of week 8 due to body weight losses and mortality. Bobwhite quail reproduction results suggest that the lowest observed effect level LOEL is 130 ppm based on reduced number of eggs produced. All 5 studies indicate reductions in the number of eggs laid. Other reproductive effects found were 9 percent eggshell thinning and fewer young. Chronic effects identified include increased adult mortality and adult body weight reduction. The guideline requirement for waterfowl reproduction tests is fulfilled. Both bobwhite studies together fulfilled the guideline requirement for an upland gamebird reproduction study."

The NOEC reported by Hakin (1990a) and Fink et al (1978a) is consistent with the result reported in the APVMA interim report (25 mg/kg diet) and both the EU and the US EPA. Australia does not have standard indicator species for different cropping situations. It should be noted that the native pacific black duck is closely related and may interbreed with the mallard, therefore the use of mallard duck is relevant. A chronic avian risk assessment has been performed using a NOEC value of 25 mg/kg diet. In terms of a daily dietary dose, this equates to 2.88 mg ac/kg bw/d (EFSA 2011), which was applied in the risk assessment.

### Mammalian toxicity values

Toxicity data for mammals were not assessed as part of the environment assessment in the interim review. Acute and reproduction toxicity data to mammals, including the data provided below in this section from two rat studies, were discussed in the chlorpyrifos interim toxicology assessment in APVMA (2000), and these results provide the basis for this updated mammalian assessment.

The acute $LD_{50}$ result is obtained from Henck and Kociba (1980) where the acute oral toxicity potential of three different batches of technical chlorpyrifos administered by oral gavage to groups of male and female Sprague-Dawley rats was tested. Two of these batches resulted in an $LD_{50}$ of 96 and 97 mg/kg to females. For this assessment, the value of 97 mg/kg bw is applied, this value is consistent with that applied by the US EPA (US EPA 2002).

The reproductive toxicity end-point is applied from a two-generation dietary reproduction study in Sprague-Dawley rats (Breslin et al 1991). In this study, the NOEL for neonatal effects was 1.0 mg/kg bw/d based on decreased body weight gain and survival. This value will be applied in the chronic mammalian assessment. The choice of study is consistent with that applied in US EPA (2002), and the end-point is also applied in EFSA (2011).

These values will be applied as surrogates to Australian native mammals (marsupials and native rodents) in the risk assessment.

## 5.2 Aquatic organisms

During the interim review (APVMA 2000), the use of 1 µg/L as the aquatic toxicity end-point for aquatic invertebrates was considered appropriate.

Even at that time, there were data from microcosm studies and literature supporting consideration of a lower ecotoxicity threshold. For example, it was observed in the interim report that differences in toxicity to fish, invertebrates and vegetation are readily apparent from multi-species testing in microcosms and ponds. Generally, 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. 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.

Further, in a statistical approach described by Giesy et al (1999), the authors calculated a 10$^{th}$ percentile of 102 ng/L (0.1 µg/L) for all 48-hour normalised species mean values for adverse acute effects in freshwater aquatic organisms. It was also indicated that results from controlled outdoor (mesocosm) studies indicate that no ecologically relevant adverse effects are expected to occur at concentrations < 0.1 µg/L.

However, at that time, the microcosm study used to determine the final aquatic invertebrate toxicity value of 1 µg/L was considered the most reliable, and had been performed as a dose/response test system with nominal test concentrations of 0.03, 0.1, 0.3, 1 and 3 µg/L chlorpyrifos.

Since the interim review, a number of additional acute laboratory toxicity studies have been reported. The interim review referenced microcosm data to determine the final aquatic end-point of 1 µg/L, but since then evidence from higher tier mesocosm studies suggest a more appropriate aquatic toxicity end-point at 0.1 µg/L. For this supplementary environment report, only high tier (microcosm and mesocosm) data have been considered, and these additional data are described in Appendix 1.

## Conclusions on the end-point from higher tier studies

The aquatic end-point has been established based on the guidance available in EU (2002), EFSA (2013) and Standing Council on Environment and Water (SCEW 2009).

EU (2002) offers further guidance in this regard. The actual assessment of the effects found in the mesocosm/microcosm studies can be grouped into five classes where class one is the lowest level (no treatment related effects demonstrated) and class five is the most severe (clear response of sensitive end-points and recovery time of these being > eight weeks after the last application; effects observed at various subsequent samplings).

A further refinement of these effects classes is provided by Brock et al (2009) where effect class three is separated as 3A being pronounced short term effects (< eight weeks) followed by recovery, whereas 3B is classified as pronounced effects and recovery within eight weeks after the last application, noting that total effect period may be longer than eight weeks because of possible responses in the treatment period where multiple treatments occur. Additionally, class five is also separated into 5A (pronounced long term effects followed by recovery), and 5B (pronounced long-term effects without recovery).

The findings from the newly evaluated higher tier aquatic studies considered above are summarised as follows:

**Table 8: Chlorpyrifos mesocosm test data—multiple application**

| Taxa | $NOEC_{population}$ | $NOEC_{community}$ | Recovery period (based on LOEC) | Reference |
|---|---|---|---|---|
| Cladocera | 0.033[1] | 0.1 | Up to 94 d | López-Mancisidor et al (2008a) |
| Rotifers | 0.1 | | | |

| Taxa | NOEC$_{population}$ | NOEC$_{community}$ | Recovery period (based on LOEC) | Reference |
|---|---|---|---|---|
| Copepoda[2] | > 1 | | | |
| Calanoida[2] | > 1 | | | |
| Cyclopoida[2] | > 1 | | | |

*LOEC = Lowest observed adverse effect; NOEC = No observed effect concentration. 1 This NOEC has significant limitations; 2 NOECs for the populations of these taxa were often noted as between 0.1 and 1 µg/L, but these were for statistically significant increases in population, not decline.*

### Table 9: Chlorpyrifos mesocosm test data—single application

| Taxa | NOEC$_{population}$ | NOEC$_{community}$ | Recovery period (based on LOEC) | Reference |
|---|---|---|---|---|
| Cladocera<br>Copepods<br>Rotifers | 0.1–1.0<br>0.1–1.0<br>0.1–1.0 | 0.1 | Up to 99 d | López-Mancisidor et al (2008b) |
| Conchostraca<br>Ostracoda<br>Cladocera<br>Copepoda<br>Insecta<br>Rotifera<br>Platyhelminths<br>Annelida<br>Mollusca[1] | 0.1<br>10<br>0.1<br>10<br>0.1–1.0<br>10<br>> 100<br>0.1<br>> 100 | 0.1 | Up to 70 d | Daam et al (2008a) |
| Microcrustaceans<br>Rotifers<br>Algae | 0.1<br>1.0<br>0.1 | 0.1 | > 35 d | van Wijngaarden et al (2005):<br>t = Mediterranean<br>1 conditions |
| Microcrustaceans<br>Rotifers<br>Algae | 0.1<br>1.0<br>0.1 | 0.1 (zooplankton); 1.0 (phytoplankton) | 14–21 d | van Wijngaarden et al (2005):<br>t = Temperate conditions |
| Microcrustaceans<br>Rotifers<br>Algae | 0.1<br>1.0<br>0.1 | 0.1 | 21–27 d | van Wijngaarden et al (2005):<br>t = Mediterranean<br>2 conditions |

*LOEC = Lowest observed adverse effect; NOEC = No observed effect concentration; t = treatment. 1 NOECs for the populations of these taxa were often noted as between 0.1 and 1 µg/L, but these were for statistically significant increases in population, not declines.*

It is clear from the above studies that significant effects were observed for more sensitive species, particularly cladocera, and that at dose levels above those determined as the $NOEC_{community}$ or $NOEC_{population}$. Recovery of these sensitive species could take longer than eight weeks following final application, ie effects could be considered as class five. The guidance from EU (2002) states that 'a NOEAEC cannot be determined if effects belonging to class four and five were observed'.

Based on these considerations, and the consistent finding among the high tier studies considered here that the $NOEC_{community}$ and (generally) lowest $NOEC_{population}$ are equal at 0.1 µg/L, this value should be used as the relevant aquatic toxicity end-point in the aquatic risk assessment.

### *Australian and New Zealand Environment and Conservation Council*

The Australian and New Zealand guidelines for fresh and marine water quality specify chlorpyrifos values (ANZECC 2000) as follows:

**Table 10: ANZECC water quality guidelines for chlorpyrifos**

| Trigger values for freshwater (µg/L) | | | | Trigger values for marine water (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| Level of protection (% of species) | | | | Level of protection (% of species) | | | |
| 99% | 95% | 90% | 80% | 99% | 95% | 90% | 80% |
| 0.00004 | **0.01** | 0.11 | 1.2 | 0.0005 | **0.009** | 0.04 | 0.3 |

The 95$^{th}$ percentile values (around 0.01 µg/L for both freshwater and marine water) are considered appropriate for the protection of slight to moderately disturbed ecosystems. These are considered high reliability values by ANZECC.

The guideline was based on a comprehensive data set of laboratory test data (pre-2000) following ANZECC methodology for data acceptability. While available mesocosm/microcosm data were assessed, they were not relied on in establishing the guideline. Most were considered to not satisfy ANZECC acceptance criteria. Three studies that did appear to be acceptable (NOEC figures of 0.06–0.1 µg/L) were not used as, at the time, it was not considered appropriate to use them to derive a guideline figure. ANZECC did observe, however, that the guideline derived from laboratory data was six to 10 fold lower than the lowest of the mesocosm NOECs.

### *United States of America*

#### US EPA

The US EPA has published water quality criteria for chlorpyrifos (US EPA 1986). Based on available laboratory toxicity data, the US EPA deemed that freshwater aquatic organisms should not be affected unacceptably if the four-day average concentration of chlorpyrifos did not exceed 0.041 µg/L more than once every three years and if the one hour average concentration did not exceed 0.083 µg/L more than one every three years. Corresponding guideline values for marine species were 0.0056 µg/L and 0.011 µg/L for four-day and one-hour average concentrations, respectively.

### CALIFORNIA

A more recent project has developed methodology for derivation of pesticide water quality criteria for the protection of aquatic life in the Sacramento River and San Joaquin River basins in California (TenBrook et al 2009). The chlorpyrifos data set was collected in accordance with the methodology described in the publication. Particular attention was given to the assessment of distributional assumptions used in Species Sensitivity Distribution (SSD) methods. The SSD software BurrliOZ was used which was the same software used in developing ANZECC guidelines where sufficient data exist, and this established the acute criterion. The acute to chronic ratio (ACR) method was used to derive a chronic criterion, and an ACR of 2.2 was calculated for chlorpyrifos.

The SSD resulted in a 95$^{th}$ and 99$^{th}$ percentile of 0.024 and 0.0082 µg/L respectively which differs from the ANZECC water quality guidelines. Some reasons for these differences were that the data were subject to different acceptance criteria, while not all data were available for consideration at the time by ANZECC. Within the data set were results not available at the time of the ANZECC calculations. The acute criterion was set based on the 95$^{th}$ percentile with a further safety factor of two applied, resulting in an acute water quality level of 0.01 µg/L.

### *Canada*

The Canadian Council of Ministers of the Environment (CCME 2008) reported a freshwater short-term exposure water quality guideline for chlorpyrifos of 0.02 µg/L, based on an SSD approach using available laboratory acute toxicity data. The freshwater long-term exposure concentration is 0.002 µg/L, which was based on the lowest acceptable end-point of a 96-h $LC_{50}$ of 0.04 µg/L for *Hyalella azteca* with a safety factor of 20.

There is no recommended Canadian water quality guideline for short term marine organism exposure to chlorpyrifos. The marine long-term exposure concentration is 0.002 µg/L, which was calculated based on a 96-h $LC_{50}$ of 0.04 µg/L to mysid shrimp with a safety factor of 20.

### *European commission*

Annex II of the EC Directive in Priority Substances (Directive 2008/105/EC) lists chlorpyrifos as one of the priority substances.

EU (2008) published environmental quality standards for their priority substances. For chlorpyrifos, the maximum acceptable concentration for both freshwater and marine water is 0.1 µg/L, while the annual average concentration is 0.03 µg/L for both fresh and marine waters.

While ANZECC and the other water quality guidelines described above have been calculated based on laboratory toxicity data; generally acute results using the application of SSD, the EC has relied on higher tier mesocosm studies in establishing their water quality standards. The data sheet for chlorpyrifos provides the following scientific basis for the establishment of the EC end-point:

> “Based on the results of micro and mesocosm studies, the Rapporteur had originally drawn the following conclusions: Concentrations of 1 µg/L and above are expected to produce relevant effects on aquatic ecosystems. Concentrations between 0.05 and 1 µg/L could affect the most sensitive taxa. The ecological relevance of these effects is expected to be related to the role of these sensitive taxa within each particular ecosystem. An overall NOEC of 0.1 µg/L was proposed. Because the multi-species test designs mostly

represented Northern European conditions, the role of invertebrate population to control algae ‘blooms’ in Southern Europe was not covered, and a safety factor of 2 on the NOEC ecosystem was agreed for covering this hazard. However, in December 2002 additional studies for covering the specific Mediterranean conditions have been submitted. Although the concern has been confirmed, the studies indicated that the level of 0.1 µg/L is also relevant for Mediterranean aquatic systems. Based on these new studies, the Rapporteur proposes a Predicted No Effect Concentration (PNEC) of 0.1 µg/L.”

Further, with regard to freshwater versus marine water, the EU concludes the following:

“Beside freshwater species toxicity tests, tests with marine fish, crustacean and algae species are reported in the monograph. No significant differences exist in the sensitivity of freshwater or saltwater species belonging to the same taxonomic group. Therefore, according to guidance outlined in the revised technical guidance document (TGD), effects data for marine and freshwater species may be pooled. As chlorpyrifos is an organophosphate insecticide with a specific mode of action, through inhibition of cholinesterase activity in the nervous system of target species, it is deemed very unlikely that marine taxonomic groups exist that are significantly more sensitive to chlorpyrifos than crustaceans. Therefore, the proposed quality standard (QS) freshwater may be considered as protective for transitional, coastal and territorial waters as well.”

Finally, because some of the microcosm/mesocosm studies reported the occurrence of transient effects at levels as low as 0.1 µg/L, the EU deemed it necessary to provide protection against longer term elevated chlorpyrifos aqueous concentrations. Therefore, an additional assessment factor of three was applied to derive an annual average quality standard of 0.03 µg/L for the protection of the pelagic community, applicable to both fresh and marine waters.

## 5.3 Summary of key ecotoxicology end points

A summary of the key ecotoxicological end-points derived in the previous section are outlined below:

**Table 11: Summary of key ecotoxicological end-points for risk assessment**

| Species | End-point |
|---|---|
| **Avian** | |
| Geometric mean, acute oral $LD_{50}$’s | Acute oral $LD_{50}$ = 28.9 mg ac/kg bw<br>HD5 from SSD of $LD_{50}$s = 9.50 mg ac/kg bw. |
| Mallard duck | Chronic dietary NOEC = 2.88 mg ac/kg bw/d (25 mg/kg diet) |
| **Mammals** | |
| Acute $LD_{50}$ (mouse, females) | Acute oral $LD_{50}$ = 64 mg ac/kg bw |
| Long-term (rat, 2 generations) | NOEC = 1 mg ac/kg bw/d |
| **Aquatic** | |
| Various (from mesocosm data) | Population and community NOEC = 0.1 µg/L water |

# 6 ENVIRONMENTAL RISK ASSESSMENT

## 6.1 Preliminary comments

The refinement of this environmental risk assessment from that described in the interim report is focussed on avian and aquatic exposure from run-off. Further, an assessment of risk to Australian native mammals has been undertaken noting international assessments identifying high risks to mammals.

The assessment has been undertaken with PERAMA (Pesticide Environmental Risk Assessment Model for Australia) software[3]. This allows for the required spatial and temporal assessments with respect to aquatic exposure from run-off, and for assessment of Australian native birds and mammals. Descriptions of the methodology applied for these different fields of environmental risk assessment are provided in **Error! Reference source not found.** and **Error! Reference source not found.**. In undertaking the risk assessment calculations, several chemical specific parameters are needed. These include a measure of sorption potential on soil and degradation measures (DT50 values) for different matrices such as soil and foliage. The choice of these values is described here.

### Choice of soil adsorption coefficient (Kd) value

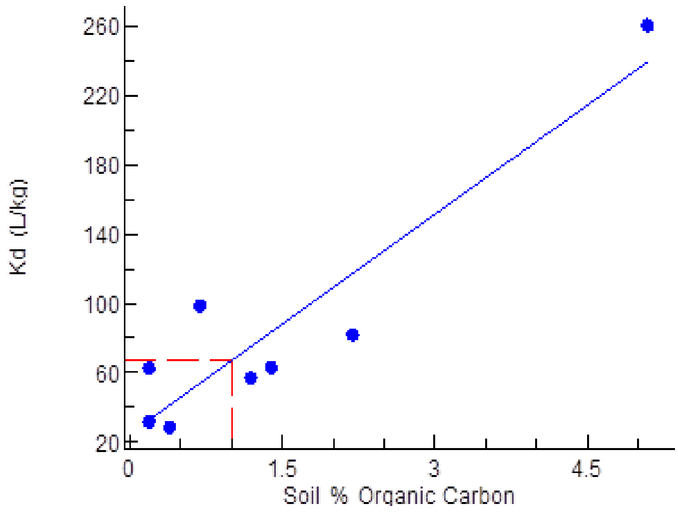
Information relating to adsorption properties of chlorpyrifos provided in the interim report can be used to derive more realistic values for application in the risk assessment, ie, Kd (soil adsorption coefficient, Kd = concentration of chemical in soil/concentration of chemical substance in water, L/kg) and Koc (soil organic carbon-water partitioning coefficient, Koc = (Kd * 100)/organic carbon). Kd or Koc indicates the mobility of chemical in soil. A very high value means it is strongly adsorbed onto soil and organic matter, and does not move throughout the soil. A very low value means it is highly mobile in soil. Kd is an important input parameter for estimating environmental distribution and environmental exposure level of a chemical substance.

The organic carbon and Koc data from the interim report have been used to develop the following relationship between organic carbon and Kd.

[3]PERAMA beta V1.0, © Australian Environment Agency Pty Ltd, 2017.

Table 12: Kd values derived from information in APVMA (2000)

| % OC | Koc (L/kg) | Kd (L/kg) |
|---|---|---|
| 2.2 | 3700 | 81.4 |
| 0.2 | 31000 | 62 |
| 0.7 | 14000 | 98 |
| 5.1 | 5100 | 260.1 |
| 0.2 | 15500 | 31 |
| 0.4 | 6910 | 27.64 |
| 1.2 | 4690 | 56.28 |
| 1.4 | 4450 | 62.3 |




*OC = Organic carbon in soil; Kd = Soil adsorption coefficient; Koc = Soil organic carbon-water partitioning coefficient*

Australia has traditionally assumed 1 per cent soil organic carbon in undertaking run-off risk assessments. This level of organic carbon results in a predicted Kd = 66.9 L/kg.

There are measured data available for total organic carbon in agricultural soils around Australia and these are published by Soil Quality Pty Ltd. While not all agricultural regions are yet represented, the data allow for a relatively good assessment of differences in organic carbon levels in different regions of States and some different agricultural uses, for example, dryland and horticulture.

The fraction of contribution of different soil organic carbon levels in different regions has been assessed to determine appropriate levels for different cropping types in different parts of the country. These are applied broadly in the run-off assessment here to differentiate between levels of organic carbon that may be found between states in dryland cropping and horticulture. The results will have a strong influence on the run-off assessment. Based on that analysis, the following organic carbon levels in the top 10 cm soil has been adopted for the different states, and the corresponding Kd from the above relationship derived for use in the run-off assessment:

Table 13: Summary of % organic carbon (top 10 cm soil) and corresponding Kd applied in the run-off assessment

| State | Horticulture | | Dryland | |
|---|---|---|---|---|
| | % Organic carbon | Kd (L/kg) | % Organic carbon | Kd (L/kg) |
| Western Australia | 2% | 108 | 1% | 66.9 |
| South Australia | 1.5% | 88 | 1.25% | 77.4 |
| Victoria | 2% | 108 | 1% | 66.9 |
| Tasmania | 4% | 194 | 4% | 194 |
| New South Wales | 2% | 108 | 1.50% | 88 |
| Queensland | 2% | 108 | 1% | 66.9 |

### Half-life values applied in risk assessment

The run-off assessment requires a representative field half-life value. The interim report notes that bare soil studies in Germany found half-lives in the order of two months with similar persistence recorded after application at 3.4 kg/ha to bare soil in Illinois, Michigan and California. Canadian studies found half-lives of two weeks in a sandy soil and two months in a muck soil seeded with carrots and radish. It is proposed for this assessment to apply a field half-life of two months (60 days) in the model.

In assessing risk to birds and mammals, a dissipation half-life for the pesticide on food items is required. The default value is set at 10 days based on EFSA (2009). This value is used in considering potential accumulation between applications in acute exposure, and in modelling the decline of residues in the diet over time in the chronic assessment.

There are data available that indicate a shorter half-life on foliage may be more appropriate for the chlorpyrifos assessment. Lu et al (2014) reports persistence and dissipation of chlorpyrifos in brassicas, lettuce, celery, asparagus lettuce (celtuce), eggplant and pepper. The application rate in the studies was 970 g ac/ha, and measured DT50s were 5.81, 3.92, 5.45, 3.90, 2.64 and 3.00 days respectively. The geometric mean of these half-lives is 3.96 days, and this will be adopted in the modelling for cropping situations.

Foliar application rates in turf can be much higher and a reduction in the turf dissipation half-life is not applied. Sears and Chapman (1979) measured persistence of chlorpyrifos in turfgrass with an application rate of 4000 g ac/ha. Based on the reported values, a half-life of 10.8 days was calculated by the APVMA. The default 10 day half-life has been maintained for application to turf as required in the risk assessment.

## 6.2 Birds

A review of literature available after the interim report found that there were international regulatory assessments including US EPA (1999) and EC (2005), which suggests that reconsideration of the interim avian risk assessment is required.

## Home garden/urban use—granular products

In the interim environment report (2000), concern was raised over risks to birds from home garden granular ant products, and mortality of pigeons that ingested granules had been reported from the Northern Territory.

Many granular ant control products do not provide an actual rate in terms of quantity per area (g/m$^2$), so there is potential for concentrated amounts of granules to be applied in home garden situations. Where rates are provided, the standard rate is around 20 g ac/100 m$^2$ (200 mg ac/m$^2$ or 2000 g ac/ha). For granular products, risk is as a function of the number of $LD_{50}$'s available/m$^2$. For the acute assessment, potential risk is identified where > 1 $LD_{50}$s/m$^2$ is calculated (10 $LD_{50}$s/m$^2$ with a level of concern = 0.1). Australia does not have indicator species for use in risk assessments. Assuming granules are spread evenly at a rate of 200 mg ac/m$^2$ (20 g ac/100 m$^2$), there is a potential risk, as this equates to approximately 7 $LD_{50}$s/m$^2$.

The 2000 interim environmental assessment report recommended varying labels to include restraints to reduce risk to birds, which may ingest the granules. Subsequently, label variations were implemented by the APVMA, including the addition of precautionary statements for protection of birds:

> DO NOT heap granules. These granules may kill birds if ingested
>
> DO NOT feed granules or otherwise expose to wild or domestic birds.

The 2000 interim report also recommended further monitoring to assess whether granular ant products were adversely affecting birds feeding in the area. The APVMA Adverse Experience Reporting Program (AERP) collects, assesses and reports on reported adverse experiences associated with the registered use of agricultural chemical products when the product is used in accordance with the approved label instructions. Since the program's inception in 1995, there have been no reported adverse effects on birds from the use of granular chlorpyrifos products although it is acknowledged that incident reports can be an unreliable basis for determining risk.

Further, the application rates for these products are high (20 g ac/100 m$^2$ equivalent to 2000 g ac/ha) and these products are mostly not incorporated into the soil. The refined avian risk assessment identifies an upper application rate of 850 g ac/ha and this finding should also apply to home garden/urban use granular products.

## Home garden/urban use products—spray products

Home garden spray products tend to contain chlorpyrifos in low concentrations (50 g/L or less) with use on lawns, garden beds and in and around the home at rates essentially the same as those for the home garden granular products. Small pack size is a limiting factor to the coverage that the products can achieve. For those products with stated application rates, based on pack sizes, coverage could range from 50 m$^2$ to 750 m$^2$ and half of the products would only have sufficient formulation for approximately 170 m$^2$ or less.

Nonetheless, there are several products that don't prescribe application rates, and some have larger pack sizes (2 L). Further, the treatment rates when these products are applied is up to 20 g ac/50 m$^2$ (4000 g ac/ha). The refined avian risk assessment identifies an upper application rate of 850 g ac/ha and this finding should also apply to home garden spray products.

### Turf

Turf situations are not well defined on many labels, and simply stated as 'Turf'. Rates can be high and range from 10 g ac/ha up to 3000 g ac/ha in all states except Tasmania. Other registered rates for all states are 350 g ac/ha, 450 g ac/ha and 2000 g ac/ha. The findings from the acute avian risk assessment are also applicable to turf uses, hence application rates at 850 g ac/ha and greater are not supported.

## 6.3 Refinement of risk assessment to birds and animals

The results from the screening assessments above indicate that the risk to mammals is lower than that to birds, and chronic risks to mammals are slightly higher than acute risks. Refinement arguments will focus on the acute risk to birds as this was the area of highest identified risk. Mitigation of risk to birds will be considered as also being protective of mammals.

### Field studies assessing avian impacts

The interim assessment describes several field studies assessing avian impacts and these won't be repeated here. Despite the tier 1 assessment identifying a potentially high acute risk to birds, significant adverse impacts in the field have not been identified.

There are several reasons why this may be the case. As described in Moore et al (2014):

- doses in the acute oral toxicity studies are administered as one large dose. In the field, most birds continuously feed throughout the day
- chlorpyrifos is rapidly metabolised by birds to less toxic metabolites. When feeding throughout the day, birds have the opportunity to detoxify and/or eliminate chlorpyrifos before it accumulates to internal doses that result in lethality
- repeated exposure to chlorpyrifos in the diet may lead to avoidance and birds can switch to sources of non-contaminated food in the field. There can be no avoidance with large single doses administered in gavage studies
- in oral exposures, chlorpyrifos is generally administered in corn oil or gelatin capsules. Such carriers have been shown to result in greater toxicity with other insecticides than occurred, when the insecticides were adsorbed to food items consumed by birds in the field (Moore et al 2014). Use of corn oil or gelatin carriers maximizes the potential for a pesticide to be absorbed rapidly, more so than would occur in the field where the pesticide is bound to food items. When pesticides are mixed with food, or when consumed at a time when the gastro-intestinal (GI) tract has other food items present, they are absorbed less efficiently than when dosed as a bolus in pure form into an empty GI tract (Lehman-McKeeman 2008).

In the studies reported in the interim assessment included application to golf courses (granular and liquid formulations tested, 4500 g ac/ha), some (but not extensive) apparent chlorpyrifos casualties were observed.

Other field studies were conducted since the interim report, and studies reported by Moore et al (2014) in brassica, citrus, apple and grapes are summarised below.

### *Brassica*

Three cabbage fields near central Poland were identified to study the effects of chlorpyrifos application on associated bird communities. Chlorpyrifos was applied twice at a rate of 950 g ac/ha with a spray interval of 14 days. Visual observations, searches for carcasses, monitoring of bird nests and radio-tracking were used to estimate adverse effects to wildlife. The study showed no signs of toxicity during the visual searches or monitoring of nests. No carcasses were recovered from the treated areas. Over the treatment period, a total of 53 birds were caught, radio-tagged and tracked for observations. Of these 53 birds, none of them experienced adverse effects in relation to chlorpyrifos application.

### *Citrus*

#### STUDY 1

A study was conducted in three citrus orchards in Spain, where chlorpyrifos was sprayed twice at 2320 g ac/ha with a 14-day re-treatment interval. Birds were captured, radio-tagged and released for pre- and post-application tracking, ie observed three days before each application and seven days after each application. Investigation included general monitoring of the activities of radio-tagged birds, monitoring of bird nests, searches for dead bodies and surveys of masses of arthropod biomass, and these activities were also used to quantify possible adverse effects to birds. Six out of 38 birds observed during the study were continuously tracked through both application periods. The tracked birds stayed approximately 33 per cent of their time in the treated orchards before and after application. A total of 3,751 sightings of birds made during the observation periods and no birds showed signs of chlorpyrifos toxicity. Three bird carcasses were detected. In one of the dead blackbird, residues of chlorpyrifos were found at 14 mg ac/kg bw in the skin and feather matrix, and at 1.2 mg ac/kg bw in its core body matrix. Another dead blackbird's (unknown species) wing contained chlorpyrifos residues at 6.5 mg ac/kg bw in skin and feathers, while their third dead bird—house martin (*Delichon urbicum*) had chlorpyrifos residues at 0.33 mg ac/kg bw in the skin and feathers. However, no chlorpyrifos was detected in the core body matrix of the second blackbird or in the house martin. There was no inhibition of acetyl cholinesterase (AChE) activity in the brain of the house martin observed. The study determined that none of the bird deaths resulted from the chlorpyrifos application.

#### STUDY 2

A study was conducted in Spain to evaluate the effects of chlorpyrifos on birds and their reproduction. Birds were observed in 10 orchards (average tree height—2.1 to 3.1 m) at the end of the main breeding season (July 6 to August 31, 2010). These orchards regularly used chlorpyrifos to control pests where a large diversity and number of birds were observed. Commonly observed bird species were serin (*Serinus serinus*), green finch (*Carduelis chloris*), and house sparrow (*Passer domesticus*), while the juveniles were barn swallow (*Hirundo rustica*), nightingale (*Luscinia megarhynchos*), and Sardinian warbler (*Sylvia melanocephala*). Sampling of arthropods following application indicated an abundance of bird food. The study identified that birds living in the citrus orchards to be highly viable.

### *Apple*

Chlorpyrifos was applied to three apple orchards at a rate of 950 g ac/ha. The first orchard received three applications, with the first and second applications spaced 14 days apart while the second and third application had a 28 days interval. The second and third orchard received two applications at 14 days apart. To quantify the effects of chlorpyrifos, telemetric surveys, visual bird observations, carcass searches and nest observations were conducted. Birds were radio-tagged and tracked for three days before applications and seven days post-applications. Birds spent approximately 50 per cent of their time in the study areas and none of the tracked birds showed signs of toxicity. No birds out of 3,616 bird observations were made during the study showed any behavioral abnormalities or signs of toxicity. A single dead bird was found that had died due to an accident. However, the chlorpyrifos applications reduced the pest (foliage dwelling and arthropods) populations by approximately 87 per cent.

### *Grapes*

A study was conducted in a vineyard in Puy du Maupas, near Puymeras, Vaucluse in Southern France, where chlorpyrifos was applied twice at a rate of 360 g ac/ha in a 15 days interval. The vineyard included eight adjacent fields with grass growing in the inter-rows. The surrounding areas were scrub, woodland, garden and grassy areas. Pre-application and 1$^{st}$, 3$^{rd}$ and 7$^{th}$ day post-application search for dead birds were conducted. Three to four days before each application, mist nests were placed in the vineyard and along the boundaries. Trapped birds were banded, sexed, measured, and radio-tagged. Once tagging, birds were tagged for several days prior to treatment and for up to 10 days post-application. The locations of birds were used to determine the proportion of time spent on the treated fields and to determine if the birds were alive.

Monitoring of the tagged birds revealed that birds spent 1/5$^{th}$ of their time on the chlorpyrifos treated fields. Some birds (cirl buntings (*Emberiza cirlus*), black redstarts (*Phoenicurus ochruros*), stonechats (*Saxicola* sp.), and jays (unknown species name)) spent more than 5 per cent of their time in the treated fields. Birds that spent their greatest proportion of time in the treated areas were alive at the end of the tracking period, except one bird whose mortality was found unrelated to chlorpyrifos. Other untagged dead birds contained residues of chlorpyrifos in skin and feather that were consistent with contact with the treated crop (0.27–1.3 mg ac/kg bw). Analysis of AchE activity in the brain of an untagged dead robin (*Erithacus rubecula*) showed no decrease in activity, revealing that mortality was not related to chlorpyrifos. There were no indications of short-term adverse effects from chlorpyrifos on birds in the vineyard during the study.

### *Telemetry—based field studies*

Brassica, pome fruit and citrus crops were treated with chlorpyrifos to determine potential effects on wild birds (Wolf et al 2010). Brassica fields (Brussel sprouts, cabbage and cauliflower) were located near Sochaczew, Poland, pome fruit fields near Belfiore, northern Italy and citrus groves in Valencia, Spain. Four or five sites were used for each crop type and fields averaged 4 ha in size.

The highest nominal rates for individual applications were 960 g ac/ha (brassicas and pome fruit) and 2400 g ac/ha (citrus), however, actual application rates slightly deviated from the nominal values. Chlorpyrifos was applied to brassicas using a tractor-mounted boom sprayer at a rate of 945 g ac/ha (two applications at three sites) and 969 g ac/ha (single application at one site). Chlorpyrifos was applied to pome and citrus fruit crops using a tractor-mounted broadcast air-assisted sprayer. Three citrus groves received two applications of chlorpyrifos at a rate of 2543 g ac/ha and another citrus grove received two applications at 2225 g ac/ha. Three pome fruit fields received two or three applications at a rate of 960 g ac/ha while another pome fruit field received three applications of chlorpyrifos at 735 g ac/ha.

All bird species regularly foraging in the crops were monitored during the study. Birds were trapped and radio-tagged (n = 201) before each application and tracked for seven days following each application. Of these birds, 133 (66 per cent) representing 15 species were small (< 50 g) insectivores; 60 of the birds (30 per cent) representing three species were either small (< 50 g) or medium (60–110 g) omnivores; and eight birds (4 per cent) represented by one small (< 50 g) granivorous species. Those tagged for earlier applications were monitored during subsequent applications if the radio-tags were still functional. Of the 242 radio-tagged monitoring periods of single birds, 194 were tracked for the full seven-day period following application. No signs of toxicity or lethality were observed. Untagged birds were also observed during the study period. No signs of toxicity were detected.

10 untagged bird carcasses were found during the study, six of which had detectable levels of chlorpyrifos. Detectable concentrations of chlorpyrifos on skin and feathers ranged from 0.3 to 14.0 mg ac/kg bw. Chlorpyrifos was only detected in the bodies of two birds (1.2 and 0.3 mg ac/kg bw). Similarly, core body concentrations of chlorpyrifos were only detected in two birds at levels of 0.1 and 1.2 mg ac/kg bw. Brain AchE activity indicated that none was likely to have died from chlorpyrifos exposure.

## Avian acute risk index

The ecotoxicity data used to establish the avian acute toxicity end-points have all been determined through gavage dosing. This makes those end-points very much worst case (single large dose), which is unlikely to reflect exposure in the field where birds are more likely to continuously forage for food during the daylight hours.

A relationship between acute toxicity of a substance to birds (through gavage dosing) and likely observed impacts in the field has been considered.

Environment Canada has undertaken work developing environmental standards for its implementation in Agriculture and Agri-Food Canada's Agricultural Policy Framework. In particular, Canada's Wildlife Toxicology Division of the Wildlife and Landscape Science Directorate of Environment Canada was tasked specifically with developing comparative environmental risk assessment tools for pesticides in support of standard development. Some of this work is described in the Environment Canada (2006) publication.

With respect to acute risk in birds, they demonstrated how field data could be used to derive an empirically based risk index, which by definition, was already validated against real-world outcomes.

This risk index approach relied on the logistic models developed in the course of previous analyses of avian field studies reported in Mineau (2002) to derive a likelihood that a given pesticide application will result in observable avian mortality. The approach appears to have become more accepted by Environment Canada with the publication of their Environmental Risk-Based Standards for Pesticide Use in Canada (Environment Canada 2009).

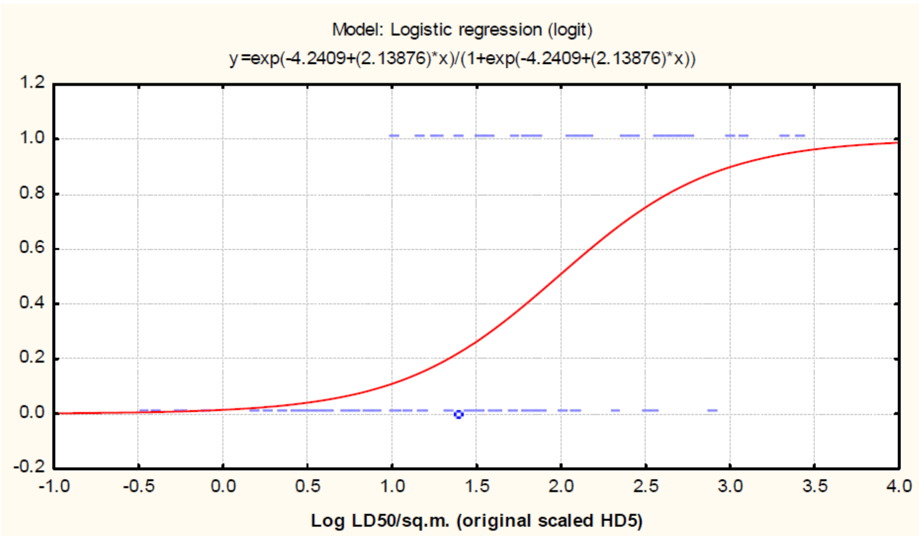
The Pesticide Research Institute is part of the team led by the IPM Institute of North America and Oregon State University's Integrated Plant Protection Center. This organisation has developed a new online tool called the Pesticide Risk Mitigation Engine, using the same logistic models and field data approach described by Environment Canada, which enables farmers to select the least-toxic pesticide for their particular local environment.

In 2010, Dr Pierre Mineau (Canadian Wildlife Research Centre, Canadian Wildlife Service) authored the White Paper for the avian acute risk index to be applied in the Pesticide Risk Mitigation Engine. This index calculates the probability that a pesticide application will provide conditions conducive to a bird kill (any compound-related mortality). It makes use of an unbiased measure of pesticide toxicity derived from laboratory acute gavage studies and principles of species-sensitivity distributions and scaling of toxicity to body mass. This toxicity measure and the application rate are used as a joint predictor in a logistic model based on a large sample of agricultural field studies where avian carcass searching was carried out.

A description of the field studies and criteria for acceptability of these studies are described in Mineau (2002). In an attempt to confirm and add credence to the available field studies, a number of sources of avian incident data were searched, namely, the US EPA EIIS database, yearly incident reports from the UK and France and sporadic publications or reports of cases from other countries. A total of 181 data points from different studies were used for the analysis.

Models developed in Mineau (2002) were modified to take into account the addition of a few more field studies and a re-evaluation of all the component agricultural studies by a panel of four evaluators mandated by the European Food Safety Authority (EFSA 2008). The final algorithm and probability curve were identified as follows:

**Figure 2: Final algorithm and probability curve—avian acute risk index**



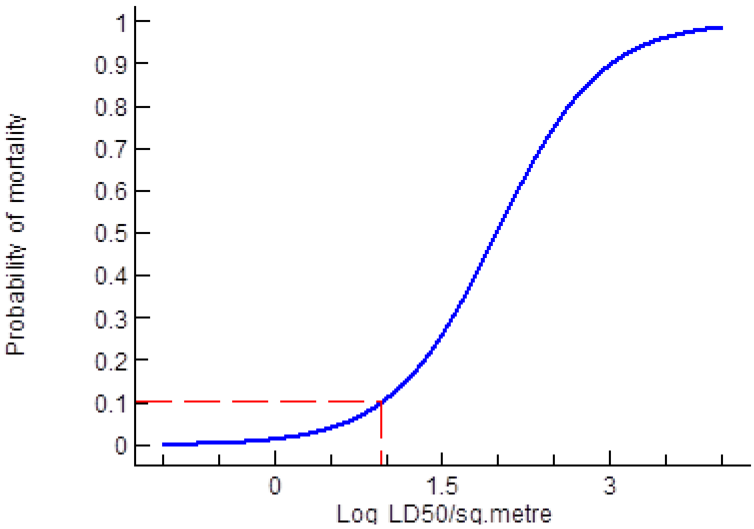

As an example, a probability of 0.20 on the Y axis indicates that, given the existing corpus of avian field studies (> 100 in agricultural landscapes combining orchard and field crops), it would be expected that avian mortality would occur in approximately one in five applications. It was argued in Environment Canada (2009) that, based on a comparison of the risk ratings with poisoning incidents, a probability of kill of > 10 per cent is associated with incidents; probabilities of kill calculated to be < 10 per cent will be considered to be *de minimus* and not carry any real risk of mortality, and probabilities > 50 per cent are typically associated with products having extensive kill records. This threshold will denote products carrying an extreme acute avian risk.

**For the choice of HD5:** In Mineau et al (2001), extrapolation factors are provided for estimating an HD5 value. This is based on a small sample approach as, for newer compounds, they are unlikely to have data for a large number of species, and the extrapolation factor then estimates the HD5 from the $LD_{50}$ value. However, for chlorpyrifos the HD5 was determined by the SSD without further extrapolation factor.

### Conclusion for avian acute risk assessment

Taking into account the range of toxicity data and a higher tier approach through application of an avian acute risk index, and considering the range of available field data, an upper application rate of 850 g ac/ha appears supported where the possibility of a bird mortality reduces significantly (less than 10 per cent). This appears supported in the range of field studies where application rates exceeding 950 g ac/ha did result in bird mortalities.

Figure 3: Acute avian risk index—chlorpyrifos applying HD5 = 9.5 mg/kg bw




## 6.4 Aquatic

### Mosquito control

Label instructions for mosquito control depend on the situation (including light, medium and heavy vegetation, and polluted water impoundments), and the life stage of the mosquito being controlled (larvae or adults). For all these scenarios, application rates are provided in terms of rate/volume/ha. The critical comments typically include directions to dilute the product with water and apply as a spray to areas (including vegetation and direct application to polluted impoundments) infested with mosquitoes. There is typically no guidance on the type of spray quality and limited restraints included on chlorpyrifos product labels, although many labels include environmental protection statements in the general instructions.

Although householder use to control mosquitoes is not a registered use, pest control operators could spray areas like backyards under current labels. In this regard, it is important to understand the mosquito ecology and habitats, and information has been obtained from the Michigan Mosquito Control Association. Larvae and pupae of mosquitoes are always found in water. The breeding source may be anything from water in discarded tyres or containers and that collected in plants, pools, puddles and swamps. ‘Permanent water mosquitoes’ can be found in various permanent habitats, such as swamps, ponds, sewage ponds/lagoons and ditches that do not usually dry up, and it should be recognised that many such habitats can occur in urban areas. Therefore, application for larvae control will need to be made directly to the water although it is clear that such water 'bodies' could be very small and may be treated by hand-held equipment and with concomitant spraying of vegetation or structures (MMCA 2013).

Large scale operations using aerial application for larvae control can also occur as has happened. For example, in the Western Australian shire of Capel, a larviciding program was conducted with s-methoprene in Forrest Beach, the headwaters of the Vasse-Wonnerup estuary, a Ramsar listed wetlands (Government of Western Australia 2016).

As described by MMCA (2013), adult mosquito control using insecticides is essentially conducted in three main ways. First, adult mosquitoes can be killed on the wing during their normal flight time (dusk and dawn) using ultra-low volume (ULV) equipment that is either hand-held, boom spray or aerial. This method is sometimes called 'cold fogging' although the droplet size of ULV application comprises a cloud that is technically not a fog.

A second approach to killing adult mosquitoes is using thermal fogs where an insecticide is heated with another combustible material (for example, kerosene) thus creating a fog that moves through the air, around vegetation and among flying insects.

The third approach is to use 'harbourage' or 'barrier' techniques, which involves spraying onto vegetation surrounding the area to be protected. This area could be a backyard, a cemetery, a park, a fairway etc.

Chlorpyrifos can be applied to polluted water impoundments for the control of larvae and adults, where rates are typically expressed in terms of a receiving water concentration. Registered application rates for direct application to water for control of mosquito larvae and adults are typically 100 µg ac/L of receiving water.

In assessing environmental aquatic risk from use of chlorpyrifos for mosquito control, the following situations are considered:

- larvae control in water in urban situations such as backyards, parks, ditches by hand-held sprayers
- adult and larval control in polluted water impoundments.

### *Larvae control in urban situations (direct application to water and vegetation)*

It appears from many of the labels registered for mosquito use in urban situations are not intended for use by householders, but urban application may be undertaken by pest control operators. Not all products carry the statement to this effect, and this needs to be clarified. Use in urban settings may occur in a wide range of situations including back yards, drains, sewage ponds and ditches by professional personnel.

### *Adult and larvae control in polluted water impoundments (direct application to water)*

The application rate for polluted water impoundments is predicted to result in water concentrations that may exceed the aquatic end-point. The application rate of 2 mL/10000 L, or 20 mL/100 $m^3$ water results in a water concentration of 100 µg ac/L, which is three orders of magnitude higher than the aquatic end-point (risk quotient = 1000). However, the actual aquatic risk is dependent on the purpose of the water impoundment (including dams or those found in urban areas such as ditches, sewage ponds and drains). Therefore, it is recommended that existing environmental protection statements on labels be expanded to include directions to limit use for control of mosquito larvae to temporary pools, as opposed to permanent water bodies, which are more likely to contain fish.

## Aquatic run-off assessment

A run-off assessment has been undertaken for urban uses with the exception of mosquito control. Run-off has been modelled following the methodology described in the APVMA's refinement of aquatic exposure estimates in environmental run-off assessments for pesticides in dryland cropping regions. Following the consultation, some amendments have been made to the methodology. These amendments relate to predicting edge of field concentrations, and not the application of the stream flow data sets that are applied at the highest tier of assessment. A description of the methodology is found in **Error! Reference source not found.**.

## Urban uses

The interim report stated that the major urban use for chlorpyrifos was for termite protection of homes with very high rates applied using manual application methods. These application have a low potential for off-site spray drift but much higher potential for run-off, particularly if heavy rain falls soon after application. Chlorpyrifos is also applied in urban areas for control of household pests such as ants and cockroaches, and garden pests such as scarabs.

Given the reduction in the aquatic end-point from 1 µg/L in the interim assessment to 0.1 µg/L in this supplementary assessment, this assessment has re-considered urban exposure in the context of aquatic risk.

### *Home garden and non-termiticide urban uses*

Chlorpyrifos is registered in home garden products in Australia for various uses including for control of ants, lawn beetles, lawn grubs, cockroaches, earwigs, black beetles and other soil insects. Both granular and liquid formulations are registered, and application can occur to pathways, lawns or recreational turf such as bowling and golf greens. Many products do not specify application rates (for example, many ant granule products simply refer to sprinkling the granules around nests and trail whenever ants are active). However, from labels where rates are stated, typical rates range from 20–40 g ac/100 $m^2$ (equivalent to 2000–4000 g ac/ha).

Specific run-off from these uses has not been modelled. There is insufficient information on quantities sold and areas treated to undertake any meaningful calculations. Uses on impervious surfaces (for example, ant granules applied to pavement areas) will be more susceptible to run-off than use in non-pervious areas. Urban uses can result in chlorpyrifos movement off-site in run-off waters and some discussion on levels found in international monitoring activities is provided below.

### *Urban run-off monitoring results*

There are no Australian monitoring results for chlorpyrifos in surface waters resulting from urban use.

On 8 June 2000, the US EPA released their revised risk assessment of chlorpyrifos and announced an agreement with registrants to phase out certain uses of this substance, including termiticide and residential indoor and lawn uses. Apart from these urban uses, the agreement would also significantly lower allowable residues on certain crops (US EPA 2000). The result of this action allowed investigation into the change in urban water quality resulting from the phase out.

National and regional studies in the United States have identified diazinon, chlorpyrifos and carbaryl as some of the most frequently detected pesticides in urban streams, suggesting that changes in the concentrations of these insecticides should be detectable on a regional basis (Philips et al 2007). It is important to consider detections in some context such as percentage of samples with a positive detection, and the concentration in the sample. For example, Philips et al (2007) state further that chlorpyrifos was detected in more than 25 per cent of samples collected from urban streams across the USA during 1992–2001, but that concentrations exceeded their acute invertebrate aquatic life benchmark (0.05 µg/L) in at least one sample from 30 per cent of those streams. This suggests that while detections may be frequent, the magnitude of the water concentrations may not be great.

This is supported in the Reregistration Eligibility Document (US EPA 2000) where monitoring data reported detections of chlorpyrifos in 26 per cent of 604 urban stream samples in 1997 and 65 per cent of 57 urban stream samples from Georgia, Alabama and Florida in 1994. While the maximum reported level was 0.4 µg/L, most detections were < 0.1 µg/L, which is below the revised aquatic regulatory acceptable level applied in this assessment. The 95$^{th}$ percentile level was 0.026 µg/L.

Smaller and more targeted studies also support the findings of low detection concentrations in urban run-off. Domagalski and Munday (2003) describe the evaluation of chlorpyrifos (and other pesticides) at selected sites in the San Joaquin Valley, California, April to August 2001. 12 sites were monitored ranging in different agricultural land uses and urban land use. One site was measured for urban run-off while urban areas were part of mixed catchments in other monitoring sites. At the urban monitoring site (Orestimba Creek), chlorpyrifos was found in 75 per cent of samples. The maximum concentration was 0.059 µg/L and the median concentration was 0.012 µg/L.

In similar monitoring to the same area (Zamora et al 2003), but through the January–February 2001 period, chlorpyrifos was detected in ~20 per cent of samples with a maximum 0.068 µg/L and all other detections < 0.01 µg/L in the Orestimba Creek site. In an urban storm drain, chlorpyrifos was found in 8/9 samples at relatively consistent levels during what appears to be a single event (25–26 January, 2001). The range of concentrations was 0.018–0.035 µg/L.

Haver et al (2008) reported pesticide detections in dry and wet weather surface run-off from single family residences in California. This monitoring program included eight single-family residential drainsheds, four in Sacramento County and four in Orange County, with 150 to 450 parcels (presumably house blocks) per site. Pesticide sampling was undertaken for various organophosphorous chemicals, synthetic pyrethroids and fipronil. Weekly grab samples were taken between October 2006 and December 2007 in Orange County, and July 2006 to December 2007 in Sacramento. In addition, biweekly grab samples were taken in both counties between January 2008 and September 2008. In the Orange Country samples, for dry weather run-off, chlorpyrifos was detected in 79 per cent of samples (150/197). While the maximum level was 0.3 µg/L, the median concentration was only 0.0016 µg/L. In wet weather run-off (26 samples), chlorpyrifos was found in 88 per cent of samples with a median concentration of 0.0028 µg/L and a maximum concentration of 0.44 µg/L.

No recent monitoring data related to chlorpyrifos in urban stormwater run-off have been obtained for Australia. However, the potentially high exposure from urban use patterns is supported by the monitoring data presented in Section 6.1.3 in the interim environmental report (APVMA 2000). Chlorpyrifos was noted as an occasional contaminant of surface waters. Several fish kills were reported in association with this use pattern in Australia with levels in water reaching several hundred parts per billion (ppb).

### *Conclusion for chlorpyrifos urban uses*

The international monitoring data described above demonstrates the movement of chlorpyrifos from its area of use as a structural pest control agent and through other household applications in urban areas to receiving surface waters can occur, and these detections suggest levels may occasionally exceed the ecotoxicity threshold. There are no equivalent Australian monitoring data, but it is noted that many products typically contain extensive environmental protection statements to manage potential risks associated with run-off of chlorpyrifos.

## Groundwater

Column leaching data described in Section 6.2.4 of the interim environment report (APVMA 2000) showed that for two silt loams and one sandy loam soils, the highest amount of leaching occurred in soil with the least organic matter, with 5 per cent found below 5 cm, while 1.3 per cent eluted through the 25 cm of the column. For the other two soils, < 1 per cent was found below 5 cm and 0.3 per cent was found in leachate, that is, > 25 cm movement. If this level of movement occurred in the field, then provided groundwater reserves are more than 25 cm below the soil surface, broadacre uses should not result in unacceptable groundwater contamination by chlorpyrifos.

There is no Australian groundwater monitoring data available. However, some groundwater contamination data from US termite treatments are described in Section 6.1.3 of APVMA interim environment report (2000). These data showed groundwater contamination was at least possible although not common. 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 one to four days after treatment where these factors were involved. Most of the incidents occurred east of the Mississippi River, with the highest incidence 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 per cent of complaints. Wells were located within 10 m of the dwelling in 70 per cent of cases.

**Table 14: Avian and aquatic (run-off) assessment outcomes in turf farms—highlighted cells (grey) indicate use cannot be supported**

| | | General conclusions for run-off risk | | | | | | Birds | |
|---|---|---|---|---|---|---|---|---|---|
| Crop | Multiple | NSW | Qld | Vic. | Tas. | SA | WA | Rate | Comments |
| Turf | | | Yes | | | | Yes | 12.5 | Bait, turf farm use only |
| Turf | Yes | Yes | Yes | | | | Yes | 1000 | Repeat not possible |
| Turf | | Yes | No | Yes | | | Yes | 3000 | Not supported in Qld in winter due to lower flow rates |
| Turf | | Yes | | Yes | No | Yes | Yes | 2000 | Not supported in Tas. in summer and autumn due to lower flow rates |
| Turf | | Yes | | Yes | Yes | Yes | Yes | 450 | |

| | | General conclusions for run-off risk | | | | | | Birds | |
|---|---|---|---|---|---|---|---|---|---|
| Crop | Multiple | NSW | Qld | Vic. | Tas. | SA | WA | Rate | Comments |
| Turf | | Yes | Yes | Yes | Yes | Yes | Yes | 350 | |

# 7 RECOMMENDATIONS

As an outcome of this supplementary environment report, several recommendations are made to ensure that chlorpyrifos products continue to be used in a manner that is safe for animals, plants and the environment.

## 7.1 Avian risk assessment

Assessment of toxicity data and a higher tier approach through application of an avian acute risk index, and field data support an application rate up to 850 g ac/ha. Also increasing re-treatment interval would result in reduced MAF value and thereby can support multiple applications. For example in apple and pears, increasing the re-treatment interval from 14 to 21 days decreased the MAF from 1.1 to almost 1, and thereby supporting the second application and reducing the risk to birds. However, short duration crops like vegetables cannot accommodate longer re-treatment intervals and so higher application rates cannot be supported for multiple applications.

### Home garden/urban use granular and spray products

Concern has been raised over potential exposure to birds which may ingest chlorpyrifos granular ant products. The products registered for home garden uses are generally in small pack sizes with limited coverage at the application rates prescribed on the product labels. However, there remain several products that may be used in the home garden or other urban applications that do not limit use to professional applicators, and pack sizes may be quite large (2 L). The indicative application rate in the treated area for the home garden/urban use granular products are high (10–40 g ac/100 $m^2$, ie. 1000–4000 g ac/ha equivalent), and these exceed the upper rate identified for an acceptable risk to birds (850 g ac/ha). Therefore, the home garden/urban use granular products class cannot be supported. A list of these products is provided in Appendix 4. For home garden/urban use spray products, there are certain uses with rates > 850 g ac/ha that cannot be supported.

## 7.2 Aquatic risk assessment

The revised aquatic risk assessment focuses on uses for the control of mosquitoes by direct application to polluted water impoundments and a run-off assessment of agricultural and urban (home garden) uses.

### Mosquito control—direct application to polluted water impoundments

Chlorpyrifos products may be applied by professional operators for the control of mosquitoes by direct application to polluted water impoundments (larval and adult control) or spray application and controlled drift over infested vegetation (adult control).

The application of chlorpyrifos products to polluted water impoundments has the potential to result in water concentrations of chlorpyrifos exceeding the aquatic end-point. To protect aquatic organisms, label restraints and environmental warning statements currently included on the majority of labels against using in water bodies which may contain fish and crustaceans appear warranted:

- PROTECTION OF WILDLIFE, FISH, CRUSTACEANS AND ENVIRONMENT:
  - VERY HIGHLY TOXIC TO FISH AND AQUATIC INVERTEBRATES

- DO NOT allow spray to drift onto sensitive areas including, but not limited to, natural streams, rivers or waterways
- DO NOT use on permanent water bodies. Product is only to be used on temporary pools
- DO NOT contaminate streams, rivers or waterways with the chemical or used container.

### Run-off—urban uses (home garden)

There is international monitoring data providing evidence that chlorpyrifos may move from its area of use as a structural pest control agent and through other household applications in urban areas to receiving surface waters. Concentrations exceeding the aquatic toxicity threshold may occur, although the evidence suggests concentrations are generally lower than this. There are no equivalent Australian monitoring data available to assess the Australian situation. The following environmental protection statements are recommended to manage the risk of run-off of chlorpyrifos into water bodies from use as a surface barrier spray for ant control and certain other products around new and existing buildings and structures, and in home garden situations.

- for under-slab 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.

It should be noted that all home garden/urban use granular products and certain uses of home garden/urban use spray products (> 850 g ac/ha) are not supported as a result of avian risk assessment.

# Appendixes

# APPENDIX 1: ADDITIONAL AQUATIC TOXICITY DATA

## Study 1

### Table 15: Study 1: Effects of chlorpyrifos in freshwater model ecosystems: the influence of experimental conditions on ecotoxicological thresholds

| | |
|---|---|
| **Reference** | van Wijngaarden et al (2005) |
| **Test guideline** | None stated |
| **Data validity** | 2*—reliable with restrictions |
| **Data relied on** | Yes—the data were considered to be critical and was relied on in this assessment |

Three experiments were conducted to determine the impact of chlorpyrifos following a single application in plankton-dominated nutrient rich microcosms. The microcosms (water volume approximately 14 litres) were established in the laboratory under temperature, light regimes and nutrient levels that simulated cool 'temperate' and warm 'Mediterranean' environmental conditions. The table below summarises the test regimes for each experiment.

### Table 16: Test regimes for microcosm experiments (van Wijngaarden et al 2005)

| | Experiment | | |
|---|---|---|---|
| | **Mediterranean 1** | **Temperate** | **Mediterranean 2** |
| Type | Warm, productive | Cool, productive | Warm, very productive |
| Mean temperature (°C) | 24–28 | 16–18 | 25–28 |
| Treatment (µg/L) | 0, 0.01, 0.1, 1.0, 10 | 0, 0.01, 0.1, 1.0 | 0, 0.01, 0.1, 1.0 |
| Replication* | n = 4 I, n = 2 (t) | n = 3 (c and t) | n = 3 (c and t) |

** c = control; t = treatment*

The effects of the chlorpyrifos treatment on the zooplankton and phytoplankton communities were analysed by the principal response curves method (PRC). Effect classes for categorising the results of microcosm were applied as follows:

- effect class 1: No effects observed
- effect class 2: Slight effects. Effects only observed on individual samplings, especially shortly after treatment
- effect class 3: Clear short-term effects. Effects observed at some subsequent sampling dates. Full recovery occurred within the study period
- effect class 4: Clear effects, no full recovery within the study period. Study duration was too short to reach control levels.

Summarising these three experiments in terms of ‘effect classes’, clear effects (class 3 and class 4) occurred in all three experiments at the 1 µg/L treatment level. Effects in Mediterranean 2 conditions generally tended to be of a longer duration, as effects on many end-points were considered to be of class 4. Class 4 effects also occurred at the 10 µg/L treatment level in Mediterranean 1 conditions. The 0.1 µg/L treatment level did not indicate any negative effects in these experiments. While there was some incidental transient density increases in the end-point categories ‘microcrustaceans’ and ‘rotifers’, these were not considered to be correlated to treatment doses. At concentrations as low as 0.01 µg/L statistical deviations occurred for the end-point category ‘community metabolism’. These involved minor deviations in pH and were considered to fall in effect class 1. All three experiments yielded community NOECs of 0.1 µg/L for structural end-points regardless of environmental conditions. Because no consistent and biologically significant effects were observed at this treatment level and lower, the 0.1 µg/L treatment level is considered to be the overall microcosm NOEC for all three experiments, ie for both ‘temperate’ and ‘Mediterranean’ conditions.

## Study 2

Table 17: Study 2: Fate and effects of the insecticide chlorpyrifos in outdoor plankton-dominated microcosms in Thailand

| | |
|---|---|
| Reference | Daam et al (2008a) |
| Test guideline | None stated. |
| Data validity | 2*—reliable with restrictions |
| Data relied on | Yes—the data were considered to be critical and was relied on in this assessment |

The experiment was performed in 12 outdoor microcosms (1 m long, 1 m wide and 1.15 m high) at the hatchery of the Asian Institute of Technology (AIT) near Bangkok. The tanks were filled with 10 cm sediment and 1 m water (1000 L), taken from the canal surrounding the AIT. The microcosms were intended to model the community of Thai farm canals. During the preparatory phase, zooplankton and macroinvertebrates were collected from the AIT canal and introduced into the microcosms. The acclimation period was six weeks. On the day of application, chlorpyrifos (as Dursban 40 EC) was applied once to the surface of eight microcosms in four duplicate treatments (nominal 0.1, 1.0, 10 and 100 µg/L). The systems were gently stirred immediately after application to mix the water column. Four other systems received water only and served as controls. Water samples were collected on days one, seven, 14 and 28 for analysis. Sediment cores were collected at the same times. Stratification in the sediment compartment was studied in the highest dose microcosm with sediment cores divided into 1.5 cm layers and extracted separately.

### End-points

Water physico-chemical properties were monitored at approximately weekly intervals, when bulk water samples were collected for analysis of phytoplankton chlorophyll a and the zooplankton community. On the day of chlorpyrifos application a bioassay was performed by placing 25 Moina micrura in a test vessel and suspending in each microcosm with its bottom at a fixed depth of around 20 cm. The numbers of individuals were counted at 24 and 48 h after application to determine mortality.

## Statistics

The NOECs were calculated for all parameters using the Williams test. The zooplankton and macroinvertebrate data sets were analysed by PRCs using the CANOCO software package. The significance of the PRC diagram was tested by Monte Carlo permutation of the microcosms. Permutation tests were performed for each sampling date to determine the significance of the treatment regime by sampling day. The $NOEC_{community}$ for zooplankton and macroinvertebrate communities were calculated for each individual sampling date.

## Results

Chlorpyrifos concentrations in the water column were not provided in the report. However, it is noted that concentrations decreased rapidly. After one week, around 25 per cent applied dose was found in the water column (suggesting an initial water half-life around 3.5 days) with < 10 per cent after two weeks. This was accompanied by a slight increase in sediment concentrations over time. In the first week post application, around 90 per cent of chlorpyrifos in the sediments was found in the top 1.5 cm. From two weeks post application, relative amounts of chlorpyrifos in the deeper layers increased, but the majority was always in the top layers. Based on a graph provided in the report, around 5 per cent and 10 per cent of the initial total dose was found in the sediments after two and four weeks respectively. No consistent treatment effects were recorded for dissolved oxygen, pH, conductivity or alkalinity.

## Zooplankton

Microcosms were dominated by Rotifera and Copepoda, followed by Cladocera and Ostracoda, in the pre-treatment period. Rotifera were also the most diverse group with seven different taxa. The three highest concentrations resulted in treatment related effects on the community with only zooplankton communities in the 1 µg/L microcosms returning to a state resembling the control tanks at the end of the experimental period (75 days). The most severely affected species was the cladoceran M. micrura, which was completely eliminated by the higher concentrations (NOEC 0.1 µg/L). Another cladoceran, Ceriodaphnia cornuta, decreased in population one week post-application (NOEC = 1.0 µg/L), but increased 8 weeks post application in the tanks with the higher concentrations (NOEC = 0.1 µg/L). A similar pattern was observed for mature stages of copepods. The M. micrura bioassay resulted in LC50s of 0.7 µg/L and 0.6 µg/L at 24 and 48 h respectively, and a NOEC for both times of 0.1 µg/L.

## Macroinvertebrates

During the experimental period, 13 different taxonomic groups were identified from pebble stone baskets. Besides insects, which were the most diverse group, flatworms, clam shrimps, oligochaetes, leeches and ostracods were found. The effects of chlorpyrifos application were evident in the highest two treatments with smaller effects found at 1 µg/L. All treated tanks returned to a state resembling that of the control within the test period (70 days post exposure). The Williams test indicated significant treatment effects at 1, 10 and 100 µg/L, so the $NOEC_{community}$ was again 0.1 µg/L. In terms of populations, the most prominent effect was an elimination of the Conchostraca (‘clam shrimps’) one week post-application in all but the 0.1 µg/L group (NOEC 0.1 µg/L). Ostracods disappeared from the highest dosage tanks (NOEC 10 µg/L). At the two highest concentrations, water boatmen (Corixidae) decreased in numbers relative to the controls (NOEC 1 µg/L). Even though these organisms were eliminated at these concentrations, they returned to control numbers eight weeks after application. Applications of 10 and 100 µg/L led to a large increase in the numbers of flatworms up to four weeks post application, after which numbers declined to values similar to the controls.

### Snails

Snails were represented by three families. Increased abundances of snails were observed at several sampling times after treatment, but no NOECs for two consecutive sampling dates could be calculated.

### Chlorophyll *a*

Chlorophyll *a* concentrations of the phytoplankton increased in all microcosms during the test period. The increase was substantially greater at 100 µg/L.

### Conclusion

Microcosm data can be difficult to interpret. At some sampling times, impacts on individual populations, particularly of zooplankton, were inconsistent. For example, statistically significant decreased abundances of M. micrura and Conchostraca as well as increased abundances of cyclopoid copepods and F. longiseta were observed at times at the 0.1 µg/L treatment level. However, these effects were noted only for one sampling date. Prolonged significant treatment effects on the dominant zooplankton species, the macroinvertebrate community, and its dominant organisms (Conchostraca) were found at chlorpyrifos concentrations of 1 µg/L and greater. Therefore, a $NOEC_{community}$ of 0.1 µg/L is appropriate for this study. The study authors conclude that 0.1 µg/L can be considered a $NOEC_{ecosystem}$.

## Study 3

**Table 18: Study 3: Ecological impact of repeated applications of chlorpyrifos on zooplankton community in mesocosms under Mediterranean conditions**

| | |
|---|---|
| **Reference** | López-Mancisidor et al (2008a) |
| **Test guideline** | None stated. |
| **Data validity** | 2*—reliable with restrictions |
| **Data relied on** | Yes—the data were considered to be critical and was relied on in this assessment |

### Materials and methods

The experiment was performed in 17 mesocosms (4 m long, 2 m wide) at the water surface, a water depth of 1.5 mm (11 m3 volume). The tanks were filled initially with 6 m3 tap water and allowed to mature over one year. Eight stainless steel trays (32.5 X 53 cm) filled with natural sediment from an unpolluted reservoir were placed in each tank one month before the first application.

The formulated product Chas 48 EC (emulsifiable concentrate) was applied to the surface of the water in the tanks four times at weekly intervals to achieve nominal chlorpyrifos concentrations of 0.033, 0.1, 0.33 and 1.0 µg/L. Each treatment was replicated three times with five tanks serving as controls. Water samples were collected (0.007, one, two, three, four, seven, nine, 11, 14, 16, 18, 21, 23, 25, 28, 35, and 49 days post first application) in every tank to measure exposure concentrations. On days that chlorpyrifos was applied, water samples were taken before and after application. The TWAC were calculated for each period of seven days in the exposure period that lasted 28 days (four weekly treatments).

## Sampling

Temperature, pH, dissolved oxygen and electrical conductivity were measured at the time of zooplankton and phytoplankton samplings. Phytoplankton were sampled from each tank on day three in the pre-treatment period and on days three, 10, 17, 24, 31, 38, 52, 66, 81, 94 and 130 after the first application. Zooplankton were sampled in parallel with the phytoplankton.

## Data analysis

Statistical differences for each group abundance/physico-chemical parameter/chlorophyll a concentration at each time between treatments and control was assessed through analysis of variance ($P < 0.05$, Williams test). The effects of chlorpyrifos at the zooplankton community level were analysed by the PRC method. The significance of the PRC diagram in terms of displayed treatment variance was tested by Monte Carlo permutation of entire time series using an F test. Monte Carlo permutation tests were also performed for each sampling date, using natural log ln-transformed treatment data as the explanatory variable to test significance of the treatment regime for each sampling date. If a significant relationship between treatment regime and species composition was found, then treatment levels differing significantly from the controls were determined to infer NOECs at the community level. To obtain the input data for the $NOEC_{community}$ analysis a principal component analysis (PCA) was performed for each sampling day. Calculations of the $NOEC_{community}$ were performed by applying the Williams test to the samples scores of the first principal component as calculated by the PCA.

## Results

Peak exposure concentrations of chlorpyrifos were generally greater than their respective nominal concentrations and usually were found after the last treatment. In terms of TWACs, the mean 28 d TWAC for the 0.033, 0.1, 0.33 and 1.0 µg/L treatment groups were 0.025, 0.107, 0.326 and 1.116 µg/L respectively. Half-lives between applications were generally less than one week although this was not always the case with half-lives of the second treatment being around 18 and 12 days respectively in the 0.33 and 1.0 µg/L treatments. No treatment related effects were found for water physico-chemical properties.

## Primary producers

In the course of the experiment a clear trend of treatment-related effects on chlorophyll *a* levels was not observed.

## Zooplankton

A total of 52 different zooplankton taxa were identified in the mesocosms during all the experimental period. The majority of the taxa were Rotifera (38), followed by Cladocera (11 with four macrocladocerans and seven microcladocerans) and Copepoda (three). The treatment related decline in the total number of taxa was observed immediately post first application and was more pronounced for arthropods (NOEC 0.033 µg/L) than for non-arthropods. A significant increase of the number of taxa for non-arthropods was found at the highest treatment levels between days 17 and 38. Total arthropod abundance decreased at the nominal treatment level of 1 µg/L at the end of the application period.

From the PRC analysis, of the total amount of variance, a significant proportion (23.4 per cent) was attributed to the treatment regime. The PRC diagram revealed dose-related effects only at the two highest treatment levels. At the third day after treatment (first sampling following the first application), the $NOEC_{community}$ was higher than the highest tested level. $NOEC_{community}$ values for days 10 to 24 were (nominal) 0.33 µg/L. This decreased to 0.1 µg/L for days 31, 52 and 66.

At the population level, dose-related toxicity was primarily observed in Copepoda followed by Cladocera (Daphnia gr. Galeata). For the total Copepoda, nauplii, and Cylopoida populations, the NOECpopulation from this study was (nominal) 0.33 µg/L. Both Cladocera, and D. gr. galeata populations decreased in a treatment-related manner. Greatest decreases occurred during the first four weeks with the lowest NOECpopulation of 0.1 µg/L for total Cladocera (days three to 10) and a NOECpopulation 0.033 µg/L for D. gr. galeata (days seven to 24). The authors note with respect to this figure, that D. gr. galeata occurred regularly at relatively low densities, and therefore the NOECs assigned to populations of this species should be interpreted with caution. The effects observed in rotifers differed between species, although no treatment related effects were observed for the total group. Of the three Rotifera species where data were presented in the study, $NOEC_{populations}$ between days 31 and 94 were generally 0.33 µg/L, although for one sampling day for one of the species, the NOECpopulation was 0.1 µg/L.

The zooplankton recovered within 12 weeks at all treatment levels except the highest (nominal) 1 µg/L.

## Conclusion

In this study, the most sensitive NOECpopulation was (nominal) 0.033 µg/L. However, this NOEC should be treated with caution as noted by the study authors. Only taxa for which a NOECpopulation was calculated on at least two consecutive sampling days were shown in the report. With the exception of the cladoceran D. gr. galeata (NOECpopulation 0.033 µg/L), the NOECpopulation for other taxa were generally (nominal) 0.1 to 0.33 µg/L.

At a community level, for zooplankton, the $NOEC_{community}$ was generally 0.33 µg/L (sampling days 10, 17, 24, 38 and 94), although for three of the sampling days (31, 52 and 66) the NOECcommunity was 0.1 µg/L (nominal). In terms of the 28 day (application period) time weighted average concentration, this was 0.107 µg/L, so in good agreement with the nominal value. At three sampling days (three, 81 and 130), the NOECcommunity exceeded 1 µg/L, the highest tested rate.

## Study 4

Table 19: Study 4: Zooplankton community responses to chlorpyrifos in mesocosms under Mediterranean conditions

| | |
|---|---|
| Reference | López-Mancisidor et al (2008b) |
| Test guideline | None stated. |
| Data validity | 2*—reliable with restrictions |
| Data relied on | Yes—the data were considered to be critical and was relied on in this assessment |

### Materials and Methods

The experiment was performed in 15 mesocosms (4 m long, 2 m wide) at the water surface, a water depth of 1.5 mm (11 m3 volume). Zooplankton and phytoplankton were introduced during the pre-treatment period (~three months), but sediment was not added. Five tanks were used as control and the treatments were performed in quintuplicate. The formulated product (Chas 48 EC) was applied by means of a spray gun allowing an even distribution of the chemical over the water surface and water samples were collected immediately following application (0.08 h). Water samples were then collected at one, four, 10 and 21 days post application from every tank to measure exposure concentrations of chlorpyrifos. Water samples were depth integrated. Physico-chemical properties (temperature, pH, dissolved oxygen and conductivity) of water in each tank were measured at the same time.

### Zooplankton sampling

Zooplankton was sampled from each experimental tank on days -17, -one, two, eight, 15, 22, 29, 43, 57, 78 and 99. Micro-zooplankton (Rotifera) was counted and identified under an inverted microscope. Macro-zooplankton (Cladocera, copepod nauplii and copepodite stadia of Copepoda) were quantified by counting the entire sample using a stereo microscope. The abundance of each group (number of individuals/L) was calculated using a correction factor to the counted samples.

### Data analysis

Before analysis, the zooplankton data were ln-transformed ln (10x + 1) (x = the abundance value) to a normal distribution. The threshold level for p was 0.05 for all statistical analyses. The NOECs at the parameter or taxon level were derived using the Williams test. Analyses were performed with the Community Analysis (CA) computer program. The effects of chlorpyrifos treatment at the community level were analysed by the PRC method. Monte Carlo permutation tests were also performed for each sampling date allowing the significance of the treatment regime to be tested for each sampling date. If a significant relation between treatment regime and species composition was found then treatment levels differing significantly from the controls were determined to infer NOECs at the community level. To obtain the input data for the NOECcommunity analysis, a principal component analysis (PCA) was performed for each sampling day. Calculations for the NOECcommunity were performed by applying the Williams test to the samples scores of the first principal component as calculated by the PCA.

## Results

Mean initial concentrations of chlorpyrifos on the day of application were 1.7 and 0.2 µg/L in the 1.0 and 0.1 µg/L nominal treatments respectively, and these higher measured concentrations may be attributed to incomplete mixing in the water volume of the mesocosm (despite the stated use of depth integrated water sampling). The initial dissipation times (DT50) calculated for the 1.0 and 0.1 µg/L treatments were very similar at 2.14 and 2.12 days respectively. The field dissipation measurement covers the losses by sorption (although sediment was not part of these mesocosms), volatilisation, photolysis, hydrolysis and biodegradation. Water parameters did not show a significant treatment related response.

## Impacts on populations

At the highest treatment level, significant treatment related effects on the number of taxa of each group and their relative contribution to the total taxa were identified on each sampling day. Percentage of Cladocera decreased in relation to the total number of taxa identified whereas for Rotifera, this value increased. The populations of cladocerans showed clear effects at 1 µg/L with a consistent NOEC of 0.1 µg/L during the post-treatment period. The population decrease was observed particularly in the Daphnia gr. galeata, which experienced the greatest decrease after application between days 0 and 22. After 99 days, this population was completely recovered.

The copepod populations (Cyclopoida and nauplii) had consistently decreased at 1 µg/L after eight days (NOEC 0.1 µg/L). Copepoda nauplii showed a clear effect at 1 µg/L with a consistent NOEC of 0.1 µg/L during most of the sampling days with a similar trend observed in cyclopoids. Recovery was observed at the end of the experiment (99 days).

Total rotifers showed a significant reduction in abundance 15–22 days after application with a NOEC value of 0.1 µg/L during that period. Different effects on other species were observed, as Keratella cochlearis was negatively affected by the highest concentration showing effects from day 22 to the end of the experiment while Brachionus angularis presented a treatment-related increase of the population density at 1 µg/L. For both species, the NOEC was 0.1 µg/L.

## Impacts on mesocosm community

Multivariate analysis reflected treatment-related effects on the zooplankton community at 1 µg/L. The PRC analysis found that percentage of total variance in the zooplankton data set related to exposure time was 42.7 per cent. Of the total amount of variance, a statistically significant 17.5 per cent was explained by treatment regimen. The PRC analysis of the zooplankton community only shows clear treatment responses at 1 µg/L compared with the controls. At this level, reductions were significant from day two to day 57 inclusive with a lowest calculated NOECcommunity of 0.1 µg/L.

## Conclusion

In this mesocosm experiment considering the effects of chlorpyrifos on Cladocera, Copepoda and Rotifera, the long-term observations (99 days post treatment) determined a NOEC of 0.1 µg/L chlorpyrifos for both the most susceptible species in the mesocosms and the total zooplankton community. Recovery of individual populations was generally observed by the end of the monitoring period of 99 days, while the community had recovered by day 78 post-treatment observation period.

## Additional results

There are other higher tier data that, although not considered appropriate for use in deriving the aquatic ecotoxicity end-point, have been considered in addition to the studies above.

### Stream mesocosms

Pablo et al (2008) describes research performed to compare the fate and acute toxicity of chlorpyrifos in laboratory and stream systems. The stream systems received either high (10 µg/L) or low (1 µg/L) nominal chlorpyrifos concentrations and control streams were also maintained. Water flow into the streams was stopped prior to dosing and left static for six hours following chlorpyrifos application. Chlorpyrifos was rapidly lost from the test systems, but the rates of loss varied considerably. Losses in the mesocosms could not be reliably predicted from the static laboratory studies, but was likely due to the mass transport of chlorpyrifos from the mesocosm via stream flow (resumed six hours after dosing). Chlorpyrifos was acutely toxic to invertebrates tested with the cladoceran species being the most sensitive. Laboratory 48-h LC50 values were 0.07–0.1 µg/L. The report notes that despite the differences in the dynamics of chlorpyrifos in the laboratory and mesocosm systems, the sensitivities of the mayfly (*Atalophelebia australis*) and the cladoceran *(Simocephalus vetulus)* were similar in the two systems. In this regard, it is reported that after six hours exposure in the stream mesocosm, all caged S. vetulus had died in both treatment groups giving a six hour LC50 < 1 µg/L, while mortality of around 88 per cent was found in caged A. Australis after six hours, giving a six hour LC50 well below 1 µg/L.

### Single concentration mesocosm data

Daam et al (2008b) describes the effects of a single and repeated application of chlorpyrifos on zooplankton and phytoplankton communities in outdoor microcosms in Thailand. Treatment levels of 1 µg/L were applied once or twice with a two week interval. Both treatments led to a significant decrease in cladocerans followed by an increase in rotifers, although the extent by which these species were affected was different. *Ceriodaphnia cornuta* was the most responsive cladoceran after the first treatment, while *Moina micrura* responded most to the second treatment. This was explained by differences in the growth phase of *M. micrura* at the time of application and an increase in *Microcystis* abundance over the course of the experiment. Several phytoplankton taxa either increased or decreased in number as a result of the chlorpyrifos induced changes in zooplankton communities. Even though chlorpyrifos disappeared rapidly from the water column, effects on plankton communities persisted until the end of the experiment (42 days). This was presumably due to the increasing population trend of *Microcystis*, favouring rotifers over cladocerans.

# APPENDIX 2: BIRDS AND MAMMALS ASSESSMENT METHODOLOGY

The Pesticide Environmental Risk Assessment Model for Australia (PERAMA) has been developed as an integrated model for undertaking environmental assessments of pesticides within the Australian regulatory framework. It is applied in the screening assessment for risk to Australian birds and mammals.

For both birds and mammals, the methodology for estimating exposure is based on the comprehensive guidance provided in EFSA (2009). Australian specific information is included with respect to native species.

## Residues on food

Initially, the tier 1 predicted environmental concentrations are based on methods described in SCEW (2009). For spray applications, the PECfood is used for assessing exposure to birds and mammals.

Pesticide concentrations in animal food items have been estimated with the focus on quantifying possible dietary ingestion of residues on vegetative matter and insects. Residues based on EFSA (2009) are applied. The Kenaga residues traditionally applied in Australian assessments are based on an old data set, which was updated in Pfleeger et al (1996). This updated set along with information from several studies has been adopted by EFSA, so would appear to provide a more suitable data set for birds and mammals assessments. Further, this data set allows a distinction between foliar and ground arthropods, something which is not possible from the Kenaga data set, which did not ever measure insect residues.

The following table shows residues on the individual dietary items based on a single application rate of 1 kg ac/ha where 90$^{th}$ percentile residues are used for acute exposure assessment and mean residue levels used for chronic exposure assessment:

**Table 20: Residues (mg ac/kg fresh weight) for different dietary components based on an application rate of 1000 g ac/ha**

| Dietary component | Residues (mg ac/kg fresh weight), 1000 g ac/ha | |
|---|---|---|
| | Acute[1] | Chronic[2] |
| Grass + cereals | 102.3 | 54.2 |
| Non-grass weeds | 70.3 | 28.7 |
| Seeds (fruiting period) | 87.0 | 40.2 |
| Fruit[3] | 41.1 | 19.5 |
| Foliar arthropods[4] | 54.1 | 21.0 |
| Ground arthropods[5] | 13.8 | 7.5 |

*[1] 90$^{th}$ percentile residue values for acute assessment; [2] Mean residue values for chronic assessment; [3] Based on large fruit from orchards. Further refinement can be made for different fruit types if required; [4] No data are available for canopy dwelling invertebrates in winter or before the leaves appear (interception would be less); [5] applications on bare soil, or ground directed applications up to principle growth stage 3, ground directed applications in orchards/vines.*

## Calculating food intake rates

Food intake rates are calculated from the daily energy expenditure (DEE) as follows:

The estimates of food intake are based on means of daily energy expenditure for free-ranging animals, energy and moisture content and assimilation efficiencies. Food item values for energy, moisture content and assimilation efficiency are provided in EFSA (2009). The food intake rate (FIR) is calculated as follows (EFSA 2009):

**Equation 1: Calculation of food intake rates (g/d, fresh weight)**

$$FIR = \left( \frac{DEE}{FE\ X\ \left(1 - \frac{MC}{100}\right)\ X\ \left(\frac{AE}{100}\right)} \right)$$

Where:

DEE = Daily energy expenditure of the indicator species (kJ/d)

FE = Food energy (kJ/dry g)

MC = Moisture content (%)

AE = Assimilation efficiency (%)

## Estimated daily exposure

The estimated daily exposure, that is, the uptake of a compound via a single food item is given by the following equation (EFSA 2009):

**Equation 2: Calculation of estimated theoretical exposure (mg/kg bw/d)**

$$ETE = \frac{FIR}{bw}\ X\ C\ X\ PT$$

In which:

ETE = Estimated theoretical exposure (mg/kg bw/d)

FIR = Food intake rate of indicator species (g fresh weight/d)

bw = Body weight (g)

C = Concentration of compound in fresh diet (mg/kg)

PT = Fraction of diet obtained in treated area (number between 0 and 1)

For the acute assessment, PT will be set at one as it is assumed all food is sourced from within the treated area.

For the chronic (reproduction) assessment, a 21-d time weighted average (TWA) concentration is obtained by multiplying peak residue by 0.53 (EFSA 2009), which assumes a default residue half-life of 10 days (foliage).

Where required, multiple application factors are applied based on the methodology in EFSA (2009).

## Birds

Birds that are NOT been considered at this stage include:

- honey eaters (these can be considered on a case-by-case basis in the event of exposure)
- shore birds and waders
- seabirds
- introduced birds.

Information on birds with respect to distribution, diets and weights has been obtained from Birdlife Australia, specifically their 'Birds in Backyards' information pages. The three groups analysed included parrots (primarily granivores, but also some mixed diet species including fruits, seeds, plant matter, insects); small insect eating birds (primarily insectivores, but also some mixed diets including seed); and birds under threat, which included a range of carnivorous birds (for example, owls, not considered further in this analysis), insectivorous, granivorous and omnivorous species.

From the information obtained, several different bird diet groups and body weights can be obtained for application in the environmental risk assessment. This exercise was not undertaken to identify focal or indicator species as it is not considered detailed enough. However, in some cases potential indicator species are identified.

The smallest birds belonged to the 'small insect eating' category. While information on larger insect eating Australian native birds has not been obtained, the use of smaller animals is considered protective of larger animals as the smaller birds are expected to have higher food intake rates and therefore have higher exposure to contaminated food items.

Granivorous birds were dominated by the parrot species and these tended to have higher body weights (range of 17 to 650 g), although several of these species are unlikely to be exposed in general farming situations. A number of parrots (n = 7) from the data set were also found to have a mixed diet of seeds and fruits.

The information available for omnivorous species is somewhat limited. Currently, two mixed diets are considered in the avian risk assessments based on a 'quail' diet and a 'mallard duck' diet. One of these is insect dominated and the other is cereal dominated. That mixture of dietary components will be maintained in this approach, but only a single small body weight bird (10 g) will be assessed for each diet.

An assessment of 'bush birds' indicates that consumption of grasses and leaves in the diet is highly unlikely, hence these birds are not assessed for residues on such food items.

An assessment of diets of almost 100 'water birds' has been undertaken from Birdlife Australia. This analysis indicates specialist herbivorous birds in Australia are also unlikely to be found. However, some species are noted as consuming land plants, which may include grasses or leaves. Examples include the grey teal, Australian wood duck, Tasmanian native hen and plumed whistling duck. Of these, the grey teal has been adopted at this stage as the best example species as it is commonly distributed throughout the country and has a lighter body weight than the other birds, which makes it the most conservative choice.

The following bird diets and body weights will be developed for the avian risk assessment:

**Table 21: Australian bird body weights, feeding guild and example species**

| Diet | Body weight (g) | Example species |
|---|---|---|
| Granivore | 15 g | Diamond firetail |
| | 100 g | Cockatiel |
| | 500 g | Long billed corella |
| Insectivore | 7 g | Grey fantail |
| | 20 g | Australian reed warbler |
| | 80 g | Grey crowned babbler |
| Omnivore, insect dominated | 10 g | Crested shrike-tit |
| Omnivore, seed dominated | 10 g | Double barred finch |
| Mixed—seeds and fruits | 150 g | Australian ringneck (parrot) |
| Herbivore | 400 g | Grey teal (only non-passerine) |

It is understood that the example species are not representative for every growing region or scenario that will be considered. However, at this stage they are thought to be a suitable surrogate for other birds where data have not been obtained.

### Allometric equations for birds

DEE for passerines and non-passerines is calculated from the following equations (EFSA 2009):

Log(DEE) = Log(a) + b X Log(BW)

Log(a) is 1.032 and 0.839 for passerines and non-passerines, respectively, while ‘b’ is 0.676 and 0.669 respectively. BW = body weight (g).

## Mammals

In Australia, there are 163 smaller species (≤ 600 g) of native mammals. The mammals are distributed evenly amongst marsupials (52), rodents (54) and bats (57) (Withers et al 2004). This reference provide numbers of mammals present based on aridity zones defined based on rainfall as: Arid zone < 250 mm/yr; semiarid zone 250–500 mm/yr; mesic zone is rainfall > 500 mm/yr. Significant dryland farming zones can occur within the rainfall band of 250–500 mm/yr. Of the 52 small marsupial species in Australia, 46 (88 per cent) can be found in semi-arid to mesic zones with 26 species (50 per cent) only found in mesic zones. Similarly with native rodents, of the 54 small mammal species, 47 (87 per cent) can be found within semi-arid to mesic zones with 31 (57.5 per cent) found only in the mesic zone. Given this, it is reasonable to assume that > 80 per cent of marsupial and native rodent species can occur within agricultural regions in Australia.

The current Australian methodology for assessing environmental risks of agricultural chemicals and veterinary medicines for the APVMA is described in SCEW (2009). The approaches in that manual have not undergone revision since the initial risk assessment manual was compiled in 2006 (first published in 2007, then again in 2009), and many aspects of the risk assessment methodology are considerably out of date.

## Native rodents

All Australian rodent species are in the subfamily Murinae, a very successful group that once occupied nearly every habitat type in Australia. Many species have suffered great reductions in distribution, with at least 11 species becoming extinct since European settlement. The rodents are a relatively diverse group with animals ranging in size from only a few grams (for example, the delicate mouse) to just over one kilogram (for example, the water rat) (NHMRC 2014).

There are 59 recognised modern species of native murids. All are essentially omnivorous with the bulk of the diet composed of plant material, mainly seeds or stems and some insect material (Watts & Kemper 1989).

Previously, mammalian assessments had simply adopted a 100 per cent grain diet for assessing risk to mammals. The residue levels for seeds calculated by the Kenaga nomogram had the highest number of values exceeding the predicted value in the field work undertaken by Pfleeger et al (1996), and these were all attributed to wheat. It was explained that the wheat head and not the individual wheat kernels were sampled. This category is heavily based on the concept of vegetative interception factors; that is, the plant tissues eaten by wildlife are partially protected from pesticide exposure by other plant tissues and therefore would generally have less pesticide residue.

Therefore, it is important to note that plant reproductive structures that are directly exposed to spray application should not be estimated under this category but rather under the long-grass category for grasses and the leaves and leafy crop category for most dicot species (Pfleeger et al 1996).

More detailed information on distributions of different native rodents and their diets is available in Breed and Ford (2007). It is difficult to find species common to the wide range of agricultural regions in Australia. However, it is noted that the diet of many species of living Australian rodents includes insects and seeds. Those species with a small body mass require more nutritious food which is essential to maintain their basal metabolic rate, thus, these species tend to consume seeds since these are more nutritious than most other available foods. Apart from seeds, plant material may consist of shoots/leaves and roots. Fungi are also noted as food sources for several species, but they are not considered within this assessment.

In performing the native rodent assessment where plant material consists of roots and leaves, non-grass weed residue data are applied. It will be assumed that consumption of this component is 50 per cent roots and 50 per cent leaves, so the residues will be halved on the assumption that the roots do not contain residues (does not account for systemic substances, but the acute assessment is assuming consumption during the day of or following treatment). Seeds will be assumed to comprise half the total diet for the smaller animals (default body weights of 10 g and 50 g).

For the larger body mass Bush rat (default body weight of 160 g), which is found in many of the agricultural areas in Australia, stems/leaves will be assumed to comprise half the diet based on residues from the non-grass weeds. Seeds will be assumed to comprise 50 per cent of the diet, other plant matter 25 per cent and insects 25 per cent of the diet. Noting that the smaller animals can change their dietary preference at different times of the year, the smaller body weight native rodents will also be assessed for an omnivorous diet with this same proportion of different components.

A mixed diet FIR/BW value has been calculated applying the energy content, water content and assimilation efficiency for weed seeds, non-grass weeds as a surrogate for the plant material component of the diet, and the arthropods for the insect component of the diet using the values reported in EFSA (2009).

The DEE has been calculated applying the allometric equation from EFSA (2009) for mammals, $DEE = 6.516 * BW^{0.715}$. The assessment is performed for the following native rodent body weights and diets:

**Table 22: FIR/BW values for foliar applied chemicals for application in assessment of risk to Australian native rodents**

| Body weight | Example species | Mixed diet FIR/BW | Diet component |
|---|---|---|---|
| **Herbivorous diet** | | | |
| 10 g | Sandy inland mouse (*Pseudomys hermannburgensis*) | 1.15 | Seeds (50%) |
| 50 g | Mitchells hopping mouse (*Notomys mitchellii*) | 0.73 | Leaves (25%) |
| | Fawn footed melomys (*Melomys cervinipes*) | | Roots (25%) |
| **Omnivorous diet** | | | |
| 10 g | Sandy inland mouse (*Pseudomys hermannburgensis*) | 0.77 | Seeds (50%) |
| 50 g | Mitchells hopping mouse (*Notomys mitchellii*) | 0.48 | Leaves (12.5%) |
| | Fawn footed melomys (*Melomys cervinipes*) | 0.35 | Roots (12.5%) |
| 160 g | Bush rat (*Rattus fuscipes*) | | Ground arthropods (25%) |

It is understood that the example species are not representative for every growing region or scenario that will be considered. For example, the bush rat is not found in Tasmania with the swamp rat being the only endemic native *Rattus* species there (Breed & Ford 2007). However, at this stage they are thought to be a suitable surrogate for other native rodents that may occur in the different areas.

## Marsupials

In terms of smaller (≤ 600 g) native mammals, in Australia there are 163 species of which marsupials account for 52 (Withers et al 2004). Of the 52 smaller marsupial species in Australia, 46 (88 per cent) can be found in semi-arid (250–500 mm rainfall/yr) to mesic (< 500 mm rainfall/yr) zones with 26 species (50 per cent) only found in mesic zones. Given this, it is reasonable to assume that a significant percentage of marsupial species can occur within agricultural regions in Australia.

The methodology proposed here places the focus on terrestrial insectivore/omnivores and terrestrial herbivores as being more relevant to agricultural situations. At this stage there are insufficient details to do allometric modelling for estimating required food intake rates by arboreal marsupials, which may be exposed during application to tree crops; marsupials that primarily live of plant exudates (pollen, nectar, gum); or the fossorial herbivores (relying on below ground plant parts and fungi). These animals are possibly less likely to be exposed through agricultural use, but methodology may be developed in the future. For the terrestrial insectivore/omnivore group, field metabolic rate data for 21 species covering 10 genera and two families (*Dasyuridae* and *Peramelidae*) have been obtained. Arthropods appear to be the principal food items of most dasyurids. It is noted that members of peramelidae family (bandicoots, bilbies) may include significant proportions of plant items in their diet (Russell et al 1989). There is insufficient information to consider mixed diets (omnivores) and develop allometric equations, so the analysis is restricted to the 16 members of the Dasyuridae family for which data are available.

For the terrestrial herbivores, the above table lists 10 different Australian genera. Field metabolic rate data for six species and a basal metabolic rate data for an additional six species have been used in developing an appropriate allometric equation. These species cover seven different genera and all from the Macropodidae family. Some macropods (mainly *Macropus* species) and wombats are grazers (Russell et al 1989), and these are reflected in available field metabolic rate data set. They are generally larger animals (adult weights > 1 kg), and the smallest marsupial in data set for metabolic rates in this group was the Rufous hare-wallaby with a body weight of ~1350 g.

Allometric equations for the two marsupial groups considered in the risk assessment remain, at this stage, proprietary information. The assessment is undertaken with the following marsupial groups and body weights:

**Table 23: Food intake rates based on body sizes for dasyurida and macropodid marsupials and example species**

| | Body weight | FIR/BW | Example species |
|---|---|---|---|
| Dasyurids | 10 | 0.57 | Common planigale |
| | 40 | 0.38 | Dusky antechinus |
| | 1000 | 0.15 | Quoll |
| Macropods | 1000 | 0.21 | Small wallaby |
| | 4000 | 0.15 | Pademelon |
| | 10000 | 0.12 | Small kangaroo |

# APPENDIX 3: DESCRIPTION OF RUN-OFF METHODOLOGY

PerAMA model has been developed as an integrated model for undertaking environmental assessments of pesticides within the Australian regulatory framework. The software incorporates relevant real-world data with respect to slopes, soil types, rainfall and stream flow rates to allow a spatial and temporal assessment of run-off risk in Australia.

Run-off has been modelled following the methodology described in the APVMA's refinement of aquatic exposure estimates in environmental run-off assessments for pesticides in dryland cropping regions.

Following the consultation, some amendments have been made to the methodology (consultation paper still to be updated). These amendments relate to predicting edge of field concentrations, not the application of the stream flow data sets applied at the highest tier of assessment. PerAMA software is based on the updated approach.

The edge of field concentration is still assessed by the following equation:

**Equation 3: Edge of field concentration equation**

$$L\%_{runoff} = \left(\frac{Q}{P}\right) X\ f\ X \exp\left(-\frac{3XLn2}{DT_{50\ soil}}\right) X\ 100/(1 + Kd)$$

The term 'f' relates to several correction factors:

f1 is the slope factor, where f1 = 0.02153 X slope + 0.001423 X (slope)2 (for slopes < 20 per cent);

f2 reflects the influence of plant interception, PI(%) where f2 = 1 – (PI/100);

f3 reflects the influence of a densely-covered buffer zone, where f3 = 0.083WBZ, and WBZ is the width of the buffer zone in metres. If the buffer zone is not densely covered with plants, the width is set to zero. Vegetative filter strips are not currently considered in Australian assessments, and thus this factor remains at zero.

The run-off assessment is performed in a tiered approach, namely, a screening level assessment, a first step of refinement where run-off curves from different cropping systems along with soil profiles for different regions are considered, and a final tier of assessment where receiving water characteristics in different use regions are considered along with regional specific rainfall values. The highest tier of assessment is undertaken in both spatial and temporal scales.

To perform these assessments, even at the screening level, a significant volume of Australian specific data have been analysed and applied. These data relate to slopes in different land use areas along with soil profiles, rainfall values and streamflow data in different regions. The following sections describe how these data were obtained and are applied in the different tiers of the run-off risk assessment.

## Australian soil profiles and influence on run-off curves

Concern was raised (and agreed by the APVMA) that the Q/P run-off curves (Q = run-off in mm; P = rainfall in mm) in the current consultation paper will underestimate run-off from soils heavier than 'loamy' soils, as the run-off curves were only available for 'sandy' and 'loamy' soils.

Consequently, a major change in the calculation of 'Q' has been adopted, using the data and approach provided by the US Department of Agriculture (USDA). A hydrologic soil-cover complex is a combination of a hydrologic soil group (soil), a land use and treatment class (cover). Tables and graphs of run-off curve numbers (CNs) assigned to such complexes are available from the USDA in their National Engineering Handbook Part 630. The chapters for this handbook are available electronically. The four hydrologic soil groups (HSGs) based on clay content are A (< 10 per cent clay), B (10–30 per cent clay), C (30–40 per cent clay) and D (> 40 per cent clay).

In addition, the Australian Grains research & Development Corporation (GRDC) and others have provided measured information on soil clay characteristics in Australian dryland cropping regions, which allows classification of these regions within the hydrologic soil group (HSG) groupings. This information can be combined with the USDA curve-number information to develop composite run-off curves for the different regions.

The clay content information can be found on the Soil Quality Pty Ltd website. The following table summarises the HSG contributions for dryland cropping for each State:

**Table 24: Fraction of different hydrologic soil groups (HSGs) in dryland cropping zones for different states**

| State | No. of measurements | < 10% clay (A) | 10–20% clay (B) | 20–40% clay (C) | > 40% clay (D) |
|---|---|---|---|---|---|
| Queensland | 97 | 0.0206 | 0.0103 | 0.1650 | 0.8041 |
| New South Wales | 575 | 0.1374 | 0.4383 | 0.3253 | 0.0991 |
| Victoria | 120 | 0.1333 | 0.4083 | 0.4000 | 0.0583 |
| Tasmania | 219 | 0.0091 | 0.1826 | 0.3607 | 0.4475 |
| South Australia | 167 | 0.1018 | 0.5030 | 0.3892 | 0.0060 |
| Western Australia | 2004 | 0.7425 | 0.1891 | 0.0619 | 0.0000 |

Composite curve numbers have been derived for the different states. Separate curve numbers are derived for the different scenarios based on the hydrologic soil group curve numbers identified in the USDA National Engineering Handbook, and the relative contribution for each soil group from the different state profiles. The formula applied is:

**Equation 4: Composite curve number**

$$Composite\ Curve\ Number = \sum (CN_i\ X\ f_i)$$

Where: CN = USDA Curve number for soil hydrological group *i*

f = fraction of contribution for soil hydrological group *i*

The above contributions are based on soil data in dryland cropping regions. In the absence of further analysis of soil clay contents for other cropping systems, at this stage PERAMA adopts them for different situations in the same states. For example, when considering Queensland production horticulture, which is undertaken on Natural Resource Management areas, the same soil profile is applied in all areas.

To maintain a conservative approach, the composite curve numbers are based on the most conservative hydrologic condition assigned to the USDA curve numbers, that is, a 'poor' hydrologic condition. This is based on combinations of factors that affect infiltration and a poor hydrologic condition adopting factors that impair infiltration and tend to increase run-off. PERAMA currently applies the following scenarios for a range of cropping categories and application types:

Table 25: Range of scenarios currently available in PERAMA and corresponding USDA cover types and curve numbers

| PERAMA scenario | USDA cover type | Curve number for USDA soil hydrologic group | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| Turf, turf farms | Pasture, fair (50–75% ground cover) | 49 | 69 | 79 | 84 |
| Turf, golf courses | Pasture, fair (50–75% ground cover) | 49 | 69 | 79 | 84 |
| Turf, playing surfaces | Pasture, good (> 75% ground cover) | 39 | 61 | 74 | 80 |
| Stubble retention/no till | Pasture, poor (< 50% ground cover) | 68 | 79 | 86 | 89 |
| Row crop, straight row | Row crops, straight row | 72 | 81 | 88 | 91 |
| Row crop, contoured | Row crops, contoured | 70 | 79 | 84 | 88 |
| Rights-of-way | Specifically derived scenario. Non-region specific. Applies CN 86 for background catchment and CN93 for rights-of-way | | | | |
| Pasture | Pasture, poor (< 50% ground cover) | 68 | 79 | 86 | 89 |
| Orchards, pasture inter row | Orchard or tree farm; 50% wooded, 50% pasture | 57 | 73 | 82 | 86 |
| Orchards, bare soil inter row | AEA derived; 50% wooded, 50% bare soil | 61 | 76 | 84 | 89 |
| Legume | Close seeded or broadcast legumes | 66 | 77 | 85 | 89 |
| Grain, straight row | Small grain, straight row | 65 | 76 | 84 | 88 |
| Fallow, crop residue | Fallow, crop residue | 76 | 85 | 90 | 93 |
| Fallow, bare soil | Fallow, bare soil | 77 | 86 | 91 | 94 |

## Determination of slope for screening assessment

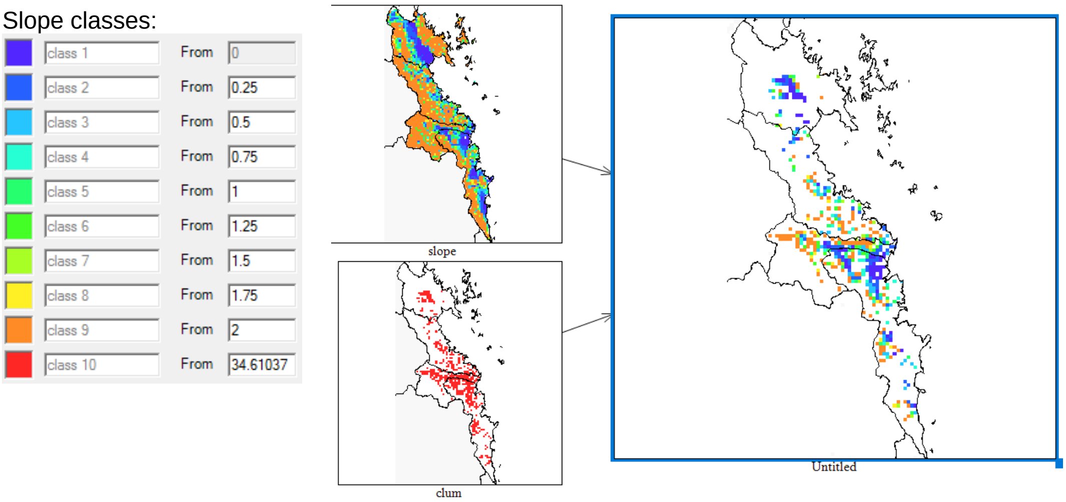
Slope values for the different cropping categories and regions have been determined based on a two-way analysis between slopes and land use from the Australian Government Department of Agriculture and Water Resources multi-criteria analysis shell (MCAS-S) tool, The MCAS data is based on the 2011 dataset with a 2 km$^2$ resolution.

In order to obtain more reliable results, 15 different slope class sizes were assessed from 0–2 per cent in 0.25 per cent increments, then from 2–2.5 per cent, 2.5–3 per cent, 3–4 per cent, 4–6 per cent, 6–8 per cent, 8–10 per cent and 10–20 per cent. To remain conservative, returned results were assumed to be at the upper value of the mean slope range being assessed. For example, the area identified in the 3–4 per cent slope class was assumed to all have a mean slope of 4 per cent.

The following figure shows this analysis for the 0–2 per cent slopes in the Mackay/Whitsunday region of Qld for sugarcane and horticultural areas:

### Figure 4: Example of slopes analysis

MCAS 2-way analysis, slopes in sugarcane and horticultural areas in the Mackay/ Whitsunday region for slopes up to 2%.




### Table 26: Land use categories applied in calculating slope values

| Cropping category | MCAS land use category (categories) applied | | |
|---|---|---|---|
| Dryland | Dryland cropping | | |
| Tropical/subtropical | Dryland horticulture | Irrigated horticulture | |
| Sugarcane | Dryland horticulture | Irrigated horticulture | Irrigated cropping |
| Horticulture, orchards | Dryland horticulture | Irrigated horticulture | |
| Horticulture, non-orchards | Dryland horticulture | Irrigated horticulture | |
| Pasture | Grazing modified pastures | Irrigated pastures | |
| Turf, golf courses | Urban | Rural residential | |
| Turf, turf farms | Dryland horticulture | Irrigated horticulture | |
| Turf, playing fields | Scenario specific. Set at 2%. | | |

There was insufficient data in the Mackay/Whitsunday region for tropical/subtropical horticulture so the data set was extended to include irrigated cropping.

While slopes for horticulture orchards and horticulture non-orchards were based on the same data set, orchard slopes in South Australia were restricted to an analysis of the Onkaparinga River Catchment, which resulted in steeper slopes than for total South Australian horticulture.

The slope data are not normally distributed. Low slope values are generally far more prevalent than high ones, and an exponential distribution is assumed.

Consequently, 90th percentile slope values have been calculated from the mean as follows:

$$90th\ percentile\ slope = -\mu\ X \log(0.1)$$

Where: µ = mean slope (%); ln = natural (base e) logarithm.

In the run-off modelling, the 90th percentile slope is applied in the first step of refinement while the mean slope is applied in the higher tier of assessment.

## Screening run-off risk assessment—water column

This is a screening assessment only. It is taken as a worst case and substances that pass this level do not require further assessment.

**Error! Reference source not found.** shows the soil profile with the highest run-off propensity is Queensland with > 80 per cent of topsoils containing > 40 per cent clay, while **Error! Reference source not found.** shows the worst case scenario based on run-off curve numbers to be a fallow, bare soil (highest curve numbers). Therefore, the worst case composite run-off curve is generated for Queensland under fallow, bare soil conditions. This composite curve number is applied in the screening assessment regardless of the situation being assessed. Substances that pass this level do not require any further assessment.

The screening level assessment is performed using the traditional standard water body scenario applied in Australian assessments whereby a 10 ha catchment feeds a 1 ha surface area water body with an initial depth of 15 cm. The rainfall value in this scenario that results in the maximum receiving water body concentration is 8 mm. At rainfall greater than this, additional run-off begins to dilute the concentration.

It is clear from the 90th percentile slope figures above that slopes can be significantly steeper in Tasmania than other horticultural/pasture/turf areas in the country. At the initial screening assessment, the slope is fixed at 8 per cent. This is expected to cover > 90 per cent of situations at the screening step. Horticultural, turf (golf courses) and pasture uses in Tasmania have 90th percentile slopes exceeding this value and in such cases, modelling run-off risk for Tasmania should proceed immediately to the Step 1 refinement.

## Step 1 run-off refinement (some spatial considerations)

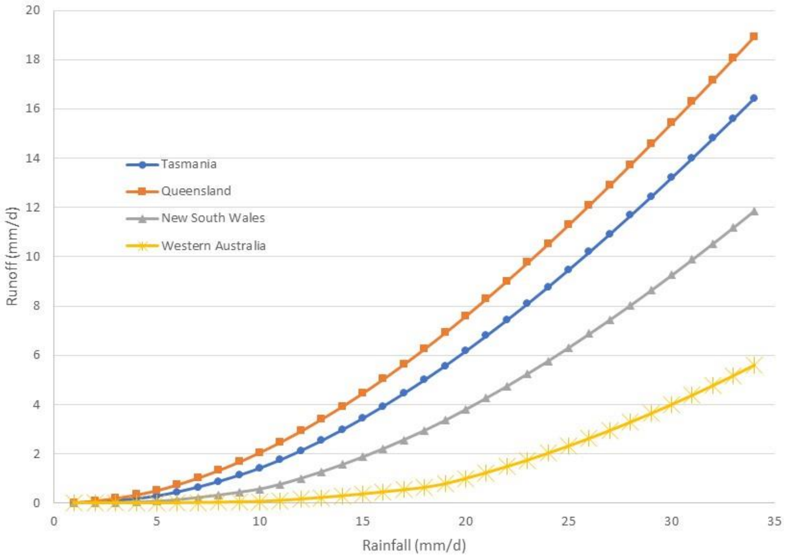
The first step of refinement from the screening assessment takes additional spatial influences into account in terms of soil profiles. These influence the run-off curve (Q/P) in Equation 3 above. This refinement step also moves from the worst case run-off curve for fallow, bare soil to more appropriate curves that consider influences of hydrologic soil-cover complexes. The range of scenarios currently available in PERAMA and corresponding USDA cover types and curve numbers are shown in **Error! Reference source not found.** above. The following figures shows the influence of soil types and cover type on predicted run-off:

## Influence of soil type on run-off curves

The profile most dominated by clay is found in Queensland and the profile most dominated by sand is found in Western Australia. For the same rainfall value, the predicted run-off rates are significantly different.

The following run-off curves for Queensland, Tasmania, New South Wales and Western Australia are shown for fallow, bare soil situation. For a given 30 mm rainfall, the predicted run-off from these different soil profiles is 15.4, 13.2, 9.3 and 4.0 mm/d. This demonstrates the importance of considering different regional characteristics in the run-off assessment rather than the 'one size fits all' approach that has traditionally been applied in Australian risk assessments.

Figure 5: Influence of different soil profiles on run-off curves




## Influence of cover type on run-off curves

The range of scenarios currently available in PERAMA and corresponding USDA cover types and curve numbers are shown in **Error! Reference source not found.** above. Composite curve numbers are calculated for each soil type based on the contribution of the hydrologic soil group. In PERAMA, a rounded curve number value was not used. Rather, a composite curve number was calculated as follows:

Equation 5: Composite Curve Number Equation

$$CCN = \sum CN_i \; X \; F_i$$

Where:

CNN = Composite Curve Number

$CN_i$ = Curve number for soil hydrologic group, *i*

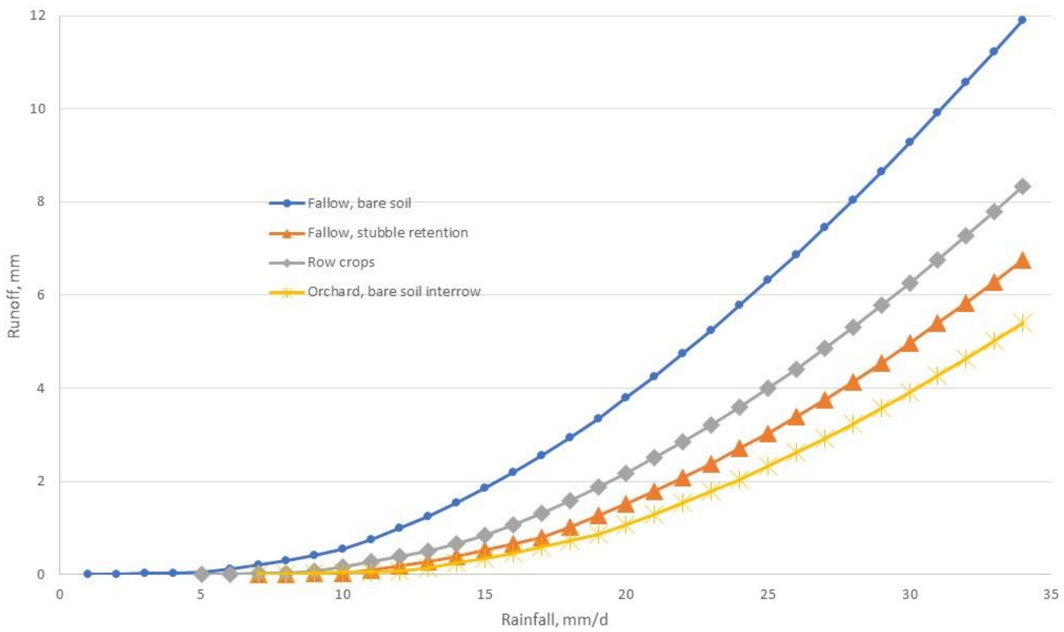
$F_i$ = Fraction of contribution of soil profile to soil hydrologic group, *i*

An example is provided as follows:

**Table 27: Development of composite curve number, Victoria, row crop, straight row, poor hydrologic condition**

| Hydrologic soil group | < 10% clay (A) | 10–20% clay (B) | 20–40% clay (C) | > 40% clay (D) |
|---|---|---|---|---|
| Curve number (USDA) | 72 | 81 | 88 | 91 |
| Contribution from state soil profile | 0.1333 | 0.4083 | 0.4000 | 0.0583 |
| SUM contribution | 83.18—final curve number applied for Victoria | | | |

**Figure 6: Influence of different soil cover on run-off curves**




For a 30 mm rain event, the different curve numbers predict run-off of 9.3 mm, 5.0 mm, 6.3 mm and 3.9 mm in fallow (bare soil), fallow (stubble retention), row crops and orchards with a bare soil inter row, respectively. This demonstrates the importance of considering different ground cover situations in the run-off assessment rather than the ‘one size fits all’ approach that has traditionally been applied in Australian risk assessments.

## Limitation of the Step 1 refinement level

While this level of refinement allows for regional consideration in terms of slopes (90$^{th}$ percentile values), soil types and their influence on the run-off curve, and ground cover from different cropping systems, it still considers run-off in the standard Australian scenario of a 10 ha catchment feeding a 1 ha pond 15 cm deep. The associated rainfall values applied are those that result in the highest predicted water concentration, and do not reflect reality. As an example, when considering run-off from the composite curve number for each state in orchards (bare soil inter-row), rainfall values of 18, 28, 28, 21, 29 and 47 mm are applied for Queensland, New South Wales, Victoria, Tasmania, South Australia and Western Australia, respectively. This is clearly unrelated to actual likely rainfall found in different regions. The likelihood of a 47 mm/d rainfall event in the orchard growing regions of Western Australia is low, but reflects the sandy soil profile. While the value in Queensland may be more realistic, at this level of refinement, it means not all regions are being considered equally.

In order for a more equal consideration, actual regional specific rainfall data require consideration. This is applied in the Step 2 level of refinement if needed. In addition, characteristics of receiving waters are also taken into account. The development of the stream flow data and rainfall data allow the assessments to be performed in both space and time.

## Step 2 Refinement (in-stream analysis; spatial and temporal consideration)

### Background catchment and its influence

There are additional factors that require consideration in analysing the rainfall and stream flow data prior to undertaking the highest level of refinement in the assessment. Firstly, the stream flow data are ‘fixed’ in that they are historic and represent the characteristics of their catchments. This means that for a given stream flow rate, any increase in rainfall will result in higher in-stream concentrations. Therefore, it is important that the rainfall value applied in the assessment is realistic.

In order to determine an appropriate rainfall value, a background catchment has been modelled, recognising that a certain amount of rain is required prior to run-off commencing. This background catchment is based on the USDA curve numbers for ‘Herbaceous—mixture of grass, weeds and low-growing brush, with brush the minor element’. The curve numbers applied for hydrologic soil groups A, B, C and D are 58, 71, 81 and 89, respectively, and composite curve numbers are then generated for each state based on their respective soil profiles.

A ‘Fair’ hydrologic condition has been applied to account for areas in the catchment that may be more susceptible to run-off. A trigger of 0.1 mm run-off was adopted such that, where run-off was predicted to be < 0.1 mm, it was not considered in determining the minimum rainfall value. The reason is that, for soils with any clay content the commencement of run-off occurs at much the same rainfall (~seven mm). This does not allow for consideration of the contribution of the higher run-off component of the soils.

Based on the above composite curves, the background rainfall values for Qld, NSW, Vic., Tas., SA and WA are set at 9 mm, 12 mm, 15 mm, 9 mm, 16 mm and 16 mm respectively. For WA, the high sand component actually predicts 23 mm required prior to the commencement of run-off, but this is considered too high to obtain meaningful results. Hence the value from SA has been applied as a default for WA.

### Determination of final rainfall values

The background catchment rainfall values are applied to the cumulative frequency distributions of historic rainfall for different regions/states to obtain 25$^{th}$ percentile and 75$^{th}$ percentile rainfall levels for application in the in-stream analysis such that the cumulative frequency distributions commence from the background rainfall value.

Rainfall statistics were obtained from weather stations within cropping areas of interest, and the number of stations assessed was proportionate to the size of the area being considered. Where > 4 stations were assessed within a region, the 90th percentile values have been applied in PERAMA, which provides a conservative value of rainfall. For smaller growing regions, for example within the Queensland production horticulture NRMs, mean rainfall values were adopted as only a small number of weather stations were assessed and variability between these was (understandably) not high.

In order to perform the temporal assessment, rainfall data were separated by season for state based assessments (dryland, horticulture, pasture, turf) and by month for tropical/subtropical production horticulture assessments. The monthly time scale was considered important due to rainfall patterns being summer dominated and the wet season time period not necessarily corresponding with standard seasons.

PERAMA assesses for a current total of 528 different rainfall values depending on cropping category, state, region, percentile stream flow being assessed or the time period being considered. The following table provides a summary of some of these rainfall values to demonstrate the variability in time and space:

**Table 28: 25th and 75th percentile rainfall values for dryland cropping in some states applied in PERAMA**

| | Queensland | | Tasmania | | Western Australia | |
|---|---|---|---|---|---|---|
| Percentile stream flow | 25th | 75th | 25th | 75th | 25th | 75th |
| Summer | 13.1 | 30.7 | 12.0 | 25.0 | 20.3 | 39.2 |
| Autumn | 12.9 | 30.6 | 11.8 | 24.4 | 19.3 | 32.0 |
| Winter | 12.7 | 29.0 | 12.1 | 22.9 | 18.5 | 27.6 |
| Spring | 12.6 | 30.1 | 11.7 | 21.9 | 18.6 | 28.1 |

It may appear curious that rainfall values for Western Australia are significantly higher than those for Queensland or Tasmania. This, however, reflects the soil profile where a much greater amount of rain is required to generate run-off in the very sandy soils found in Western Australia. These figures still do not include a measure of probability of the rainfall values. Rainfall probability is not assessed further in PERAMA, but may be a further refinement option if required. For example, the 75th percentile rainfall value in Western Australia in summer is 39.2 mm/d. This is compared to the 75th percentile stream flow rate. Stream flows in Western Australia in the dryland areas are very small, but may still occur. However, the likelihood of a 39.2 mm rainfall event is low. Based on rainfall data from 45 weather stations throughout the Western Australian wheat belt and applying 90th percentile results, the probability of any day actually being wet (> 0.1 mm rain) is only 8.9 per cent. The probability of any of these wet days resulting in rainfall exceeding 39.2 mm is only 2.6 per cent. Therefore, the overall probability of a rainfall event in the summer months of 39.2 mm/d is 0.2 per cent. Even with the lower 25th percentile value of 20.3 days, the overall probability of exceeding this in the summer months is < 1 per cent.

Conversely, in the summer rainfall dominated Queensland dryland cropping regions, the probability of a wet day in summer is 22.1 per cent and the probability of exceeding the 13.1 mm/d value on a wet day is relatively high at 21.1 per cent.

## Stream flow rates—consideration of base flow

In addition to run-off waters entering the stream/river, flow rates can already exist from other sources such as stream base flow and run-off waters originating from elsewhere in the catchment. In rainfall run-off models used to estimate design floods, rainfall run-off/filtration is classified as quick flow (surface run-off) and base flow is essentially the result of groundwater flow (Tularam & Ilahee 2005). The methodology described for refined run-off assessments in this document focuses on in-stream concentrations that result from quick flow, which is a direct result of rainfall.

An important component of the stream analysis, both in the proposed methodology here and that described in the European FOCUS[4] stream scenarios, relates to base flow. If there was no consideration of a baseflow component, stream flow rate percentiles would be based on the cumulative frequency distribution curves using the total dataset and therefore overestimation of in-stream concentrations would be likely. This is because the increased flow resulting from rainfall induced run-off would not be considered as an additional flow rate. However, the rainfall value used to predict run-off concentrations would remain the same, so in-stream concentrations would be overestimated.

In the FOCUS scenarios, to derive a baseflow component to the hydrological flows feeding the surface water bodies, parameters quantifying the catchment 'Base Flow Index' (BFI) were needed. The BFI quantifies the fraction of long-term total flow in a catchment that is represented by base flow. This parameter was derived from an estimated soil hydrological class at each representative field site for the scenarios available in Europe. Estimated soil hydrological classes have associated set of empirically-derived coefficients describing stream flow characteristics. Based on the soil hydrological characteristics for each of the FOCUS surface water scenarios, BFI values of between 0.17–0.79 were adopted.

Such a classification tool is not available in Australia. To remain conservative, a simple method for calculating an individual baseflow index for each monitoring station during each separate season has been applied. For the analysis, positive flow is considered to be > 0.001 m/s (~0.09 km/h). Using the standard stream of 3 m wide and 15 cm deep, this equates to a flow rate in terms of volume of around 1.15 L/s (0.1 ML/d) and this low rate has been used as the positive flow cut-off in an attempt to reduce possible inconsistencies in measuring low flow conditions between the different monitoring stations.

All the long term monitoring flow data have been separated by season and the time (%) of positive flow determined for each season.

The probability of rainfall within the season of interest for each region has been obtained by taking the lower 10$^{th}$ percentile of rainfall probability for each season. This is a likelihood of 'any' rainfall, not rainfall that could generate run-off as that value will be highly variable depending on other factors such as soil type and slopes within different catchments.

A unique BFI has then been calculated for each monitoring station for each season as the difference between the time (%) in positive low and the probability of any rainfall. In many cases, particularly in drier seasons, the stream flow data showed positive flow periods to be less than the frequency of rainfall. This is not surprising as the rainfall

[4]FOCUS—FOrum for Co-ordination of pesticide fate models and their USe. Approved versions of FOCUS simulation models and FOCUS scenarios are available at: esdac.jrc.ec.europa.eu/projects/focus-dg-sante

likelihood was for any rainfall, not the amount resulting in run-off (which would be a lower likelihood). In these instances, the BFI was set at 0 meaning that any flow in these systems is assumed to be the result of quick-flow only. It demonstrates the conservatism of the approach. If the probability of rainfall resulting in run-off was considered, the probability is significantly reduced which would in turn lead to a higher BFI (less conservative for in-stream concentrations).

The stream flow data for South Australia were sparse. In this regard, there is essentially no surface water in South Australian dryland cropping regions west of the Spencer Gulf. Victorian dryland stream flows have been applied as a surrogate for South Australia at this stage.

Similarly, there appear to be stream flow data available within Tasmania, but the data are not easily obtained. Currently, Victorian dryland stream flows are used for in-stream analysis in Tasmania. Efforts are underway to compile an appropriate Tasmanian stream flow data base and PERAMA will be updated accordingly when possible.

## Stream flow rates—cumulative frequency curves

To model the in-stream concentrations, the in-stream equation in Probst (2005) has been applied as an extension to Equation 3 as follows:

**Equation 6: In stream calculation module**

$$\mathrm{Pc} = \mathrm{L\%run-off\ X\ Pa\ X}\left(\frac{1}{\mathrm{Qstream\ X\ \Delta T}}\right)$$

Where:

Pc = simulated mean pesticide in-stream concentration (µg/L)

L% run-off = % of application dose available in run-off water as dissolved substance (Equation 3)

Pa = amount of pesticides applied to the simulation area (µg)

Qstream = peak stream flow during rain events (L/s)

$\Delta$T = duration of heavy rain event (seconds)

The standard assumption is that the intensity over short periods is much more than the intensity determined over a 24 h period, and in this method, the 24 h rainfall event is assumed to all occur over a duration of one hour for purposes of mixing with in-stream flow rates to predict the in-stream concentration (that is, $\Delta$T = 3600 seconds). This is considered to be a conservative assumption but is thought to be applicable in predicting higher-risk ‘first flush’ events and is applied in PERAMA for the 25$^{th}$ percentile flow rates. A two hour rainfall intensity is applied for the 75$^{th}$ percentile flow rates.

For a given state or region being assessed, all stream flow rates from individual monitoring stations are considered to derive a cumulative frequency curve of in-stream concentrations for any given time period or stream flow percentile. In its totality, this is a complex and time consuming process.

## Example of total step 2 refinement process

A worked example is provided here to demonstrate the total methodology that is applied for PERAMA to predict a percentage of receiving waters in a given region at a given time where the in-stream concentration remains below an aquatic toxicity threshold. The examples are based on a fictitious residual herbicide with a soil half-life of 26 days, Kd = 0.40 L/kg and an aquatic regulatory acceptable level of 6 µg/L. The application rate is 1500 g ac/ha. A fallow with stubble retention/no till scenario is modelled for Tasmania for the 25$^{th}$ percentile stream flow value in autumn only:

1. Calculate Q/P from Equation 3—this is based on the composite run-off curve developed with the Tasmanian soil profile:

Q = (((-0.000099 * ([Rainfall] ^ 3)) + (0.0162 * ([Rainfall] ^ 2))) + (-0.137 * [Rainfall]))

The rainfall value was determined to be 11.8 mm/d, Q = 0.476; Q/P = 0.04,

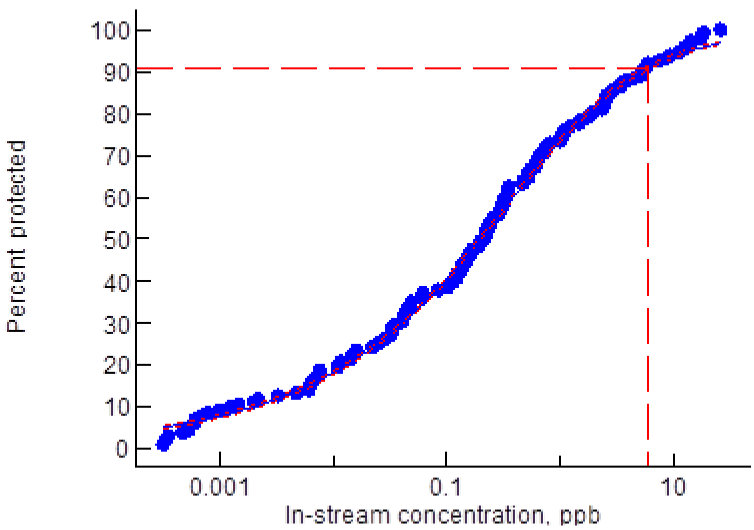
2. Calculate % run-off: Filling out Equation 3, % run-off = 0.015 in the dissolved phase.

3. Calculate in-stream concentrations based on real world stream flow data.

This step is performed for every monitoring station within a region being assessed. Victorian streamflow data are being applied as a surrogate data set for Tasmania in PERAMA at this stage and that data library contains stream flow data from 145 individual monitoring stations. For all stations, the 25$^{th}$ percentile stream flow rate is calculated. A cumulative frequency curve for in-stream concentrations is then constructed:

**Figure 7: Tasmania, percent protected, autumn application, fallow, stubble retention**

Percent protected is predicted to be 91 per cent of receiving waters.

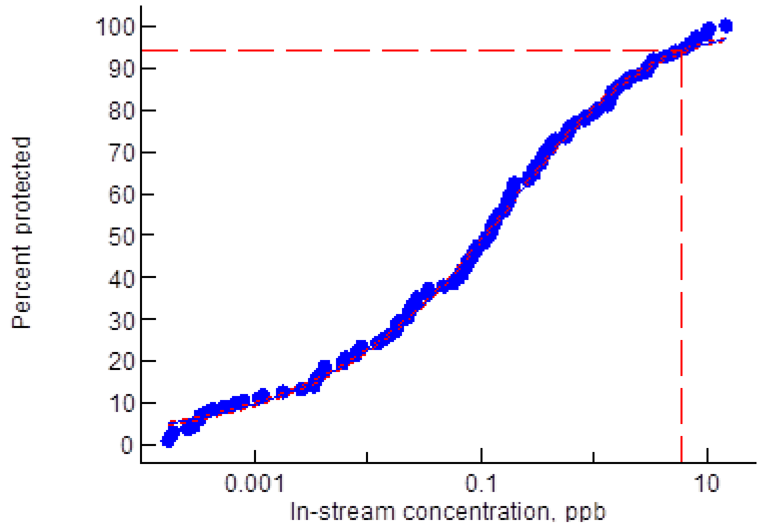


With the software, the same exercise can rapidly be performed to see the change in protection level if the pre-emergence application is made to formed fields rather than those still in fallow—the following distribution is based on the composite curve number for grains, straight row:

**Figure 8: Tasmania, percent protected, autumn application, grains, straight row**

Run-off is predicted to decrease to 0.008 per cent in the dissolved phase with the same rainfall amount.

Percent protected is predicted to be 94 per cent of receiving waters.




This short example has required calculations of 145 in-stream concentrations for two scenarios and the underlying non-linear regression modelling to determine percent of protection. Done long hand, this in itself is a time consuming exercise. To undertake a single scenario assessment for a state based assessment, a total of 871 in-stream concentrations are calculated for two stream flow percentiles across all states. Distributions are developed for six states, four seasons and two stream flow percentiles (48 distributions) for a single scenario.

When considering tropical and subtropical situations, distributions are developed for nine different regions, two stream flow percentiles and 12 time periods because the assessment is undertaken monthly. This totals 216 different distributions for a single scenario.

The time required for such refined assessments is a limiting factor, and the scope for human error is large given the high number of different curve numbers, slope values, rainfall values and stream flow values that need to be included. However, all the distribution algorithms have been developed and incorporated into PERAMA. It is now possible to undertake single scenario assessments rapidly and compare scenarios rapidly and consistently.

# APPENDIX 4: HOME GARDEN/URBAN USES OR PRODUCTS NOT SUPPORTED

Table 29: Home garden/urban uses or products not supported

| Product number | Product name | Concentration | Unit | Use | General comments |
|---|---|---|---|---|---|
| 33198 | Heiniger Banant Granules | 50 | g/kg | Ant granules | Around homes and gardens |
| 39222 | David Grays Antex Granules | 30 | g/kg | Ant granules | Home garden |
| 45227 | Surefire Antout Granular Insecticide | 50 | g/kg | Ant granules | Around homes and gardens |
| 45449 | Brunnings lawn Grub Destroyer | 10 | g/L | Lawn beetles spray uses only | Lawn |
| 47528 | Heiniger Lawn Beetle Blitz Insecticide | 50 | g/kg | Lawn beetle granules | Lawns and turf |
| 49315 | Richgro Garden Products lawn Beetle and Grub Killer | 10 | g/kg | Various pests | Garden beds, lawns, bowling greens, golf greens, tennis courts |
| 49666 | Barmac Chlorpyrifos G Granular Insecticide | 50 | g/kg | Various pests | Turf (golf greens, bowling greens, lawns); domestic, commercial, industrial, public areas; outdoor areas including gardens |
| 51769 | Garrards Ant Killer 50 | 50 | g/kg | Ant granules | Outside of houses, gardens, commercial and industrial buildings |
| 52167 | Munns Lawn Grubs, Lawn Beetle Grubs & Slater Killer With Long Life Organically Advanced Weta-Lawn | 10 | g/kg | Various pests | Lawns, bowling greens, garden beds, golf greens and tennis courts |
| 52564 | David Grays Antex 50 Granular Professional Insecticide | 50 | g/kg | Ant granules | Exterior of domestic buildings and gardens |
| 55444 | Searles Ant Kill 50 Granules | 50 | g/kg | Ant granules | Exterior of domestic buildings and gardens |
| 55961 | Searles Lawn Grub Killer Granules | 50 | g/kg | Lawn beetle granules | Lawns |
| 56209 | Superway Grub, Ant And Pest Controller | 50 | g/L | African black beetle spray uses only | Lawns |

| Product number | Product name | Concentration | Unit | Use | General comments |
|---|---|---|---|---|---|
| 56495 | Richgro Home Garden Ant Killer | 10 | g/kg | Ants granules | Fences, garden beds garden paths, rockeries, garden beds, lawns |
| 56616 | Amgrow Patrol Lawn Grub & Beetle Killer Granules | 50 | g/kg | Lawn beetle granules | Lawns and garden beds |
| 57758 | David Grays Lawn Beetle & Grub Killer Insecticide | 50 | g/L | African black beetle spray uses only | Lawns |
| 58188 | Surefire Lawn Grub.Ant and Outdoor Pest PCT Insecticide | 50 | g/L | African black beetle spray uses only | Lawns |
| 58286 | Richgro Ant Killer | 30 | g/kg | Ant granules | Fences, garden beds, paths, lawns |
| 58287 | Richgro Slater Killer | 40 | g/kg | Slaters, millipedes, ants, earwigs granules | Garden beds, pots, rockeries, gardens |
| 58294 | Richgro Lawn Beetle Killer | 40 | g/kg | Lawn beetle granules | Lawns |
| 58479 | Grass Gard Lawn Beetle & Grub Spray | 50 | g/L | African black beetle spray uses only | Lawns |
| 61354 | Searles Lawn Grub Killer Hose On | 10 | g/L | Lawn beetles spray uses only | Lawns and garden beds |
| 61533 | Amgrow Sir Walter Buffalo Lawn Pest Control | 50 | g/kg | Lawn beetle granules | Lawns and garden beds |
| 64936 | Amgrow Patrol Fix Ant | 50 | g/kg | Ant granules | Fences, garden beds, paths, rockeries, lawns |
| 67249 | Searles Lawn Grub Killer | 50 | g/L | African black beetle spray uses only | Lawns |
| 83025 | Delfos 5G Insecticide | 50 | g/kg | Ant granules | Fences, garden beds, paths, rockeries, lawns |

# ABBREVIATIONS

| | |
|---|---|
| ACR | Acute to chronic ratio |
| AERP | Adverse Experience Reporting Program |
| ac | Active constituent |
| ANZECC | Australian and New Zealand Environment and Conservation Council |
| AgDISP model | Agricultural Dispersal model |
| APVMA | Australian Pesticides and Veterinary Medicines Authority |
| CAS | Chemical Abstracts Service |
| $Cr_{Soil\ surface}$ | Concentration on soil following degradation and partitioning |
| EPHC | Environment Protection and Heritage Council |
| EC | European Commission |
| EU | European Union |
| $F_{int}$ | Amount of foliar intercepted pesticide |
| $f_{OC}$ | Mass fraction of soil organic carbon content |
| $F_{ret}$ | Amount of foliar retained pesticide |
| ha | hectare |
| $K_d$ | Partition (or distribution) coefficient |
| $K_{OC}$ | Soil adsorption coefficients |
| $K_{ow}$ | Octanol/Water partition coefficient |
| LC | Lethal concentration |
| LD | Lethal dose |
| LOC | Levels of concern |
| LOEL | Lowest observed effect level |
| MMCA | Michigan Mosquito Control Association |
| MRID | Master Record Identification Number |
| NOEC | No Observed Effect Concentration |
| OECD | Organisation for Economic Co-operation and Development |

| | |
|---|---|
| PCA | Principal Component Analysis |
| PEC | Probable Effects Concentration |
| $pK_a$ | Acid Dissociation Constant |
| PMRA | Pest Management Regulatory Agency of Health Canada |
| PNEC | Predicted No Effect Concentration |
| ppb | Parts per billion |
| ppm | Parts per million |
| PRC | Principal Response Curves |
| QS | Quality Standard |
| RQ | Risk Quotient |
| SCI-GROW | Screening Concentration in Ground Water |
| SoE | State of the Environment |
| SSD | Species Sensitivity Distribution |
| STP | Sewage Treatment Plant |
| TCP | 3,5,6-Trichloro-2-Pyridinol |
| TGD | Technical Guidance Document |
| TMP | 3,5,6-Trichloro-2-Methoxy Pyridine |
| TWAC | Time Weighted Average Concentration |
| ULV | Ultra-Low Volume |
| US | United States |
| US EPA | US Environmental Protection Agency |

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