ECOLOGICAL RISK ASSESSMENT IN A TASMANIAN AGRICULTURAL CATCHMENT

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DECLARATION

I declare that this thesis contains no material which has been accepted for a degree or diploma by the University of Tasmania or any other institution, and to the best of my knowledge and belief contains no copy or paraphrase of material previously published or written by another person except where due acknowledgement is made in the text of the thesis.

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ABSTRACT

In the Huon Valley, southern Tasmania, Australia, large volumes of pesticides are applied to the region's apple orchards. The broad objective of this study was to determine whether regional aquatic ecosystems are being adversely impacted by the use of orchard pesticides. The subcatchment of Mountain River was chosen as the study area, and a regional risk assessment was completed to gain an understanding of the environmental issues in the region.

A Tier 1 risk assessment identified the insecticide, chlorpyrifos, as being of particular concern to aquatic ecosystems. The risk hypothesis for research on chlorpyrifos was that spray drift from chlorpyrifos applications in orchard located on river flats was resulting in aquatic ecosystems being exposed to potentially harmful concentrations of pesticide.

Chlorpyrifos exposures in Mountain River were characterised using data from seasonal sampling and sampling at the time of spray application. Seasonal results showed intermittent, low-level detections of chlorpyrifos in Mountain River. Sampling at the time of spraying provided unique field data describing the magnitude and duration of pulse exposures at a site directly exposed to spray drift. The concentrations measured compared well with the spray drift model, AgDRIFT™.

Chlorpyrifos effects in Mountain River were characterised using multiple lines of evidence. Probabilistic risk assessments using cumulative frequency distributions of exposure and effects data, and @Risk® software simulations of probability distributions functions fitted with BestFit® software showed that aquatic species were not adversely impacted by the exposures measured.

Field studies validated the outcomes of the probabilistic risk assessment for fish species. *In situ* investigations on the blood chemistry and acetylcholinesterase activity of rainbow trout (*Oncorhynchus mykiss*) were used to assess acute effects. A maximum aquatic concentration of 0.163µg/L was measured soon after the commencement of spraying, but no significant changes in blood chemistry parameters or cholinesterase activity were detected. Body burdens and histology of native fish caught from localities surrounded by orchards confirmed exposure to pesticides but it was difficult to assess the severity of chronic effects, given the multiple stressors to which fish in agricultural areas are exposed.

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THESIS FORMAT

The thesis is composed of ten chapters divided into four sections:

- Project Background
- Preliminary Investigations and Research Background
- Project Work
- Thesis Synthesis

At the start of each chapter, there is a chapter background, which details the aims and objectives of the work described in the chapter, and summarises the chapter content.

Six research papers have been written in the course of this project. These papers have been included as thesis chapters with submission details given in the chapter background. To avoid repetition of some background material, some papers have been edited and the thesis chapter is not the submitted paper in its entirety.

PROJECT BACKGROUND

CHAPTER 1. INTRODUCTION

Chapter Background: This chapter describes the background and broad objectives of the project, and introduces the history and principles of ecological risk assessment.

BROAD OBJECTIVES OF THE PROJECT

The Huon Valley is an intensive horticultural region in southern Tasmania, Australia, and has been recognised as a significant orcharding district for over 130 years. Currently the State produces approximately 20% of the total Australian apple crop (Australian Horticultural Corporation, 2000) and 60% of Australian apple exports (Tasmanian Apple and Pear Growers Association, 1998). Pesticides are an essential management option in modern apple orchards, but pollution of soil, waterways and groundwater has been an issue of concern in the Huon Valley.

Compared to the United States, Canada and Europe, there has been very limited monitoring of the distribution or impact of pesticides in the Australian environment. The majority of pesticides research in Australia has been focused on the environmental fate and effects of endosulfan used in the cotton industry (LWRRDC, 1998). There is a scarcity of field measurements available for other pesticides and other industries. An important component of this project was to collect pesticides field data from an intensive orcharding region.

The project attempted to extend the understanding of how pesticides behave in the environment by placing particular emphasis on the aquatic and aerial dissipation of a pesticide pulse exposure. The focus of the study was on the insecticide chlorpyrifos, a chemical with a variety of agricultural, domestic and industrial applications. Field measurements of a chlorpyrifos pulse exposure from a typical orchard application have not been previously undertaken. Characterisation of *in situ* pulse exposures is generally an area that has received limited attention, due to the logistical difficulties involved.

The overall objective of collecting field data on chlorpyrifos was to assess the environmental impact of an important apple pesticide used in the Huon Valley. Assessment of environmental impact was not possible without a structured environmental decision-making framework. Ecological risk assessment was chosen as a decision-making framework for the purposes of understanding the extent and severity of chlorpyrifos impact on the Huon Valley aquatic environment.

DEFINITION OF RISK ASSESSMENT

Risk assessment is used to evaluate and manage the potential of unwanted circumstances in a large array of areas, from finance to human health. In environmental applications risk assessment is the process of assigning magnitudes and probabilities to the adverse effects of human activities or natural catastrophes (Suter, 1993a). Risk assessments in health and environmental fields are conducted to estimate how much damage or injury can be expected from exposures to a given risk agent, and to assist in judging whether these consequences warrant increased management or regulation (American Chemical Society, 1998).

THE ORIGINS OF RISK ASSESSMENT

Aversion to risk and the quest for certainty are overriding themes of human history (Rowe, 1999). The ancients of all cultures consulted oracles, priests, mentors and prophets in an effort to know what would happen in the future. However, despite humanity's preoccupation with seeking certainty in the face of the unknown, it was only relatively recently that the potential of science and mathematics for describing the future was realised. In the West, it was not until the adoption of the Hindu-Arabic numbering systems about 800 years ago that there was a conceptual basis for development of the laws of probability. Mathematicians who have played pivotal roles in the development of modern probability and risk theory include Blaise Pascal, Pierre de Fermat, Jacob and Daniel Bernoulli, Abraham de Moivre, Thomas Bayes, Francis Galton and Harry Markowitz. The history of risk and the societal implications of its development are well described by Berstein (1996).

The formal process of risk assessment gained acceptance in banking, insurance, and business long before it spread to other disciplines. Applications in human health and safety emerged in the early decades of this century. By the 1930s, a substantial body of scientific evidence had been collected regarding the quantitative relationships between occupational exposures to hazardous substances and their effects on human health. In subsequent decades, scientific research aimed at identifying appropriate safety margins for human exposures has become well-established (American Chemical Society, 1998).

ECOLOGICAL RISK ASSESSMENT

The practice of ecological risk assessment evolved from developments in the area of human health risk assessment. Modern, quantitative methods of ecological risk assessment emerged in the mid-1970s (American Chemical Society, 1998). Since then ecological risk assessments have been completed for a variety of environmental issues e.g. effects of hypothetical oil spills on seabird populations (Samuels and Ladino, 1983); atrazine in North American surface waters (Soloman *et al.*, 1996) and tributyltin exposures in US surface waters (Cardwell *et al.*, 1999).

The development of ecological risk assessment as a environmental management and regulatory tool has been largely driven by the United States Environmental Protection Agency (US EPA) which has released key documents outlining the principles and practice of ecological risks assessment (US EPA, 1992a; US EPA 1996; US EPA 1998). In the *Proposed Guidelines For Ecological Risk Assessment* (US EPA, 1996), ecological risk assessment was formally defined as 'a process for organising and analysing data, information, assumptions, and uncertainties to evaluate the likelihood of adverse ecological effects' (US EPA, 1996).

THE CONCEPT OF UNCERTAINTY IN ENVIRONMENTAL ASSESSMENT

The US EPA definition of ecological risk assessment highlights one of the fundamental premises of ecological risk assessment, that of uncertainty. Ecological risk assessment differs from other schools of environmental assessment in that it incorporates the concept of uncertainty into environmental management.

In making scientific predictions, there are always uncertainties. Uncertainty stems from ignorance (lack of knowledge or incomplete understanding), fallibility (e.g. inaccuracy in measurements) and the stochastic (random) properties of living ecosystems (Suter, 1993a). It is because scientists recognise the uncertainty of predicting responses in the field that the concept of ecological risk has supplanted environmental impact as the dominant assessment paradigm (Suter, 1998).

Despite an incomplete understanding of ecological systems, society must make regulatory and management decisions based on imperfect scientific information (Suter, 1993a; Ruckelhaus, 1983; Moghissi, 1984). The objective of risk-based environmental regulation is to balance the degree of risk to be permitted against the cost of risk reduction and against competing risks. It is impossibly expensive to eliminate all the environmental effects of human activities (Suter, 1993a) so society must be prepared to adopt a risk-based approach to environmental management.

ADVANTAGES OF ECOLOGICAL RISK ASSESSMENT

Recognition of uncertainty in prediction of ecological responses is one of the fundamental premises of ecological risk assessment. In ecological risk assessments, a conscious decision is made to estimate uncertainty rather than adopt conservative assumptions. The continued use of conservative assumptions in environmental decision-making frameworks is invalid for a number of reasons (Paustenbach, 1990). Firstly, it is always possible to conceive of a worse and more improbable case so "worst case" assumptions are inconsistent. Conservative assumptions tend to hide uncertainty and error from the decision-maker by burying it in the estimates of exposure and effects. Finally, conservatism assumes that there are no societal or environmental costs of regulating false positives. Regulation or remediation often results in inter-media transfers of treated pollutants or replacement of one product with another whose properties are not well studied (Suter, 1993a). For these reasons, conservative assumptions are generally not used in ecological risk assessments. The major exception is the use of conservative assumptions in the screening of hazards to quickly eliminate chemicals and routes of exposure that are clearly trivial from further assessment (Suter, 1993a).

Further advantages of ecological risk assessment over other environmental decision-making paradigms include prioritisation of risks and research aimed at understanding/mitigating these risks, and generation of quantitative outcomes which can be objectively compared with outcomes from other assessments (Suter, 1993a). Risk assessments aim to separate the scientific process of estimating the magnitude and probability of effects (risk analysis) from the process of choosing among alternatives and determining acceptability of risks (risk management). The result of this separation is reduced likelihood of analyses that are biased to fit desired decisions and greater credibility for both the scientists and the policy makers (Suter, 1993a).

STRUCTURE OF ECOLOGICAL RISK ASSESSMENT

The structure outlined in the *Framework for Ecological Risk Assessment* published by the US EPA (1992a) is widely recognised as the basis for most risk assessment. Ecological risk assessments involve three main components: problem formulation, analysis and risk characterisation (Figure 1.1).

Within problem formulation, important areas include identifying goals and assessment endpoints, preparing the conceptual model, and developing an analysis plan. Potential assessment endpoints for ecological risk assessments are: abiotic (air and water quality standards); population (extinction, abundance, yield/production, frequent gross morbidity, contamination, massive mortality); community/ecosystem (market/sport value, recreational quality, change to less useful/desired type) (Suter, 1990).

Some of these endpoints have both biological and societal impact, for example, the extreme scenario of species extinction. Prevention from extinction of rare and endangered animals is a goal clearly understood by the public. However, a target of maintaining community structure in the presence of a particular environmental stressor is less easily understood. Choosing air and water quality standards as assessment endpoints means that goals are clearly defined by regulatory boundaries, but may be of unknown biological significance (Suter, 1990).

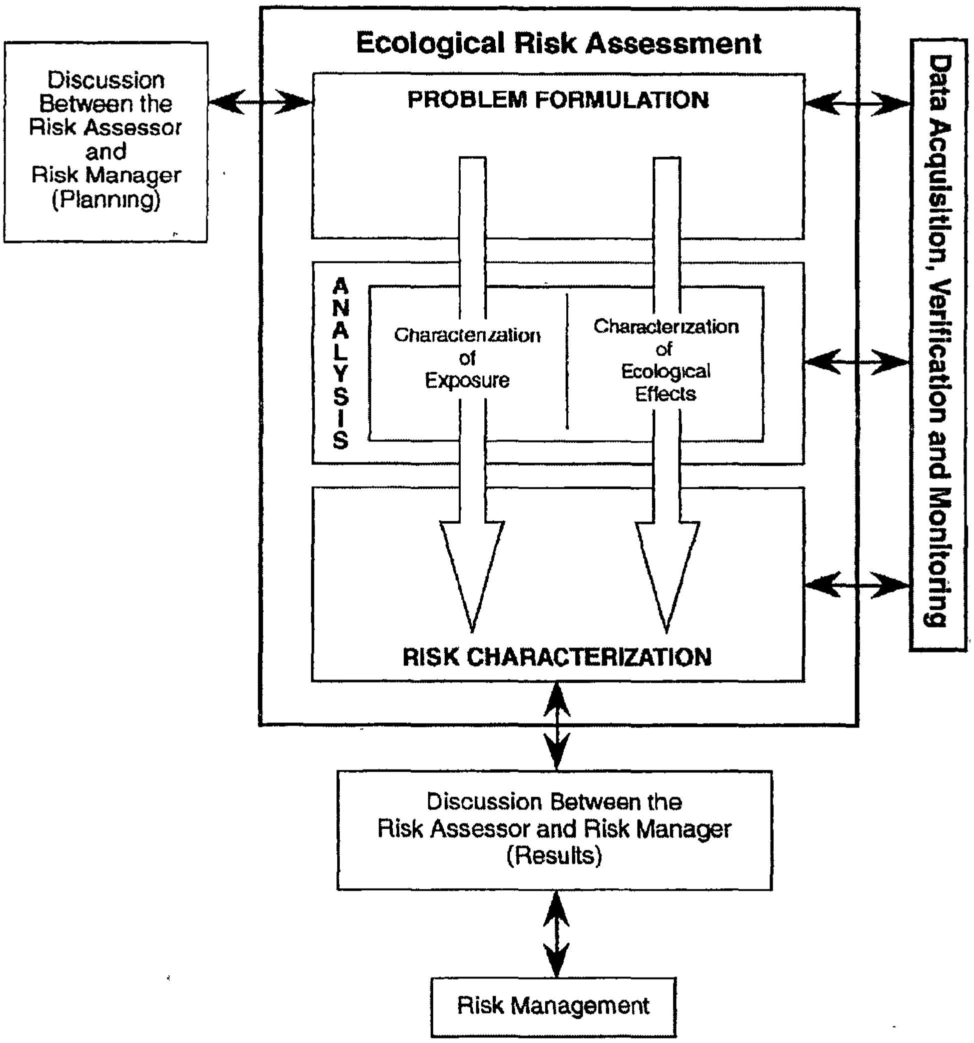


Figure 1.1 Framework for ecological risk assessment used in most formal risk assessments. From US EPA, 1992a.

The risk analysis phase involves evaluating exposure to stressors and the relationship between stressor levels and ecological effects. Chemical stressors are most often studied, but biological and physical stressors may also be considered (Renner, 1996). Both laboratory and field studies (including field experiments and observational studies) can provide useful data for evaluating exposure to environmental stressors and the relationship between stressor levels and ecological effects (US EPA, 1996).

Risk characterisation is the final stage of the process where all risk analyses are considered to determine whether exposure is sufficient to cause adverse effects on the environment, and if so, the nature, extent and severity of the effects. Key elements of estimating risk are through integration of exposure and stressor-response profiles, describing risk by discussing lines of evidence and determining ecological adversity, and preparing a report. The uncertainties associated with the risk assessment are also considered (US EPA, 1992a; US EPA, 1996; US EPA 1998). For most assessments, multiple, independent lines of evidence are better than any single approach (Suter, 1993).

The scientific process of risk assessment concludes with risk characterisation. The outcomes of the scientific assessment are then considered along with economic, technological and legal, political and social considerations to arrive at a decision and decide upon a course of action (US EPA, 1996; Suter, 1990). For risk managers to effectively utilise the outcomes of a scientific risk assessment it is essential that the character, strengths and limitations of the analytical methods are understood (US EPA, 1996). Considerations in risk management – issues of risk acceptability, economic and social consequences of achieving specific environmental objectives, and how to balance trade-offs among competing interests – are beyond the technical/scientific debate (NRC, 1983) and have not been considered in this project.

The final concept in risk assessment is risk communication, which is vital for conveying the outcomes of a scientific risk assessment and risk management process to non-technical stakeholders and communities. Public risk perceptions can be extremely influential in shaping the public's reaction to a hazard – even to the point of overpowering scientific findings about the magnitude of the risk. For example, pesticide residues in food and the operation of nuclear power plants continue to be very prominent public concerns – both of which scientific risk calculations indicate to be relatively small hazards. Although scientific findings consider high-fat diets or exposure to radon to be more serious public health concerns, they draw far less public attention (American Chemical Society, 1998). Risk communication is emerging as a specialist area and is beyond the scope of this project. Concepts in risk communication are well described by Lundgren and McMakin (1998).

In risk assessments for chemicals, a tiered approach is generally adopted (Figure 1.2). A tiered approach provides increasing refinement of the exposure and risk estimates in a logical, step-wise process (Oliver *et al.,* 2000). The advantages of a tiered approach include cost effectiveness, reliability, flexibility and minimised completion times (Parkhurst *et al.,* 1994). In Tier 1 conservative assumptions are adopted and resources can be prioritised to focus on the chemicals that pose the greatest risks. In higher tiers research efforts can be directed at collection of site-specific and species-specific data, depending on the objectives of the risk assessment.

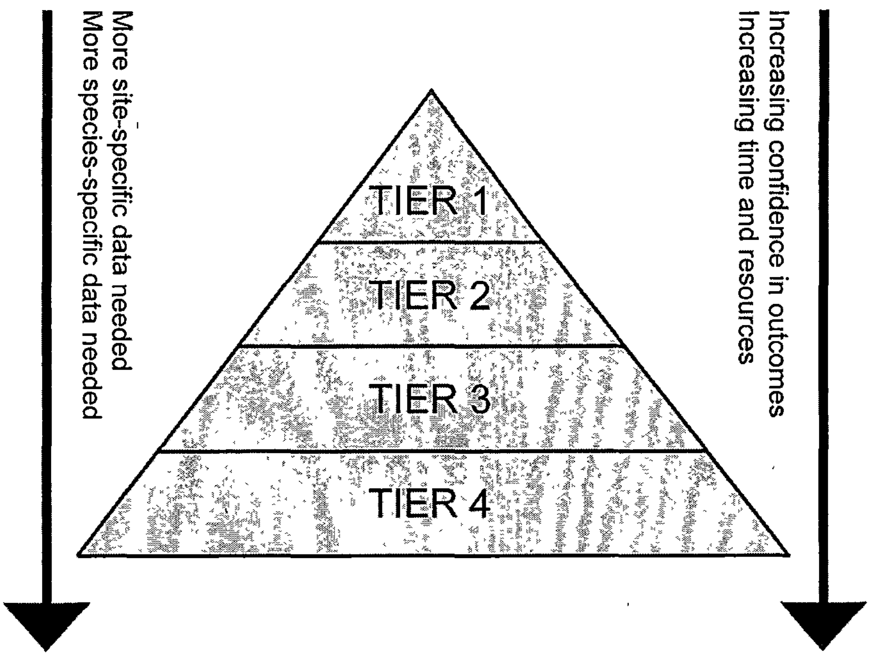


Figure 1.2 Tiered approach to pesticides ecological risk assessment. This approach is adopted so that resources are prioritised to research pesticides with the greatest potential for adverse ecological impacts.

Risk assessments may be prospective or retrospective. Prospective ecological risk assessments are largely employed by regulatory agencies and many of the developments in ecological risk assessment methodology have been in the area of prospective assessments. However, there has been a shift in emphasis to assessments of the effects of pollution that began in the past and may have ongoing consequences such as waste sites, acid rain and existing pesticides (Suter, 1993a). Retrospective ecological risk assessments evaluate the likelihood that observed ecological effects are associated with previous or current exposures to stressors. Many of the same methods and approaches are used for both prospective and retrospective assessments.

PESTICIDES RISK ASSESSMENT

Ecological risk assessment has been widely adopted for pesticides risk assessment. Pesticides risk assessment recognises that although modern pesticides provide many benefits in agricultural, domestic and industrial applications (e.g. Stapley 1969; Pedigo, 1996; Ware 2000), there is also a human health and environmental risk associated with their use (e.g. Carson 1963; Perring and Mellanby, 1977; Snelson, 1979; OCED, 1986).

Prospective assessments are used for pesticides that are undergoing registration. Measures of exposure and effects tend to be based on models, and limited laboratory testing. Retrospective assessments are used for pesticides that have been previously registered and are under review, or for pesticides which have been recognised to have potential for adverse effects in a particular region, industry or application. Measures of exposures and effects come from field monitoring programs as well as modeling, and there is generally more toxicological data available.

Specific technical guidance for analysis and risk characterisation in pesticides ecological risk assessments has been issued by the Aquatic Risk Assessment and Mitigation Dialogue Group (1994). Their approach involves refining both environmental exposures and effect endpoints, and progressing in a tiered manner from simple screening methods to geographically specific, probabilistic techniques at the highest tier level.

The United States leads developments in the field of pesticides risk assessment. The US EPA Office of Pesticides Programs (OPP) has been a driving force in the completion of human health, occupational exposure and ecological risk assessments for many pesticides registered in the United States. Under the Federal Government Food Quality Protection Act (1996) the OPP is charged 'to protect public health and the environment from the risks posed by pesticides and to promote safer means of pest control' (OPP, 2000). The recommendations from several OPP risk assessments have had significant implications for agriculture and agri-business.

Ecological risk assessment of pesticides is also used in Europe, and is gradually gaining worldwide acceptance. The Australian environmental regulatory authority, Environment Australia, has adopted ecological risk assessment as a process for assessing risks from new and existing chemicals released into the environment, but at this stage only simplistic lower tier assessments are conducted (Holland, 1999).

Currently there is tremendous scope to refine the use of ecological risk assessment methods used Australia. Formal ecological risk assessments conducted to date in Australia have been limited and include assessments for deltamethrin (Thomas *et al.*, 1999), tebuthiuron (van Dam *et al.*, 1999), chemicals in Sydney stormwaters (Bickford *et al.*, 1999) and for the management of contaminated sites (Ng *et al.*, 1998; Ooi *et al.*, 1999; Cox *et al.*, 1999).

ECOLOGICAL RISK ASSESSMENT IN THIS PROJECT

In view of the limited research in the field of ecological risk assessment in Australia, the work presented in this thesis attempts to extend the understanding of ecological risk assessment in Australia by applying a variety of ecological risk assessment strategies to an issue where the outcomes were important to apple growers, local community and the agricultural chemical industry.

Different ecological risk assessment approaches were used to progress from a preliminary regional risk assessment where assessment endpoints were developed using stakeholder values, to a Tier 4 geographically specific risk assessment for the insecticide chlorpyrifos. In this way, the project was a case study of different ecological risk assessment methods, based on their applicability to current understanding of pesticides in the Australian environment. The merits of the different ecological risk assessment methods used are considered in the Discussion chapter.

CHAPTER 2. THE MOUNTAIN RIVER CATCHMENT: REGIONAL DESCRIPTION

Chapter Background: This chapter briefly describes the physical, climatic, social, economic and environmental characteristics of Mountain River catchment relevant to this project.

PROJECT LOCATION

Fieldwork for this project was conducted in the Mountain River catchment southern Tasmania, Australia (Figure 2.1). Mountain River rises in the Wellington Range and flows south, out of the foothills of Trestle Mountain. It is a small river, a tributary of the Huon River, which is one of the largest rivers in southern Tasmania. The catchment has been mapped in the Tasmap 1:25,000 map series Longley 5024 and Huonville 5023. Grove, one of the principal settlements in the catchment, is located at latitude 42 °59′, longitude 147°06′ (Figure 2.2).

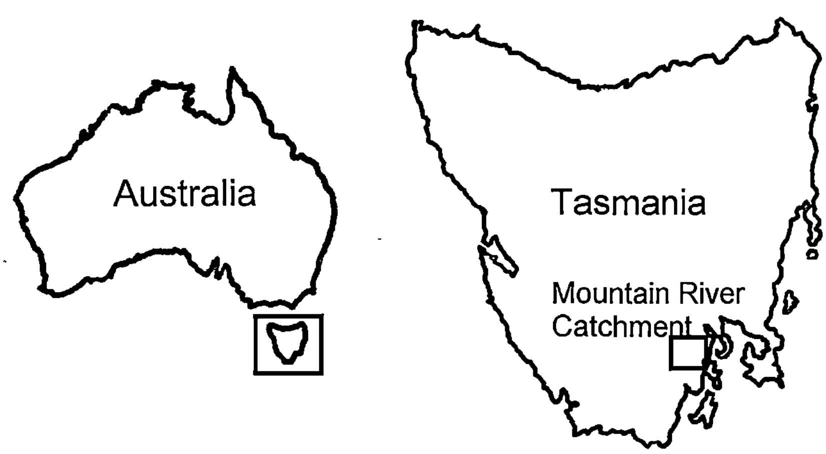


Figure 2.1 Location of Mountain River catchment, southern Tasmania, Australia.

Mountain River catchment is located within the region known generally as the Huon Valley. The catchment area of the Huon River covers an area of approximately 3,900 square kilometres in southern Tasmania (Figure 2.2). The catchment incorporates four areas of general use. The top end of the catchment is part of the Gordon power scheme comprising a dam on the Huon River at Scott's Peak. The western section of the catchment is part of the World Heritage Area (Southwest National Park, Hartz Mountains National Park, and South West Conservation Area). The central section is land dedicated as State Forest and managed by Forestry Tasmania, while the Eastern section is private land, principally in agricultural production (HHRP, 1997).

Within the catchment there are 20 subcatchments: World Heritage/State Forest area (above Arve River), Little Denison River, Russell River, Judds Creek, Mountain River, Kellaways Creek, Agnes Rivulet, Nicholls Rivulet, Garden Island Creek, Clarkes Rivulet, Prices Creek, Fleurtys Creek, Castle Forbes Rivulet, Kermandie River, Esperance River, Lune River, D'Entrecasteaux River, Catamaran River, Huon River, Huon Estuary.

Orcharding occurs within several of these subcatchments. In choosing where to undertake fieldwork, all of the regional 1:25,000 maps were studied. Several days were spent driving around the Valley investigating ease of access to sampling sites in different catchments. Mountain River was chosen for the following reasons:

- Greater intensity of orcharding activity in the Mountain River catchment compared with other catchments
- Easy public access to sampling sites along the length of the river. Access to waterways in other areas was through private land, and bringing field equipment down to the river may have been problematic.
- Several previous studies have been conducted on Mountain River so that there was a knowledge base about the river on which to draw.

Within the Mountain River catchment, Grove, Ranelagh, Lucaston, Crabtree and Mountain River Township are the most populated areas. Huonville is the nearest country town.

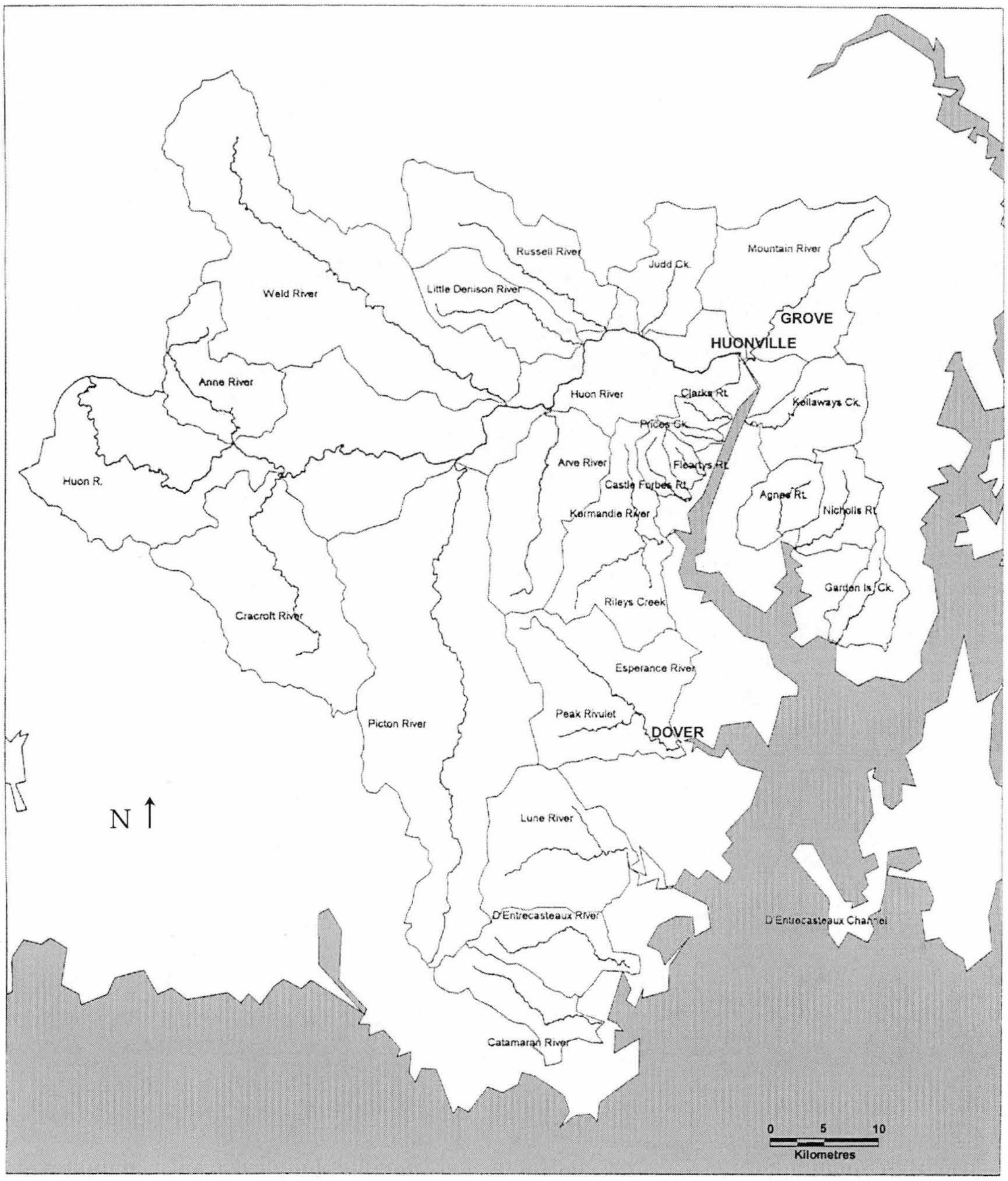


Figure 2.2 The catchment of the Huon River, southern Tasmania, Australia. Mountain River is located to the north of Hounville, the largest town in the region. Major tributaries of the Huon are the Weld, Russell, Mountain, Cracroft, Picton and Kermandie Rivers. The Huon River becomes estuarine a little way above the principal settlement of Huonville, and drains to the D'Entrecasteaux Channel.

PHYSICAL AND CLIMATIC CHARACTERISTICS OF MOUNTAIN RIVER CATCHMENT

The catchment area of Mountain River is 186 square kilometres (Davies, 1988). Mountain River originates in alpine heath between Collins Bonnet and Thark Ridge in the Wellington Range and flows for 25km (Robson, 1995) before joining the Huon River at Huonville.

Hydrology

Mountain River is a perennial fourth order tributary of the Houn River (Robson, 1995). Stream flow has been monitored in the past, but is currently not being monitored. A bankfull discharge event occurs approximately once every fifteen years (Robson, 1995).

Water quality in the river is generally good. Occasional low dissolved oxygen levels and elevated faecal coliform counts have have been recorded during periods of low flow. Water quality parameters were measured as part of seasonal sampling during the 1997 summer (Appendix 1). This water quality data was collected from five sites along Mountain River (locations described in Chapter 6) and these results were generally indicative of good water quality along the course of Mountain River.

Climate

The annual mean maximum temperature measured at Grove is 16.8°C and the mean minimum is 5.7 °C. The average annual rainfall is 764.7mm. (Bureau of Meteorology, 2000). Winter is the season of maximum rainfall with January, February and March being the driest months.

Geology

The floor of the Huon Valley and the lower section of the surrounding hills consist of a bedrock of Permo-carboniferous mudstones and Triassic sandstones, from which the bulk of the cultivated soils are derived. Intrusions of diasbase and, immediately adjacent to the Mountain River, of basalt are found outcropping, generally in small areas.

Basic igenous rock composes most of the geology (55%) followed by 19% fine-grained sedimentary rock, 13% medium-grained sedimentary rock and 13% being complexes of other rock types (Davies, 1988).

Soils

Along Mountain River, alluvial soils occur with Huon sand, and Huon loam and Huon silty loam occurring beyond the river flats. Some of the most productive apple growing soils in the Huon Valley occur within the Mountain River catchment (Taylor and Stephens, 1935).

The alluvial topsoil is usually a sandy loam and occasionally a loam. The depth of topsoil varies between 70-120cm. Subsoils include deep sand, loam over sand and a deep sandy loam. The depth of subsoil varies between 4.8m and 7.2m and the subsoils overlie river gravel of variable texture. Due to the high sand fraction (>70%), the alluvial soils tend to be well drained and suited to irrigation. The typical pH for the alluvial soils ranges from 6.2 to 6.8 (Stephens, 1935).

The Huon series of soils have high clay content in the subsoils and this can restrict drainage in some areas. Lucaston and Grove sands are also found in the Mountain River catchment. They tend to be less productive apple growing soils with an impermeable hardpan that restricts drainage and root growth (Stephens, 1935).

Vegetation

The priority vegetation associations identified in Mountain River are *Eucalyptus ovata* (on any substrate), *E. tenuiramis* (on sedimentary substrate), *E. amygdalina* on sandstone and grassy *E. globulus* communities (TasVeg 2000 map series). Mountain River occurs within the southern ranges bioregion in the Interim Biogeographic Regionalisation of Australia (IBRA). Within this bioregion, *E. ovata* communities on sandstone are recognised as a priority vegetation type. *E. ovata* on sandstone occurs in several small pockets in the forested regions of the catchment.

REGIONAL BACKGROUND

The Huon Valley is one of Tasmania's most intensive horticultural regions. The Huon Valley produces approximately 65% of the Tasmanian apple crop (Tasmanian Apple and Pear Growers Association, pers. comm. 1999) with a market value of around $40 million. Other intensive horticultural operations in the Valley include cherries, berry fruits and floriculture.

Other industries in the Huon Valley, which are also directly related yet impinging on the quality of the environment, include aquaculture, forestry and tourism. Aquaculture, which is entirely dependent on regional water quality, is a major industry currently with an annual value of $45 million (HHRP, 1997). In the upper reaches of various catchments, there are significant forestry actives with an annual value of $42 million. The annual value of tourism is currently $12 million and predicted to expand (HHRP, 1997). The Valley has many scenic areas and is a base for many outdoor pursuits such as hiking, climbing and water sports.

A regional risk assessment was conducted to put catchment issues in context and to gain a better understanding of social and environmental issues in the catchment. Land use patterns were mapped and environmental issues studied. This is described in the following chapter.

PRELIMINARY INVESTIGATIONS AND RESEARCH BACKGROUND

CHAPTER 3. ENVIRONMENTAL ISSUES IN MOUNTAIN RIVER CATCHMENT

Chapter Background: Regional ecological risk assessment is concerned with describing and estimating risks to environmental resources at the regional scale or risks resulting from regional-scale pollution and physical disturbance (Hunsaker *et al.*, 1989). Regional risk assessment represents an unconventional form of ecological risk assessment because of the need to spatially and temporally integrate toxic effects with other factors operating in the region (Suter, 1993a). Method development for regional risk assessments is in its infancy due to the complexities involved in integrating spatial and temporal components into the assessment. One framework that has been proposed for regional risk assessment is the Relative Risk Model (Landis and Wiegers, 1997).

This chapter describes a regional risk assessment using the Relative Risk Model, which was conducted to:

- Gain an overview of land use patterns within the Mountain River catchment study area.
- Gain an understanding of regional environmental issues, with an emphasis on orchard production systems.
- Gain an understanding of the processes involved in conducting a regional risk assessment, and assess the utility of the Relative Risk Model as a regional risk assessment tool.

In this chapter, the process of utilising the Relative Risk Model as a regional risk assessment tool is described. A critique of the Relative Risk Model and its applicability to the Mountain River catchment is given in the Discussion chapter.

The Relative Risk Model assessment described in this chapter is to be published in the international journal *Human and Ecological Risk Assessment* with the following reference: Walker R Landis WG Brown PH. 2001. Developing a regional risk assessment: A case study of a Tasmanian agricultural catchment. *Human and Ecological Risk Assessment.* in press.

Abstract

A regional ecological risk assessment was conducted for the Mountain River catchment in Tasmania, Australia. The Relative Risk Model was used in conjunction with geographic information systems interpretations. Stakeholder values were used to develop assessment endpoints, and regional stressors and habitats were identified. The risk hypotheses expressed in the conceptual model were that agriculture and land clearing for rural residential are producing multiple stressors that have potential for contamination of local waterbodies, eutrophication, changes in hydrology, reduction in the habitat of native flora and fauna, reductions in populations of beneficial insects in agricultural production systems, increased weed competition in pastures, and loss of aesthetic value in residential areas. In the risk analysis, the catchment was divided into risk regions based on topography and land use. Stressors were ranked on likelihood of occurrence, while habitats were ranked on percentage land area. Risk characterization showed risks to the maintenance of productive primary industries were highest across all risk regions, followed by maintenance of a good residential environment and maintenance of fish populations. Sensitivity analysis was conducted to show the variability in risk outcomes stemming from uncertainty about stressors and habitats. Outcomes from this assessment provide a basis for planning regional environmental monitoring programs.

INTRODUCTION

There are various stressors impinging on the quality of the environment in any catchment region. Without a framework, it is difficult to objectively assess the risks associated with multiple stressors. The Relative Risk Model as developed by Landis and Wiegers (1997) is a framework for ranking and comparing the risks associated with multiple stressors. It is a useful tool for describing and comparing risks to valued resources within a catchment.

The Relative Risk Model was developed for a regional risk assessment for the Fjord of Port Valdez, Alaska (Wiegers *et al.,* 1998) and is currently being used for a large regional risk assessment of the Willamette and McKenzie Rivers, Oregon (Landis *et al.,* in press). This paper reports on the application of the Relative Risk Model in a more localized region in southern Tasmania, Australia. The aim of this work was to use the Relative Risk Model as a tool to put catchment issues in context, and highlight issues that needed to be further addressed.

Relative Risk Model methodology essentially mirrors the traditional three-phase risk assessment approach: problem formulation, analysis, and risk characterization, but requires a modification of the traditional approach. Expanding an assessment to cover a region requires consideration of larger scale, regional components: sources that release stressors, habitats where the receptor live, and impacts to the assessment endpoints.

In the problem formulation phase of the relative risk assessment, the scope of the assessment is defined; at this stage, the values of regional stakeholders are influential in determining assessment endpoints. Generic goals for regional risk assessment include: explanation of observed regional effects, evaluation of an action with regional implications, and evaluation of the state of a region (Suter, 1990). Regional stressors and habitats are identified in the problem formulation phase.

In the risk analysis phase the stressors and habitats are ranked based on their likelihood of occurrence within the risk region. The interaction between stressors and habitats is considered when total relative risk calculations are made for each stressor and habitat. In the risk characterization phase, the risks for stressors and habitats are compared. Stressors with greatest potential for ecological impact and habitats most at risk are both identified. This provides a basis for discussions about management of the region.

It is particularly apparent at the regional scale that not all components of the environment can be measured, tested, modeled, or otherwise assessed (Suter, 1993b).

In addition, there is a large degree of spatial and temporal variability. On a regional scale, there is a large degree of uncertainty in a preliminary risk assessment such as this. However, this should not stop the assessment from proceeding. Uncertainty should be recognized as an inherent component of each stage of the risk assessment and addressed at each stage, rather than at the conclusion of the risk analysis. A sensitivity analysis can be performed at the conclusion of the risk analysis to determine how uncertainty is influencing the overall risk rankings.

PROBLEM FORMULATION

The Risk Region

As noted by Suter (1993b), a catchment lends itself to being an easily defined risk region for aquatic borne contaminants. The catchment considered in this assessment is the Mountain River catchment in southern Tasmania, Australia. The Huon Valley is a major horticultural region. The main horticultural crops are apples, cherries, stone fruit, and berries. Other primary industry enterprises include beef cattle production, mushroom farming, herbs, honey, and cut flowers. The Huon Valley is a popular residential locality for urban commuters who have no financial dependence on the land but value the aesthetic and lifestyle benefits of living in a rural environment.

There is a significant level of public interest and concern in the Huon Valley about environmental issues generally, and waterways in particular. Catchment management in the Huon Valley was formally instigated with the establishment of the Huon Healthy Rivers Project initiated in 1995 with funding provided through federal and local governments. The Huon Healthy Rivers Project is an ongoing project that aims to promote environmental awareness and provide a resource base for community projects.

Information in this assessment was obtained from a number of sources, particularly publications produced by the Huon Healthy Rivers Project and personal communication with Huon Healthy Rivers project officers who facilitated various community forums. There has been no extensive or consistent environmental monitoring of freshwater bodies within the Valley, other than basic water quality data available through State agencies.

Defining Assessment Endpoints within the Mountain River Catchment

Assessment endpoints represent the social values to be protected, and serve as a point of reference for the risk assessment. The values to be protected in a region may be described in terms of characteristics of its component populations and ecosystems or in terms of characteristics of the region as a whole (Suter, 1993b).

The goals of the local community were used in this regional risk assessment as a starting point for developing assessment endpoints. A community forum, held in 1998 to identify water values for Mountain River as a starting point for setting environmental flows for the River, identified the following issues as important: improve water quality (particularly decreased *E.coli* counts), maintain/establish water of drinkable and irrigable quality, maintain habitats for aquatic animals, maintain water in suitable volumes to sustain agriculture, maintain catchment quality for town water supply, maintain water for swimming, maintain water for trout fishing, maintain and/or improve beauty of the river, and maintain seasonal nature of the river.

In a 1999 catchment community forum, locals created an image of their preferred catchment having the following characteristics: clean water which is safe for drinking and swimming; sustainable landuse practices; optimum stream flow; natural vegetation along the riverbanks; an active and responsible community; and an attractive settings for picnics. As noted by Steel *et al.*. (1994), analysis of survey data should consider relationships between survey responses and stakeholder backgrounds. Length and location of residence, occupation, education, and other factors can influence stakeholder values. This particular "community" forum was not well attended by local farmers, and the values stated may not necessarily represent priorities for primary producers. It is vital that assessment endpoints be determined with a conscientious and intelligent effort to represent the values of the entire community.

Beginning with the water body and expanding across the catchment, assessment endpoints were identified based on the views expressed by stakeholders, discussion with resource managers, and expert judgement. The assessment endpoints were identified as:

- **Water quality parameters to meet or better Australian and New Zealand Guidelines for Fresh Water Quality**
- **Maintenance of local fish populations***
- **Maintenance of adequate environmental stream flow** §
- **Maintenance or increase of native streambank vegetation, and reduction of weed density to less than 10% groundcover** Φ
- **Maintenance of productive primary industries**
- **Landscape aesthetics and maintenance of a good residential environment**

* Criteria are currently being established by the regulatory body, Tasmanian Inland Fisheries.

§ Criteria are currently being established by the regulatory body, Department of Primary Industries, Water and Environment.

Φ Weeds are defined as non-native species growing where they are not wanted.

Suter (1990) states that good assessment endpoints should have the following characteristics: social relevance, biological relevance (function of its implications for the next higher level of biological organization), unambiguous operational definition, accessible to prediction and measurement, and susceptible to the hazard. We compared the above assessment endpoints to Suter's criteria. 'Water quality parameters to meet or exceed Australian and New Zealand Guidelines for Fresh Water Quality (2001)' and 'Maintenance or increase of native streambank vegetation, and reduction of weed density to less than 10% groundcover' are currently the only assessment endpoints that meets all of Suter's criteria. At the time of writing the State fisheries agency was in the process of establishing quantitative goals for Tasmanian brown trout fisheries, which is the State's most popular inland fishery. Quantitative goals have currently only been set for the recovery plans of the rare and endangered native galaxias (Crook and Sanger, 1997), none of which occur in Mountain River. Also at the time of writing, the State environmental agency was in the process of establishing an environmental flow for Mountain River.

The assessment endpoint of maintenance of productive primary industries and landscape aesthetics are intuitively understood but not well defined. These endpoints do not meet Suter's criteria, but clearly an imperfect definition must not exclude them;

'maintenance of productive primary industries' is of utmost importance in a primarily agricultural catchment. For the purposes of this preliminary relative risk ranking, this assessment endpoint is not operationally defined; instead, general knowledge of good soil and water management practices is applied to it. Recent work by Landis and McLaughlin (2000) is providing a conceptual framework for quantifying sustainability, although it is unlikely that an unambiguous operational definition for quantifying sustainable agriculture will be achieved because of the huge diversity of inputs to agriculture. It is possible, however, to quantify the sustainability parameters of individual inputs to agriculture, for example, using water quality criteria and regional soil databases.

Similarly, landscape aesthetics is not operationally defined, but can be understood as meaning that Mountain River is a nice place to live. Other assessment endpoints directly impinge on this, particularly the quality of the natural environment as measured through water quality, water flow, weed infestation, aquatic life, and factors affecting agriculture such as soil stability and climate.

Identifying Stressors in the Region

The issues of environmental concern identified in the Huon Healthy Rivers project were categorized in terms of the stressor and corresponding ecosystem response variable (Table 3.1). With the exception of seasonal flooding, all the stressors identified were anthropogenic. The effects of seasonal floods can be enhanced or mitigated by regional land management practices.

Out of all the stressors identified for the Huon Catchment in Table 3.1, the only stressors considered relevant in the risk assessment for Mountain River catchment were agriculture and land clearance for rural residential development. No large-scale forestry activities occur within the catchment, although it is possible there may be some paddock-scale tree plantations on individual farms. No aquaculture occurs within the catchment. Mountain River is too small for boating, and recreational pursuits in the catchment are mainly hiking, horseriding, fishing, and swimming, which were considered to have negligible impact.

Agricultural stressors in the Mountain River catchment were identified as: pesticides used in orchards, fertilizers (pasture, orchards and other cropping activities), pumping irrigation water from the river, weed infestation, and clearing of native bush for farmland (Table 3.1). Another stressor that could be included under the umbrella heading of 'agriculture' is contaminated sites because of possible copper, lead, and arsenic residues in the soil from previous use of orchard pesticides containing these elements. It was decided to omit contaminated sites from this risk assessment because the focus is on risks associated with current agricultural practices. In addition, introducing contaminated sites into the risk assessment involves considerable uncertainty. Currently the actual extent of contamination, if any, is unknown. An intensive regional soil-testing program is required before contaminated sites should be considered as a stressor.

Stressors resulting from land clearing for rural residential were identified as: bacteria from septic tank effluent, clearing of native bush for residential purposes, nutrients from households, pumping water from the river for garden and household use, and weed infestation.

Identifying Habitats in the Region

Human exclusion from ecosystems has been symbolic of a long held belief that somewhere there exists a reference, pristine ecosystem. It is more realistic to recognize that humans are participants in most ecosystems; indeed agricultural ecosystems are created and maintained by humans. It was decided in this risk assessment to recognize anthropogenic habitats in the same way as natural habitats. This has recently been considered as a valid risk assessment approach because changes in ecological systems result in risks to cultural resources, economic activity, and quality of life because of the numerous and important services of nature (Suter, 1999a). Moreover, ecological risks can often be considered as risks to the sustainability of the activities being assessed (Suter, 1999b).

Table 3.1 Anthropogenic stressors and ecosystem response variables identified in the Huon Valley. Information from the Huon Healthy Rivers Project (HHRP) (1997) was used as a basis for this table.

ANTHROPOGENIC STRESSOR	**ECOSYSTEM RESPONSE VARIABLE**
LAND CLEARANCE AND RURAL SUBDIVISION	Species and habitat destruction Soil erosion and landslips Increase in frequency of erosive flood events Increase in environmental weeds – willows, blackberries, ragwort, gorse, pampass grass
INTENSIVE AGRICULTURE Fertilizers and animal waste	Agricultural runoff causing eutrophication of freshwater bodies Toxic algal blooms in the estuary affecting estuarine species
Pesticide contamination of soils and water through spray drift, spillage and runoff	Mortality, immunological and reproductive health of local species Contaminated Sites – it is possible that the lead, copper and arsenic sprays used earlier this century may have left residues in the soils in older orcharding areas.
Soil and water management	Soil erosion and landslips Soil compaction and reduction in biological diversity of the soil Irrigation water pumped from local waterways reducing stream flow and changing hydrology affected microhabitat of aquatic species
RURAL AND COASTAL AREA DEVELOPMENT	River and coast modification altering the habitat of local species Wetland degradation. Reduction of the "biological filtering" capacity of the estuary Septic Tank effluent– effluents from improperly maintained septic tanks have contaminated waterways and ground water in various locations.

ANTHROPOGENIC STRESSOR	ECOSYSTEM RESPONSE VARIABLE
RURAL AND COASTAL AREA DEVELOPMENT	Refuse disposal site leachate - current public sites are located at Huonville, Geeveston, Cygnet. Former sites were located at Glen Huon and Judbury. Older and former public and private sites are spread throughout the municipal area. Contaminants of unknown types and quantities discharged to waterways. Pumping drinking and household water from local waterways, reducing stream flow and changing hydrology affecting the microhabitat of aquatic species. Nutrient input from sewage. Sewage treatment plants are located at Ranelagh, Cygnet, Geeveston. Sewage lagoons at Huonville, Dover, Southport. Franklin sewage is currently discharged into the Huon River. Solid waste management -public landfill facilities at Geeveston and Cygnet. Waste transfer stations at Cygnet, Southport, Dover and Huonville. A private contractor provides recycling facilities at each site. Untreated stormwater containing unknown types and quantities of contaminants
FORESTRY	Soil erosion and landslips Nutrient runoff Road building causing siltation of waterways Environmental weeds
AQUACULTURE	Nutrients from fish waste, uneaten food and disposal of net wash effluent causing nutrient enrichment of the estuary and increasing probability of toxic algal blooms Escaping fish possibly competing with native species
RECREATIONAL PURSUITS	Ballast water introducing pest species Boat pollution (fuel, sewage waste, rubbish) Soil compaction or increases in soil erosion Contamination of waterways with exotic bacteria

Based on land use in the catchment, five different habitat categories were identified (Table 3.2). Given the diversity of stressors there is a variety of impacts that could occur within each habitat.

Interaction of Stressors and Habitats - Risk Hypotheses in the Conceptual Model

At this point in our preliminary risk assessment, stressors and habitats in the region have been identified. The values of various stakeholder groups have been considered in the formulation of assessment endpoints. A conceptual model of the region showing the interaction of stressors, habitats, and the potential for impacts on chosen assessment endpoints is given in Figure 3.1. The conceptual model describes the approach that will be used for the risk analysis phase. It is a graphical summary of the risk hypotheses being assessed within the catchment (US EPA, 1992a). Conceptual models are representations of the assumed relationships between sources and effects (Suter, 1999a). The conceptual model shown in Figure 3.1 represents assumed interactions of stressors and habitats within the catchment. It contains uncertainty; however, it is adopted as an operating tool in the absence of more complete knowledge.

The risk hypotheses shown in Figure 3.1 assume that agriculture and land clearing for rural residential areas produce multiple stressors that have potential for contamination of local waterbodies, eutrophication, changes in hydrology, reduction in the habitat of native flora and fauna, reductions in populations of beneficial insects, increased weed competition in pastures, and loss of aesthetic value in residential areas.

Particular emphasis has been placed in this regional risk assessment on the conceptual model as a tool for visually interpreting the relative risk calculations. This is described in the Risk Analysis section.

Table 3.2 Habitats identified within the Mountain River catchment

HABITAT	DESCRIPTION	MAJOR IMPACTS WITHIN
Aquatic	All waterbodies are included in this category, although the emphasis is on larger waterways in the catchment, in particular Mountain River and Crabtree Rivulet	Contamination of the waterbody Eutrophication Changes in hydrology
Native vegetation	This includes all native vegetation types mapped in the TasVeg 2000 series. The priority vegetation associations in the Mountain River catchment are *Eucalyptus ovata, E. amygdalina, E. tenuiramis, E. globulus.*	Reduction in the habitat of native flora and fauna
Orchard	This includes all land mapped as orchard. Major orchard crops are apples, followed by cherries.	Reductions in populations of beneficial insects Weeds competing with orchard trees, especially during establishment.
Pasture	This category includes all pastures used for grazing sheep, horses, goats and for cutting hay. There is limited crop production in Mountain River catchment but any occasional cropping that does occur is also included in this category.	Weeds competing with pasture and crop species. Weeds can also decrease quality of pasture and decrease price of cut hay.
Residential	This category includes the area around each residence that is actively used or maintained by the resident. It also includes the residence.	Loss of aesthetic value

RISK ANALYSIS USING THE RELATIVE RISK MODEL

Much of the input data for the risk analysis in this assessment came from land use patterns shown in the Tasmania 1:25,000 Series. The maps sheets used were Longley 5024 (Edition 2, 1988) and Huonville 5023 (Edition 2, 1987). Digitized map data are supplied to the Australian public on a cost recovery basis and there is only a limited amount of digitized data available. Land use themes, including vegetation, were not available in digital format so it was necessary to digitize vegetation patterns from paper maps. The maps were scanned and on-screen digitized. Vegetation themes were transformed from scan unit co-ordinates to the Universal Transverse Mercator projection using Shape Warp 2.2. ArcView® version 3.1 (Environmental Systems Research Institute, Redlands, CA, USA) was the geographic information systems (GIS) software used in this assessment.

Identifying Risk Areas

The ranking criteria described below for stressors and habitats are primarily based on land use. Land use patterns generally change dramatically between the upper and lower reaches of a catchment. It would be unrealistic and unachievable to attempt a risk ranking for the entire catchment. It is more practical and relevant to divide the region into subareas or risk regions so that stressors and habitats within a specific subarea can be better considered. This also allows comparison of risks from different stressors to specific habitats within different catchment areas.

An incremental gradient of human activity occurs as Mountain River flows down through the catchment. The intensity of agriculture, orcharding, and residential development increases. The risk regions in Figure 3.2 were chosen to match this gradient of human activity as well as the natural boundaries determined by contours and tributaries flowing into Mountain River. Aligning risk regions with the flow of tributaries to Mountain River was very important. Although two tributaries may at some point only be separated by a few kilometers, they may flow through very different land use activities before they join the main channel, ultimately contributing very different inputs to the main channel.

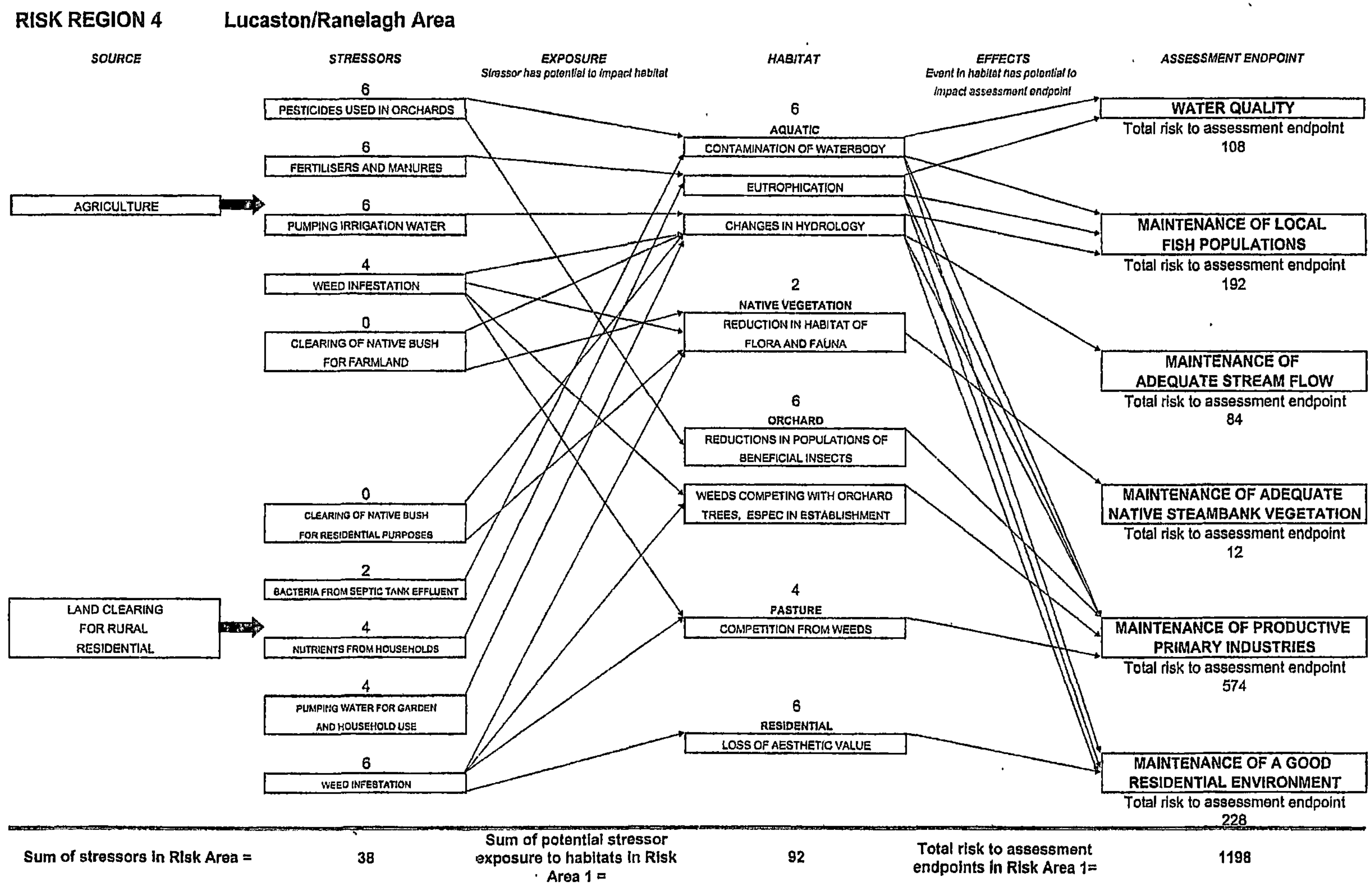


Figure 3.1 Conceptual model for the Mountain River catchment showing hypothesized interactions between stressors and habitats in Mountain River. The rankings and calculations are for Risk Region 4.

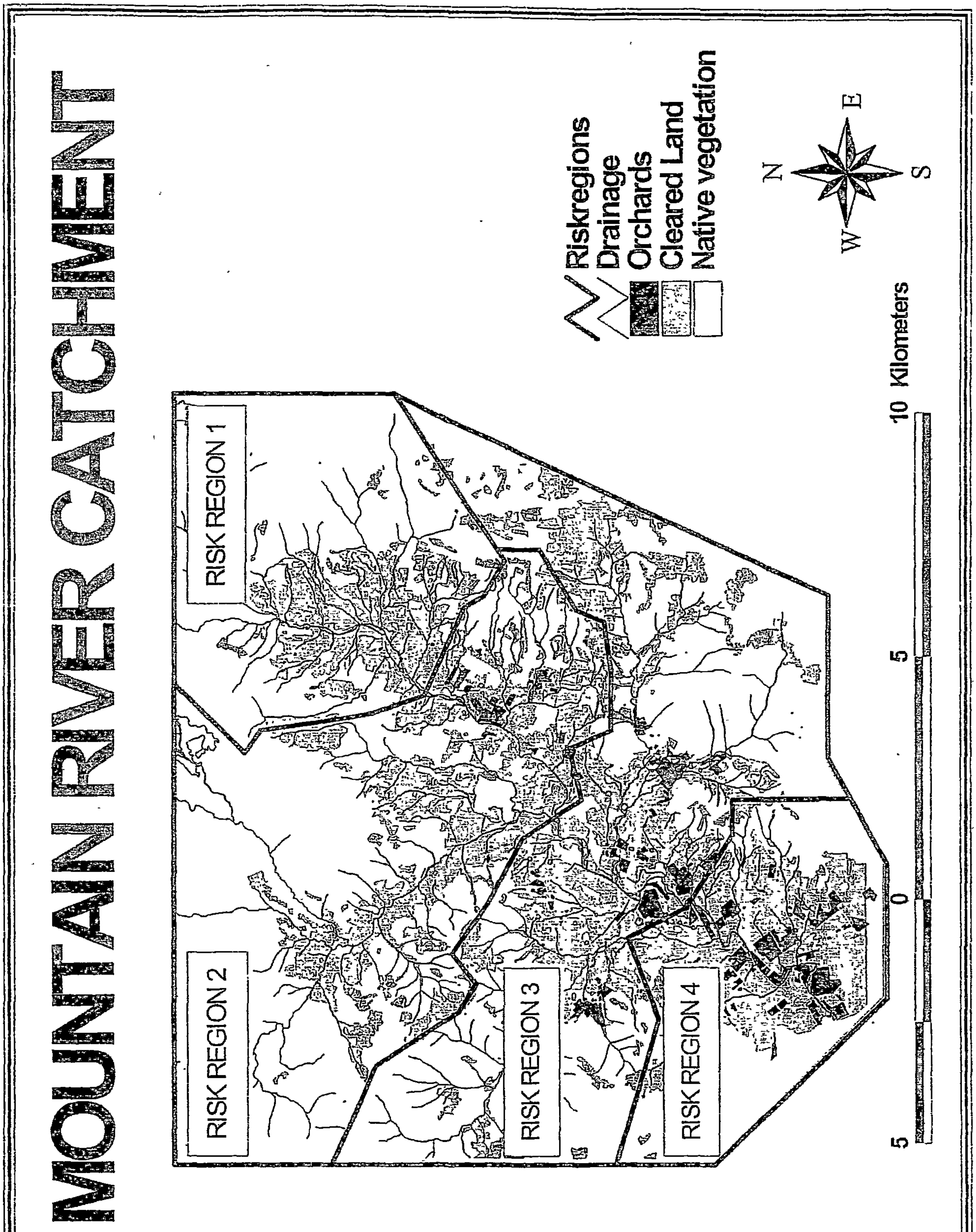


Figure 3.2 Mountain River catchment risk regions. Risk regions were mapped according to the flow of tributaries into Mountain River, and the incremental gradient of human activity in the lower reaches of the catchment.

Ranking Stressors

The most accessible data about the Mountain River catchment came from the 1:25,000 map series. However, it was not possible to quantify the extent and severity of each stressor by simply studying land use maps. Some quantitative data were available for the Mountain River catchment, although the lack of coordination between government agencies made it difficult to access. Surprising gaps in the knowledge about potential environmental stressors were discovered. The local council did not have a database that could identify how many people lived within the physical catchment, nor how many septic tanks were installed within the catchment, although they could make approximations. A total of 39 household pumps are installed along the river, although locations of the pumps could only be estimated based on residential density along the river.

To collect quantitative data about the extent and severity of each stressor in each risk region is a task not warranted for a preliminary risk assessment of the catchment. All data currently available about the catchment were collated, but no additional field data were collected for this preliminary risk assessment. We decided in this preliminary risk assessment to use expert knowledge of the region and land use maps to qualitatively rank stressors. The ranking criteria and points assigned were:

6 Likely to occur

4 Possibly could occur

2 Unlikely to occur

0 Very unlikely to occur

The 'distance between' risk categories was assumed equal i.e. stressors ranked 6 were not by definition three times larger than those ranked 2. This also applied to the habitat ranking criteria given in Table 3.3.

Uncertainty is obviously a significant consideration at this point of the risk assessment. However, it was planned to undertake a sensitivity analysis to determine if the stressor rankings had a significant effect on the relative risk ranks. In this way, the effect of an incorrect stressor ranking on the overall relative risk outcomes could be compared. The sensitivity analysis is described in the Risk Characterization section.

The ranking criteria and points assigned for severity of weed infestation was based on standard categories for mapping weed density as used in the survey conducted by the Huon Healthy Rivers Project.

6 Heavy >50% groundcover

4 Moderate 25-50% groundcover

2 Light weeds 10-25% groundcover

0 Scattered weeds <10% groundcover

Ranking Habitats

Habitats were ranked according to the proportion of a particular habitat within a region. To determine the proportion of a particular habitat within a risk region, map themes were manipulated and planimetric areas measured using ArcView software. Habitat ranks and uncertainties associated with the ranking are described in Table 3.3.

The major source of uncertainty in establishing the ranking criteria for habitats stems from the 1:25,000 maps. The content of these maps was determined from aerial photography undertaken in 1986. Obviously, there would have been changes in land use since that time, so the exact proportion of different vegetation and land use types would have changed. However, in the absence of other map data, the 1:25,000 series maps must be used. Since 1986, the major changes in land use in the catchment have been the subdivision of pasture into rural residential blocks. The number of residences in the catchment is now greater than indicated on the maps, and consequently the true extent of pasture may have been overestimated. However, there have not been other significant land use changes in the catchment, and for the purposes of this preliminary risk assessment the 1:25,000 maps were considered adequate.

Relative Risk Calculations Using the Conceptual Model

Figure 3.1 is the conceptual model for this risk assessment. Visually it describes all the interactions between stressors and habitats being considered in this risk assessment. It has been produced as a spreadsheet so that it can simultaneously mathematically describe the risks associated with the stressors and habitats found in each risk region, based on the assumed interactions between stressors and habitats. These assumed interactions are indicated by the exposure and effects arrows.

Table 3.3 Ranking criteria for Mountain River habitats

HABITAT	RANK CRITERIA AND ASSIGNED POINTS	UNCERTAINTY
Aquatic	6 – The aquatic habitat was given a single, high ranking because all activities that occur within a catchment ultimately impinge on the waterway. In addition, the risk regions all include a section of the waterway so aquatic habitat was considered a highly ranked habitat in all risk areas.	Assumption that a high ranking is justified across all regions
Native Vegetation	6 23-37%..........of total catchment native 4 11-22% vegetation found within 2 10% the risk region 0 <1%	Accuracy of 1:25,000 maps
Orchard	6 41-46%..........of total catchment 4 15-40% orchards found within the 2 1-14% risk region 0 <1%	Accuracy of 1:25,000 maps
Pasture	6 29-35%..........of total catchment 4 16-28% pastures found within the 2 1-15% risk region 0 <1%	Accuracy of 1:25,000 maps Classification of pasture vs. vacant land and home gardens
Residential	6 Many ratepayers (approx >5000) 4 Not so many ratepayers (approx >3000 2 Few ratepayers (approx >1000) 0 No ratepayers	No localized population data available for different areas of the catchment. Assumption is that all residences are contributing equally to the source

There is a number above each stressor and habitat category in Figure 3.1. These numbers are the risk rankings for the stressor and habitat in a given risk region (the example reproduced here is for Risk Region 4). This number describing risk ranking is in a cell that is part of a spreadsheet formula. Spreadsheet formulas are used to calculate the risks indicated in Figure 3.1, that is, the sum of stressors within the risk region, sum of potential stressor exposure within the risk region, total risk to assessment endpoints within the risk region, and total risk to each assessment endpoint. Incorporating spreadsheet calculations into the conceptual model means it is easy to compare total risks between different risk regions and for different rankings of stressors and habitats. The assumed interactions between stressor and habitat remain constant; only the risk rankings change.

The spreadsheet formulas used for calculating risk are:

Sum of stressors in risk region = Σstressors

*Sum of potential stressor exposure in risk region = Σ(stressor *habitat)*

for interactions where an exposure arrow indicates the stressor has potential to impact habitat

*Total risk to assessment endpoint = Σ(stressor *habitat)*

for interactions where an exposure arrow indicates the stressor has potential to impact habitat AND an effects arrow indicates that an event in the habitat has potential to impact assessment endpoint.

Total risk to assessment endpoints in risk region = Σ(total risk to assessment endpoint)

The use of exposure and effects arrows serves to ensure that only realistic interactions are included in the conceptual model and the risk ranking. Not every stressor has the potential to impact every habitat, nor has every stressor the potential to impact every assessment endpoint. A relative risk ranking cannot simply be a sum of stressor * habitat; the interactions assumed in the conceptual model must be accounted for. These interactions are indicated by the linking arrows in Figure 3.1.

When Wiegers *et al.*. (1997) did their relative risk calculations for the Port Valdez regional risk assessment, they used an exposure filter and effects filter to ensure that only realistic interactions were included in the risk calculations. Their filtering method was to include 1 in the risk calculations that represented realistic interactions and 0 in the interactions that represented unrealistic interactions. Their method did not use the conceptual model as visual reference so the filtering method involved individually assessing each stressor/habitat/impact interaction and questioning whether it was a realistic scenario.

RISK CHARACTERIZATION

A comparison of risks to assessment endpoints in Risk Region 4 is shown in Figure 3.3. This is where most agricultural and residential development in the catchment has occurred. Risks to productive primary industries are greatest which is not surprising considering the diversity of inputs to agriculture. After primary industries, risks to the residential environment and maintenance of fish populations are greatest. Degradation of water quality in the region had the greatest impact on assessment endpoints. Initially it was surprising that risks to native vegetation were comparatively low, given the development that has occurred in the region. However, this risk outcome is accurate because there is actually very little native vegetation remaining in the region (habitat rank is 2) so risks to this habitat type are relatively low.

A comparison of risks to assessment endpoints in different Risk Regions is shown in Figure 3.4. The same general trends appear throughout the catchment with risks greatest to productive primary industries, followed by residential environment and maintenance of fish populations. Generally, risks to all assessment endpoints are greater in Risk Regions 3 and 4 because more agricultural and residential development has occurred there.

It is important when interpreting the risk outcomes to remember that *relative* risks form the basis of the relative risk model. A risk outcome in itself has no meaning unless compared to other risk outcomes; in this way, risks are prioritized. One limitation of the relative risk model is that stressors and habitats are ranked on relative likelihood of

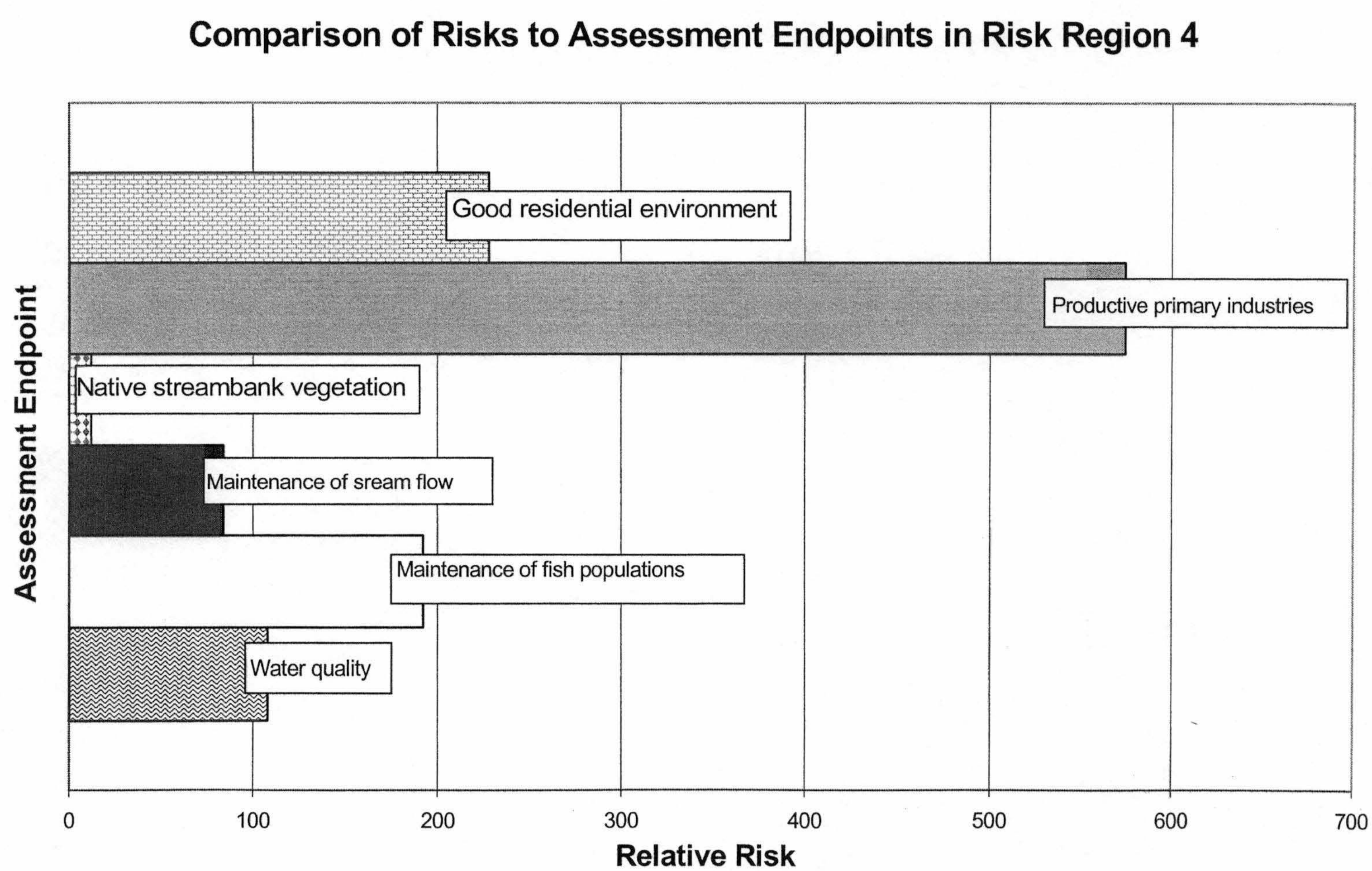


Figure 3.3 Comparison of risks to assessment endpoints in Risk Region 4. Relative risks rather than absolute values describe environmental conditions in the catchment.

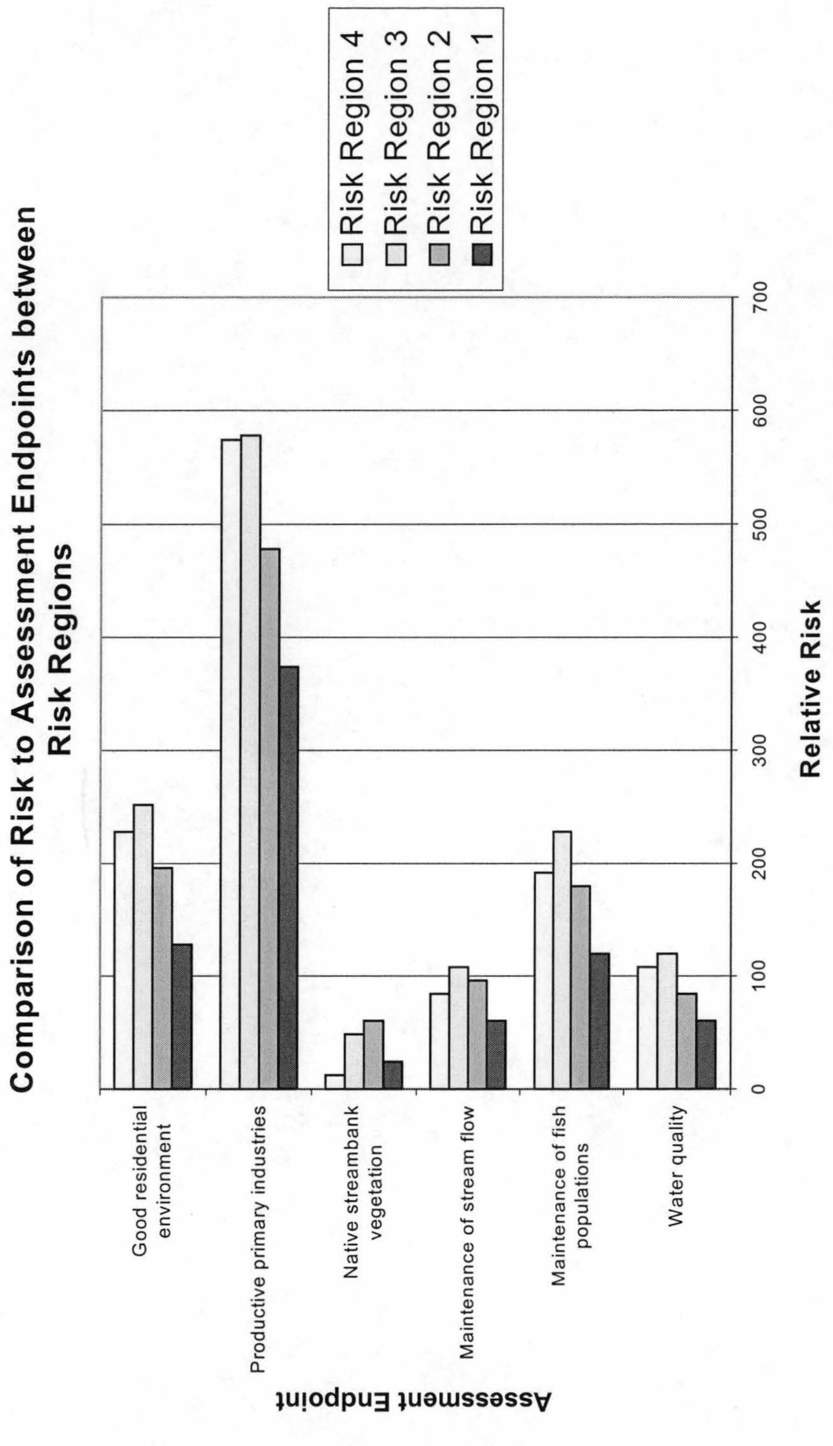


Figure 3.4 Comparison of risks to assessment endpoints between Risk Regions. The increased risks to assessment endpoints in Risk Region 3 and 4 reflect the increased level of human activity in these parts of the catchment.

occurrence, not on relative consequence of occurrence. Different stressors can have different effects with different consequences for the habitat of concern. Ranking of stressors based on 'consequence of occurrence' was not attempted in this preliminary study, due to a limited understanding of ecological processes within the catchment. With limited scientific data available, rankings of ecological consequence would tend to be value-driven, rather than factual.

Sensitivity Analysis

As previously mentioned the ranking of stressors is a major source of uncertainty in the assessment. Sensitivity analysis is a means to assess the robustness of the model - how would the risk outcomes change if we had new knowledge that allowed more precise ranking of the stressors?

Weed infestation is a significant stressor in the catchment, particularly as it has been included as a stressor to agricultural and residential environments. The initial rankings of weed infestation came from a 1999 Huon Healthy Rivers Weeds survey. However, this survey was preliminary. Weed cover was only estimated along a few roads in each Risk Region and only certain weed species were included in the survey. No survey was conducted along the banks of Mountain River where crack willows, blackberries, hawthorn, and thistles have taken over in many places. It is likely that the true extent of weed infestation was underestimated in the initial rankings. Weed infestation was given a higher ranking in each Risk Region, and the risks to assessment endpoints recalculated. The results are shown in Figure 3.5.

Weed infestation is a stressor with considerable uncertainly. The true extent of pasture cover is a habitat type with considerable uncertainty. This stems from using 1987 1:25,000 maps to calculate pasture cover. As previously mentioned, since 1987 various farms have been subdivided and the pasture converted to rural residential blocks. It is possible that the calculated land areas overestimate the true extent of pasture cover. Pasture cover was given a lower ranking in each Risk Region, and the risks to assessment endpoints recalculated (Figure 3.5).

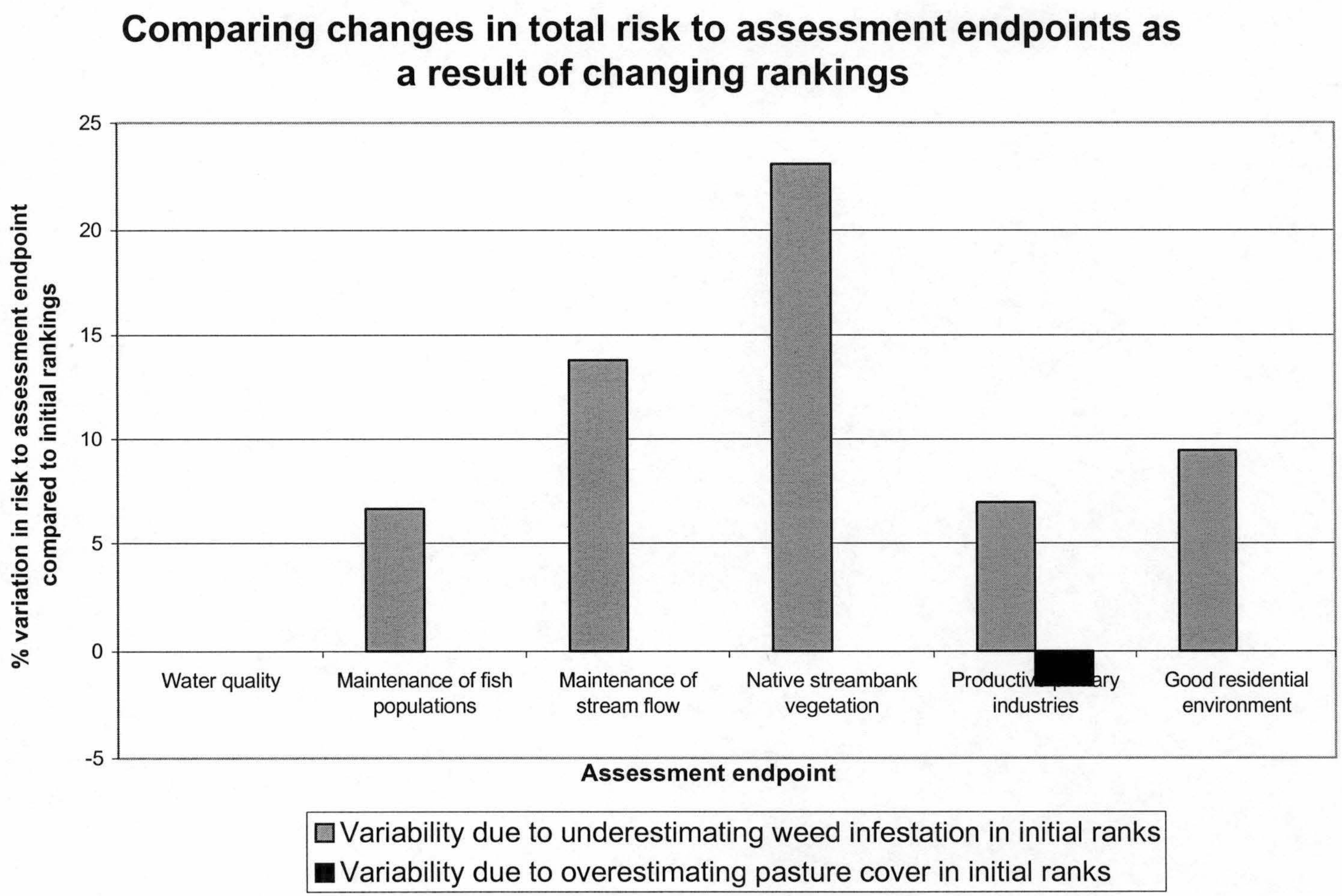


Figure 3.5 Sensitivity analysis. This shows the effect that changing initial rankings has on the risk outcomes. The conceptual model is sensitive to changes in rankings of weed infestation but insensitive to changes in ranking of pasture cover. Uncertainty in some parameters is more critical than uncertainty in others.

Uncertainty in the ranking of weed infestation (stressor) can have considerable effect on the risk outcomes (Figure 3.5). If the true extent of weed infestation is actually greater than initially estimated, then the actual risks to several assessment endpoints are greater. The risks to native streambank vegetation are increased by 23% and the risks to maintenance of stream flow increased by nearly 14%. This occurs because more weeds are competing with native vegetation and more willows are interfering with natural watercourses.

Figure 3.5 also shows that uncertainty in the ranking of pasture cover (habitat) has negligible effect on the risk outcomes. If the true extent of pasture cover is actually less than initially estimated, the actual risks to assessment endpoints remain unchanged except for a 2% decrease in risk to productive primary industries. This is explained by the fact that pasture is an input to agriculture, and if there is less pasture cover there is less risk to productive agriculture. Obviously this does not account for competition between agricultural and residential land uses. If there is less pasture cover it may be that agriculture is actually at more risk because there is less viable land for farming.

A Basis for Action

The sensitivity analysis shows that the conceptual model is more sensitive to uncertainties in some parameters than in others. An on-paper exercise such as this can be used to highlight the most important knowledge gaps about the catchment. In the example seen in Figure 6, obviously it is more important to invest time and money into a comprehensive weeds survey rather than precisely determining the percentage cover of each land use type.

A preliminary study such as this can also provide a basis for establishment of environmental monitoring programs. Monitoring programs should be concentrated in Risk Region 3 and 4 as this is where most environmental stressors are impacting. Maintenance of productive primary industries is most at risk, so monitoring should focus on the stressors that are having an impact on this assessment endpoint. In the conceptual model (Figure 3.1) it is clear that changes in the aquatic habitat (water contamination, eutrophication, and hydology) have a major impact on this assessment endpoint. There is a priority to monitor the stressors that are impacting the aquatic environment. Nutrient levels, bacterial counts, and pesticide residues should be included in routine water quality monitoring programs.

The risk analysis can also provide information for local environmental groups who undertake activities in the catchment. Figure 3.1 reinforces that weed control is one of the most effective means for the community to achieve its environmental goals.

DISCUSSION

The relative risk model is a straightforward approach to risk assessment - more than anything it is a framework for data collection and decision-making. In a preliminary risk assessment such as this, perhaps the most important function is collation of information about the region, and focus on what stakeholders want for the region. Identification of assessment endpoints represents a crucial but difficult part of this process. Currently practical regional risk assessments are somewhat limited by the generalist goals that are chosen in the absence of more specific baseline data. Minimal scientific and regulatory information was available for Mountain River and this greatly hindered the definition of concise assessment endpoints.

The conceptual model formed the basis of the entire risk assessment. The risk outcomes were based entirely on the interactions between stressors and habitats assumed in this model. This particular conceptual model is unique to the Mountain River catchment. The conceptual model for another catchment would be different based on the interactions that occur in that environment. For example, soil erosion and salinity caused by tree removal are not considered to be environmental problems in the Mountain River catchment, but are significant issues in many other Australian catchments, therefore their inclusion would require development of an entirely different conceptual model.

The model was formulated based on all available knowledge about the region, but it is possible that different risk assessors with a similar knowledge of the region might propose a different conceptual model as the basis of the risk assessment. The risk outcomes might be different, but the framework provided by the relative risk model means there is a tangible basis for discussion of regional environmental priorities.

The Relative Risk Model framework provided an effective utilization of time and resources for gaining an understanding of ecological issues within the Mountain River catchment. Preliminary risk assessments such as this are valuable tools in planning expensive fieldwork and ground truthing projects.

CHAPTER 4. TIER 1 RISK ASSESSMENT FOR APPLE PESTICIDES

Chapter Background: Increased community awareness of environmental issues, expansion in rural residential population and the development of a major aquaculture industry in the Huon Valley have focussed attention on the impact of agricultural chemical use on the region's river systems. Community surveys (HHRP, 1997) and the regional risk assessment of Mountain River catchment (Chapter 3) have identified pesticides as significant environmental stressors. However, no monitoring of agricultural pesticides has previously been undertaken in the Huon Valley.

Prior to undertaking any monitoring of orchard pesticides, it was necessary to gain an understanding of pesticide usage in Huon Valley apple orchards by asking the questions: 'What products were being applied, how regularly, and in what volume?' Local horticultural advisors and agricultural chemical sales representatives were interviewed, and provided information about regional pesticide usage.

Given the limited resources available for the project it was important to have a system to rank the apple pesticides based on their potential environmental impact and to focus on those pesticides for which monitoring was a priority. Early tier risk assessments of chemicals provide a framework for ranking potential environmental impact.

This chapter describes a Tier 1 risk assessment for the apple pesticides used in Huon Valley production systems which was conducted to:

- Gain an understanding of pesticide usage in apple production systems in the Huon Valley.
- Identify pesticides of primary ecological concern to the aquatic environment
- Gain an understanding of the processes involved in conducting a Tier 1 pesticides risk assessment.

This chapter has been submitted as a paper 'Environmental risk rankings for apple pesticides used in Tasmania's Huon valley: Identifying contaminants of potential environmental concern.' to the international journal *Air, Soil and Water Pollution* authored by Walker R and Brown PH.

Abstract

The Huon Valley in Tasmania is one of Australia's most productive apple growing regions. Many of the orchards are planted on river flats and there is potential that pesticides used in apple production may pollute local waterways. A tiered ecological risk assessment approach was used to identify pesticides of potential environmental concern to aquatic ecosystems. The hazard quotient method was chosen as the most appropriate means for rating risk to aquatic species. Pesticide use patterns and physiochemical data were also included in the overall assessment of risk to the aquatic environment. Based on its hazard quotient for aquatic species, physiochemical properties and volume of usage in the Huon Valley, chlorpyrifos was identified as the orchard pesticide currently most likely to adversely impact the aquatic environment..

Azinphos-methyl and carbaryl are other insecticides of potential concern. The fungicides that had the highest risk rankings were thiram, ziram, mancozeb and dithianon. From an aquatic risk point of view the herbicides used in the Huon Valley are of little significance. Pesticides monitoring programs conducted in the Huon Valley should focus on these pesticides identified as being contaminants of potential environmental concern.

INTRODUCTION

This paper describes preliminary research undertaken to determine whether aquatic ecosystems in the Huon catchment region in Tasmania were at risk from current apple orchard spray practices. Contamination of waterways by pesticides is a pertinent issue in the Huon Valley because many commercial orchards in the Huon catchment are located either adjacent to or in close proximity to waterways which feed into the Huon estuary. The Huon estuary supports a $45 million aquaculture industry (HHRP 1997). Waterways of particular concern for pesticide pollution include Mountain River, Kermandie River, Agnes Rivulet and Nicholls Rivulet.

Pesticides are an essential management option in modern orchards, but one for which the industry faces consumer concerns over health and environmental standards. In 1992 the Australian Apple and Pear Growers' Association signed a charter with the Australian Consumers' Association to reduce pesticide use by 50% by 1996 and 75% by the year 2001 (Apple and Pear News 1992)

The Pesticides Charter, government regulation and market pressures have all been factors driving industry research and development towards sustainable production practices. For a decade there has been a concerted push for change in pesticide use patterns, but there has been little monitoring undertaken to measure the impacts that pesticide usage is having on the environment. It is important to document how current pesticide usage is impacting the environment, so that this can be used as a gauge to assess the environmental merits of future crop protection practices.

The aim of this research was to identify which pesticides should be included in a pesticides monitoring program assessing risks to aquatic environments from current apple orchard spray practices. In the tiered approach to pesticides risk assessment recommended by the Aquatic Risk Assessment and Mitigation Dialogue Group (1994) screening studies such as described here are Tier 1 risk assessments. Initial screening risk assessments have been used previously to identify contaminants of potential environmental concern (COPCs), screen out other contaminants, define data requirements, and gain focus in a large scale risk assessment (Cook *et al.* 1999). Basic risk rankings for pesticides used in the cotton industry were conducted prior to implementation of extensive field monitoring (Batley and Peterson 1992; Bowmer 1993) but no Tier 1 risk assessment studies have been published for intensive horticultural production regions; this paper provides a case study for preliminary pesticide risk assessments in such regions.

METHODS

Sources of pesticide contamination

Tier 1 risk assessment involves analysis of potential sources of contamination within the system under examination. Potential sources of pesticide contamination in the

Huon Valley include drift contamination from orchard spraying, run-off from spray sheds where orchard sprayers are filled, run-off/leaching from sprayers where excess spray is drained off following spraying, and drainage from post-harvest fruit dips (including diphenyl amine, benomyl, iprodione and imazilil) in packing sheds during grading, packing, and storage.

Best management practices can greatly reduce the off-target impact of pesticides. Throughout Australia apple growers have recognised the importance of responsible chemical management practices and their trade implications as evidenced by the fact that 80% of growers have adopted some integrated pest and disease management practices (HRDC 1998). In Tasmania, all growers participating in the statewide quality assurance scheme are required to complete farm chemical users training courses and to maintain spray diaries.

Responsible handling, mixing and disposal of pesticides by qualified workers reduces the likelihood of spray run-off and drainage from post-harvest dips. Drift from orchard spraying can be minimised to some extent, but it is the form of environmental contamination over which even the most responsible grower has least control. In this risk assessment it was decided to assess risks from production practices used by growers implementing best management practices, and assume that run-off from filling stations and dips was minimal. Hence, the focus was on pesticides applied as part of the routine spray schedule that could cause drift contamination of nearby waterways or which could move to waterways via leaching or runoff after application.

Data collection

The starting point for identifying potential sources of spray drift contamination was to document pesticide usage in the region. Interviews conducted with Department of Primary Industries and Fisheries staff, local horticultural advisers and with the largest local agricultural chemicals retailer were used to gain information about pesticide formulations, rates, and annual usage in the Huon Valley. Responses from Primary Industries staff were based on local experience and data collated from twenty grower spray diaries, while the major local agricultural chemical retailer supplied annual sales figures. Due to the confidential nature of some of this information, usage rankings rather than specific figures are given in this paper. Based on the interviews conducted, the pesticides shown in Table 4.1 were included in the risk assessment. This background research was conducted in 1997, and more recently released formulations and new chemicals are not included.

Methods for measuring the environmental impact of pesticides

Strategies to identify COPC specific to the apple industry include the Pesticide Index (Penrose *et al.*, 1994), a pesticides ratings system designed for facilitating Integrated Fruit Production. The Index incorporates variables such as environmental impact, occupational health and safety, the potential for residues and the importance of the pesticide in a particular crop protection system. Other authors (e.g. Weber 1977; Kovach *et al.* 1992; Dushoff *et al.* 1994) have proposed environmental ranking systems for pesticides which are applicable across a variety of agricultural production systems. Each ranking system has a specific emphasis depending on the purpose for which it was designed.

Since the aim of this work was to focus solely on risk to the aquatic environment, it was decided to use a less comprehensive method that did not attempt to integrate risks arising from worker exposure and human health considerations. The method considered most appropriate for the apple production systems of the Huon Valley was the quotient method as first developed in the United States Environmental Protection Authority by Urban and Cook (1986). The quotient method has been widely adopted as a method to estimate potential hazard to the aquatic environment (Nabholz 1991; Aquatic Risk Assessment and Mitigation Dialogue Group 1994; Calow 1995; Holland 1999). An estimated environmental concentration (EEC) is calculated for the worst case of direct overspray to a waterbody, and the EEC is divided by the lowest LC50 value obtained in ecotoxicity tests. This provides a hazard index called Q (quotient). If Q is less than 0.1, it means that environmental concentrations should be one-tenth or less of the lowest LC50 value, and it is assumed that adverse environmental effects are unlikely. If Q is greater than 0.1 further investigation is necessary.

An alternative method designed to rank pesticide impacts to the aquatic environment is the Pesticide Impact Ranking Index (PIRI) developed in Australia by Kookana *et al.*

(1998). This system rates the impact of a pesticide on a waterbody on the basis of the value of the water resource threatened, the pesticide load reaching the waterbody and pesticide transport parameters. Because of a lack of pesticide input data PIRI has had limited validation (Kookana *et al.* 1998), although validation in vegetable production systems is currently being conducted. In the future PIRI may prove to be a useful tool for orchard production systems, but in this research PIRI was not an appropriate method to use for the Huon Valley because it requires a large amount of specific data about the quantity of pesticide applied per unit area per unit time that was not available.

Using the quotient method for assessing toxicity to aquatic species

Estimated environmental concentrations (EECs)

The standard Australian method for estimating environmental concentration is to assume a body of standing water 1 ha in area with a depth of 15cm, having a volume of 1500m^3. It is assumed that there is a direct overspray of this water body at the maximum label rate. Estimated environmental concentrations are always calculated for active ingredient (Holland 1999).

The direct overspray calculations are for aerial applications which is an unrealistic orchard scenario. To use the quotient method for waterbodies within orcharding districts it is more realistic to assume concentrations that occur as a result of spray drift. In these scenarios, the Australian government environmental regulatory authority assumes that 10% spray drift is applicable (Holland 1999). In the calculations shown in Table 4.1, 10% spray drift is factored into the Estimated Environmental Concentrations shown.

Toxicity data

Registration of pesticides requires comprehensive ecotoxicity data, although there is limited toxicity data available for Australian species. For some chemicals there has been extensive toxicity testing, although the scientific rigour varies between tests. Toxicity data from the Pesticides Manual (Tomlin, 1994) and the US EPA AQUIRE database (US EPA 1994) were used in this study. *Oncorhynchus mykiss* (rainbow trout) and *Daphnia magna* (water flea) were chosen as representative aquatic species with toxicity data retrieved for 96-hour LC 50 exposures and 48-hour EC50 exposures respectively. Because toxicity data for Australian aquatic species is currently very limited (Warne et al 1998) the risk assessment did not include species indigenous to the catchment region.

Calculating hazard quotient, Q

The Q value is calculated by dividing the Estimated Environmental Concentration (mg/L) by the LC50 (mg/L). Q values are shown for *Oncorhynchus mykiss* and *Daphnia magna* (Table 4.1).

Bioaccumulation potential

Another indicator of risk to aquatic organisms is the tendency for the compound to bioaccumulate as indicated by the octanol-water partition coefficient. The octanol-water partition coefficient is a physical property used extensively to describe a chemical's lipophilic or hydrophobic properties. It is the ratio of a chemical's concentration in the octanol-phase to its concentration in the aqueous phase of a two-phase system at equilibrium, and the logarithm (log Kow) is commonly used to characterise its value. Increased octanol-water partition coefficients indicate a greater propensity for the pesticide to bind to organic tissue, particularly fats, and to be carried through the food chain.

Physiochemical properties of pesticides for assessing risk to aquatic ecosystems

One approach to predict water pollution potential is to estimate each chemical's inherent tendency to undergo leaching or runoff based on its physical and chemical properties. The SCS/ARS/CES pesticide properties database (Wauchope *et al.* 1992; Augustijn-Beckers *et al.* 1994) is one of the comprehensive pesticides databases available; the water solubility, half life, soil adsorption coefficients (Koc) and vapour pressure values given in Table 4.1 are drawn from this database. Some of the azole compounds are not included in the database and where possible physiochemical properties for these pesticides were taken from the Pesticides Manual (Tomlin, 1994) and the SRC environmental fate database CHEMFATE.

The four properties given in the SCS database have been used to estimate pesticide leaching, adsorbed runoff and runoff solution potential for the Huon Valley apple pesticides using the algorithms defined by Goss & Wauchope (1990).

Pesticide leaching potential algorithm:

Large:	If log (Half-life)*(4-log(Koc)) ≥2.8
Small:	If log (Half-life)*(4-log(Koc)) ≥1.8
Very Small:	If log (Half-life)*(4-log(Koc))<0.0 or Solubility<1 and Half-life≤1
Medium:	All other values

Pesticide adsorbed runoff potential algorithm:

Large:	If Half-life≥40 and Koc ≥1000 or
	If Half-life≥40 and Koc≥500 and solubility ≤0.5
Small:	If Half-life≤1 or If Half-life≤2 and Koc≤500 or
	If Half-life≤4 and Koc≤900 and solubility≥0.5 or
	If Half-life≤40 and Koc≤500 and solubility≥ 0.5 or
	If Half-life≤40 and Koc≤900 and solubility≥2
Medium:	All other values

Pesticide runoff solution potential algorithm

Large:	If solubility≥1 and Half-life>35 and Koc<100000 or
	If solubility≥10 and solubility <100 and Koc≤700
Small:	If Koc≥1000000 or
	If Koc≥1000 and Half-life≤1 or
	If solubility <0.5 and Half-life<35
Medium:	All other values

RESULTS

Biological risk potential Q values allow quick comparison of the aquatic risk potential of pesticides. The Q values for insecticides were much higher than for fungicides and herbicides (Table 4.1). When *Oncorhynchus mykiss* was used as the surrogate test organism for fish, chlorpyrifos was the most hazardous pesticide followed by azinphos-methyl (Figure 4.1). Higher hazard quotients were expected for organophosphorous compounds due to their high acute toxicities stemming from their anti-cholinesterase properties. The dithiocarbamates and diathianon were the fungicides that posed the highest risk to fish communities. The azole fungicides posed little risk to fish, as did the herbicides.

	INSECTICIDES						FUNGICIDES									HERBICIDES	
PROPERTY / PESTICIDE	chlorpyrifos EC	chlorpyrifos WP	azinphos-methyl SC	azinphos-methyl WP	carbaryl	parathion-methyl	thiram	ziram DF	mancozeb	dithianon WP	dithianon SC	penconazole	myclobutanil	hexaxonazole	flusilazole	amitrole	diuron
CAS number	2921-88-2	2921-88-2	86-500-0	86-500-0	63252	298-00-0	137-26-8	137-30-4	8018017	3347-22-6	3347-22-6	66246-88-6	88671-89-0	79983-71-4	85509-19-9	61-82-5	330-54-1
Maximum label rate (quantity/100L)	100	50	196	100	150	140	150	120	120	120	40	25	12	40	15	570	80
% active ingredient (a i)	50	50	20	50	80	50	80	76	80	75	75	10	40	5	20	25	90
Amount a i applied per hectare with an airblast sprayer delivering 2000 L/ha (g)	1398	500	1190	1000	2400	1400	2400	1824	1920	1800	948	50	96	40	60	2850	1440
EEC (mg/L)	93 20	33.33	79.33	66 67	160 00	93 33	160 00	121 60	128.00	120 00	63.20	3.33	6.40	2.67	4 00	190 00	96 00
Rainbow Trout 96 hr LC50 (mg/L)	0 003	0 003	0 02	0 02	1 3	2 7	0 048	0.048	0 46	0 1*	0.1*	1.7	4 2	3 4	1 2	243	5 6
Q value for Rainbow Trout	31067	11111	3967	3333	123	35	3333	2533	278	150*	79*	1 96	1.52	0 78	3 33	0 78	17
Daphnia magna 48 hr EC50 (mg/L)	0.0017	0 0017	0 0011	0 0011	0 006	0 0073	0 21	0 21	1 3	2 4	2 4	7	11	2 9	3 4	215	12
Q value for Daphnia magna	54824	19608	72121	60606	26667	12785	762	579	98	50	26	0.48	0 58	0.92	1 18	0 88	8
Usage ranking for the Huon Valley	5	2	8	5	4	7	1	3	6	5	5	5	5	8	8	5	5
log Kow	5 11	5 11	2.96	2.96	1 59	3	1 73	1 086	0 62	3 20	3.20	3 72	2 94	3.9	3 74	-0 65	2 85
Water solubility (mg/L)	0.4	0 4	29	29	120	55	30	65	6	0 5	0 5	73	142	17	54	280	360,000
Half life (pH 7)	30 days	30 days	10 days	10 days	10 days	40 days	15 days	30 days	70 days	12.2 hrs	12.2 hrs	v stable	25 days	v stable	v stable	stable	14
Koc (mL/g)	6070	6070	1000	1000	300	5100	670	400	>2000								100
Vapour pressure (mPa)	2.27	2 27	0 0267	0 0267	0 159	0 2	<0 013	0 013	0	0 066	0.066	0 21	0 213	0 01	0 039	0.055	0 059

Table 4.1 Properties of apple pesticides used to identify contaminants of potential concern to the aquatic environment.

For dithianon LC50 data for *Oncorhynchus mykiss* was not available so the data shown is the 96 hour LC50 for *Cyprinus carpio* (common carp). EEC = estimated environmental concentration. Toxicity values drawn from the Pesticides Manual (Tomlin 1994) and the AQUIRE toxicity database (US EPA 1994). Physiochemical data drawn from SCS/ARS/CES pesticide properties database (Augustijn-Beckers *et al* 1994; Wauchope *et al* 1992), CHEMFATE database (SRC 2000), Interactive LogKow (SRC 2000) and Pesticides Manual (Tomlin 1994).

When *Daphnia magna* was used as the surrogate test organism for invertebrates, azinphos-methyl was the most hazardous pesticide, followed by chlorpyrifos (Figure 4.2). Carbaryl and parathion-methyl also had potential to adversely impact invertebrate populations. The risks to invertebrates from fungicide and herbicides were similar to those for fish.

Octanol-water partition coefficients indicate that chlorpyrifos was the pesticide most likely to bioaccumulate. Following chlorpyrifos the azole fungicides were the pesticides most likely to bioaccumulate, however they were far less toxic to aquatic species than the organophosphates.

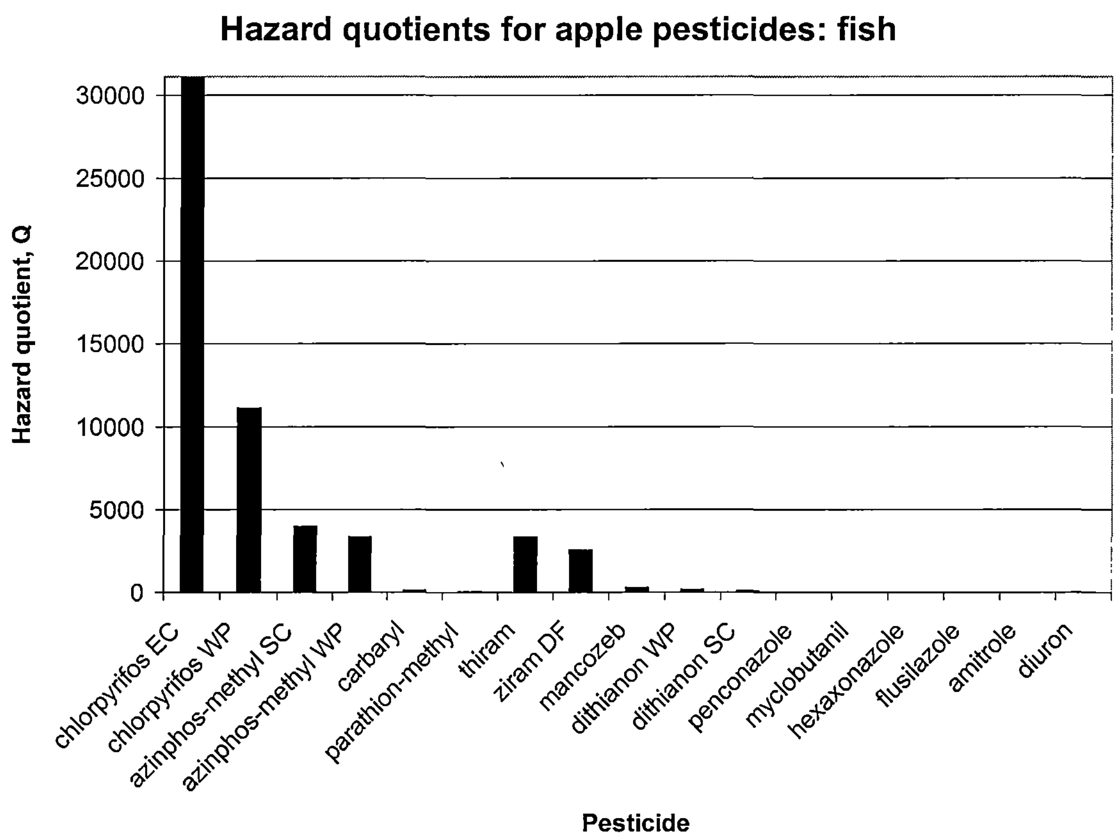


Figure 4.1 Hazard quotient values, Q, for apple pesticides calculated using *Oncorhynchus mykiss* (rainbow trout) as the non-target aquatic organism.

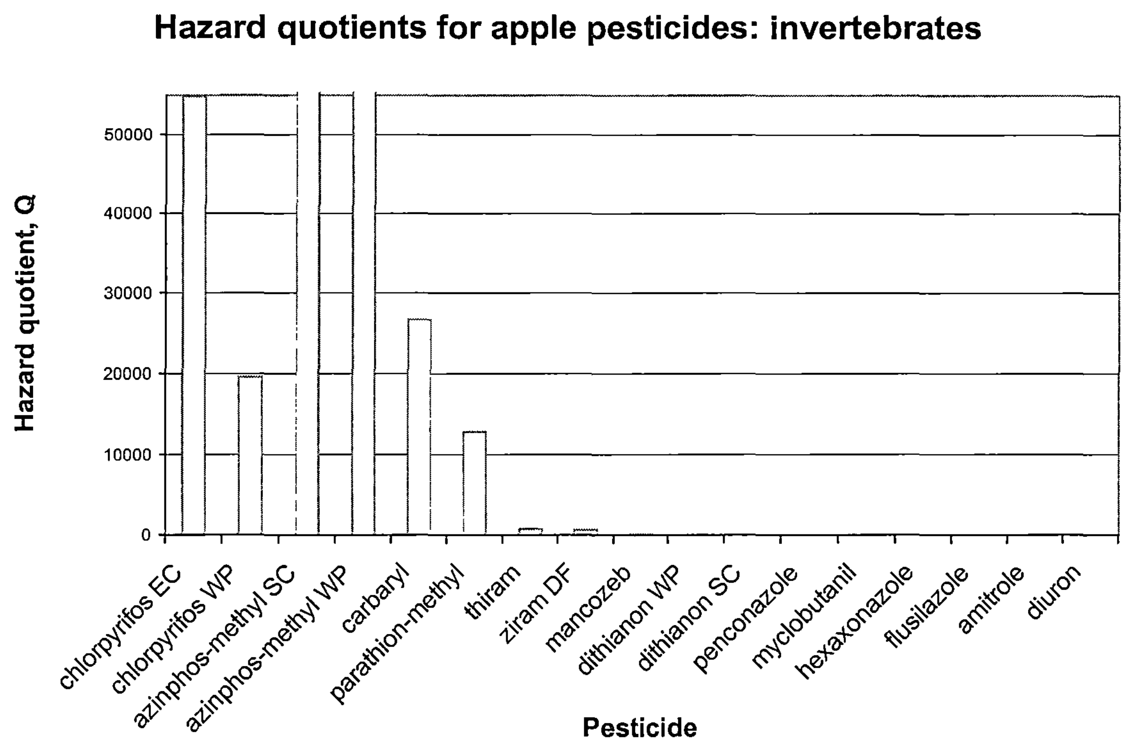


Figure 4.2 Hazard quotient values, Q, for apple pesticides calculated using *Daphnia magna* (water flea) as the non-target aquatic organism.

Pesticide movement to water based on physiochemical properties

Based on the pesticide property algorithms of Goss and Wauchope (1990) ziram had the greatest potential for leaching to waterways; azinphos-methyl and mancozeb had the greatest potential for adsorbed runoff; and azinphos-methyl, thiram and ziram had the greatest potential for surface runoff (Table 4.2). Koc values for some products were not available in all databases searched, and these products are omitted from Table 4.2. When vapour pressures are considered, chlorpyrifos has the greatest potential to volatilise (Table 4.1) indicating a tendency to move off-site as vapour drift.

Table 4.2. Aquatic pollution potential of selected apple pesticides
S = small, M = medium, L = large. Parathion-methyl and ziram properties calculated according to the algorithms of Goss and Wauchope (1990). All other values drawn from Goss and Wauchope (1990).

Potential for aquatic pollution	chlorpyrifos	azinphos-methyl	carbaryl	parathion-methyl	thiram	ziram	mancozeb	diuron
Pesticide leaching potential	S	S	S	S	S	M	S	M
Pesticide runoff solution potential	M	L	S	M	S	M	L	M
Pesticide adsorbed runoff potential	M	L	M	M	L	L	M	L

DISCUSSION

Based on the outcomes of this risk assessment a number of pesticides were identified as contaminants of potential environmental concern in the orcharding system. The hazard quotients clearly indicate that a number of pesticides have potential for adverse biological impact, and the physiochemical properties of some pesticides indicate that they are likely to be partitioned to waterways. The pesticide of most concern in the Huon Valley was chlorpyrifos, which had potential for the greatest adverse impact on the aquatic environment due to its high volume of usage, toxicity, bioaccumulation properties and tendency to volatilise. Its physiochemical properties indicate that it is unlikely to pollute waterways via leaching or runoff, but the basis of this risk assessment was an assumption that growers were using best management practices and that aerial spray drift was the form of environmental contamination most difficult to mitigate against.

Azinphos-methyl is another organophosphate which has similar aquatic risk potential to chlorpyrifos, however it was used in far smaller volumes in the Huon Valley. The relatively high estimated environmental concentrations of carbaryl when used as an insecticide mean it has potential to adversely impact invertebrate communities.

The fungicides of potential environmental concern in the Huon Valley were the dithiocarbamates: thiram, ziram and mancozeb. Dithianon also had potential to impact on fish populations. From an aquatic risk point of view the herbicides used in the Huon Valley were of little significance.

There is no published record of regular pesticide monitoring programs in Australian apple-growing districts. The only ongoing monitoring of pesticides in the apple industry is in the National Residue Survey. Although this survey is conducted with human health rather than environmental standards as the focus, it is interesting to note that maximum residue levels (MRL) exceedences in the industry have been for chlorpyrifos, azinphos-methyl and dithiocarbamates (National Residue Survey 2000) indicating that these are chemicals for which strict adherence to best management practices is a necessity.

Problems in data generation, collection and interpretation restrict the extent to which environmental hazard can be predicted from ecotoxicity and physiochemical data (Bowmer *et al.* 1996). Despite using the AQUIRE toxicity database and the SCS/ARS/CES pesticide properties database (Augustijn-Beckers et al 1994; Wauchope et al 1992), both considered to be among the most comprehensive databases available, it was still not possible to locate consistent data for every pesticide. On a regional level it is also important that accurate information about pesticide usage patterns is available in order to assess risks. This means that agricultural chemical retailers must be prepared to disclose sales records, and that growers maintain and disclose spray diaries.

The hazard quotient can only be used as an estimate to give a relative ranking of potential for adverse impacts. When the hazard quotient approach was developed by Urban and Cook (1986) they recognised the method had a number of weaknesses. These include: no compensation for the differences between laboratory tests and field populations; no consideration for the effects of incremental dosages; the method cannot be used for estimating indirect effects of toxicants (e.g. food chain interactions) and does not account for other ecosystem effects (eg. predator-prey relationships, community metabolism, structural predator-prey relationships, community metabolism, structural shifts etc.) and the method does not quantify uncertainties. In addition, the tests on exotic species may not reflect toxicity to native species, recognised test procedures may not allow for Australian environmental conditions, and laboratory tests may not simulate real conditions (Curnow *et al.* 1993). Furthermore, the hazard quotient method is very conservative. No risk-benefit analysis was undertaken here, but in assessments for commercial industries, the risks associated with being too conservative should also be considered. If risks are overestimated and this conservatism extended to restrictive regulation of management practices, then the financial viability of an operation may be jeopardised.

In a tiered risk assessment approach, measurement of field concentrations and comparison of these with estimated environmental concentrations provides increased confidence in the outcomes of the assessment. Considerable time and resources must be invested into field measurements of pesticides. Commercial pesticide analysis costs may be as much as $200 per sample, so it is essential that the decision about which pesticides to include in a monitoring program be based on fact rather than presumption. A preliminary risk assessment such as described here is a useful means of refining the monitoring program to focus on the priority chemicals to include in sampling programs.

CHAPTER 5. PROBLEM FORUMULATION FOR CHLORPYRIFOS RISK ASSESSMENT

Chapter Background: Ideally, higher tier risk assessments would be conducted for all those pesticides identified as chemicals of potential environmental concern in the Tier 1 risk assessment. However, due to the limitations of monitoring and analytical resources, and the literature review required, it was decided to devote project time and resources to one chemical which clearly had potential to adversely impact aquatic systems in the Huon Valley.

This chapter presents the background research undertaken in the problem formulation phase for the aquatic risk assessment of chlorpyrifos used in Tasmanian apple orchards. The problem formulation phase of a risk assessment establishes the goals, breadth and focus of the assessment (Parkhurst *et al.*, 1994). The risk assessment proceeds according the facts and assumptions established in the problem formulations phase. This chapter comprises a general literature review of chlorpyrifos characteristics, a description of the conceptual model and a review of assessment endpoints conducted prior to selection of endpoints for this project.

ENVIRONMENTAL STRESSOR CHARACTERISTICS

Chlorpyrifos formulations

Chlorpyrifos [*O,O* -diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate] is a widely used, broad-spectrum organophosphorothioate pesticide that displays activity against a broad range of insect pests and is used in a wide variety of global markets (Giesy *et al.*, 1999). The chemical structure of chlorpyrifos is shown in Figure 5.1. Chlorpyrifos was developed in 1962, and commercial production of the chemical commenced in 1965 (Giesy *et al.*, 1999). The widespread use of chlorpyrifos has resulted in a large volume of research on its environmental fate and ecotoxicology. In 1993 Racke noted that a survey of the published literature on chlorpyrifos resulted in nearly 12,000 citations and over 3500 proprietary research reports issued for the manufacturer, Dow AgroSciences (formally known as DowElanco and originally known as the Dow Chemical Company).

Chlorpyrifos has been used in Australia for approximately two decades and there are currently 161 products containing chlorpyrifos are registered with the National Registration Authority (NRA, 2000a). Chlorpyrifos registration has recently been reviewed under the National Registration Authority's Existing Chemical Review program (NRA, 2000b).

Chlorpyrifos is used in a formulated form as a broad-spectrum insecticide for the control of *Coleoptera, Diptera, Homoptera* and *Lepidoptera* in soil or on foliage in a wide range of crops. Crops include fruit (pome, stone and citrus fruit, strawberries, figs, bananas), nuts, vines, vegetables (potatoes, asparagus), grains (rice, cereals, maize, sorghum), cotton, mushrooms and ornamentals. Chlorpyrifos formulations are available as emulsifiable concentrates (EC), baits, granules, ultra-low volumes (ULV), liquid concentrates (LC), wettable powders (WP) and dusts (NRA, 2000b).

Chlorpyrifos formulations used in Tasmania's apple orchards include Lorsban® 750 WG and Chlorpyrifos 500 EC. The label for Lorsban® 750 WG is shown in Appendix 2. In Tasmania chlorpyrifos is registered for control of light brown apple moth, and is used for early season butt sprays for woolly aphid. Approximately six to eight sprays per season are applied under a fortnightly calendar spray schedule (Department of Primary Industries, GregAdams, *pers. comm*).

Physiochemical properties

Persistence of chlorpyrifos in the environment has been observed to vary widely, depending on site specific and climatic conditions as well as application practices. Aquatic half-lives are usually less than a few days but have been reported up to several weeks, depending on environmental conditions (Racke, 1993). Chlorpyrifos water solubility has been recorded as ranging from 0.4 mg/L (Wauchope *et al.*, 1992) to 2 mg/L (Tomlin, 1994). Chlorpyrifos is moderately hydrophobic with a partition coefficient of log K_{ow} = 5.11 (Pesticides Manual, 1994). Chlorpyrifos occurs in an non-ionised form in the environment but is strongly sorbed to soil solids and sediments and has an mean sorption coefficient (Koc) of 8498 mL/g in a variety of soils (Racke, 1993). Chlorpyrifos is very resistant to leaching in soil (Marshall and Roberts, 1978; Goss and Waucahope, 1990; Tomlin, 1994). Increased degradation of chlorpyrifos occurs with higher soil temperatures, lower organic content, high pH and free cupric ions (CHAST, 1988). Although chlorpyrifos has an intermediate vapour pressure (2×10^{-5} mm Hg at 25°C), volatilisation has been shown to be a significant mechanism of dissipation from certain environmental surfaces (i.e. plant foliage, pond water), as summarised by Racke (1993). The rate of chlorpyrifos volatilisation observed in the environment is greatly influenced by the nature of the environmental matrix in which it is present and by other partitioning processes e.g. adsorption and absorption (Racke, 1993). The physical and chemical properties of chlorpyrifos are summarised in Table 5.1.

Species sensitivity

In laboratory tests under constant exposure conditions, chlorpyrifos exhibits significant acute toxicity to many aquatic organisms. This raises a concern for potential impact to aquatic ecosystems. An extensive database on the toxicology of chlorpyrifos to aquatic and terrestrial organisms has developed since product discovery. Comprehensive reviews of chlorpyrifos toxicology have been conducted by Marshall and Roberts (1978) and Barron and Woodburn (1995). Based on laboratory LC50 data, chlorpyrifos is acutely toxic to both freshwater and saltwater fish at concentrations between 0.5 and 1000 µg/L. The most sensitive freshwater species tested is the freshwater bluegill (*Lepomis macrochirus*) with a 96 h LC50 of 1.7-10 µg/L (Barron and Woodburn, 1995). The most resistant freshwater species tested are the freshwater mosquito fish (*Gambusia affinis*), certain cyprinid species and the channel catfish (*Ictalurus punctatus*) with LC50 values greater than 100 µg/L (Barron and Woodburn 1995).

Mechanism of action

The mode of action of chlorpyrifos is non-systemic. Exposure via contact, ingestion and/or inhalation affects the nervous system by inhibiting the activity of the enzyme acetyl cholinesterase (NRA, 2000b). This enzyme is essential for the hydrolysis of acetylcholine, a neurotransmitter of nerve impulses. The direct toxicity of chlorpyrifos results from initial metabolic activation to form chlorpyrifos oxon, with the subsequent inactivation of acetylcholinesteratse (AChE) at neural junctions. Inactivation of AChE occurs by oxon phosphorylation of the enzyme

Table 5.1 Summary of physical and chemical properties of chlorpyrifos.

PROPERTY	VALUE
CAS number	2921-88-2
IUPAC name	O,O -diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate
Molecular weight	350.6
Molecular formula	$C_9H_{11}Cl_3NO_3PS$
Melting point	41 to 43.5°C[A]
Colour	white/colourless crystalline solid
Odour	odourless
Physical state	Crystalline solid
Specific gravity	1.38 g/cm^3 at 46 °C[A]
Water solubility	2mg/L at 25 °C[B]
	0.4mg/L at 25 °C[C]
	1.39mg/L at 25 °C[D]
Partition coefficient (log P_{ow})	5.11[B]
Volatility	2 27 mPA
Mean Sorption coefficient	6070mL/g[C]
	8498mL/g[D]
Dissociation constant	Chlorpyrifos does not contain any readily dissociable groups
Stability	Chlorpyrifos is stable in air (non-volatile) and is not sensitive to UV radiation. It is stable in neutral and weakly acidic solutions, but it is hydrolysed by strong bases. Chlorpyrifos is thermally sensitive to temperatures over 50 °C, and undergoes violent exothermic decomposition above 130 °C. [A]
Hydrolysis	The rate of chlorpyrifos hydrolysis increases with both pH and temperature.
	At 25 °C: pH 8 $t_{½}$ = 23 days; pH 7 $t_{½}$ = 35 days; pH 5 $t_{½}$ = 63 days
	At pH 7.0: 35 °C $t_{½}$ = 12 days; 25 °C $t_{½}$ = 35 days; 15 °C $t_{½}$ = 100 days. [A]
Aqueous photolysis	Average $t_{½}$ 30d under midsummer sunlight at ~40°N latitude. [E]
Soil photolysis	Wide range of values, from no observed degradation to $t_{½}$ 17d on moist soil. [E]
Aerobic soil metabolism (25 °C)	Variable, average $t_{½}$ 30-60 d [E]
Anaerobic aquatic metabolism (25 °C)	Variable, $t_{½}$ 40-50 d to 150d [E]

[A]National Registration Authority (2000b); [B]Tomlin (1994) ; [C]Wauchope *et al.*, (1992)
[D]Racke (1993); [E] Giesy *et al.* (1999)

active site and is rapidly reversible (Figure 5.1). In some fish species, AChE can become irreversibly inhibited through dealkylation of the phosphorylated AChE, a process that renders it resistant to hydrolysis (Chambers and Chambers, 1989) (Figure 5.1). AChE inactivation is dose- and exposure- dependent, and results in overstimulation of the peripheral nervous system and subsequent toxicity (Marshall and Roberts, 1978).

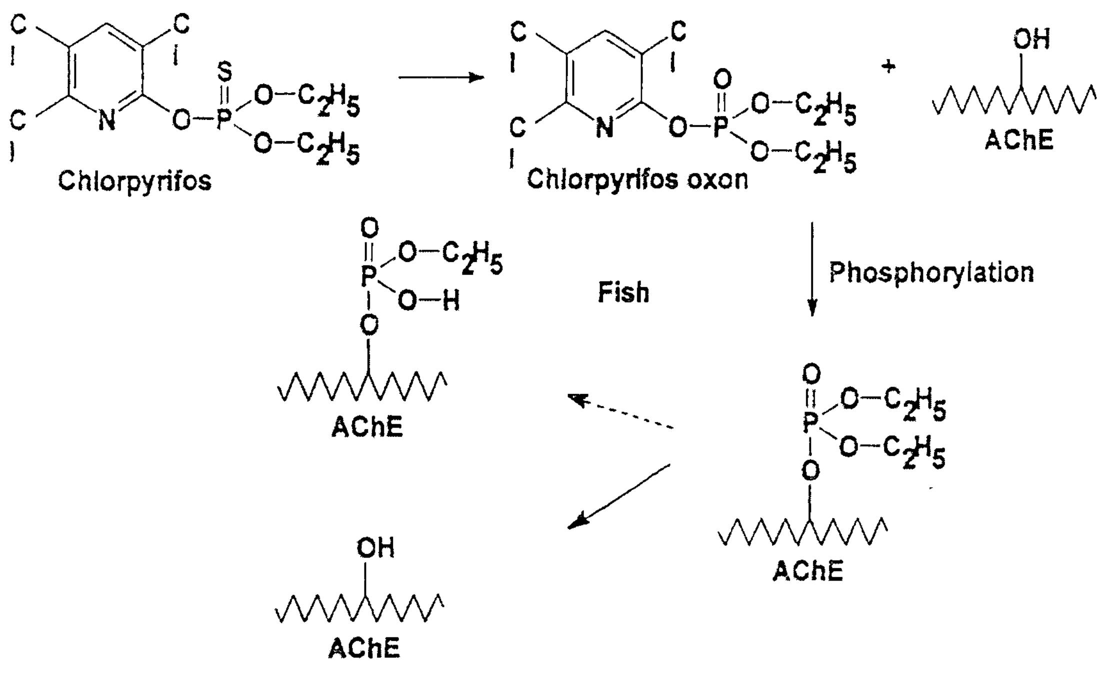


Figure 5.1 Activiation of chlorpyrifos to the oxon form, phosphorylation, and recovery of acetylcholinesterase (AChE). In some fish dealkylation of the phosphorylated AChE results in irreversible enzyme inhibition. From Giesy *et al.* (1999), pp 13

Individual and species sensitivity to chlorpyrifos is related to the presence and sensitivity of AChE to inactivation by the chlorpyrifos oxon. Species differences in behaviour, feeding ecology, ecological relationships (competitor, predator effects) and pharmokinetics, in combination with pharmacodynamic differences, result in a greater than one million-fold variation in sensitivity across species (Marshall and Roberts, 1978).

Metabolic fate and environmental behavior

Chlorpyrifos will degrade by both abiotic and biotic transformation processes in terrestrial and aquatic environments. The metabolic fate of chlorpyrifos in soil, water, plants and animals is similar, with oxidative dealkylation or hydrolysis to diethyl phosphorothioate and 3,5,6-trichloro-2-pyridinol being the major route of detoxification. 3,5,6-trichloro-2-pyridinol is conjugated as they glycosides or glucuronides in plants and animals. De-ethylation is not a major route of detoxification in mammals. Activation by desulfuration to the active acetylcholinesterase inhibitor, chlorpyrifos oxon, occurs in both animals and plants but the compound is often not detected owing to its rapid hydrolysis. Dechlorination of the chlorpyrifos ring also occurs in the environment, principally by hydrolysis (Roberts and Hutson, 1999).

The main route of chlorpyrifos metabolism in plants is via cleavage of the P-O-pyridinol function to give 3,5,6-trichloro-2-pyridinol that is then sequestered by the plant as glycoside conjugates. Chlorpyrifos is lost rapidly from leaf surfaces after its foliar application, mainly owing to volatilisation. Iwata *et al.* (1983) reported half-lives of 2.4 to 3.4 d after chlorpyrifos was applied to citrus foliage, while Racke (1993) reported half-lives of <1 to 9 d. Smith *et al.* (1967) reported very little translocation within cranberry, bean and maize plants.

The main route of chlorpyrifos metabolism in animals is cleavage to give 3,5,6-trichloro-2-pyridinol, which is then conjugated and excreted, principally in the urine (Roberts and Hutson, 1999). Proposed routes for the metabolism of chlorpyrifos in plants and animals are shown in Figure 5.2. The metabolic products of chlorpyrifos are more soluble than the parent molecule (Barron and Woodburn, 1995). Typically organophosphorous pesticides do not bioaccumulate to levels which exert toxicological effects (Ware, 2000).

The principal degradation product of chlorpyrifos in soils is 3,5,6-trichloro-2-pyridinol (Thiegs, 1966) which is then broken down to CO_2 (Bidlack, 1977). Microbial degradation of 3,5,6-trichloro-2-pyridinol results in an average soil half-life of 73 days at 25°C (Bidlack, 1976). Hydrolysis is an important inactivating reaction in soils. Hydrolytic degradation of chlorpyrifos is accelerated under alkaline conditions, although in testing of 37 different soils Racke *et al.* (1996) found that hydrolytic rate constants varied greatly (0.004 to 0.063 d^{-1}). The pH and moisture content of the soil greatly influences the

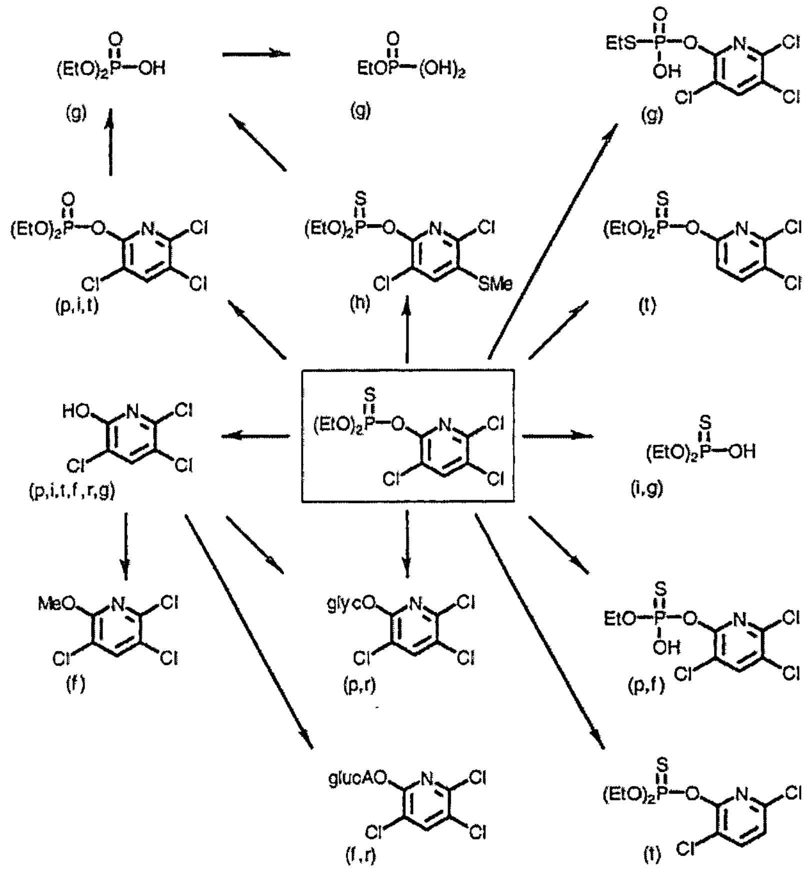


Figure 5.2 Proposed routes for the metabolism of chlorpyrifos in plants (p), insects (i), termites (t), fish (f), rats (r), goats (g) and humans (h). From Roberts and Hutson (1999), pp 241.

rate of degradation of chlorpyrifos. The reported half-lives of chlorpyrifos in soil range from 8 to 279 d with an average of 69 days (Marshall and Roberts, 1978). Typical field dissipation half-lives for soil-surface and soil-incorporated applications at agricultural use rates range from 1 to 2 weeks and 4 to 8 weeks respectively (Racke, 1993).

Hydrolysis of chlorpyrifos to 3,5,6-trichloro-2-pyridinol is the most important degradation reaction occurring in most compartments of aquatic systems. The degradation rate of chlorpyrifos in water normally follows pseudo first-order kinetics and can be dependent on temperature, light intensity, and the chemical composition of the water. The reported half-lives of chlorpyrifos associated with hydrolysis in relatively pure waters range from 10 to 100 days at temperatures between 15 and 35°C in the pH range of 5 to 9.

As for other organophosphates, the mechanism of hydrolysis and the nature of the products are pH-dependent. *O*-dealkylation predominates at acid and neutral pH values and in alkaline solution the main mechanism is cleavage of the P-O-aryl bond. The mechanism for base-catalysed hydrolysis is via S_N2 hydroxide attack on phosphorous, whereas under acid and neutral conditions the nucleophile is water and the rate is pH-independent with a half-life of 72.1 days and 72.9 days being reported at pH 5 and pH 7 respectively (Roberts and Hutson, 1999). Chlorpyrifos oxon was much more easily hydrolysed (Kenaga, 1971). Pathways for the hydrolytic degradation of chlorpyrifos in acid and base solution are shown in Figure 5.3.

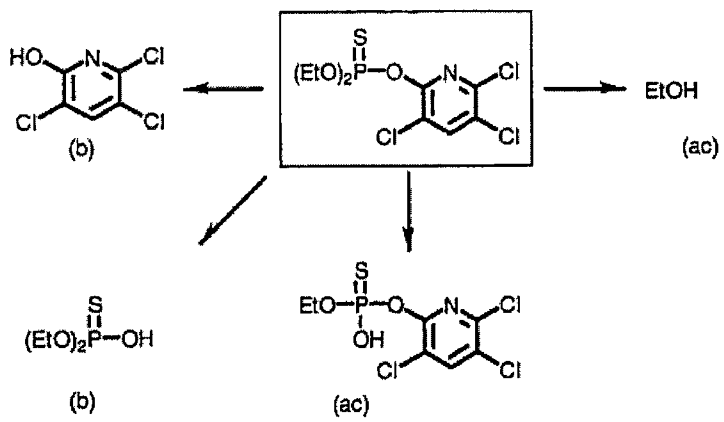


Figure 5.3 Hydrolysis of chlorpyrifos in acidic (ac) and basic (b) solution. From Roberts and Hutson (1999), pp 237.

In addition to hydrolysis, chlorpyrifos is also removed from the water column via hydrolysis, biodegradation, sorption to sediment, volatilisation and photodegradation. Dilling *et al.* (1984) reported that in surface water at 40°N latitude chlorpyrifos is degraded in the environment via photolysis with an aqueous half-life of 31 days and 3,5,6-trichloro-2-pyridinol is degraded with an aqueous half-life of about 4 minutes.

In natural waters, the apparent half-life of chlorpyrifos is much shorter (Schaefer and Dupras, 1970). Racke (1993) reported water column half lives ranging from 0.08 to 5 days and sediment half lives of 0.8-16.3 days from a number of field investigations. The more rapid decrease in concentrations under field conditions is likely caused by additional dissipation and degradation forces such as volatilisation and surface- and metal-catalysed hydrolysis that operate in natural waters and sediments and are not assessed under laboratory conditions (Giesy *et al.*, 1999).

Macalady and Wolfe (1985) found that chlorpyrifos in the sorbed state is much less (approximately 10-fold) susceptible to base-catalysed hydrolysis than dissolved chlorpyrifos. Racke *et al.* (1996) also found the rate of chlorpyrifos hydrolysis in most soils was significantly slower than that observed in water maintained at a similar pH. These results both indicate a general retardation of (presumably base-catalysed) hydrolysis of chlorpyrifos in soils due to sorption onto organic and mineral components in soils and sediments (Racke *et al.*, 1996). Chlorpyrifos oxon, the highly toxic activation product of chlorpyrifos, is very unstable in water and unlikely to be encountered.

The general conclusion from this review of the literature on environmental fate and metabolism is that none of the transformation products of chlorpyrifos are likely to be sufficiently toxic or persistent in the environment to be of toxicological concern (Giesy *et al.*, 1999).

THE CONCEPTUAL MODEL

The conceptual model describes the approach that will be used for the risk analysis phase. It is a graphical summary of the risk hypotheses being assessed (US EPA, 1992a). (Figure 5.3). It contains uncertainty, however, it is taken as an operating tool in the absence of more complete knowledge.

Chlorpyrifos applied by airblast/airshear sprayers is distributed throughout the orchard canopy, onto the soil and into the atmosphere. Spray landing in the orchard canopy is effective against target pests but also impacts on populations of beneficial insects. A notable exception is the predatory mite, which is resistant to organophosphate sprays. Spray landing on the soil is quickly and effectively bound to soil and organic particles. With a mean soil sorption coefficient of 8498 mL/g (Racke, 1993) chlorpyrifos is relatively resistant to soil leaching, so that aquatic contamination via leaching to groundwater is negligible. Given its propensity for sorption, chlorpyrifos also would not be expected to migrate over the soil surface (runoff) with moving water (Racke, 1993). As described in Chapter 4, chlorpyrifos is ranked as having a small pesticide leaching potential, medium adsorbed runoff potential and medium solution runoff potential (Goss and Wauchope 1990; Wauchope *et al.*, 1992).

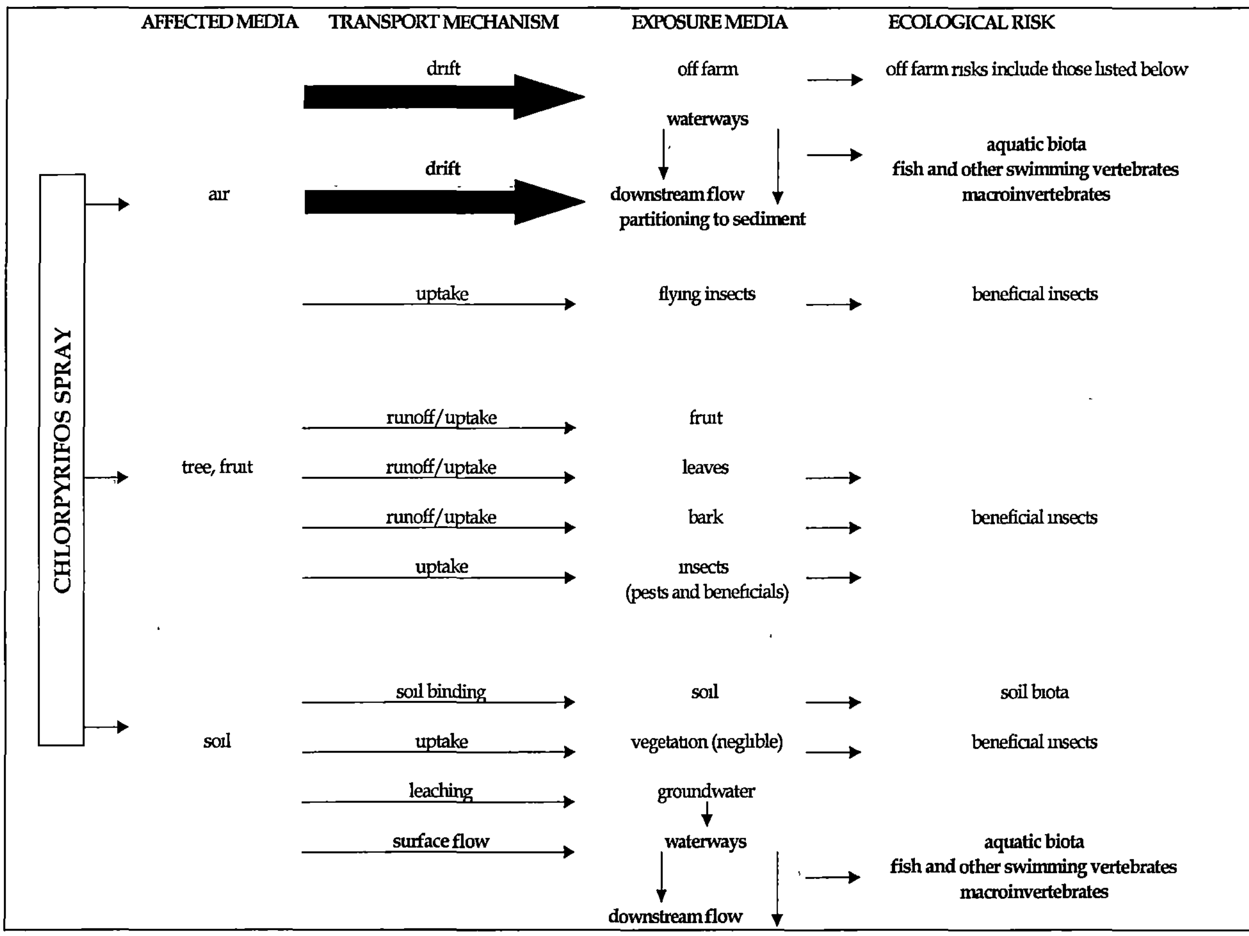


Figure 5.4 Conceptual model for chlorpyrifos sprayed onto an orchard adjacent to Mountain River. The conceptual model represents assumed interactions of chlorpyrifos sprays in the environment

Because of the strong soil and organic binding properties of chlorpyrifos, and the spray application method, aerial drift is expected to be the most significant mechanism of off target chlorpyrifos transport into waterways in the Huon Valley. This pathway is emphasised in the conceptual model.

REVIEW OF ASSESSMENT ENDPOINTS RELEVANT TO THIS PROJECT

Assessment endpoints are defined as explicit expressions of the environmental value to be protected" (US EPA, 1992a). On some occasions, the concept of assessment endpoint may be difficult to understand. An alternate is to describe the situation as a hypothesis to be tested. For example, an assessment endpoint such as "Maintenance of fish growth rates in Clear Creek" could be expressed as the hypothesis "Zinc in Clear Creek affects fish growth rates." This approach has been adopted in the Methodology for Aquatic Ecological Risk Assessment used by the Water Environment Research Foundation (Parkhurst *et al.*, 1994).

The assessment endpoints represent the social values to be protected, and serve as a point of reference for the risk assessment. Often societal goals are presented in ambiguous terms such as protection of endangered species, protection of a fishery, or the even more vague 'preserve the structure and function of an ecosystem' (Landis and Yu, 1999). This is clearly demonstrated in the espoused aim of catchment management in the Huon Valley: *"To protect the ecological balance of the Huon Catchment through sustainable use, development and management of natural resources."* (Huon Healthy Rivers Project, 1997). Such a statement is best regarded as a "mission statement" for the catchment rather than a defined and tangible objective. To define and measure "ecological balance" is a scientific impossibility. "Ecological balance" is a term like "ecosystem health" which is ecologically unrealistic (Suter, 1993b; Landis *et al.*, 1994). Such conceptual anomalies in environmental assessment stem from analogies with human health assessment (Calow 1992; Calow 1995; Renner 1996).

Identifying quantitative assessment endpoints from environmental "mission statements" is one of the challenges faced by risk assessors. The practical difficulties of generating quantitative assessment endpoints were all too clearly highlighted in Chapter 3, where only one out of six assessment endpoints could fulfil Suter's criteria for good assessment endpoints (Suter, 1990). As a basis for formulating assessment endpoints for the chlorpyrifos aquatic risk assessment, it was valuable to review assessment endpoints chosen for other aquatic risk assessments.

In an ecological risk assessment of chlorpyrifos in North American aquatic environments, Giesy *et al.* (1999) chose "population persistence (function of survival, growth and recruitment)" as their assessment endpoint for fish populations. They chose a generic assessment endpoint because their assessment addressed a broad range of ecosystem types and exposure patterns. This assessment endpoint did not explicitly address ecosystem structure or function, but the implication was that ecosystem integrity would be protected if fish populations and invertebrate communities were protected.

Giesy *et al.* (1999) chose "community productivity" as their assessment endpoint for invertebrate populations. They noted that for most invertebrates, even changes at the population level may not be ecologically, economically, or socially significant, except in the case of endangered species, if the overall productivity of the invertebrate community and its ability to support higher trophic levels are maintained.

In a comprehensive site specific risk assessment for Clinch River, Tennessee, the assessment endpoint for the fish was "No reduction in species richness or abundance or increased frequency of gross pathologies in fish communities resulting from toxicity" (Suter *et al.*, 1999). The risk assessors focused on the fish community as an endpoint entity because it was considered ecologically and socially important, susceptible to the hazard and on a scale appropriate to the site. The societal importance was due to recreational fisheries. The ecological significance came from the fact that fish are a major nutrient pool in temperate reservoirs. In the same study, the assessment endpoint for the invertebrates was "a 20% or greater reduction in species richness or abundance of benthic macroinvertebrate communities resulting from toxicity." (Jones *et al.*, 1999).

In a regional risk assessment for the Willamette and McKenzie Rivers, Oregon, USA, Landis *et al.*, (in press) chose a generic assessment endpoint based on stakeholder values. The generic assessment endpoint was that "There are sufficient numbers of desirable fish to support an active recreational fishery." In addition, specific quantitative assessment endpoints were set for important fish species e.g. For summer steelhead the assessment endpoints were: No reduction of allowable catch of sport fish; Population meets Department of Fish and Wildlife basin fisheries plan (maintain a potential sport catch of 250 in the mainstem above Willamette Falls); and maintain an annual catch of 1200 on the McKenzie River.

These three studies illustrate different approaches for definition of assessment endpoints. Only Landis *et al.,* (in press) put quantitative figures on the assessment endpoints. They were able to do this because the regional regulatory authority had already invested considerable time into quantifying the fishery; and this is to be expected as they were dealing with a popular recreational fishery with large fish species. Landis *et al.,* (in press) only established assessment endpoints for the fish species that were recognised as being important to the stakeholders. Quantitative criteria were not set for unfished species such as the lamprey. These species were ignored in the risk assessment.

Suter *et al.* (1999) took a different approach. They considered all fish species as being important and did not establish quantitative criteria for particular species. Instead, they chose a level of effect on the assessment endpoint properties to provide a benchmark for design and interpretation of studies. A 20% or greater reduction in one of the endpoint properties measured in the field, or a 20% reduction in survivorship, growth, or reproduction in a toxicity test is considered potentially significant. This was a policy judgement concerning values, not science (Suter *et al.,* 1999).

Giesy *et al.* (1999) did not explicitly state any quantitative basis for their assessment endpoint, but in their risk analysis they constructed exceedence profiles and used the 10th centile of species sensitivities as the assessment endpoint. Exceedence profiles were constructed for selected sites by combining the frequency distributions for the probability of a concentration being exceeded with the probability of a species being affected to generate a graphical expression of the percent exceedence of LC50/EC50 values against the probability of a species being affected (Giesy *et al.,* 1999). Giesy *et al.* (1999) state that an advantage of the probabilistic methods applied is that the analysis is independent of the *a priori* selection of acceptable probabilities of exposure and response for the decision-making process.

REVIEW OF MEASUREMENT ENDPOINTS RELEVANT TO THIS PROJECT

Measurement endpoints are the parameters that are actually quantified as indicators of the effects of the stressor (US EPA, 1996). Although all risk assessments must have assessment endpoints, there may not necessarily be measurement endpoints (Suter, 1990). In some cases, measurements may be unnecessary or impossible. For example, if the assessment endpoint for an assessment of a proposed power plant is the probability of exceeding an air quality standard, then there is no environmental response to measure and, assuming that good local meteorologic data and source terms are available, models based on atmospheric theory are adequate predictors. In this case the assessment is based on theory and assumptions about the relationship between the hazard and the assessment endpoints. In the absence of measurement endpoints, the assessment is limited by uncertainty and can only be used to suggest areas worthy of study rather than actually predicting effects (Suter, 1990).

In the chlorpyrifos risk assessment conducted by Giesy *et al.* (1999) LC50 data was used as the main source of effects data. Suter *et al.* (1999) also used single chemical toxicity data but considered four other distinct lines of evidence which were combined in a weight of evidence approach for the final risk conclusions. In addition to single chemical toxicity tests, they also considered fish community surveys, fish body burdens, toxicity tests of ambient waters and suborganismal bioindicators. The risk assessment being undertaken by Landis *et al.*, (in press) is not yet complete. They plan to calculate condition factors for individuals using length and weight measurements, and calculate organosomatic indices for autopsied fish to identify stress-related symptoms. If, or how, this work will relate to the quantitative assessment endpoints that they have established is not clear.

RISK ANALYSIS PLAN

An ecological risk assessment for chlorpyrifos in Mountain River catchment is a retrospective risk assessment. As such, environmental exposure data forms a critical component of the risk analysis. Typically, risk assessments of pesticides involve the use of pesticide fate models to estimates environmental exposures. These models include

Ground Loading Effects of Agricultural Management Systems (GLEAMS), Exposure Analysis Modeling System (EXAMS), Leaching Estimation and Chemistry Model-Pesticides (LEACHEM), Pesticide Root Zone Model (PRZM), and other published models (e.g. Jury *et al.*, 1984; Mackay *et al.*, 1986; Taylor and Spencer, 1990; Leonard, 1990; Mackay 1994; Shukla, 1996).

At the start of the project, modeling was considered as option for estimating environmental exposures, but it was felt that risk outcomes from real-world data rather than theoretical maximums could be used with greater confidence. In addition, one of the objectives of this project was to collect field data describing the extent of pesticide contamination in Huon Valley waterways. No monitoring of agricultural pesticides had been conducted in the Huon Valley; the only published pesticides monitoring data for Tasmania was for forestry areas (Barton and Davies, 1993; Davies and Cook, 1993; Davies *et al.*, 1994a) and some monitoring of chlorothalonil in NE Tasmania (Davies, 1984).

Field monitoring of chlorpyrifos in Mountain River (Chapter 6) was undertaken with the premise that concentrations and temporal nature of the data would be considered in light of the already established toxicology of chlorpyrifos. Existing knowledge of chlorpyrifos toxicology was used to assess the potential for adverse impacts in Mountain River using probabilistic methods (Chapter 7) and site-specific field studies (Chapter 8). The specific assessment endpoints chosen for probabilistic and field assessments are described in the relevant chapters.

PROJECT WORK

CHAPTER 6. CHARACTERISATION OF ENVIRONMENTAL EXPOSURES

Chapter Background: This chapter describes characterisation of the environmental exposures of chlorpyrifos occurring in Mountain River. Seasonal and pulse exposures are described, and the levels measured in Mountain River compared with the spray drift model, AgDRIFT™ and other chlorpyrifos monitoring programs.

In smaller tributaries such as Mountain River, the concentrations of pesticide are strongly skewed distributions and there is great temporal variability (Richards and Baker, 1993). A temporal description of the exposure profile is particularly important for a toxicant such as chlorpyrifos which is acutely toxic (Giesy *et al.,* 1999). A large part of the fieldwork described in this chapter was devoted to characterising the temporal nature of chlorpyrifos dissipation in Mountain River.

This chapter has been submitted as a paper in the international journal *Environmental Monitoring and Assessment* with the following reference: Walker R Brown PH Nowak BF Dorr G. in press. Chlorpyrifos aquatic concentrations in an intensive orcharding region - pulse, modeled and seasonal exposures.

Abstract

The organophosphate insecticide chlorpyrifos is commonly applied in apple orchards, and there is potential for spray drift from orchard sprayers to contaminate nearby waterways. Pulse exposure monitoring for a routine chlorpyrifos spray application in an adjacent orchard was conducted on two occasions in Mountain River, southern Tasmania, Australia. Pesticide concentrations peaked at an average of 0.147 μg/L approximately 10 minutes after spraying commenced. Concentrations above 0.01 μg/L persisted for less than 40 minutes after spraying. Three hours after spraying chlorpyrifos concentration at the site exposed to spray drift was 0.002 μg/L, the limit of

detection by GC-MS/MS. Pesticide concentrations measured downstream peaked at an average of 0.03 μg/L. These results have implications for ecological risk assessments that use toxicological parameters based on a minimum of 24 or 48-hour exposures. The practical logistics of pulse exposure sampling are complex and it was found that simulations using the spray drift modeling program, AgDRIFT™, were comparable with field results so that modeled pulse exposure data could justifiably be used in lower tier risk assessments. Low levels of chlorpyrifos were intermittently detected during seasonal monitoring in Mountain River.

INTRODUCTION

Chlorpyrifos (*O,O-diethyl O-(3,5,6-trichlor-2-pyridyl) phosphorothioate*) is an broad spectrum organophosphate insecticide, with a wide variety of applications for different pest control situations (Havens *et al.*, 1998). Contamination of waterways by chlorpyrifos is potentially a serious environmental issue, given that chlorpyrifos is highly toxic to many aquatic species (Marshall and Roberts, 1978; US EPA, 1989; Tomlin 1994; Barron and Woodburn, 1995). One of the greatest limitations in exposure assessment is the availability of empirical information on environmental concentrations (Giesy *et al.*, 1999). Additional information to describe environmental exposures, duration of pulses, and short-term as well as seasonal variation in surface water is needed.

In Tasmanian apple orchards liquid and wettable granule formulations of chlorpyrifos are applied for control of light brown apple moth using airblast/airshear orchard sprayers. Spray drift from airblast sprayers can result in off target movement of pesticide. Aerial movement of chlorpyrifos is recognised as one of the main dissipation pathways (Racke, 1993) but chlorpyrifos spray drift onto flowing water has not been previously studied. Spray drift has not been included in previous risk assessments because of difficulties in accounting for localised factors, although it is acknowledged that spray drift can be important in transient exposures of aquatic organisms to chlorpyrifos (Giesy *et al.*, 1999).

Although pulsed exposures commonly occur in aquatic ecosystems, limited information is available for evaluating the effects of pulsed exposures relative to continuous exposure (Giesy *et al.*, 1999). Analysis of chlorpyrifos concentrations measured in Lake Erie, one of the largest chlorpyrifos exposure data sets available, found that 85% of the reported pulses lasted 48 hours or less (Giesy *et al.*, 1999). Toxicity profiles observed during prolonged constant concentration exposure in the laboratory may not accurately reflect toxicological responses to pulsed and rapidly declining concentrations in water under field conditions (Barron and Woodburn, 1995).

The aim of this research was to measure the extent and duration of the chlorpyrifos pulse in a river system when an orchard block adjacent to a flowing river was sprayed, and to gain a better understanding of the concentration fluxes occurring in aquatic ecosystems in orcharding regions. As noted by many authors (e.g. Spalding and Snow, 1989; Davies et al., 1994; Kreuger, 1995; Liess *et al.*, 1999) exposure of stream biota to pesticides typically occurs by a combination of short-term spikes of high concentration following spraying and rain events, and longer term chronic exposure in streams that drain areas sprayed repeatedly or sprayed with more persistent materials. In addition to the pulse exposure monitoring, intensive seasonal monitoring was conducted in Mountain River over two seasons to gain an estimate of the chronic chlorpyrifos exposures occurring in orcharding districts.

MATERIALS AND METHODS

All sampling for this work was conducted in Mountain River, a small perennial river flowing through the Huon Valley region, Tasmania, Australia. The Mountain River catchment is 186 square kilometres (Davies, 1988). The intensity of orcharding in this small catchment with many orchards located directly adjacent to the river and relatively low summers flow combine to make this waterway a representative 'worst case scenario' for chlorpyrifos contamination of waterways in orcharding districts.

Pulse exposure sampling

Sampling site

Pulse exposure sampling was conducted in Mountain River at one of the largest commercial apple orchards in the Huon Valley. The block being sprayed was approximately 4.5 ha in size and planted with 4-year-old centre leader trees (Pink Lady and Red Delicious varieties). Spacing between rows was approximately 4.5 m, and trees averaged 2.5 to 3 m in height. The canopy was relatively open.

Sampling was conducted at sites in Mountain River, along the perimeter of the orchard block. A simplified schematic of the orchard block and the water sampling sites is shown in Figure 6.1. At the target site the edge of the orchard block was 10 m from midstream.

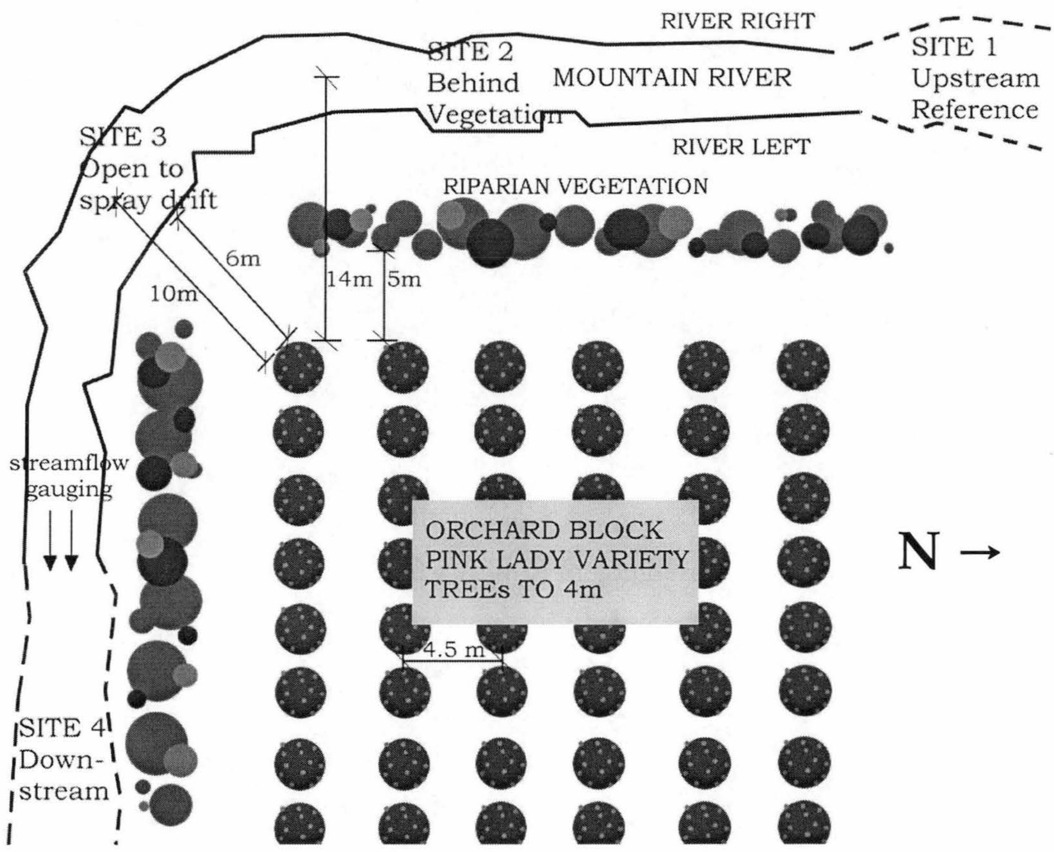


Figure 6.1 Pulse exposure sampling sites in Mountain River. The schematic diagram shows orchard layout and sampling sites for pulse exposure sampling.

Sampling sites were:

Site 1 -reference site, located upstream from all sprayed blocks. The reference site was approximately one kilometre above Site 3 (target site).

Site 2 - behind vegetation. Spray drift reaching this site had to pass through, over or around vegetation buffer.

Site 3 - target site. Open to spray drift with no buffering from streamside vegetation. Represents a "worst-case scenario" for spray drift contamination of waterways in orcharding regions.

Site 4 – downstream site, located approximately 600m downstream of Site 3. (In 1999 sampling the downstream site was located approximately 200m downstream of Site 3).

Streamside vegetation was dense, typical of the unmanaged vegetation that grows along many waterways in the Huon Valley. In addition to native grasses, *Acacia* species (5-10 m) and *Eucalyptus* species (to 25 m), there were many weed species including willows (to 15 m), hawthorns (to 5m), blackberries, and introduced grasses. Adjacent to the river near Site 4, there was an avenue of poplars reaching up to 30 m.

Sampling protocol

Pulse exposure sampling was conducted twice at the site; 5 January 1999 and 12 January 2000. In the first experiment, Lorsban® 500 WP was applied at the rate of 1 kg/ha (500 g/ha active ingredient.). The sprayer was a Silvan Electromiser delivering 250 L/ha. The following season, the formulation had been replaced with Lorsban® 750 WG and this was applied at the rate of 660 g/ha (495 g/ha active ingredient). The sprayer was a Silvan Cropliner delivering 1500 L/ha. It took approximately one hour to spray the target block.

Water and sediment samples were taken by assistants standing in thigh-depth water, in sections of typical stream flow (i.e. riffles or still eddies were not sampled). One litre water grab samples were collected in solvent-rinsed amber glass sampling bottles with teflon-lined screw tops. Bottles were filled 10 cm below the water surface. Sediment grab samples (approximately 100 g) were collected in glass jars with foil lined screw tops. After sample collection water bottles and sediment jars were stored on ice. Upon return to the laboratory samples were stored at 2°C prior to extraction. All samples were extracted with 48 hours of collection. Baseline samples were collected at all sites before spraying commenced. Sampling schedules at all sites commenced with the start of spraying (0 min). In the 1999 sampling 3 samples were collected at Site 1, 6 at Site 2, 14 at Site 3 and 8 at Site 4 over a two hour intensive sampling period. In the 2000 sampling 3 samples were collected at Site 1, 13 at Site 2, 22 at Site 3 and 15 at Site 4 over a three hour intensive sampling period.

A stream flow gauging was conducted immediately prior to commencement of spraying, and at 120 min. An Ott Meter C31 with a current meter monitor and calibrated wading rod was used for the gauging. Stream flow was calculated using Hydrol Time Series Manager Vers. 3.6.2.0 software (Hydro-Electric Corporation, Hobart, Tasmania, Australia).

Local wind speed and direction were also measured throughout the course of the experiment. Wind speed was measured every 5 min using a handheld anemometer. Wind direction, as estimated by compass alignment with a wind tether, was recorded at the same time.

Chlorpyrifos extraction and analysis

Extraction from water: 1000 mL water spiked with 100 μL of Base Neutral Surrogate (Ultra Scientific, North Kingston, RI, US) was extracted three times using 90 mL pesticide grade dichloromethane, dried through Na_2SO_4 (anhydrous) and evaporated to 1000 μL under N_2 atmosphere. Extraction recovery from water samples was greater than 75% (S.D.±21%) (see Appendix IV).

Extraction from sediment: sample was mixed thoroughly and sticks, leaves, root matter and rocks discarded. A sub-sample was taken to determine % dry weight of the sediment. Approximately 30g of sample was spiked with 100 μL of Base Neutral Surrogate (Ultra Scientific, North Kingston, RI, USA) mixed with Na_2SO_4 (anhydrous) until freeflowing, and extracted three times using 90 mL pesticide grade pesticide grade dichloromethane:acetone (1:1, v/v). Between extractions samples were placed on a rotary shaker for 15 min. Extract was dried through Na_2SO_4 (anhydrous) and evaporated to 1000 μL under N_2 atmosphere. Extraction recovery from sediment samples was greater than 46% (S.D.±14%) (see Appendix IV).

Blank (tapwater and uncontaminated sediment) and blank recovery samples were extracted and analysed for every twenty samples. Two replicates of water samples collected in November 1999 were analysed by Analytical Services Tasmania, Government laboratory as a quality assurance measure. Chlorpyrifos spike for recovery analysis was 10 μg per sample. Chlorpyrifos standard (99.8% purity) was obtained from the Australian Government Analytical Laboratory.

Analysis for all samples was by GC-MS/MS using conditions that were optimised for detection of chlorpyrifos and the surrogate and the internal standard, *n*-pentadecane. Analysis was using a Varian Saturn 4D iontrap GC-MS. Gas chromatography conditions were as follows: 30-m VA-5MS capillary column, 0.25mm i.d., 0.25 μm film thickness and helium carrier gas at a constant flow of 1.0 mL/min. The temperature program was as follows: injector temperature 280°C, initial temperature 40 °C, hold 20 min, 10 °C/min to 160 °C, hold 9 min, 20 °C/min to 280 °C, hold 6 min. MS/MS conditions were: segment 1 0-14 min in electron ionisation mode and segment 2 14-20 min in MS/MS mode. The ions monitored for chlorpyrifos were 314, 286, 258 m/z. The method detection limit was 0.002 μg/L.

For all chlorpyrifos quantities discussed, the results were corrected for surrogate recovery. Correction for recovery improves data consistency and facilitates comparison between sites and times. The use of recovery corrected results in risk assessments gives greater confidence in the risk outcomes.

For the purpose of presentation all results for water samples below the limit of detection (LOD) were plotted as half the LOD (0.001 μg/L). Non-detects (nd) for sediment samples were recorded as such.

Seasonal exposure sampling

Sampling sites

Five sampling sites in Mountain River were chosen for seasonal monitoring. The sites were chosen to match the gradient of orcharding activity in the catchment, with no orcharding in the upper reaches of the catchment and intensive orcharding in the lower reaches of the catchment (Figure 6.2).

The sampling sites shown in Figure 6.2 are:

1) Top Ford. No agricultural or forestry activity upstream of this site.

2) Bridge at Sawyer's Creek. Orchard immediately adjacent to Mountain River.

3) Crabtree Road. Below influx of Sawyers Creek and Dip Creek.

4) Bridge at Lucaston Road. Below influx of Parsons Creek and Fourteen Turn Creek.

5) Bridge at Ranelagh. Below influx of unnamed natural and artificial drainages. Last site suitable for monitoring before Mountain River joins Huon River.

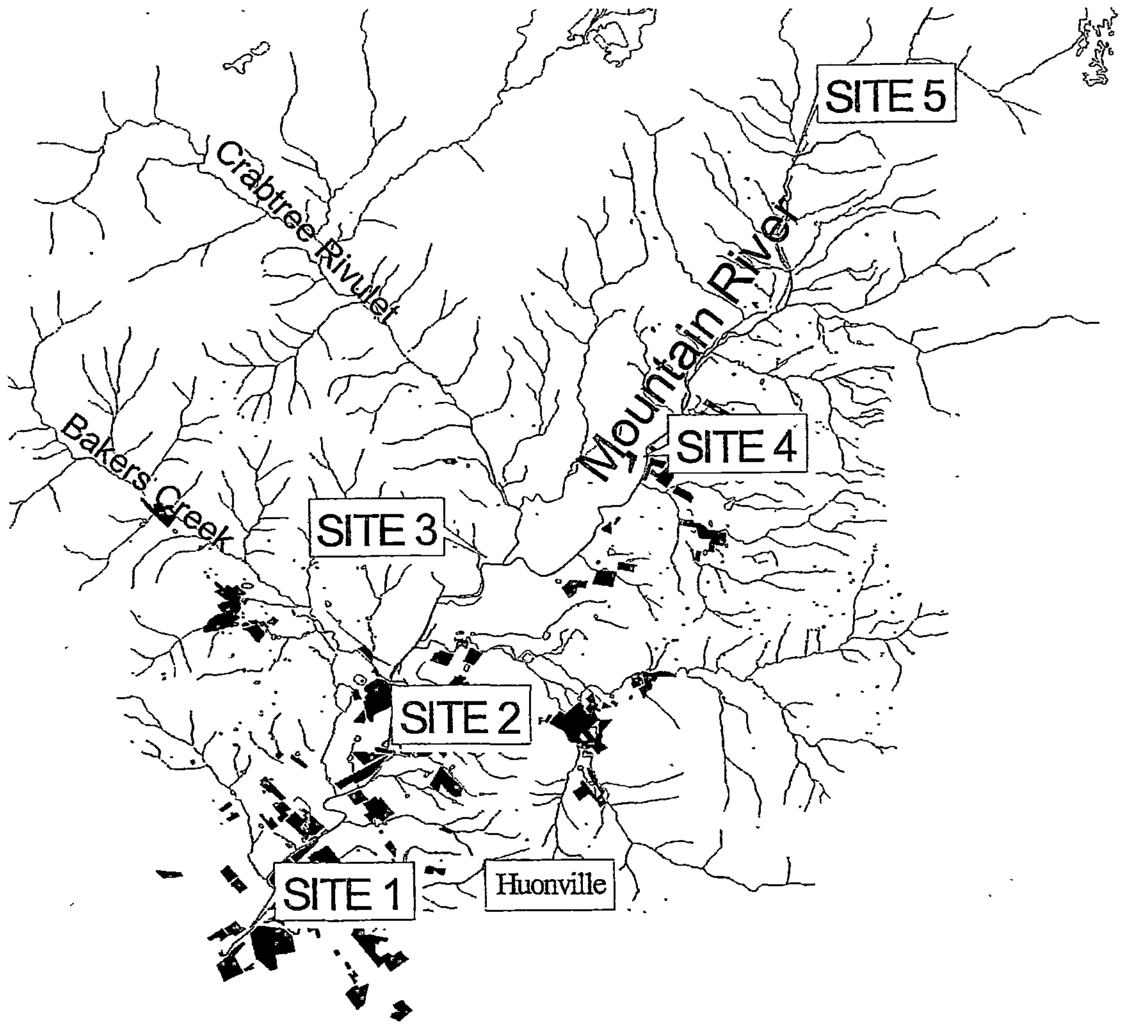


Figure 6.2 Seasonal sampling sites in Mountain River. The catchment map shows drainage lines, seasonal exposure sampling sites and location of orchards (shaded in black) in the Mountain River catchment.

Sampling protocol

The five sites were sampled over the 1997/98 summer and the 1998/99 summer. Sites were sampled at approximately fortnightly intervals during the chlorpyrifos spray season (October to February). At each site 1 L water grab samples were collected in amber glass sampling bottles with teflon-lined screw tops. Bottles were filled at approximately 10 cm below the water surface. River level was measured against an indicator at each site. Sediment grab samples (approximately 100 g) were collected in glass jars with foil lined screw tops. Crabtree and Top Ford sites had a rocky substrate and it was not possible to collect sediment at these sites. After sample collection water bottles and sediment jars were stored on ice. Upon return to the laboratory samples were stored at 2°C prior to extraction.

Water quality measurements

There was limited baseline water quality data available for Mountain River and for the 1997/98 summer routine water quality measurements were conducted at each site. Temperature, conductivity and dissolved oxygen were measured at each site using WTW meters. pH was measured using a Mettler pH meter. Turbidity was measured using a Model 21OOP Turbidmeter.

Water quality parameters were all within the acceptable range for Tasmanian streams and routine water quality monitoring was not continued in the 1998/99 summer.

Chlorpyrifos extraction and analysis

The methods used for extraction and analysis of seasonal water samples were the same as those described above for pulse exposure sampling.

RESULTS

Pulse exposure sampling

Surface water concentrations

In the 1999 sampling chlorpyrifos was detected in the water 2 min after spraying commenced (Figure 6.3). Concentrations at the target site (Site 3) peaked at 10-20 min after spraying commenced with a maximum concentration of 0.129 μg/L. The maximum concentration reached at Site 2 was 0.045 μg/L, approximately three times less than the maximum at Site 3. The pesticide pulse was detected downstream at approximately 20 min after spraying commenced, and peaked at 0.030 μg/L.

In the 2000 sampling chlorpyrifos was detected at the upstream site throughout the sampling period, indicating that pesticide from upstream orchards was moving through the sampling area. Contamination from upstream would explain the low concentrations detected immediately prior to the commencement of spraying. Concentrations at the target site peaked at 10 min after spraying commenced, with a maximum concentration of 0.164 μg/L (Figure 6.3). After 40 min, concentrations had dropped to 0.003 μg/L and continued close to the limit of detection for the duration of sampling. The maximum concentration measured at Site 2 was 0.014 μg/L, approximately ten times less that the maximum at Site 3. Levels at Site 2 remained slightly higher than at Site 3 after 40 min. Site 2 was located within a section of the river with less stream flow, which explains why pesticide dissipated more quickly at Site 3 than at Site 2. The pesticide pulse was detected downstream at approximately 80 min after spraying commenced. The maximum concentration of the downstream pulse was 0.033 μg/L measured at 140 min after spraying commenced. This was much later than for the 1999 downstream pulse measurement, but this was because the downstream sampling was moved approximately 400 m further downstream to reduce the risk of aerial drift contamination of the site.

The results from the 1999 and 2000 sampling were consistent, particularly considering the extent of factors in the field that could influence results. All comparable results are of the same order of magnitude, and the timing of peak exposures was similar. Of particular interest was the timing of peak concentrations at Site 3 that occurred 10 min after spraying commenced on both sampling occasions. The maximum concentration measured in 1999 was 0.129 μg/L and 0.164 μg/L in 2000. It is possible that maximum concentrations in 1999 were similar to the 2000 levels were also reached, but they were not detected due to the lower frequency of sampling. The sampling intensity was increased in 2000 in order to detect peak concentrations, particularly in the first 40 min after spraying commenced. The 2000 results emphasise the temporal nature of chlorpyrifos concentrations in flowing streams. Over a 2 min sampling interval concentrations varied by more than five-fold.

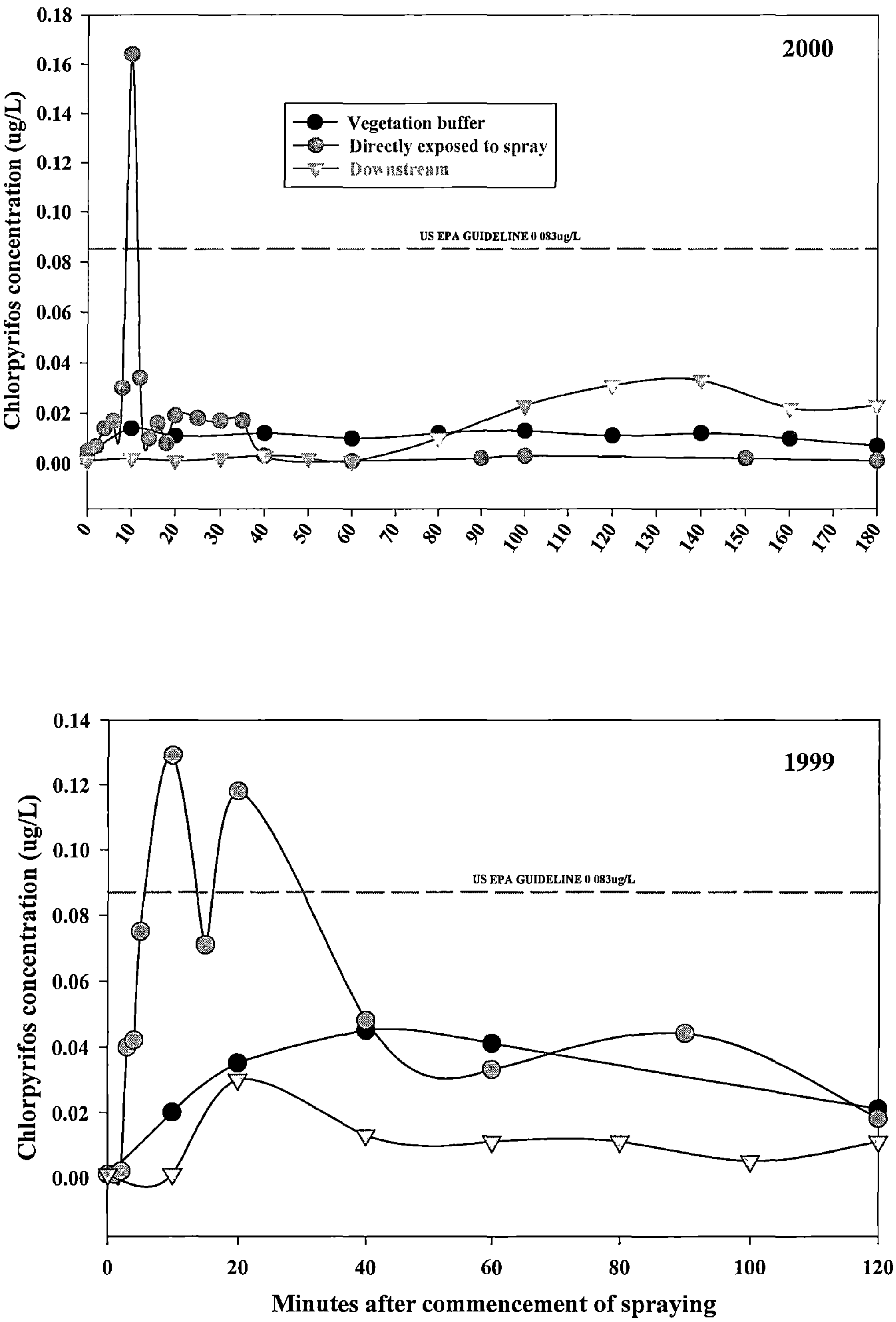


Figure 6.3 Chlorpyrifos surface water concentrations (µg/L) measured during pulse exposure sampling in 1999 and 2000.

Wind speed and direction

During both experiments the prevailing wind direction was N to NE which blew spray drift directly onto the river. The wind speed was light (0.1-3.8 m/s) for the duration of both experiments (Appendix 3).

Stream flow

In 1999 the mean flow velocity was 0.30 m/sec. The distance between Site 3 and Site 4 was approximately 200 m; water flowing directly downstream would take approximately 11 min to reach Site 4. In 2000 the mean flow velocity was 0.18 m/sec. The distance between Site 3 and Site 4 was approximately 600 m; water flowing directly downstream would take approximately 55 min to reach Site 4. In reality it is difficult to predict downstream transport times on the basis of streamflow alone due to the effect of localised currents and eddies along the river.

Sediment concentrations

Mountain River has a rocky substrate and sediment samples were difficult to collect. At Site 3 the substrate consisted of river rocks and it was not possible to collect enough sediment for analysis. The variability in the sediment results (Table 6.1) may stem from the fact it was difficult to collect much sediment at any of the sampling sites, and the samples analysed are a composite of all sediments at that locality in the river.

Table 6.1 Sediment concentrations (ng/g dry wt) measured in Mountain River during chlorpyrifos pulse exposure sampling.
nd=non detect. na=not sampled. [a]Time (min) measured from the started of spraying

Sampling date	Time[a] (min)	Sediment concentration of chlorpyrifos (ng/g dry wt)		
		Upstream site Site 1	Vegetation buffer Site 2	Downstream site Site 4
Jan 5, 1999	0	nd	0.5	nd
	60	na	1	0.5
	120	na	2.4	0.1
Jan 12, 2000	0	0.9	0.1	0.2
	60	na	0.4	0.7
	120	na	0.1	0.3
	180	na	na	0.2

Chlorpyrifos has a mean sorption coefficient (Koc) of 8498 mL/g and is strongly adsorbed by soil and sediment (Racke, 1993). Sorptive equilibrium in soil-water systems is reached quickly, generally within 2-4 hours (Felsot and Dahm, 1979); adsorptive equilibrium may be reached as quickly as 15 minutes in sediment/water systems (Macalady and Wolfe, 1985). The results collected for Mountain River sediments are not adequate to describe chlorpyrifos partitioning, but when compared against the values for toxicity of sediments the concentrations measured in Mountain River are very unlikely to be of any toxicological significance (Table 6.2).

Table 6.2 Concentration ranges for chlorpyrifos toxicity of sediments

Source: Brown *et al.* (1997) cited in Giesy *et al.* (1999).

Whole sediment chlorpyrifos concentration	Potential for adverse effect
< 100 ng/g	Not probable
100 to 500 ng/g	Possible
> 500 ng/g	Probable

Comparison of field data with AgDRIFT™

Currently there is limited understanding of how pesticides dissipate instream, but it is an area of increasingly important research. The AgDRIFT™ model ™ (Spray Drift Task Force. 1998. Ver 1.07. Missouri, USA) incorporates a stream assessment option for estimating downstream pesticide concentrations resulting from spray drift onto the river. This model was developed by the Spray Drift Task Force in response to a directive from the USEPA to conduct a series of field and laboratory studies to develop a database and spray drift model to assist in the registration of agrochemicals. The Spray Drift Task Force committed some $US 20 million to the project to develop a model to assist regulatory authorities assess off target risks based on realistic input parameters instead of prescriptive threshold values. The model, AgDRIFT™, is primarily designed as an aerial predictive model for risk assessment purposes.

AgDRIFT™ utilises a three-tier approach. Tier I is designed to "yield conservative exposure estimates for downwind deposition values...as a preliminary screen for aerial, ground and orchard airblast spraying" (Teske et al., 1997). Tier II and Tier III permit increasing assess to more model details for aerial spraying only. Input data concerning application, meteorology and the environment can be included. As the level increases, the level of input data increases. At this stage AgDRIFT™ can only calculate Tier I assessments for airblast applications, and there is no facility for Tier II and Tier III airblast applications.

Tier I simulations for an airblast sprayer estimate that for a waterbody 7 m wide, 0.7 m deep (approximate to Mountain River average) an initial average concentration of 0.168 µg/L for a.i. applied at 0.495 kg/ha. This value compares very well with the peak concentration of 0.164 µg/L recorded at Site 3.

AgDRIFT™ has the facility to introduce a pond or wetland at various downwind distances to determine concentrations of deposit in water bodies. There is also a stream assessment module for certain applications, which includes dilution and mixing effects in the analysis of downwind deposition. One of the limitations of AgDRIFT™ is that the flowing stream assessment option does not operate for airblast applications but estimates based on low boom spray applications are comparable if the rate of a.i. applied is corrected for. For a waterbody 7 m wide, 0.7 m deep and flowing at 0.18 m/s AgDRIFT™ estimates a peak concentration of 0.108 µg/L at Site 3 for a.i. applied at 0.495 kg/ha, which was also comparable to the measured concentration.

The AgDRIFT™ simulation for downstream movement of the pesticide pulse is shown in Figure 6.4. AgDRIFT™ predicts a peak concentration of 0.115 µg/L at Site 4 600 m downstream which was slightly more than the initial peak concentration. AgDRIFT™ assumes continuous input of spray drift throughout the simulation while in the Mountain River experiment spray drift was only being directed over the river for a matter of minutes when the sprayer was working in the rows closest to the river.

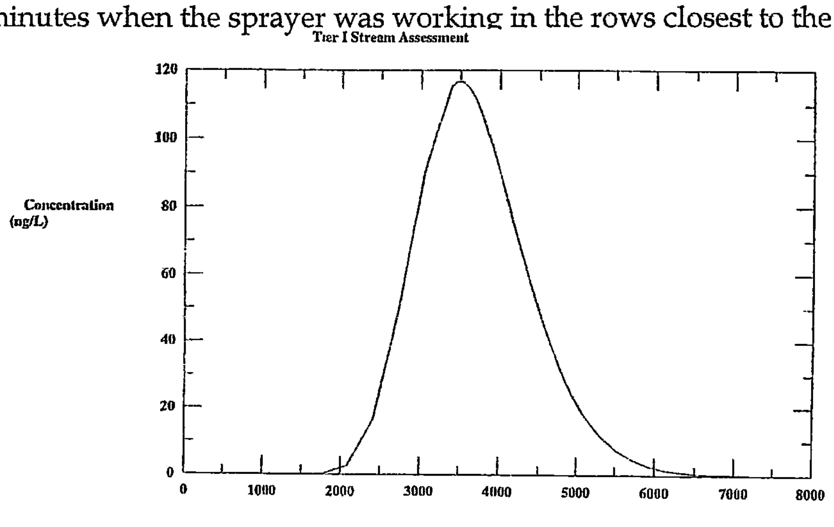


Figure 6.4 AgDRIFT™ stream assessment simulation for pesticide movement downstream

Seasonal exposure sampling

Seasonal chlorpyrifos concentrations

There was considerable variability between sampling sites (Figure 6.5) and between the range of concentrations detected between seasons (Figure 6.6). Low level aquatic concentrations were detected intermittently throughout the spray season. There were more detections in the first year of sampling which was a dry year with low flows occurring frequently throughout the summer months. For the period 1 October 1997 to 1 March 1998 there was a total of 249 mm rainfall recorded, while for the corresponding period in 98/99 there was a total of 402 mm rainfall recorded (Bureau of Meterology daily data for Grove Research Station, Site number 094069). Concentrations correlated with the area of orcharding upstream of the sampling site (Figure 6.7).

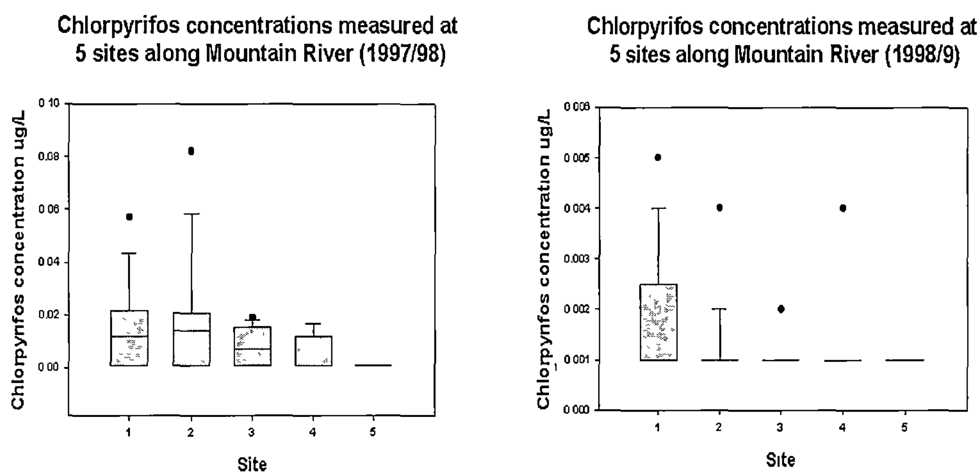


Figure 6.5 Box plots showing average surface water concentrations (µg/L) measured over two years sampling in Mountain River, Tasmania, Australia.

Over the two years of seasonal sampling average concentrations (± S.E) measured in the sediment were: 0.62 ng/g (± 0.38) at Site 1; 0.52 ng/g (± 0.17) at Site 2; and 0.15 ng/g (± 0.02) at Site 4. Rocky substrates at Sites 3 and 5 precluded the collection of sediment at these sites. The sediment concentrations measured in the seasonal sampling were all below the concentrations deemed to have potential for adverse effects (Table 6.2) (Brown *et al.*, 1997).

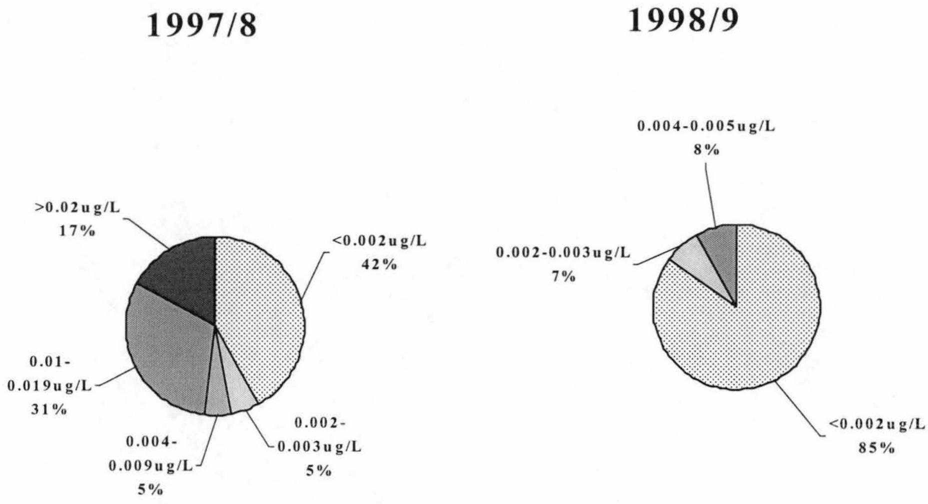


Figure 6.6 Breakdown of average seasonal exposures measured in Mountain River, Tasmania, Australia.

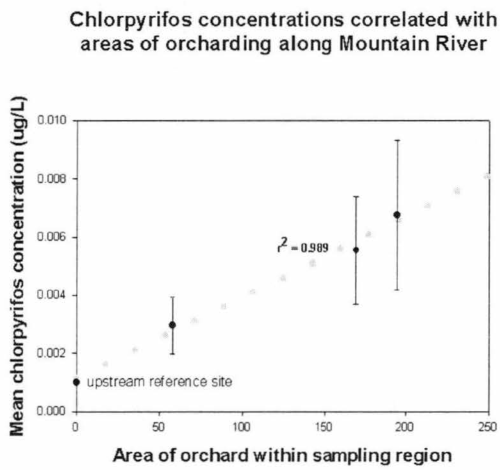


Figure 6.7 Correlation of average surface water concentrations (µg/L) measured over two years with area of orchard upstream of sampling site. For purposes of this correlation, the Mountain River catchment was broken down into 4 subcatchments and average surface water concentrations at a site plotted against area of orchard in that subcatchment. Because there was minimal orcharding upstream of Site 3, Sites 3 and 4 were combined in this correlation. The area of orchard within each subcatchment was calculated using ArcView® version 3.1 (Environmental Systems Research Institute, Redlands, CA, USA).

DISCUSSION

In both experiments described here elevated chlorpyrifos levels occurred very soon after commencement of spraying and dissipated rapidly. This finding is in agreement with the work of many authors (Knuth and Heinis, 1992; Racke, 1993; Giddings *et al.*, 1997). Within approximately 40 min after the sprayer passed by the target site chlorpyrifos was only detectable in trace amounts. These results have important implications for ecological risk assessments, which currently use toxicological parameters based on 24 or 48 h exposures. The exposures which are being tested in the laboratory for a minimum of 24 h may actually only occur in the field for a matter of minutes. For example, the only endemic Australian species for which chloryprifos toxicity tests have been conducted is the Australian freshwater shrimp *Paratya australiens* which had a 24 hour EC50 of 0.1 μg/L (Abdullah *et al.*, 1993). In the 2000 sampling a concentration of 0.030 μg/L was measured at 8 min, 0.164 μg/L at 10 min and 0.034 μg/L at 12 min. There was less than a 4 min interval during which the water concentration could have exceeded the EC50 to which *Parataya* had been exposed for 24 h. The same discrepancy in laboratory exposure vs. field exposure is also seen for the Australian *Ceriodaphnia dubia* which has a 24 h EC50 of 0.13 μg/L (Foster *et al.*, 1998). These two examples are the only studies to date where chlorpyrifos has been tested on Australian species.

Generating such field data is expensive and logistically complex so it is understandable that more studies of this type are not undertaken. However, the reality for many ecological risk assessments is that they should be undertaken for pulse exposures in flowing, rather than stationary, waterbodies. Comparisons of the Mountain River field data with AgDRIFT™ simulations indicate this model is a valid tool for estimating pulse aquatic pesticide concentrations resulting from spray drift on the waterway. Given the resources required for field monitoring of pulse exposures, it is useful to have a model that can be used for preliminary risk assessments.

Seasonal exposures of chlorpyrifos in the U.S. Midwestern corn belt have been simulated using the Dow AgroSciences Geographical Assessment System (DEGAS). This simulation was for at-plant application of granular chlorpyrifos applied to corn (Havens *et al.*, 1998) and is not applicable for modeling seasonal exposures resulting from orchard spray drift. In the absence of a valid modeling system, field measurements for chronic chlorpyrifos exposures in orcharding districts are important, and should be conducted more frequently. The seasonal exposure results from Mountain River indicate that chlorpyrifos contamination of waterways in orcharding regions does occur, although at very low levels and the detections are infrequent.

Chlorpyrifos has been detected in several other Australian pesticide field monitoring programs. Monitoring in a horticultural catchment in South Australia showed that chlorpyrifos exhibited a seasonal detection pattern coinciding with the growing season extending from October to February. The maximum concentration detected throughout a three year sampling program was 4.30 µg/L, and a concentration of 5.20 µg/L was detected following a runoff event (Thoma and Nicholson, 1989). It was concluded that chlorpyrifos concentrations were sufficient to adversely affect aquatic environments. In 1996 Sydney Water Corporation conducted urban pesticide monitoring in major sewage overflows, sewage treatment plants and stormwaters around Sydney (Bickford *et al.*, 1999). Chlorpyrifos was detected at concentrations ranging from 0.05 to 0.38 µg/L (A. Lovell, personal communication) and identified as being a cause of toxicity in toxicity identification evaluations for discharges from sewage treatment plants (Bailey *et al.*, 2000). In rural New South Wales the Central and NorthWest Regions Water Quality Monitoring Program (CNWRWQP) sampled 28 sites for pesticides in the Border, Gwydir, Namoi, Macquarie, and Darling River catchments. Sampling was conducted on 23 occasions throughout 1996/97. Chlorpyrifos was detected twice throughout the program, in mid-summer. Concentrations measured were 1.2 µg/L and 0.4 µg/L (Muschal, 1997). CNWRWQP recorded a total of 10 chlorpyrifos detections in the years 1994-1996 although concentrations were not given. Chlorpyrifos exceeded 0.001 µg/L on several occasions during sampling of the Murrumbidgee and Colembally Irrigation Areas but the concentrations measured were not reported (Korth *et al.*, 1994).

Overseas chlorpyrifos has been detected in a pesticide monitoring program conducted in the Negro River basin, Argentina in 1986 (Natale *et al.*, 1988). A maximum concentration of 0.134 µg/L was measured although concentrations of 0.040 to 0.08 µg/L were more typical. The most comprehensive monitoring for chlorpyrifos has been conducted in North America. Chlorpyrifos concentrations measured in surface water monitoring programs in Lake Erie, the U.S. Midwest, California and various agricultural watersheds and urban watersheds sampled under the National Water Quality Assessment Program (NAWQA) have been extensively characterised (Giesy *et al.*, 1999). The range of chlorpyrifos concentrations measured in the USA is too extensive to describe here but monitoring programs have generally shown infrequent occurrences of low levels of chlorpyrifos residues from non-point sources (Havens *et al.*, 1988). In Canada chlorpyrifos was measured at 4.4 µg/L in one of 19 rural ponds sampled in Ontario (Frank *et al.*, 1990). This concentration caused fish kills and was the result of accidental spillage into the pond. Chlorpyrifos was present in only 3 samples out of 949 stream water samples collected from 11 agricultural watersheds in southern Ontario between 1975 and 1977. The maximum concentration detected was 1.6 µg/L (Braun and Frank, 1980).

The results from the Mountain River seasonal monitoring and the other pesticides monitoring programs described demonstrate the variability associated with random sampling of pesticides in the environment. When environmental pulse exposures regularly occur, such as from orchard airblast applications, it is difficult and expensive to carry out a sampling program sufficiently detailed to obtain a reliable estimate of the average over time of the rapidly fluctuating concentrations (Richard and Baker, 1998). Generally it is difficult to know whether field monitoring studies are completely representative of the actual use of chemical within a given region (Havens *et al.*, 1998).

Three dimensions must be considered when estimating exposure: intensity, time and space (US EPA, 1996). This paper describes the intensity and duration of a pesticides pulse, but another aspect that requires consideration in understanding the true pulse exposures to which organisms are exposed to is the vertical distribution of the pesticide. Vertical mixing of chlorpyrifos has been measured in littoral enclosures dosed with an overspray of chlorpyrifos (Steffert *et al.*, 1989). All of the chlorpyrifos was found in the top 7.6 cm of the water column 20 min after application, and none was detected near the bottom of the water column (1.1 m) until 1 h after application. The distribution remained constant for the next hour, and at 2 hours 55% of the chlorpyrifos still remained in the top 7.6cm of water, while 3.6% had reached the bottom (Steffert *et al.*, 1989).

A further consideration is that chlorpyrifos has a low water solubility of 0.4 mg/L (Wauchope *et al.*, 1992) and a log Kow (octanol:water partitioning coefficient) of 5.11 (Tomlin, 1994) indicating that it does not readily partition to water. It would be expected that a percentage of chlorpyrifos spray drift landing on the water surface would never be incorporated into the water body but rather remain on the surface microlayer and dissipate through volatilisation and photolysis. In studies on volatilisation from pond water it was found that volatility losses from water represented the primary route of chlorpyrifos dissipation from water (McCall *et al.*, 1984). Chlorpyrifos fate in outdoor pond microcosms has been studied: for an overspray calculated to correspond with a nominal concentration of 0.1 μg/L the water concentration 2 h after spraying was 0.088 μg/L and for a nominal concentration of 0.3 μg/L the 2 h water concentration was 0.246 μg/L (Giddings *et al.*, 1997). An initially rapid loss of chlorpyrifos from water bodies is generally attributed to volatilisation from the surface water (Steffert *et al.*, 1989; Knuth and Heinis, 1992; Racke, 1993). Physiochemical interactions at the air-water interface are complex and more detailed studies are needed to understand chlorpyrifos behaviour at the surface microlayer and subsequent incorporation into the water body, particularly for flowing waters.

Globally there is a scarcity of data describing the pulse exposures of chlorpyrifos that occur following application or runoff events. Given the rapid toxic action of chlorpyrifos it is appropriate that pesticide monitoring programs with limited time and resources should focus on pulse exposure monitoring at the time of application or following a runoff event, rather than conduct routine monthly or quarterly sampling programs. In the absence of reliable chronic exposure data, pulse 'worst case' exposure data is needed to conduct ecological risk assessments of pesticides. This type of data is representative of the most toxic concentrations that actually occur in the field.

CHAPTER 7. PROBABILISTIC ASSESSMENT OF RISKS TO AQUATIC SPECIES IN MOUNTAIN RIVER

Chapter Background: The assessment of risk involves determining the probability of the concentration to which organisms are exposed exceeding the concentration of toxicant that will cause an unwanted effect, as determined from the dose-response relationship (Solomon *et al.*, 1996).

Due to a scarcity of toxicological testing for Australian species, the chlorpyrifos dose-response relationships for most Australian species are unknown. In this assessment, an international data set was used to assess risks to species in Mountain, with the assumption that the distribution of species sensitivity in Mountain River approximates the distribution of species sensitivity in exotic species. This chapter is a case study for similar applications in Australia where risk assessments have to be made using datasets for exotic species.

Exceedence plots and simulations based on probability distributions of aquatic exposures were used to estimate the probability of a particular target levels being exceeded in Mountain River. The target levels were chosen based on a literature review of chlorpyrifos effects in aquatic studies.

The merits of probabilistic risk assessment are discussed in the Discussion and Conclusions chapter.

This chapter forms the basis of a paper submitted to the journal *Environmental Toxicology and Assessment* with the following reference: Walker R Nowak BF. Probabilistic risk assessment for aquatic species exposed to chlorpyrifos sprays in an Australian orcharding region.

Abstract

In Australia, ecological risk assessment of pesticides is limited by the availability of exposure and effects data. With an increasing requirement to complete ecological risk assessments of pesticides for their Australian applications, there is a necessity to extrapolate from overseas toxicity data. Probabilistic risk assessment is a useful tool for such circumstances because it does not require direct comparison between endemic and exotic species. Probabilistic methods were used to assess effects of chlorpyrifos on aquatic species in a stream located within a region of intensive orcharding in southern Tasmania, Australia. Risks were characterised using using exceedence plots and @Risk® simulations. Probabilistic outcomes indicate that fish are unlikely to show chronic or acute responses to seasonal or pulse chlorpyrifos exposures. There is potential that aquatic invertebrates will be acutely affected by exposures occurring as a result of spray drift deposition onto waterways at the time of spray application.

INTRODUCTION

In recent years a number of pesticides including atrazine (Solomon *et al.*, 1996), chlorpyrifos (Giesy *et al.*, 1999), diquat bromide (Ritter *et al.*, 2000) and diazinon (Giddings *et al.*, 2000) have undergone extensive probabilistic risk assessments for their applications in the United States of America. These large-scale risk assessments have been for generic applications and habitats. There is a growing global demand for more intensive ecological risk assessments applicable to the specific circumstances of pesticide usage within a region/industry.

In Australia, ecological risk assessment of pesticides is limited by the availability of exposure and effects data. There is a scarcity of laboratory and field ecotoxicology data available for Australian species under local conditions (Chapman *et al.*, 1993; Pusey *et al.*, 1994; Wu, 1996; Warne *et al.*, 1998). With an increasing requirement to complete ecological risk assessments of chemicals for their Australian applications, there is a necessity to extrapolate from overseas toxicity data. Probabilistic risk assessment is a useful tool for such circumstances because it does not require direct comparisons between endemic and exotic species. Instead, an existing international data set can be used with the assumption that the distribution of sensitivities of exotic species approximates the distribution of sensitivities of Australian species (Parkhurst *et al.,* 1995). To date there is not enough data to validate this assumption. However, in the limited research conducted for short term responses of fish to pesticide exposure, it has been concluded that it is not strictly necessary to determine toxicity to native Australian species in order to derive water quality criteria (Sunderam *et al.,* 1992; Davies *et al.,* 1994). Although not ideal, the use of international toxicity data is acceptable for Australian applications.

This paper is an application of probabilistic risk assessment methods to characterise the probability and significance of effects of chlorpyrifos on aquatic species in a stream located within a region of intensive orcharding in southern Tasmania, Australia. In the Huon Valley, southern Tasmania, Australia, chlorpyrifos is used for control of light brown apple moth in apple orchards. Given the toxicological properties of chlorpyrifos, there is potential for adverse impacts on aquatic communities in the Huon Valley. Spray drift from chlorpyrifos applications to apple orchards has been shown to result in detectable concentrations of pesticide in waterways within the region (Chapter 6).

Ecotoxicological research with chlorpyrifos in Australia has been very limited (Pusey *et al.,* 1994). The only endemic species for which chlorpyrifos has been tested are *Paratya australiensis* (Abdullah *et al.,* 1993; Olima *et al.,* 1997) and *Ceriodaphnia dubia* (Foster *et al.,* 1988). Exotic species have been extensively tested for chlorpyrifos sensitivity. There is an comprehensive data set available through the scientific literature for chlorpyrifos toxicity to aquatic invertebrates which has been reviewed by several authors (Marshall and Roberts, 1978; Barron and Woodburn, 1995; Giesy *et al.,* 1999).

The objective of this risk assessment was to use probabilistic methods and international toxicity data to estimate the likelihood of adverse ecological effects occurring in Huon Valley waterways as a result of chlorpyrifos use in nearby apple orchards. The risk assessment is presented in the standard format: problem formulation, risk analysis, risk characterisation. In the risk characterisation the literature on chlorpyrifos was reviewed to characterise ecological relevance of the exposures.

PROBLEM FORMULATION

Assessment endpoints

Assessment endpoints are defined as explicit expressions of the environmental value to be protected (US EPA, 1992). Measurement endpoints are the parameters that are quantified as indicators of the effects of the stressor (US EPA, 1998). In this paper endpoints are considered in terms of fish and invertebrates found in Mountain River.

The assessment endpoint was set as the upper limit of risk for all species. The general assessment endpoint was 'for aquatic species to be protected aquatic exposure must not exceed to the 10^{th} centile of species sensitivity'. For the assessments based on cumulative frequency distributions of exposure and effects, the specific assessment endpoint was 'for aquatic species to be protected the 10^{th} centile of exposure must not exceed to the 10^{th} centile of species sensitivity'. The choice of a 10% level of effect is consistent with that recommended and used by other researchers (Aquatic Risk Assessment and Mitigation Dialogue Group, 1994; Solomon *et al.*, 1996; Solomon and Chappell, 1998; Giesy *et al.*, 1999). Given the asymptotic nature of probability distributions, exposure concentrations would have to become infinitely small to include 100% of all possible species (Giesy *et al.*, 1999). No rare or endangered fish or aquatic invertebrates are known to occur in Mountain River but if they did then a smaller centile could be used as the assessment endpoint in order to make the risk estimates more conservative.

In risk assessments of chemicals the most commonly used measurement endpoints are survival and sometimes growth or reproduction of individual organisms, as determined in laboratory toxicity tests and reported in the scientific literature. Acute toxicity (usually expressed as the LC50) is particularly relevant in a chlorpyrifos risk assessment because its toxic effects are rapid and exposures are of relatively short duration in surface waters (Giesy *et al.*, 1999). Median effect levels (LC50) data was used in this assessment because it was the only threshold value widely available in the literature. LC50 data is commonly used in ecological risk assessments because the level of uncertainty is minimised at the midpoint of the regression curve (US EPA, 1996).

Conceptual Model

The conceptual model for interaction of chlorpyrifos sprays in the Mountain River environment was described in Chapter 5. Spray drift landing on the water surface either volatilises or is incorporated into the water column. The direct toxicity of chlorpyrifos to aquatic organisms results from initial metabolic activation to form chlorpyrifos oxon, with the subsequent inactivation of acetylcholinesteratse (AChE) at neural junctions. Inactivation of AChE occurs by oxon phosphorylation of the enzyme active site and is rapidly reversible. AChE inactivation is dose- and exposure-dependent, and results in overstimulation of the peripheral nervous system and subsequent toxicity (Marshall and Roberts, 1978). Only fish and aquatic invertebrates were included in this risk assessment. The potential exposure of amphibians, reptiles, birds and mammals to chlorpyrifos is small because the chemical does not biomagnify to a significant extent (Giesy *et al.*, 1999).

RISK ANALYSIS

Characterisation of exposures

The exposure data used in this analysis came from field data collected in Mountain River, southern Tasmania. Mountain River is a perennial stream flowing through an area of intensive orcharding in the Huon Valley apple-growing region. Water samples were collected for analysis of seasonal and pulse exposures (Chapter 6).

Seasonal concentrations were measured at five sites in Mountain River on a fortnightly basis during the apple spray season (October to February). Over the two years of seasonal sampling there was considerable variability between sampling sites and between the range of concentrations detected between seasons. In the first year of sampling 42% of samples collected were below the limit of detection, 17% of samples greater than 0.02 μg/L and 41% of samples in the range 0.002 to 0.019 μg/L (Figure 6.6) In the second year of sampling 85% of samples collected were below the limit of detection, 8% of samples greater than 0.004 μg/L and 7% of samples in the range 0.002 to 0.003 μg/L (Figure 6.6). In the second year of sampling the rainfall was approximately double that in the first season so it is probable that residues were diluted and dissipated much more quickly than in the first season of sampling (Chapter 6).

Pulse concentrations were measured twice in Mountain River while a routine chlorpyrifos spray was being applied in an orchard immediately adjacent to the river. Chlorpyrifos concentrations peaked at 0.163 μg/L approximately 10 minutes after spraying commenced. Concentrations above 0.01 μg/L persisted for less than 40 min after spraying. Three hours after spraying chlorpyrifos concentration was 0.002 μg/L, the limit of detection by GC-MS/MS (Chapter 6).

For the purposes of the distributional analysis, concentrations reported as non-detects, below the limits of detection (LOD) of GC-MS/MS were assigned a value of zero (Solomon *et al.*, 1996; Giesy *et al.*, 1999). The probabilistic procedure assumes that non-detects are distributed from the limits of detection to zero, in a continuation of the distribution of the detected concentrations. Assigning a value of ½ LOD to the non-detects is common practice that was not used in this assessment because it represents an unrealistic occurrence and has been shown to been statistically biased (Newman *et al.*, 1989).

Characterisation of effects

The toxicity data set used in this analysis came from a comprehensive review of chlorpyrifos ecotoxicology (Barron and Woodburn, 1995). LC50 values for fish ranged from 4.7 μg/L for bluegill (*Lepomis macrochirus*) to 1039 μg/L for mosquitofish (*Gambusia affinis*). LC50 values for aquatic invertebrates ranged from 0.001 μg/L for the mosquito (*Aedes aegypti*) to 141 μg/L for the ostracod (*Chlamydotheca arcuata*) (Figure 7.1). In general, crustaceans and insect larvae were the most sensitive aquatic species. Rotifers, molluscs and annelids were generally the least sensitive aquatic invertebrates in both laboratory and field studies (Giesy *et al.*, 1999). For consistency all values in the data set were normalised to 48 h exposures using reciprocity equations relating concentration and time. The normalised 48 h data used in this assessment from obtained from (Giesy *et al.*, 1999).

Two probabilistic methods were used to analyse risks to aquatic species: 1) Exceedence plots based on cumulative frequency distributions; 2) Assessments based on simulated probability distribution functions

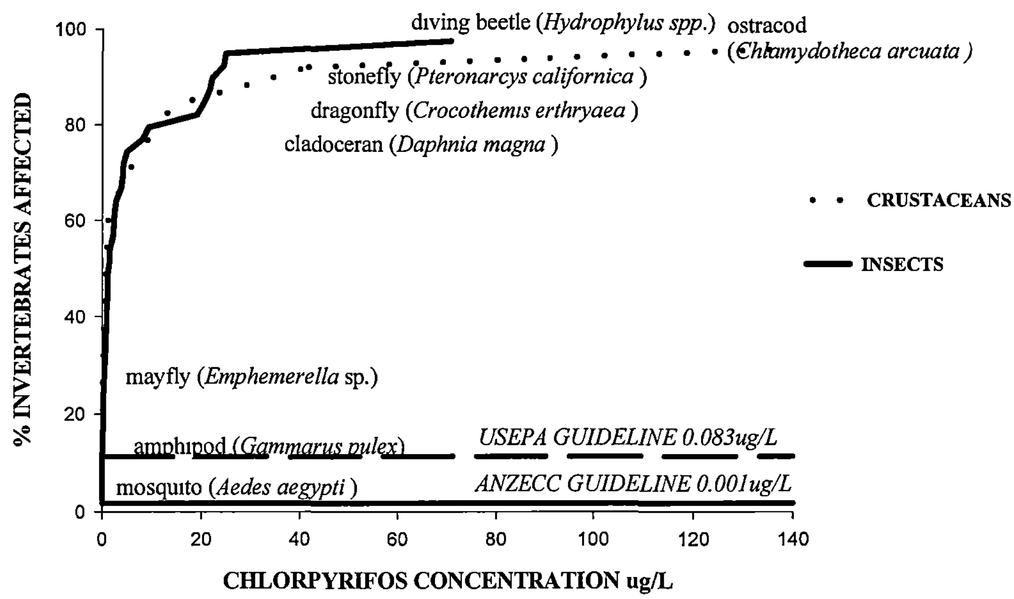


Figure 7.1 Distribution of acute sensitivities of aquatic arthropods and crustaceans to chlorpyrifos (48 h exposures). Selected species are shown to illustrate the range of chlorpyrifos sensitivities of tested species.

Exceedence plots based on cumulative frequency distributions

Details of generating exceedence plots have been given in several publications (e.g. Parkhurst *et al.*, 1995; Solomon *et al.*, 1996; Solomon and Chappell, 1998). Both the exposure data and effects data were ranked and expressed as cumulative frequency distributions. The cumulative frequency distributions were transformed to linear axes to enable regression calculations to solve for a concentration which affected a particular % of species, and then the % exceedence of this concentration was calculated from the distribution of exposure data.

Risks were expressed as exceedence plots, which illustrate how often exposures exceed the LC50 for sensitive species. Mountain River chlorpyrifos concentrations exceeded the 10th centile of all freshwater species 2% of the time during the spray season and 10% of the time during a spray event (Figure 7.2). Concentrations exceeded the 10th centile of fish species 0.006% of the time throughout the spray season and for 0.02% of the time during a spray event (Figure 7.3). When the exposure data for Mountain River was compared with the distribution of invertebrate sensitivities, concentrations exceed the 10^{th} centile of invertebrate species 3% of the time throughout the spray season, and 19% of the time during a spray event (Figure 7.4).

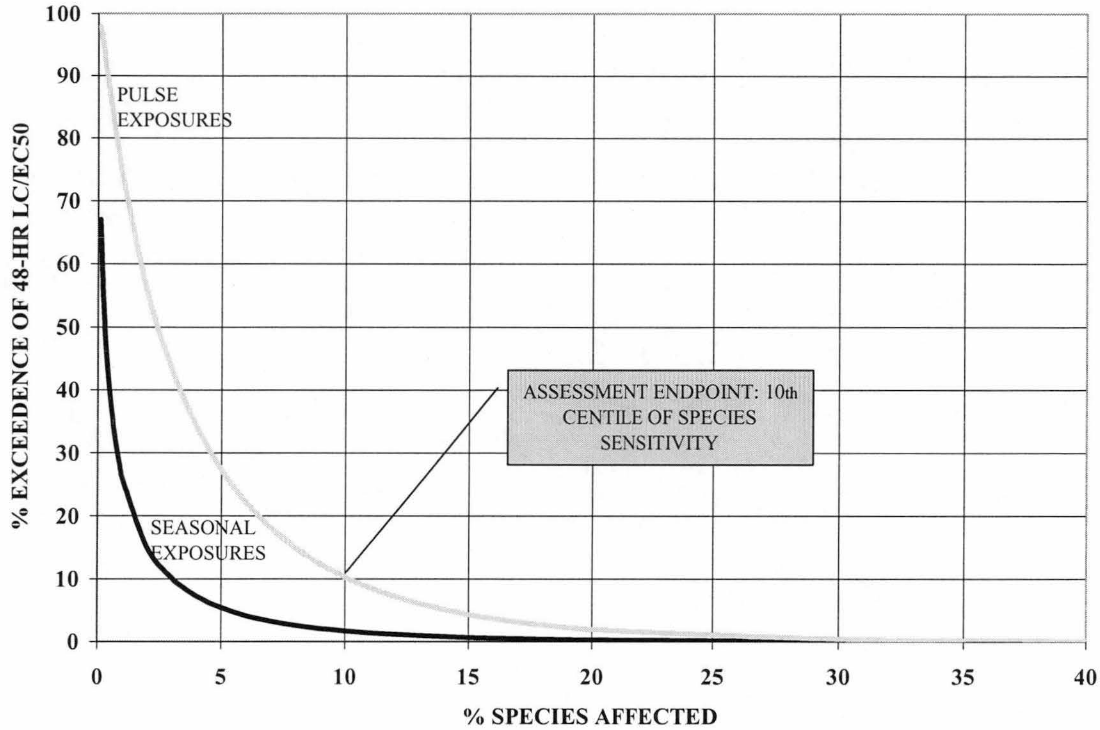


Figure 7.2 Chlorpyrifos exceedence profiles for seasonal (October-February) and pulse (2 h) exposures in Mountain River: All Freshwater Species.

The exceedence plots showed that the assessment endpoint for aquatic invertebrates was not achieved during the pulse exposures measured in Mountain River. Exceedences for all freshwater species were at the level of the assessment endpoint (10%). Exceedences for fish species were well below the assessment endpoint.

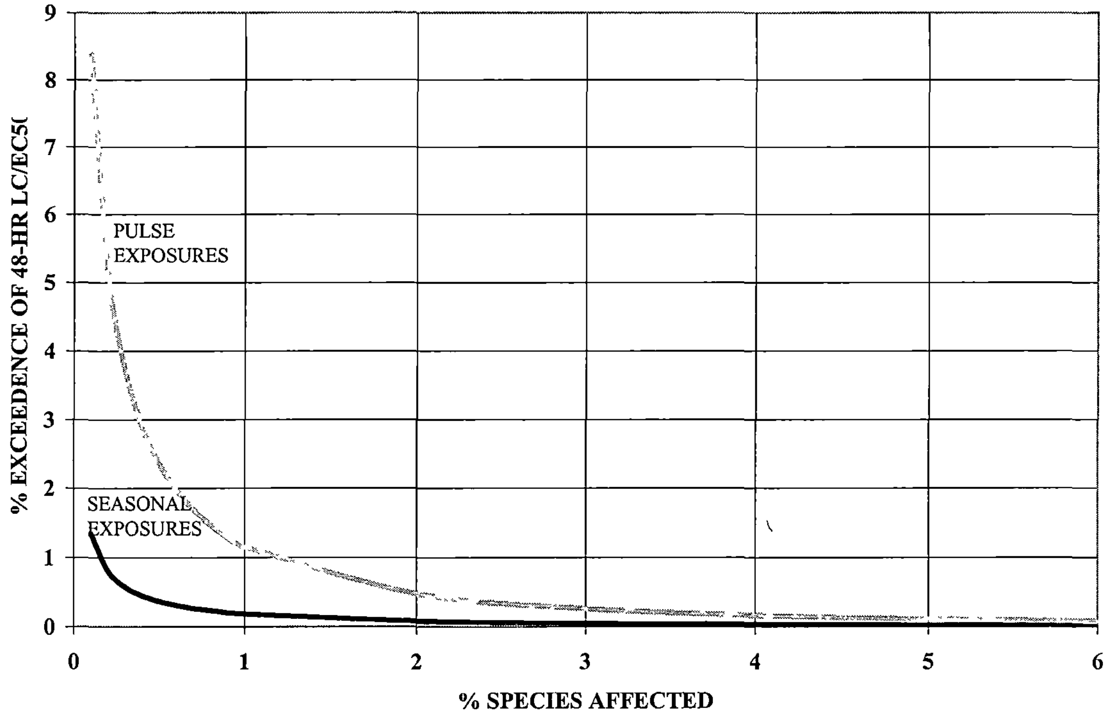


Figure 7.3 Chlorpyrifos exceedence profiles for seasonal (October-February) and pulse (2 h) exposures in Mountain River: Fish Species.

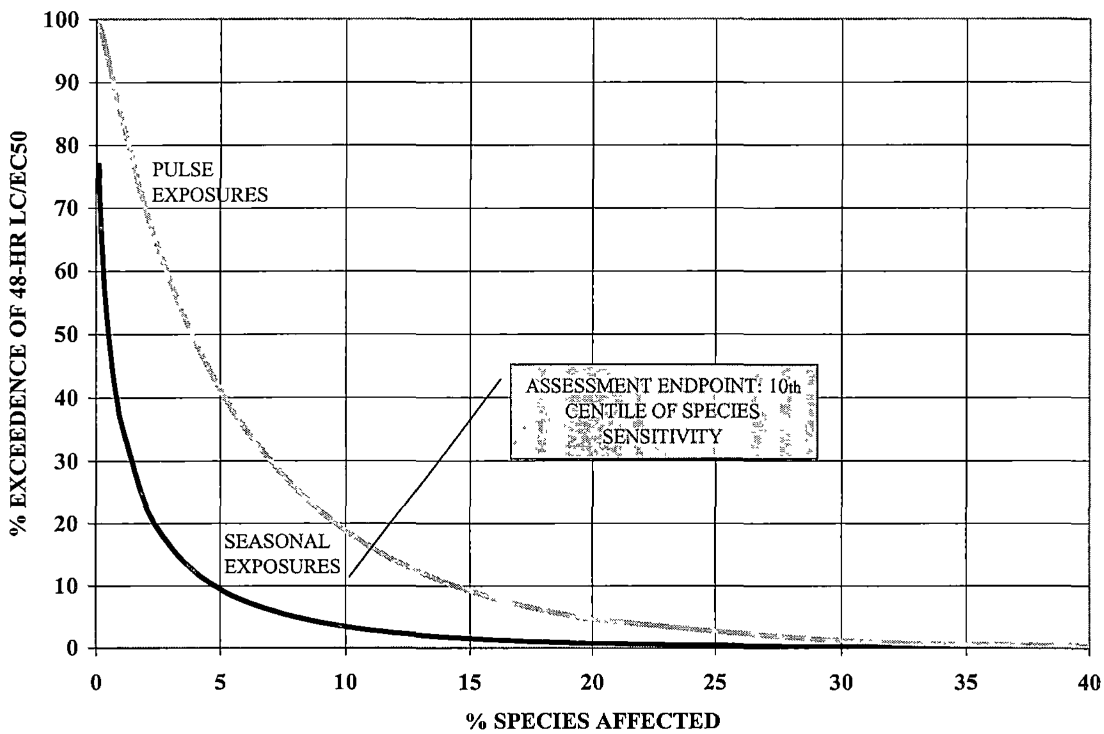


Figure 7.4 Chlorpyrifos exceedence profiles for seasonal (October-February) and pulse (2 h) exposures in Mountain River: Aquatic Invertebrate Species.

Assessments based on simulated probability distribution functions

Knowledge of the unique probability distribution function of exposure data for a particular locality means it is possible to conduct simulations based on what would be expected at that particular site. As such it is possible to assess high risk and low risk localities on the basis of their individual characteristics. This is a requirement of Tier 4 risk assessments (Aquatic Risk Assessment and Mitigation Dialogue Group, 1994).

Probability distribution functions for the Mountain River pulse exposure data were fitted using the commercial software package Best Fit® (Palisade Corporation, 1996). A total of 34 water samples were taken at the target site during pulse exposure sampling. The maximum value of the distribution was set at 0.168 µg/L with is the maximum value modeled by AgDRIFT™ for the site (Chapter 6). The maximum value measured at the site was 0.164 µg/L. The goodness-of-fit test used in the distribution fitting was the Kolmogorov-Smirnov (K-S) test with $p<0.1$.

The five distributions that were ranked highest by the K-S test were simulated using the commercial software package @Risk® (Palisade Corporation, 1996). Ten simulations with 1000 iterations per simulation were run. Latin Hypercube sampling was used. These simulation settings were based on the field scenario of a maximum of 10 sprays being applied throughout the season (under a chlorpyrifos calendar spraying schedule 6-8 sprays might be applied), with 1000 pulse exposure water samples collected at each time of spray application.

For each of the Mountain River pulse exposure PDFs, the probability of exceeding particular target water concentrations was calculated. Values from acute and chronic toxicity tests were used as target water concentrations. Unless otherwise stated the critical water concentrations used were endpoints given in the review of chlorpyrifos ecotoxicology (Barron and Woodburn, 1995). If several test concentrations for one species were given or a range of values was reported, the lowest concentration was always chosen as the target water concentration.

The @Risk simulations for all freshwater aquatic species (Table 7.1) showed that there was 87 to 90% probability of pulse exposures exceeding the Australian ANZECC environmental trigger value for chlorpyrifos (0.001 µg/L) (Australian and New Zealand Guidelines, 2000). There was 9 to 12% probability of exposures exceeding the US EPA Clean Water Act guideline for chlorpyrifos (0.083 µg/L) (US EPA, 1986). In a comprehensive characterisation of chlorpyrifos effects on freshwater species, the 10th centile of acute effects was calculated to be 0.102 µg/L (Giesy *et al.*, 1999). A similar concentration of 0.1 µg/L was identified as the mesocosm NOEC, based on an extensive review of chlorpyrifos mesocosm studies (Giesy *et al.*, 1999). There was a 6 to 10% probability that pulse exposures in Mountain River would exceed the 10th centile for freshwater species and the mesocosm NOEC.

Table 7.1 Probability of pulse exposures of chlorpyrifos in Mountain River exceeding various target water concentrations: General Targets for All Freshwater Species.

Species	Target Concentration	% Probability of Exceeding Target Concentration[a]				
		Gamma	*Pearson VI*	*Weibull*	*Lognormal*	*Lognormal 2*
ANZECC Guideline	0.001 µg/L	86.9	89.8	88.3	89.4	89.2
US EPA Guideline	0.083 µg/L	9.5	11.6	9.2	12.1	11.9
Mesocosm NOEC [b]	0.1 µg/L	6.6	9.2	6.6	10.1	10.0
10th centile all freshwater species [b] (48 h normalised LC50)	0.102 µg/L	6.3	9	6.5	9.9	9.8

[a]Probability distributions are for concentrations measured in Mountain River at the time of spray application in an orchard adjacent to the sampling site. Distributions fitted using BestFit® and ranked by the K-S test. Distributions simulated using @Risk®.
[b]From (Giesy *et al.*, 1999)

The @Risk® simulations for fish (Table 7.2) showed that there was a 0 to 4% probability of pulse exposures exceeding the inhibition concentration (IC25) for bluegill (*Lepomis macrochirus*) survival and total biomass (Giddings *et al.*, 1997). Bluegill was used in microcosm studies to study the effect of chlorpyrifos on growth and survival because it is the most sensitive freshwater fish species chlorpyrifos (Barron and Woodburn, 1995). There was 0% probability that pulse exposure concentrations would exceed the 96 h LC50 for rainbow trout (*Oncorhynchus mykiss*). Risks to rainbow trout were estimated because it is one fish species found in Mountain River for which a chlorpyrifos toxicity test has been conducted. There was a 0-0.4% probability that concentrations would exceed the 96 h LC50 for bluegill. The longest duration for any chronic tests with fish was a 200 d test with fathead minnow (*Pimephales promelas*). There was a 4 to 8% probability of pulse concentrations exceeding this value. However, the duration of the pulse exposure was so much shorter than this test that any interpretations were very limited. There was a 0 to 0.1% probability that pulse exposures in Mountain River would exceed the 10th centile for fish species.

The @Risk® simulations for aquatic invertebrates (Table 7.3) showed a 87 to 90% probability of pulse exposures exceeding the 24 h LC50 of the mosquito, *Aedes aegypti*, which was the most sensitive species tested for chlorpyrifos toxicity. There was a 22 to 25% probability of aquatic concentrations exceeding the 96 hour NOEC of 0.04 µg/L for *Paratya australiensis* (13). Significant depression in AChE activity of *Paratya australiensis* has been shown to occur at both acute levels (>1 µg/L) and at sublethal concentrations (0.1 µg/L) (Olima *et al.*, 1997). The @Risk™ simulations showed a 6 to 10% probability of aquatic concentrations exceeding 0.1µg/L. There was a 16 to 18% probability of exposures exceeding the 21 d life cycle NOEC for *Daphnia magna* of 0.056 µg/L. The Australian *Ceriodaphnia dubia* has a 24 h EC50 of 0.13 µg/L (Foster *et al.*, 1998). There was a 3 to 8% probability of exposures exceeding this concentration.

Table 7.2 Probability of pulse exposures of chlorpyrifos in Mountain River exceeding various target water concentrations: Targets for Fish Species.

Species	Target Concentration	% Probability of Exceeding Target Concentration[a]				
		Gamma	*Pearson VI*	*Weibull*	*Lognormal*	*Lognormal 2*
Primephales promelas[b] (200d NOEC)	0.12 μg/L	4.4	7.3	4.7	8.4	8.4
Lepomis macrochirus[c*] (30 d IC25 survival and biomass)	0.26 μg/L	0.3	2.2	0.6	3.6	3.6
Lepomis macrochirus[c*] (96 h IC25 survival and biomass)	0.4 μg/L	0	1.1	0.1	2.1	2.1
Lepomis macrochirus[b*] (96 h LC50)	1.1 μg/L	0	0.2	0	0.4	0.4
10th centile fish[d] (48 h normalised data)	5.4 μg/L	0	0	0	0.1	0
Oncorhynchus mykiss[b] (96 h LC50)	7 μg/L	0	0	0	0	0

[a]Probability distributions are for concentrations measured in Mountain River at the time of spray application in an orchard adjacent to the sampling site. Distributions fitted using BestFit® and ranked by the K-S test. Distributions simulated using @Risk®.
[b]From Barron and Woodburn, 1995; [c]From Giddings *et al.*, 1997; [d]From Giesy *et al.*, 1999.
*Most sensitive fish species tested for chlorpyrifos toxicity.

Table 7.3 Probability of pulse exposures of chlorpyrifos in Mountain River exceeding various target water concentrations: General Targets for Aquatic Invertebrates.

Species	Target Concentration	% Probability of Exceeding Target Concentration[a]				
		Gamma	*Pearson VI*	*Weibull*	*Lognormal*	*Lognormal 2*
Aedes aegypti [b†] (24 h LC50)	0.001 µg/L	86.9	89.8	88.3	89.4	89.2
Paratya australiensis [c*] (96 h NOEC)	0.04 µg/L	25.2	25.0	23.1	22.0	21.8
10th centile invertebrates [d] (48 h normalised LC50	0.055 µg/L	17.7	18.4	16.3	17.2	17.1
Daphnia magna [b] (life cycle 21 d NOEC)	0.056 µg/L	17.3	18	16.0	17.0	17.0
Paratya australiensis [e*] (24 h inhibition of AChE)	0.1 µg/L	6.6	9.2	6.6	10.1	10.0
Ceriodaphnia dubia [f*] (24 h EC50)	0.13 µg/L	3.5	6.5	3.9	7.8	7.7
Zooplankton community structure [g*] (NOEC in field experiment)	0.5 µg/L	0	0.7	0	1.5	1.5

[a]Probability distributions are for concentrations measured in Mountain River at the time of spray application in an orchard adjacent to the sampling site. Distributions fitted using BestFit® and ranked by the K-S test. Distributions simulated using @Risk®.
[b]From Barron and Woodburn, 1995; [c]From Olima *et al.*, 1997; [d]From Giesy *et al.*, 1999; [e]From Abdullah *et al.*, 1993; [f]From Foster *et al.*, 1998; from [g]Simon *et al.*, 1995.
*Research conducted in Australia.
†Most sensitivity invertebrate species tested for chlorpyrifos toxicity.

In other Australian studies with chlorpyrifos, it has been found that chlorpyrifos doses above about 1 to 2 µg/L cause a marked change in zooplankton community structure. A significant increase in rotifer numbers and a decrease in cladocerans was seen, which coincided with an algal bloom of *Anabaena flos-aquae.* Concentrations below 0.5 µg/L had no effect on community structure (Simon *et al.*, 1995). There was a 0 to 1.5% probability of exposures exceeding 0.5 µg/L.

RISK CHARACTERISATION

The assessment endpoint was for aquatic species to be protected exposures must not exceed the 10th centile of species sensitivity. The risk analysis using exceedence plots showed that freshwater species were considered as a composite, the assessment endpoint would be achieved during seasonal and pulse exposures. Risks to fish were always well within the assessment endpoints. Risks to invertebrates were higher, which is to expected because chlorpyrifos is an insecticide. During pulse exposures the assessment endpoint was not achieved for invertebrate species.

The risk estimates from the @Risk® simulations were similar to those predicted from the exceedence plots. The assessment endpoint was not achieved for four of the target concentrations for invertebrates. Probabilities of Mountain River pulse exposure concentrations exceeding the Australian and US EPA guideline concentrations are relatively high, but in this paper the guidelines were not used as assessment endpoints. The ANZECC (1992) guideline value of 0.001 µg/L is below the method detection limit for all currently used methodologies. To set an assessment endpoint that 'chlorpyrifos levels do not exceed the environmental trigger value' is not achievable (Suter, 1990), given available chemical methods.

The probabilistic risk estimates described in this paper are conservative. One of the largest sources of conservatism is temporal. The toxicity data used in this assessment was for 48 hours. Chlorpyrifos concentrations measured in Mountain River dissipated to levels below the limit of detection (0.002 µg/L) three hours after spraying. It is difficult to compare toxicities and exposures because of the different temporal scales. It would be unrealistic to relate the 200 d chronic test results to any exposures that occur in Mountain River.

The probabilistic outcomes indicate that risks to aquatic invertebrates are greater than risks to fish. However, the life histories of aquatic invertebrates are generally characterised by short life spans, rapid rates of intrinsic population increase, and resting stages. As such they are typically resilient and capable of rapid recovery from short-term disturbances (Woodburn, 2000). In addition, aquatic invertebrates from unexposed refuges can readily repopulate impacted areas (Giesy *et al.*, 1999).

In this application of probabilistic risk assessment, the protection of ecological communities was founded on protecting 90% of the species present. This approach acknowledges that transient changes in the absolute or relative numbers of individuals in a population in the short-term can often be accommodated without altering the functioning of the ecosystem (Giesy *et al.*, 1999; Solomon and Chappel, 1998). In practice, it would be arbitrary to choose any centile less than the 10^{th} centile, because even the 10^{th} centile of species sensitivity to chlorpyrifos is below the limits of chemical detection.

Probabilistic risk assessment is only one line of evidence in a larger process (Solomon and Giddings, 2000). The results of probabilistic risk assessments need to be interpreted in the context of ecological relevance (Giesy *et al.*, 1999).

Implications for changes in community structure

Short-term changes in community structure have been studied in littoral enclosures treated with nominal chlorpyrifos concentrations of 0.5, 5.0 and 20.0 µg/L (Steffert *et al.*, 1989). Four days after pesticide application, the percentage of similarity between chlorpyrifos treated enclosures and controls declined to 74-78% (Steffert *et al.*, 1989). Prior to pesticide application percentage of similarities between treatments and control ranged from 83 to 88%. Using the assumption that a percentage of similarity of 85% or higher would be expected for two stream communities that are structurally similar (Brock, 1977), the authors concluded that species composition had changed as a result of the chlorpyrifos application. An Australian study in artificial streams showed that a pulse of chlorpyrifos at 5 µg/L for 6 h caused invertebrate drift but 0.1 µg/L for the same time did not affect drift or community structure (Pusey *et al.*, 1994). The concentrations used in both these effective treatments far exceed those measured in Mountain River.

Long term changes in community structure as a result of exposure to chlorpyrifos alone have not been studied. One study that is directly applicable to the Huon Valley orcharding district compared aquatic communities in orchard drainage ditches before and after intensive pesticide application on surrounding orchards (Heckman, 1981). Species abundance and diversity was compared to that which existed 25 years earlier, prior to the intensive application of pesticides in orchards. There were small reductions in absolute number of species of Porifera, Ectoprocta, Hirudinea, Bivalva, Copepoda, Branchiura, Decapoda, Emphemeroptera, Heteroptera, Neuroptera, Lepidoptera and larger reductions in numbers of Acari, Odonata, Trichoptera and Coleoptera. There were small increases in the absolute number of species of Tricladida, Araneae, Collembola and a large increase in the species diversity of Diptera. Generally decreases in the populations of individual species were infrequent. Most of the fauna either maintained their population densities or disappeared completely from the ecosystem.

The author concluded that under continuous influence of pesticides, sublethal effects were no longer a factor for populations that had developed resistance. Those species that were susceptible to the pesticides had been completely eliminated. Elimination of many competitors and predators that did not successfully develop resistance to pesticides resulted in abundant populations of resistant organisms. The results from a long-term study such as this are very different to the results usually obtained during short-term investigations, where great fluctuations in the populations of susceptible species are nearly always encountered.

In the orchard drainage ditches, the odonatans, several families of predatory beetles and the water mites were particularly affected by pesticides (Heckman, 1981). In contrast, dipterans increased in number. Habitats where agricultural chemicals have reduced the numbers of predatory beetles and odonatan larvae are ideal places for populations of flies, mosquitoes and midges to develop (Heckman, 1981).

Potential for secondary effects

Suppression of zooplankton by organophosphorus pesticides has been recognised as a major factor contributing to the formation of algal blooms (Hulbert, 1975; Butcher *et al.*, 1977). The @Risk® simulations showed a very small probability of chlorpyrifos concentrations exceeding the algal bloom trigger level of 0.5 µg/L (Simon *et al.*, 1995).

Because pesticides are often more toxic to zooplankton and macroinvertebrates there is potential for pesticides in aquatic ecosystems to affect fish diet and subsequent growth (Johnson and Finley, 1980). In littoral enclosures treated with a single application of chlorpyrifos applied at concentrations of 0.5, 5.0 and 20.0 µg/L, growth rates of larval fathead minnows, *Pimephales promelas* were significantly reduced during a 32 d study period. The greatest differences between treatment groups were observed 15 d post treatment and corresponded with the most significant reductions in cladoceran, copepod, rotifer and chironomid populations. The authors concluded that reductions in the populations of chlorpyrifos sensitive invertebrate forage species forced dietary changes that led to reduced growth of minnow larvae (Brazner and Kline, 1990). The @Risk® simulations showed a very small probability of chlorpyrifos concentrations exceeding 0.5 µg/L. It is unlikely that exposures in Mountain River would result in reduced fish growth as a result of dietary changes.

Implications for change in ecosystem metabolism

Continuos measurements of oxygen, pH and temperature were taken in outdoor experimental ditches treated with chlorpyrifos to determine if chlorpyrifos altered ecosystem function (Kersting and van den Brink, 1997). The main effect of chlorpyrifos treatment was a decrease in system respiration at a concentration of 44 µg/L that led to elevated oxygen concentrations and pH. A lack of statistical power made it difficult to conclusively demonstrate ecosystem metabolism effects at lower concentrations (Kersting and van den Brink, 1997). It is very unlikely that concentrations of 44 µg/L would be seen in agricultural environments, unless there was an accidental spillage.

Uncertainty analysis

Uncertainties exist at every level of the risk assessment process (Suter, 1993a; Landis *et al.*, 1998). Uncertainties in the exposure data include uncertainty about the true value of concentrations below the limit of detection, analytical error, temporal and spatial variability and field effects such as sediment absorption. In order to minimise uncertainties in exposure data, it is important that monitoring programs are well designed. Monitoring programs for chlorpyrifos should have detection limits of 0.5 μg/L or better to be adequately indicative of potentially harmful exposures. The sampling schedule should match to temporal and spatial distribution of chlorpyrifos.

In the @Risk® simulations there was uncertainty arising from the lack of knowledge about the true probability distribution of pulse exposures in Mountain River. Only 34 data points were available to characterise the pulse exposure. It is possible that the probability distribution functions fitted by BestFit® do not accurately describe the pulse exposures. A much larger data set is needed to reduce uncertainties regarding the underlying probability distribution. In instances where the exposure data forms part of a potentially controversial risk assessment, efforts should be made to quantify the extent of uncertainty in the analytical procedure by running a number of standard curves, and quantifying their variability. This variability should be then factored into the aquatic concentrations used in the distribution fitting.

Uncertainties in the toxicity data are numerous. A major source of uncertainty is whether the distribution of toxicity data for the Mountain River species approximates that of the international data set used in the effects characterisation. However, until more toxicity data is available for Australian species there is no means of reducing this uncertainty. Another source of uncertainty is that the species tested in the international data set are not representative of typical ecosystems. Species used toxicity data are not necessarily chosen because of their environmental significance or sensitivity to toxicants, but more likely for their amenability to laboratory culture and handling (Chapman *et al.*, 1993). The international database used in this assessment lacked data on dormant stages of invertebrates or for juvenile and adult amphibians (Giesy *et al.*, 1999).

In addition to the uncertainties in the chlorpyrifos data set, generic uncertainties in toxicity testing also apply to this assessment. Laboratory toxicity tests are usually conducted under conditions where exposures to the toxic substance are maximised.

This is done by making exposure homogeneous; by excluding absorptive matrices such as sediment, macrophytes, or particulates that could reduce exposures; and by maintaining toxicant concentrations constant throughout the study (Chapman *et al.*, 1993). Laboratory conditions are not consistent with habitat variability in the field. The duration of laboratory exposures are not generally not consistent field exposures. A further source of variability is in the calculation of LC50 values, depending on the method of statistical analysis (Stephen, 1977).

In this assessment, no consideration has been given to the toxicity of chlorpyrifos in sediments. Sediment residues were measured in Mountain River during seasonal and pulse sampling. Whole sediment concentrations of less than 100 ng/g have been shown unlikely to produce adverse effects in aquatic organisms (Brown *et al.*, 1997). All residues measured in Mountain River were less than 100 ng/g and it is very unlikely that toxic effects would result from exposure to sediment residues (Chapter 6).

Sensitivity analysis

Sensitivity analysis for the assessments based on cumulative frequency distributions of exposure and effects data is of limited value without further characterisation of the uncertainties described above. However, sensitivity analysis for the @Risk® simulations is useful because it describes how changes in input parameters are likely to affect the risk outcomes.

Sensitivity analysis was conducted for the @Risk® simulations using the logic that if an input distribution does not account for much variation in the outcome, then the lack of data does not have that much impact, to the extent that the data were used to determine the input distribution. On the other hand, if the input distribution was a major contributor to variation in the outcome, then the lack of data implies a greater uncertainty in the risk outcomes (Haimes *et al.*, 1994).

BestFit® generated different probability distributions to describe the pulse exposures measured in Mountain River. The five distributions that were ranked highest by the K-S were Gamma, Pearson VI, Weibull, Lognormal and Lognormal 2. These distributions and their defining parameters were used in the @Risk® simulations.

It is generally recognised that concentrations of environmental contaminants approximate a lognormal distribution (Solomon *et al.*, 1996; Solomon and Chappel, 1998). Although lognormal was one of the distributions fitted to the Mountain River pulse exposure data, it was not the most appropriate according to BestFit® outputs. The advantage of using probability distribution software such as BestFit® is the ability to fit distributions to the unique parameters of a particular site, so the risk outcomes are site-specific.

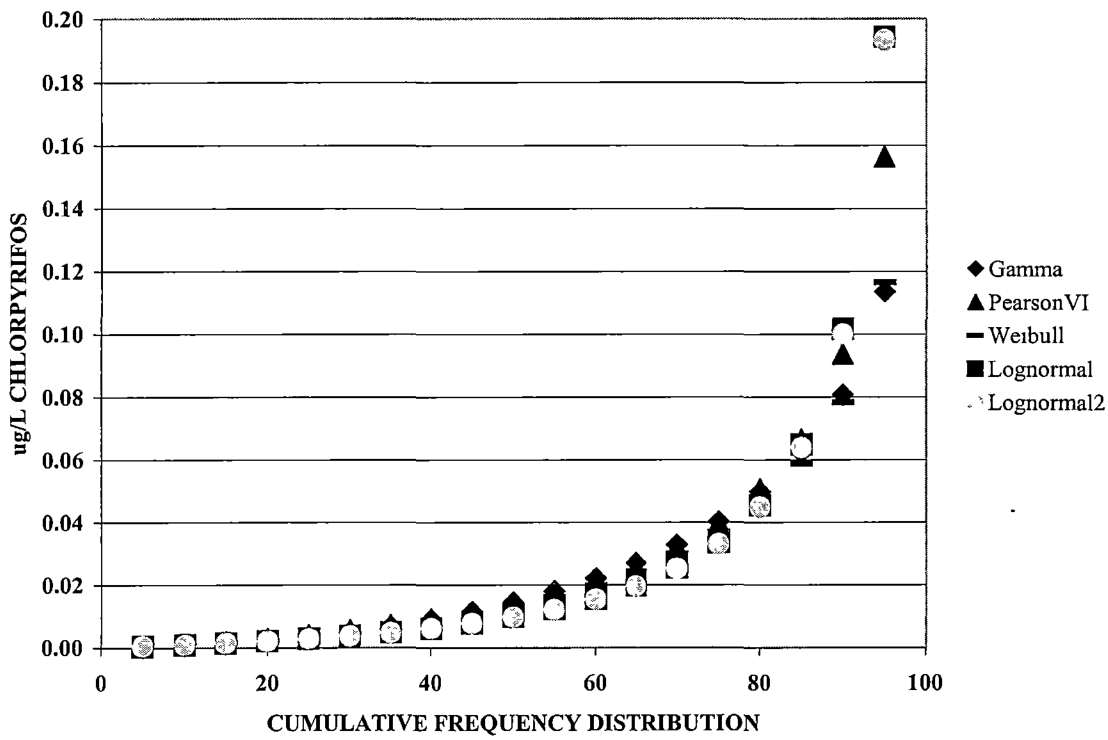


Figure 7.5 Cumulative frequency distributions for five probability distribution functions fitted to the Mountain River pulse exposure data.

In order to compare whether the input distribution had a significant effect on the risk outcomes, the simulation results for all five distributions are shown in the risk tables (Tables 7.1 to 7.3). The risk outcomes for different distributions are always within 4% of each other. Given the other uncertainties in the assessment, these differences are negligible. A plot of Mountain River pulse exposures based on the cumulative frequencies of the different distributions confirmed that all of the @Risk® simulations produced similar outputs (Figure 7.5). Descriptive parameters of the @Risk®

simulations showed that there was less spread in the statistical parameters describing the Gamma and Weibull distributions. The greatest spread was in the lognormal distributions (Figure 7.6). It was concluded that for the relatively small data set describing pulse exposures in Mountain River (34 data points), any of the five probability distribution functions described could be used to reasonably estimate risks to aquatic species. The best risk estimates would be from simulations using Gamma and Weibull distributions.

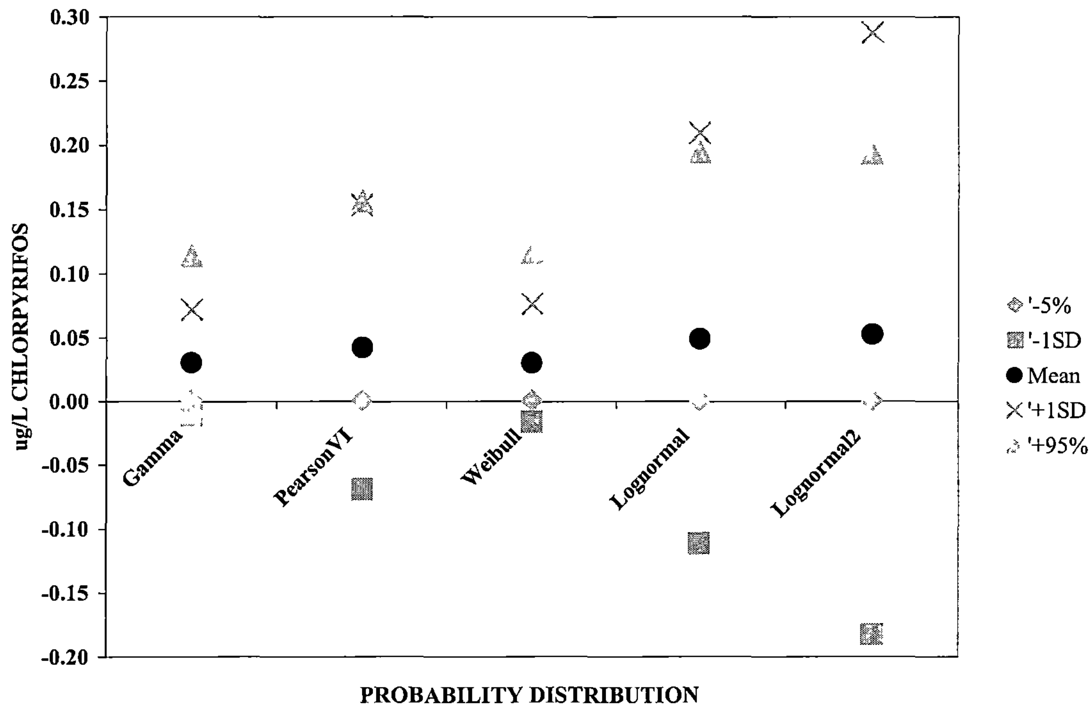


Figure 7.6 Statistical descriptions (mean, ±SD, 95% confidence intervals) for five probability distribution functions fitted to the Mountain River pulse exposure data.

Real world considerations

There are economic and practical consequences associated with overestimating ecological risks. Real-world mitigating factors must be considered before any regulatory or management decisions are made on the basis of probabilistic risk outcomes. In the Huon Valley there are several practical considerations which imply that the outcomes from the probabilistic assessment are overly conservative. Firstly, the exposures resulting from spray drift at the time of spray application are those with greatest potential to adversely impact aquatic ecosystems. If a routine calendar spray schedule is being followed, chlorpyrifos sprays could be applied fortnightly. The worst case scenario is that every fortnight aquatic invertebrates are subject to the pulse exposures characterised in this study. Secondly, the pulse exposures characterised here were measured at a site directly exposed to spray drift from an adjacent orchard. At other sites, streambank vegetation reduces deposition of spray onto waterways (Chapter 9). Finally, many growers in the Huon Valley have adopted integrated pest management (IPM) strategies, and have greatly reduced their use of chlorpyrifos. Of those growers still using chlorpyrifos, very few are applying fortnightly sprays.

CONCLUSIONS

Probabilistic risk estimates indicate that fish in Mountain River are unlikely to show chronic or acute responses to seasonal or pulse chlorpyrifos exposures. There is potential that aquatic invertebrates in Mountain River will be acutely affected by exposures occurring as a result of spray drift deposition onto the waterway at the time of spraying. Aquatic species in Mountain River most likely to be affected by chlorpyrifos sprays are mites, chironomids and odonates. The risk estimates in this assessment are conservative because of temporal variability between field exposures and laboratory tests. To fully characterise risks from chlorpyrifos in intensive orcharding regions, higher tier risk assessments incorporating site-specific investigations are necessary.

CHAPTER 8. SITE-SPECIFIC FIELD STUDY OF CHLORPYRIFOS EFFECTS ON FISH

Chapter Background: The probabilistic risk estimates described in the previous chapter indicate that risks to aquatic species from chlorpyrifos sprays in the Mountain River catchment are small. However, probabilistic risk assessments are only one line of evidence (Giesy *et al.*, 1999; Solomon and Giddings, 2000). Field studies were necessary to validate the outcomes of the probabilistic risk assessment, and provide increased confidence in the assessment outcomes. Recently it has been argued that validation of probabilistic risk assessment predictions is uncommon (de Vlaming, 2000). This chapter describes field data for fish populations that is consistent with the outcomes from probabilistic risk assessment discussed in the previous chapter. Field studies were conducted to assess acute and chronic effects of chlorpyrifos exposure in Huon Valley fish species. Acute effects were measured in caged fish held in Mountain River during spray application in an adjacent orchard (Chapter 6). Chronic effects were assessed in fish collected from Mountain River, and other Huon Valley waterways surrounded by orchards.

This chapter forms the basis of a paper submitted to the journal *Australasian Journal of Ecotoxicology* authored by Walker R, Nowak B F, and Powell M. The findings of a fish survey of Mountain River conducted by Morton (1998) are included in this chapter with the consent of the author. As the survey was not part of this project, only the findings are discussed, and the results are not presented here.

INTRODUCTION

The risk hypothesis for this study was that spray drift from chlorpyrifos applications in orchard located on river flats was resulting in aquatic ecosystems being exposed to potentially harmful concentrations of pesticide. Chlorpyrifos spray drift landing on the water surface either volatilises or is incorporated into the water column. Chlorpyrifos in water moving across the gills has the potential to exert toxic effects in fish, through inhibition of acetylcholinesterase. In mammals death is caused by asphyxiation (O'Brien, 1960; Murphy and Lutenske, 1986) but the exact mechanism of acute toxicity in fish is less well understood, since as long as water crosses the gills, transfer of oxygen occurs. Direct effects of chlorpyrifos on fish survival occur shortly after the exposure and are not additive with additional exposures (Giddings *et al.*, 1997). Fish absorb, metabolise and eliminate chlorpyrifos rapidly. The chlorpyrifos clearance rate half-life is 66 hours in rainbow trout (*Oncorhynchus mykiss*) (Murphy and Lutenske, 1986).

In this study the assessment endpoint used was 'for fish populations to be maintained there should be no reduction in species richness or abundance, or increased frequency of physiological and pathological abnormalities in fish communities resulting from chlorpyrifos exposure'. The assessment endpoint used was generic, and based on endpoints used in other risk assessments (Suter *et al.*, 1999).

Measurement endpoints were chosen to reflect the mode of action of chlorpyrifos. The measurement endpoints chosen as indicators of acute exposure were *in-situ* respiratory physiology and cholinesterase activity. The measurement endpoints used as indicators of chronic exposure were species richness and abundance, fish body burdens and histopathology.

Species richness and abundance was not indicative of exposure to chlorpyrifos alone, but served to assess whether there were differences in fish populations between reference sites and sites located within areas of intensive orcharding. Histological condition was indicative of exposure to pesticides but could not be used to directly estimate the assessment endpoint (Suter *et al.*, 1999).

MATERIALS AND METHODS

Species richness and abundance in Mountain River (from Morton, 1998)

A fish survey of Mountain River was conducted in 1998 as part of a concurrent project describing distribution of fish species in Huon Valley streams (Morton, 1998). Fish were surveyed using electrofishing and sampling sites corresponded to those used for seasonal sampling of chlorpyrifos aquatic concentrations (Figure 6.2, described in Chapter 6).

Seasonal and pulse exposures of chlorpyrifos in Mountain River

The environmental exposures of chlorpyrifos in Mountain River were measured throughout the spray season and at the time of spray application (pulse exposures). The sampling protocol and analysis of water samples has been previously described (Chapter 6). Seasonal concentrations were measured at five sites in Mountain River on a fortnightly basis during the apple spray season (October to February). Pulse concentrations measured on January 5, 2000 were those to which the fish used in the acute effects experiments described below were exposed.

Experimental fish used for in-situ acute effects experiments

Fish used in the pulse exposure experiment were 5-month-old rainbow trout (*Oncorhynchus mykiss*) cultured in the Aquatic Centre, School of Aquaculture, University of Tasmania. Ideally *in situ* biological effects would have been studied on native fish species but as no cultured populations were available it would have been necessary to collect test fish from wild populations. This was not done due to the variability associated with sampling from fish of unknown age and previous pesticide exposure. Previous work has shown a marked difference in brain cholinesterase activity between fish of different ages, and recommended that fish of similar age be used for tests involving brain cholinesterase activity (Zinkl *et al.*, 1987). In addition, the small size of the native galaxids (mean fork length typically < 60 mm) made catheterising problematic.

Rainbow trout used in the trial were of uniform weight (200-300g) and had never been exposed to any pesticides. Fish were transported to the site in a fish transporter in oxygenated water and held in a river cage for 24 h prior to any experimentation commenced. The experimental cage in which the catheterised fish were held during spraying was located in a section of the river open to spray drift from the adjacent orchard. Previous research has shown that chlorpyrifos remains near the top of the water column up until several hours after deposition on the water surface (Steffert *et al.*, 1999). Spray deposition on the water surface close to the location of the experimental cage was measured using glass-fibre filter papers and water-sensitive papers (Chapter 6).

In-situ respiratory physiology

The dorsal aorta of 10 rainbow trout (mean fork length 302 mm ± sd 12) were catheterised according to the method of Soivio *et al.* (1975) under benzocaine anaesthetic (100 mg/L). Fish were recovered and maintained in black polyethylene tubes suspended in the current 5 cm below the water surface in the river. Water temperatures ranged from 23°C during the day to 18°C at night. Recovery at such high temperatures was remarkably good and of the 10 fish catheterised, 7 catheters remained patent. Fish were recovered for 24 h prior to exposure to chlorpyrifos.

A 500 µL blood sample was withdrawn from the catheters and an equivalent of heparinised (100 IU/mL ammonium heparin) replaced the lost volume. Samples were taken prior to exposure (control baseline), after the peak over-spray onto the river (approximately 20 min from the commencement of the spraying) and after 6 h post-exposure. PO_2 was determined using a Cameron Instrument Company (Port Aransas Texas) E101 oxygen electrode maintained at ambient water temperature and calibrated using a 2% sodium sulphite solution (zero) and air saturated water. Arterial pH was determined using an Activon ACTP 336 pH probe maintained at ambient water temperature and calibrated with Radiometer precision buffers. Both oxygen partial pressure (PO_2) and pH readings were relayed to a Cameron Instrument Company BGM 200 blood gas analyser. Total oxygen content was determined according to the method of Tucker (1967) and total CO_2 content was determined using a Cameron Instruments Capni-con 5. Unfortunately due to the malfunction of the Capni-con particularly at the high temperatures experienced in the field (air temperature of 36°C), reliable total CO_2 measurements could not be obtained. Haematocrit was determined in microcapillary tubes with EDTA as the anticoagulant. Total blood haemoglobin (Hb) concentration was determined using a commercial haemoglobin assay kit (Sigma Chemical Company).

In-situ cholinesterase activity

Fish were collected from the river cage prior to exposure (control baseline), and approximately 90 min and 180 min after the commencement of spraying. Five fish were collected on each sampling occasion. Fish were killed with an acute blow to the head and immediately dissected. All tissue was stored on dry ice before return to the laboratory where it was stored at -80°C. Brain cholinesterase activities of fish stored at -68°C are not affected for up to 55 d of storage (Zinkl *et al.*, 1987). Cholinesterase activity was analysed in triplicate using commercial MPR 2 test kits (Roche Diagnostics, Nunawading, Australia) based on the method of Ellman *et al* (1961). Acetylthiocholine was used as the substrate so it is likely that the enzyme assayed was acetylcholinesterase (Sturm *et al.*, 2000) however no other characterisation of other selective inhibitors was performed so the activities measured are referred to as cholinesterase (ChE). Quality control was using the commercially available Precinorm® U solution (Roche Diagnostics). All spectrophotometric analysis was done at 25°C and 405 nm using a temperature controlled Varian DMS 100 spectrophotometer. Approximately 20 mg of tissue was used for each analysis, and the enzyme activity was corrected for weight of tissue analysed.

Gill and liver tissues for histology were also taken from the experimental fish. Samples were processed for histology using the same procedure as described below for wild fish.

Fish body burdens and histopathology in regional populations

Fish were collected by electrofishing and anaesthetised without recovery in 100 mg/L benzocaine. Fish were immediately placed on ice and kept frozen until dissection for extraction. Fish species collected were *Salmo trutta, Pseudaphritis urvillii* and *Anguilla australis.* Fish were collected from an upstream reference site on Mountain River (upstream of all agricultural activity), and downstream sites located within orcharding areas on Mountain River, Nicholls Rivulet and Judd's Creek. The downstream sites were chosen as representative of locations in the Huon Valley orcharding district where fish could be exposed to pesticides. At each site, five fish of the same species were collected. The species collected varied between sites.

Tissue for histology was dissected out immediately after the fish were killed, and placed in 10% formalin fixative. The collected fish were transported on ice to the laboratory and stored at -20°C until analysis. Fish for analysis were thawed, composited by species and tissue type, and tissue for analysis ground in a glass mortar. Gill, liver and muscle tissue were analysed. Pesticide from fish tissue was extracted using a commercial matrix solid phase dispersion (MSPD) kit (Varian Sample Preparation Products, Harbor City, CA). A known weight of tissue was used for extraction. Mean extraction recovery (± S.E) calculated for spiked gills from fish collected from the upstream reference site was 54% (±5.4%). Samples were analysed using GC-MS/MS under conditions previously described for analysis of chlorpyrifos in water and sediment samples (Walker *et al.*, submitted). The results are given as recovery corrected based on recovery of a 100 µL spike of Base Neutral Surrogate (Ultra Scientific, North Kingston, RI, US) which was included in every sample.

Samples were processed for histology using routine procedures. The tissue was trimmed and blocked in paraffin wax. Five micron thick sections were cut using a microtome. Following staining with haematoxylin and eosin the sections were mounted and examined under compound microscope using magnification X400. One section was examined from each block.

Statistical analysis

Data for respiratory physiology was analysed using a repeated measures analysis of variance SigmaStat *vers.* 1.02 software (Jandel Scientific) with a significance level of 0.05. Data for cholinesterase activity was analysed using analysis of variance SAS *vers.* 6.12 software (SAS Institute Incorporated, Cary, N.C.) with a significance level of 0.05.

RESULTS

Respiratory physiology

There were no significant effects of chlorpyrifos exposure on blood pH, oxygen content or haematocrit (Table 1). There was no significant change in the estimated O_2/Hb ratio even though the pre-exposure ration represented only 70% saturation of haemoglobin. This suggests that despite exposure to chlorpyrifos over-spray, there was no evidence of hypoxaemia compromised oxygen transport. O_2/Hb ratios all represented between approximately 70 and 104% saturation. Disparities in the O_2/Hb ratio are probably reflective in small errors in measuring haemoglobin content. However, there was a significant decrease in haemoglobin concentration between the pre-exposure and 6 hours post-exposure (Table 8.1). This decrease is not likely to have been reflective of the effects of repeated blood sampling since blood haematocrit was not significantly affected over the duration of the experiment. Potential over estimations of haemoglobin content in the pre-exposure samples may have accounted for the unusually high MCHC and lower-than-expected O_2/Hb ratio in the

Table 8.1 Effects of an *in situ* chlorpyrifos exposure on mean (sd) arterial oxygen tension (P_aO_2), arterial pH (pH_a), whole blood oxygen content (C_aO_2), plasma total CO_2 content (C_aCO_2), haematocrit (Hct), whole blood haemoglobin concentration ((Hb)), estimated O_2 bound to haemoglobin (O_2/Hb) and the mean cell haemoglobin concentration index (MCHC) in rainbow trout. Superscripts of different letter denote significant difference.

	Pre-exposure	Post-exposure	6 h Recovery
PaO_2 (mmHg)	ND	ND	126.9 (14.3)
pH_a	8.026 (0.136)	7.937 (0.094)	7.861 (0.109)
C_aO_2(mL O_2/dL)	11.78 (3.21)	8.70 (2.58)	8.77 (3.09)
C_aCO_2 (mM)	ND	ND	ND
Hct (%)	23.3 (4.4)	24.1 (4.1)	25.7 (6.1)
(Hb) (g/dL)	11.10 (1.63)^{a}	8.93 (2.73)^{ab}	7.19 (2.24)^{b}
O_2/Hb (mL/g)*	0.86 (0.23)	1.04 (0.39)	1.31 (0.54)
MCHC†	0.49 (0.10)^{a}	0.36 (0.11)^{ab}	0.28 (0.06)^{b}

**estimated value since does not take into account the fraction of O_2 dissolved in the plasma. † calculated by (Hb)/Hct. ND Non-determinable*

pre-exposure samples. The reasons for this are unknown but it seems unlikely that the disparities are due to the effects of chlorpyrifos. Due to equipment failure it was not possible to determine the potential effects of chlorpyrifos exposure on plasma CO_2 content. However, with no significant effects on blood pH (all of which appeared to be within the normal range for trout), it would seem unlikely that there would have been any significant effects detected.

Cholinesterase activity

There were no significant differences in brain ChE, pre-exposure, 90 min post exposure and 180 min post exposure (Table 8.2).

Table 8.2 Brain cholinesterase activity in rainbow trout exposed to a chlorpyrifos pulse exposure. No significant difference between times was detected ($p \leq 0.05$, n=5).

Time since fish were exposed to chlorpyrifos spray	Mean cholinesterase activity ± SE (nmol/min/mg protein)
Pre-exposure	183.5 ± 32.3
90 min post exposure	254.9 ± 94.8
180 min post exposure	264.4 ± 52.1

Fish body burdens and histology

Chlorpyrifos residues were detected in *Salmo trutta* and *Pseuaphritis urvillii* collected from all of the downstream sampling sites (Table 8.3). No residues were detected in *Anguilla australis*. The highest residue detected in Mountain River was 36 ng/g in *Salmo trutta* gill tissue. The highest residues detected in native *Pseuaphritis urvillii* were in Nicholls Rivulet. Composite gill, liver and muscle tissue from *Pseuaphritis urvillii* in Nicholls Rivulet had respective concentrations of 7, 13, and 9 ng/g. Two out of three individual *Pseuaphritis urvillii* from Nicholls Rivulet also had relatively high residue levels in the gills (20 ng/g and 32 ng/g). These results are not unexpected because the Nicholls Rivulet sampling site was immediately downstream of a very large orchard.

No histopathological changes were detected in organs of experimental caged fish, with the exception of epithelial lifting and telangiectasis in the gills of fish. These changes were most likely due to surgery, handling or sampling procedures and not related to the exposure to chlorpyrifos.

Wild fish sampled from the Huon Valley waterways had relatively mild pathological changes and no pathogens could be detected using histological methods. Two of the *Salmo trutta* sampled at Mountain River had inflammation in their gills. This is a response to tissue injury, which could be due to gill irriation or presence of pathogens (Mallat, 1985). Four out of five *Salmo trutta* collected from Mountain River and two out of five *Salmo trutta* collected from Judds Creek showed focal hyperplasia of respiratory epithelium in their gills. This hyperplasia resulted in lamellar fusion in all fish in Judds Creek and two of the *Salmo trutta* from Mountain River. Lamellar fusion is a result of gill irritation and if extensive can affect respiration (Mallat, 1985). Two out of four *Pseuaphritis urvillii* collected from Mountain River also showed focal hyperplasia of respiratory epithelium. Four out of five *Salmo trutta* from Mountain River and four out of five *Salmo trutta* from Judds Creek had abundant black melanomacrophages present in their liver. This suggests that the fish were stressed in the past. Melanomacrophages number and pigment content increases usually in response to infection or tissue damage (Mallat, 1985). Most fish displayed telangiectasis and a few had lifted epithelium, both most likely a result of sampling or fixation delay.

Table 8.3. Chlorpyrifos tissue residues for fish collected from three rivers in the Huon Valley orcharding district. nd=non detect.

Year and Sampling Site	Fish Species	Chlorpyrifos Tissue Residue (ng/g)	
1999 Mountain River (upstream reference site)	*Salmo trutta* composite sample	Gill	nd
		Liver	nd
		Muscle	nd
1999 Mountain River	*Salmo trutta* composite sample	Gill	7
		Liver	1
		Muscle	1
	Pseuaphritis urvillii composite sample	Gill	1
		Liver	nd
		Muscle	nd
	Anguilla australis individual	Gill	nd
		Liver	nd
		Muscle	nd
2000 Mountain River	*Salmo trutta* composite sample	Gill	1
		Liver	3
		Muscle	3
	Pseuaphritis urvillii composite sample	Gill	5
		Liver	nd
		Muscle	5
	Salmo trutta individual #1 109.0 g	Gill	36
	Salmo trutta individual #2 135.4 g	Gill	nd
	Salmo trutta individual #3 334.4 g	Gill	7
2000 Judds Creek	*Salmo trutta* composite sample	Gill	1
		Liver	nd
		Muscle	nd
2000 Nicholls Rivulet	*Pseuaphritis urvillii* composite sample	Gill	7
		Liver	13
		Muscle	9
	Pseuaphritis urvillii individual #1 13.2 g	Gill	20
	Pseuaphritis urvillii individual #2 37.1 g	Gill	32
	Pseuaphritis urvillii individual #1 12.1 g	Gill	nd

DISCUSSION

Species richness and abundance in Mountain River (From Morton, 1998)

Species diversity data collected by Morton (1998) showed that the Mountain River fish community was similar to other Tasmanian streams. *Salmo trutta* (brown trout), a salmonid widely distributed throughout Tasmanian waterways, was the only introduced species found in Mountain River. Native species found in Mountain River were *Anguilla australis* (eel), *Pseudaphritis urvillii* (sandy), *Galaxias maculatus* (jollytail), *Galaxias truttaceus* (spotted galaxias), *Galaxias brevipinnis* (climbing galaxias), *Neochanna cleaveri*, *Gadopsis marmoratus* (blackfish) and *Geotria australis* (pouched lamprey).

None of resident species found in Mountain River were rare or endangered. *Salmo trutta* was the only species regularly fished in the river. No chlorpyrifos toxicity tests have been developed for any of the native fish in Mountain River. Two of the endemic species found in Mountain River, *Galaxias maculatus* and *Pseudaphritis urvillii*, have been used in studies of sublethal responses to pesticides, however chlorpyrifos was not among the pesticides tested (Davies *et al.*, 1994b).

Species richness data indicated that Mountain River is similar to other Tasmanian streams, and the impact of agriculture has not reduced diversity in the fish community (Morton, 1998). Abundance data collected for Mountain River was difficult to interpret in relation to agricultural impacts, given the natural patterns of fish migration and distribution in Tasmanian waterways (eg. estuarine species such as *Pseuaphritis urvillii*. found in downstream Mountain River; large numbers of *Salmo trutt*a moving from upstream spawning). The limited distribution of native species made it difficult to consider abundance across all sampling sites on Mountain River. Although *Salmo trutt*a is an introduced species, it was by far the most abundant species throughout Mountain River. Biomass data for *Salmo trutta* showed there was reduced biomass at the two sampling sites located within the areas of greatest orcharding intensity. However, these results were confounded by a number of factors, and it is likely that results are not solely attributable to pesticides, but to all the stressors identified in Chapter 2 as impacting fish communities in Mountain River catchment.

Respiratory physiology

Oxygen content values fell within an acceptable range similar to reported values (Perry *et al.*, 1993) and O_2/Hb ratios were all consistent with that reported for rainbow trout arterial blood (Perry *et al.*, 1993) suggesting no diffusive limitations to oxygen diffusion across the gills. While it was not possible to accurately determine PO_2 in the pre- and post-exposure samples, the blood PO_2 measurements made at 6 h post-exposure fall within the expected range for rainbow trout (Perry *et al.*, 1993).

Although the technical challenges of this study limited some of the variables that could be measured, the results indicate that chlorpyrifos spray deposition on to the water where the trout were being held had no detrimental effect on the respiratory or acid-base physiology of rainbow trout. This is in contrast to previously reported research where trout were acutely exposed in the laboratory to chlorpyrifos (Bradbury *et al.*, 1993). This study represents a more realistic assessment of the effects of chlorpyrifos at concentrations likely to arise from recommended agricultural use. Bradbury *et al.* (1993) exposed rainbow trout to mean chlorpyrifos concentrations of 0.208 mg/L which resulted in death after 43.8 h of exposure. Concentrations of 0.2 mg/L are very unlikely to occur in Huon Valley waterways as a result of spray drift. Such high concentrations would only be likely to occur as a result of accidental spillage.

Brain cholinesterase

Exposure to chlorpyrifos in Mountain River had no effect on brain cholinesterase activity in rainbow trout. In other field measurements of AChE, enzyme depression was seen in *Fundulus heteroclitus* exposed fortnightly to chlorpyrifos oversprays (Thirungnanam and Forgash, 1977). Enzyme depression continued throughout the fortnight between spray applications. In the Mountain River experiment it would have been desirable to continue ChE measurements for days, rather than hours, after spray application but logistically this was not possible.

Variability between ChE activity of individual fish (n=5) may have confounded the results of this experiment. Similar problems with variability in ChE have been reported (Ernst and Julien, 1994). Larger sample sizes or elevated pesticide concentrations are required to accurately measure changes in enzyme activity. In one study using 48 h exposures of high chlorpyrifos concentrations (0.1 mg/L), variability among test individuals was not reported although the sample size was three individuals (Boone and Chambers, 1996). In this study the test concentration was 67% of the LC50 for the test species, mosquitofish (*Gambusia affinis*). In another study concentrations of 1 μg/L chlorpyrifos resulted in 19% inhibition of AChE when fish were exposed for 24 hours, however only two individual fish were tested (Thirungnanam and Forgash, 1977). Fish exposed to 2.1 μg/L for 24 hours showed a 100% AChE inhibition and severe toxic symptoms, but there was no fish mortality (Boone and Chambers, 1996). The relationship between AChE inhibition in brain and muscle and toxicity is not well understood (Boone and Chambers, 1996). Several authors (Weiss, 1961; Gibson *et al.*, 1969; Boone and Chambers, 1996) have found a lack of correlation between the *in vivo* AChE inhibition and toxicity in fish, and it has proposed that fish do not require as much functional AChE to sustain life as do mammals (Boone and Chambers, 1996).

Fish body burdens and histopathology

Although only the gills of six individual fish were analysed, those fish with chlorpyrifos residues all had pathological changes in the gills and liver. Correlation between residue level and biological effects have been shown for endosulfan where ultrastructural changes in the liver of catfish *Tandarus tandanus* were related to endosulfan residue levels (Nowak, 1996). Chlorpyrifos exposures of 2000 μg/L produced shrunken glomeruli, vacuolated blood cells, dilated renal tubules, and necrosis in freshwater catfish *(Heteropneustes fossilis)* (Srivastava *et al.*, 1990).

None of these signs were seen in fish collected from Mountain River. The only histological changes seen in Mountain River fish were minor abnormalities, which were consistent with exposure to pesticides. Similarly these abnormalities could be attributed to a number of non-chemical stressors including variable water conditions and pathogens. Wild fish often have some background level of pathological changes attributable to non-chemical stressors (Nowak, 1996). The incidence of histological abnormalities was higher in the larger fish suggesting that cumulative environmental factors were the cause of the observed abnormalities.

Different tissues may accumulate different levels of organic contaminants. Rates of depuration vary between different tissues and are related to their relative abilities to metabolically transform the chemical (Nowak, 1997). Chlorpyrifos residues were typically higher in the gill for both *Salmo trutta* and *Pseuaphritis urvillii*. This is to be expected as fish exposure to chlorpyrifos is via water.

The biological significance of xenobiotic residues in fish has been reviewed (Connell, 1988; Nowak 1997) but to date there has been limited quantification of benchmarks for effects of pesticide as indicated by body burdens. McCarty and Mackay (1993) proposed the concept of a 'critical body residue' as an estimate of biological response. For acute effects of chlorpyrifos to be seen the critical body residue was estimated at 2.2 mmol/kg. This equates to 771 mg/kg, which is an extreme body burden. It is not comparable with the concentrations seen in the Huon Valley fish where 36 ng/g was the highest residue measured.

In this study, the chlorpyrifos residues found in *Salmo trutta* and *Pseuaphritis urvillii* serve to confirm that the Mountain River sites selected for seasonal sampling (Chapter 6) were consistent with sites where fish were exposed to chlorpyrifos. Macek *et al.* (1972) found that accumulation of chlorpyrifos residues in bluegills (*Lepomis macrochirus*) and largemouth bass (*Micropterus salmoides*) was a function of chemical concentration in the water. In US rivers measurements of chlorpyrifos residues in fish were correlated with concentrations measured in surface waters (US EPA, 1992b).

Although only chlorpyrifos residues were measured in this study, wild fish often contain residues of different compounds. Their potential interactions include synergisms, potentiation, antagonisms or additvity of effects (Nowak, 1996) which all confound a chemical specific risk assessment.

CONCLUSIONS FROM MULTIPLE LINES OF EVIDENCE

Measures of acute effects indicated that the assessment endpoint for this risk assessment was being achieved in Mountain River. There were no significant changes in respiratory physiology or brain cholinesterase activity as a result of exposure to chlorpyrifos.

Measures of chronic effects were more difficult to interpret. Chlorpyrifos residues confirmed that fish in the Huon Valley orcharding region are exposed to chlorpyrifos in regional waterways. Body burdens were probably indicative of the locality from which fish were collected, with fish collected close to large orchards having elevated residue levels. The histology of fish with residues showed some signs consistent with exposure to pesticides, but these signs could also be attributable to natural environmental stressors such as temperature and fluctuations in food resources.

Further field studies are required to confirm the chronic effects of chlorpyrifos in fish species in the Huon Valley orcharding district. However, given the very low risk estimates predicted in the probabilistic risk assessment (Chapter 7) and the inconclusive chronic effects observed in field studies, it is unlikely that chronic effects directly attributable to chlorpyrifos could be identified in the Huon Valley. Measures of chronic effects in fish in the Huon Valley are likely to be indicative of exposure to various anthropogenic stressors, given the level of agricultural activity within the catchment.

CHAPTER 9. AERIAL MOVEMENT OF CHLORPYRIFOS AND POTENTIAL FOR RISK MITIGATION USING SPRAY BUFFERS

Chapter Background: Previous chapters have described potential risk to aquatic organisms in orcharding districts. Although the risks are small, it is desirable for risks to be minimised in all situations. Given that chlorpyrifos is potentially highly toxic to aquatic organisms, drift mitigation must be considered if the product continues to be used in situation where there is potential for spray drift onto waterways.

In this chapter aerial movement of chlorpyrifos was studied with the objectives of:

- Describing the typical drift profile for an orchard application
- Assessing the effectiveness of riparian vegetation as a spray buffer to protect aquatic ecosystems
- Comparing field measurements with the spray drift model, AgDRIFT™

The Aquatic Risk Assessment and Mitigation Dialogue Group (1994) recommends buffers as one of the most effective risk mitigation options for achieving reductions in off-target pesticide movement. The height, density, composition and siting of vegetative buffers can significantly influence their effectiveness in trapping spray particles. Strategies for optimising the risk mitigation properties of buffers in orcharding districts are discussed in this chapter.

This chapter forms the basis of a paper submitted to the *Journal of Environmental Quality* with the following reference: Walker R Brown PH Dorr D Woods N. Chlorpyrifos spray drift and effect of spray buffers in orcharding districts.

Abstract

Off target orchard spray drift onto an adjacent waterway was measured in the Huon Valley, Tasmania, Australia. Measured deposits of the insecticide chlorpyrifos onto Mountain River were compared with estimates from water sensitive papers, estimates used by regulatory authorities and estimates simulated using the spray drift model

AgDRIFT™. Comparisons of field data from Mountain River with AgDRIFT™ indicate this model is a valid and useful tool for estimating aerial drift in orcharding districts. The effect of a vegetative buffer as a spray drift risk mitigation strategy to protect aquatic environments was studied using stream surface deposition measurements and drift tower measurements. The buffer significantly reduced spray drift, approximately halving the amount of drift moving offsite. In this and other studies, it has been found that vegetative buffers with an optical porosity of 0.2 result in approximately 50% reduction in off-site movement of spray. Characteristics of vegetation spray buffers that are most effective in minimising the impact of orchard pesticides on aquatic environments are considered.

INTRODUCTION

Pesticide application in intensive orcharding systems in Australia generally involves the use of airblast or airshear sprayers. Improvements in the design of spray units have contributed to the increased efficiency of pesticide application in apple orchards, but the potential for significant movement of pesticide to off-target sites under certain conditions has been demonstrated (e.g. Spray Drift Task Force, 2000; Ganzelmeier *et al.*, 1995, Ganzelmeier and Rautmann, 2000) The risk of drift contamination of the aquatic environment is particularly high in older orcharding districts where many orchards have been established adjacent to waterways on river flats. Pesticide contamination of waterways from apple orchards is a serious environmental issue because many of the insecticides used, particularly organophosphates and carbamates, are highly toxic to aquatic organisms (Warne *et al.*, 1998; Davies *et al.*, 1994b; Tomlin, 1994).

Mitigation activities are defined as actions taken to reduce or eliminate pesticide concentrations in aquatic and terrestrial habitats (Aquatic Risk Assessment and Mitigation Dialogue Group, 1994). Despite the development of spray application guidelines (DPIF, 1999; CPAS, 2000) and increasing pressure on growers to adhere to best management practices for pesticide use, the drift mitigation potential of vegetative buffers in orcharding districts in Australia has received limited attention.

The Spray Drift Task Force (SDTF) in the United States of America has been responsible for developing a spray drift model to assist in the registration of agrochemicals. The model, known as AgDRIFT™, is designed to assist regulatory authorities assess off target risks based on realistic input parameters instead of prescriptive threshold values. AgDRIFT™ is primarily designed as an aerial predictive model for risk assessment purposes. Its outputs are curve-fits of data collected by the Spray Drift Task Force. To date its potential application in Australian orchard production systems has not been considered.

The aims of this experiment were to measure the drift profile resulting from a typical orchard application of pesticide; assess the effectiveness of a vegetative buffer in reducing orchard drift; and compare field measurements with the AgDRIFT™ model.

MATERIALS AND METHODS

Sampling site

An experimental site typical of a 'worst case scenario' for spray drift contamination of waterways in orcharding regions was chosen in the Mountain River catchment, southern Tasmania, Australia. The sprayed block was part of one of the largest commercial apple orchards in the Huon Valley and located directly adjacent to Mountain River. The Mountain River field site was an ideal locality for studying both pesticide spray drift and the effect of typical regional streamside vegetation in mitigating drift. Mountain River flowed around the perimeter of the block, with a section of the river directly open to the orchard and a section of the river buffered by streamside vegetation (Figure 9.1). Sampling sites were: (1) Buffered site (vegetative spray buffer present. Spray drift reaching the river had to pass through, over or around vegetative buffer), (2) Exposed site (no vegetative spray buffer present. Waterway open to spray drift with no buffering from streamside vegetation).

The orchard block being sprayed was approximately 4.5 ha in size and planted with 4 year old centre leader trees (Pink Lady and Red Delicious varieties). Spacing between rows was approximately 4.5 m, and trees averaged 2.5 to 3 m in height. The canopy was relatively open.

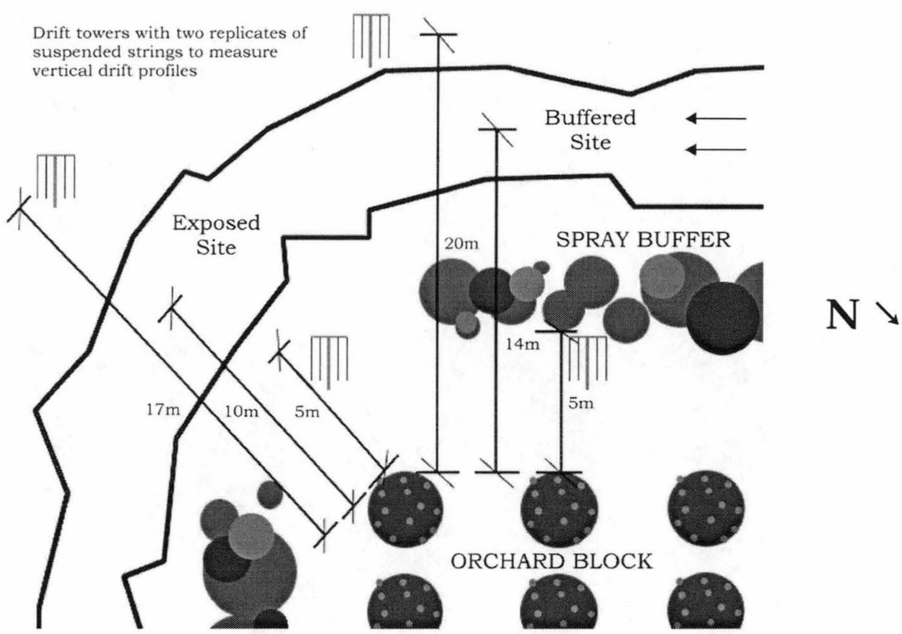


Figure 9.1 A simplified schematic of the orchard block and the location of drift towers.

Streamside vegetation was dense; in addition to native grasses, wattles (5-10 m) and gum trees (to 25 m), there were several weed species including willows (to 15 m), hawthorns (to 5 m), blackberries, and introduced grasses. The average optical porosity of the buffer was visually estimated to be 0.2. The average width of the buffer was approximately 7 m.

Sampling protocol

Drift sampling was conducted on 12 January 2000. Lorsban® 750 WG was applied at the rate of 660 g/ha (495 g/ha active ingredient) using a Silvan 820 CV Cropliner (1500 L) with air output of 87, 000 m^3/h. The nozzles were Albuz ceramic nozzles at 10 bar pressure. Spraying commenced at 1320 hrs. The sprayer was operating for one hour in the orchard.

Drift towers were located on both sides of the river at the two sites (exposed and buffered), so as to compare drift differences with/without vegetation buffer (Figure 9.2). The drift towers were 7 m tall; above this height it was difficult to maintain stability in the event of windy conditions. Other Australian drift sampling in cotton-growing districts has been up to 20 m, but purpose-built mechanised drift towers have been used (Woods *et al.*, 1998). Two 1 mm diameter untreated cotton strings were suspended from each tower to collect drift. The strings were anchored at ground level so that they remained fixed through the trial.

After spraying each cotton string was cut at one metre intervals so that the intervals 0-1 m, 1-2 m, 2-3 m etc. could be sampled to give a vertical drift profile. Each one metre length of string was wrapped in foil and placed in a labeled ziplock bag and stored at 2°C prior to extraction. At the base of each drift tower three replicates of 70 mm glass-fibre filter papers were placed on level plywood. These were used to measure horizontal deposition on the streambank.

Spray deposition on the water surface was measured with 70 mm glass-fibre filter papers and 76 x 52 mm Novartis® (Spraying Systems Co. Wheaton, Illinois, USA) water-sensitive papers pinned to foil-covered polystyrene floats, set to float just above the water surface. Spray deposition on the water surface was measured for the intervals 0–60 min and 60–120 min. Three replicates of filter papers and three replicates of water sensitive papers placed on each floating platform were used for each time interval. Sampling schedules at all sites commenced with the start of spraying (0 min).

Local wind speed and direction were also measured throughout the course of the experiment. A fixed anemometer with automatic logging was used but due to technical problems the data could not be downloaded. Fortunately measurements were also taken with hand held instruments as backup. Wind speed was measured every 5 minutes using a handheld anemometer. Wind direction, as estimated by compass alignment with a wind tether, was recorded at the same time. Throughout the experiment the wind was light (less than 1.5 m/sec and blew from the northern quarter (Appendix 3) which directed spray across the river. The temperature range on the day of sampling was 13.2 - 29.6°C. The relative humidity was 76% (Bureau of Meterology Grove Station, 3pm readings).

Chlorpyrifos extraction and analysis

Extraction from string sections and glass fibre filter papers was achieved following transfer of the samples to conical flasks using tweezers. 50 mL pesticide grade dichloromethane and 100 μL of base neutral surrogate (Ultra Scientific®, Smith St, North Kingston, RI) were added to the flask. After approximately ten minutes, the flask was gently shaken and the solvent dried through Na_2SO_4 (anhydrous) and evaporated to 1000 μL under N_2 atmosphere. Extraction recovery from string sections and filter papers was greater than 90%.

Analysis for all samples was by GC-MS/MS using conditions that were optimised for detection of chlorpyrifos, base neutral surrogate and the internal standard, *n*-pentadecane. Analysis was using a Varian Saturn 4D iontrap GC-MS. Gas chromatography conditions were as follows: 30-m VA-5MS capillary column, 0.25 mm i.d., 0.25 μm film thickness and helium carrier gas at a constant flow of 1.0 mL/min. The temperature program was as follows: injector temperature 280°C, initial temperature 40 °C, hold 20 min, 10 °C/min to 160 °C, hold 9 min, 20 °C/min to 280 °C, hold 6 min. MS/MS conditions were: segment 1 0-14 min in electron ionisation mode and sediment 2 14-20 min in MS/MS mode. The ions monitored for chlorpyrifos were 314, 286, 258 m/z. The method detection limit was 0.002 μg.

Water sensitive paper analysis

Image analysis with SwathKit (Droplet Technologies, USA http://www.droptech.com/) was used to analyse the water sensitive papers. The spread factor was based on the equation used for water landing on water sensitive paper, and was used in estimates for droplet size and rate.

RESULTS

Results from the drift towers show a clear difference in drift across the river between the buffered and exposed site (Figure 9.2). A paired sample *t*-test showed that on the near bank there was no significant difference between the buffered and exposed ($p = 0.13$, $d.f = 6$). On the far bank, drift at the buffered site was significantly different ($p = 0.0003$, $d.f = 6$) and approximately half that of the exposed site. Significant differences were recorded in the transmission ratios for the two sites (Figure 9.3). The transmission ratio is the ratio of drift measured behind a buffer to that measured in front of the buffer. The average transmission ratio for the buffered site was 0.15 compared to 0.27 at the exposed site. The transmission ratio at the buffered site was significantly different to the transmission ratio at the exposed site ($p = 0.004$, $d.f = 6$) indicating that there was a significant reduction in spray drift due to the buffer.

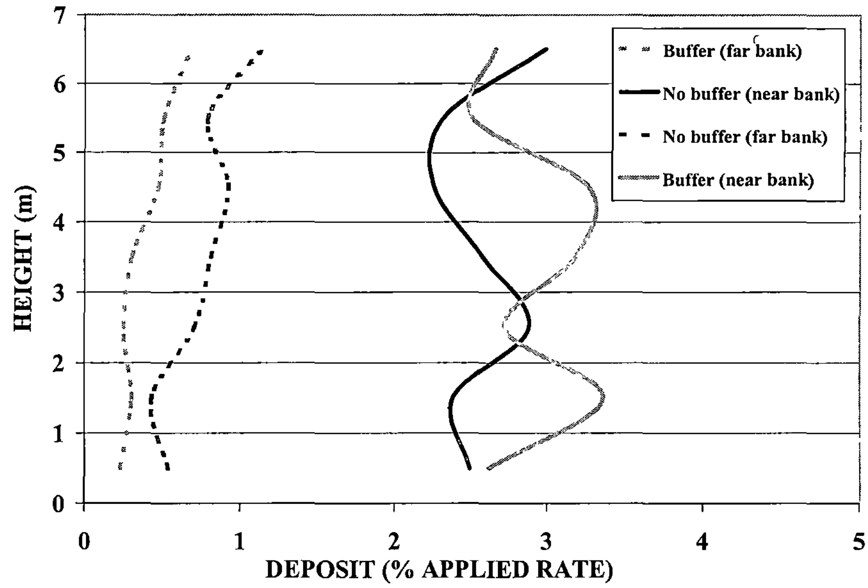


Figure 9.2 Aerial deposit (expressed as % of applied rate a.i.) measured with drift towers located at the exposed site and the buffered site. Measurements are shown for the midpoint of each height interval.

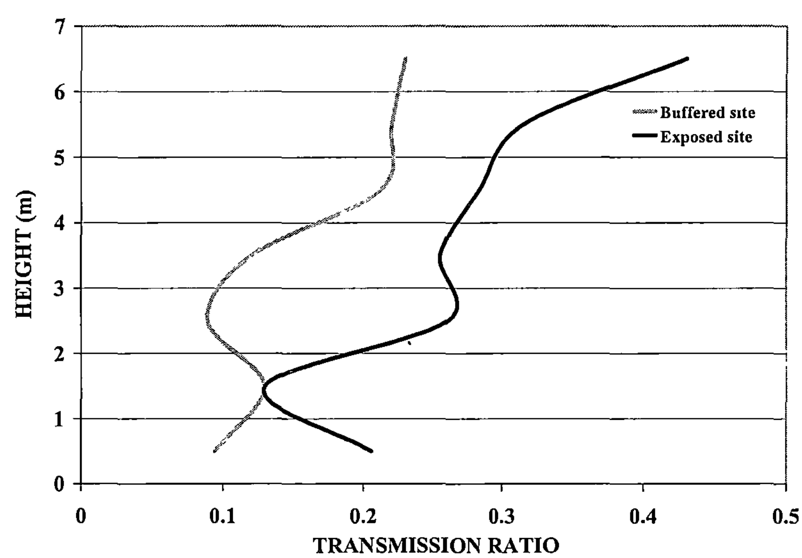


Figure 9.3 Transmission ratios for the buffered and exposed sites. The transmission ratio is calculated as (deposit behind buffer/deposit in front of buffer). Measurements are shown for the midpoint of each height interval.

Stream surface deposition

Average midstream deposition at the exposed site was approximately three times greater than at the buffered site during the first hour and approximately double during the second hour (Figure 9.4). Measurable deposition occurred after spraying had ceased indicating that chlorpyrifos remained in the atmosphere after release.

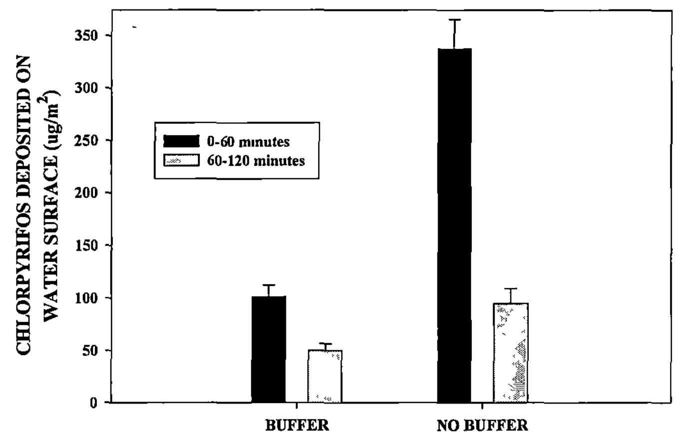


Figure 9.4 Mean midstream (+ SE) chlorpyrifos deposition at the buffered site and exposed site during the first hour (0-60 minutes) and the second hour (60-120 minutes) after spraying commenced.

In addition to field measurements, there are a number of different ways to estimate stream surface deposition (Table 9.1). The AgDRIFT™ model (described below) can be used to estimate spray deposition onto the water surface. AgDRIFT™ (Spray Drift Task Force. 1998. Ver 1.07. Missouri, USA) predicted the midstream deposit to be about half of the measured deposit (Table 9.1). An estimated deposit based on a standard drift factor of 10% overestimated the midstream deposit by about 15 times (Table 9.1). The deposition estimate based on water sensitive paper underestimated the midstream deposit by about 117 times (Table 9.1). Underestimation with the water sensitive papers is to be expected because droplets less than about 50 µm will not stain the papers so the total deposit on the paper is not recorded (Ciba-Geigy, 1985).

Table 9.1 Comparison of estimated and measured chlorpyrifos deposition (µg/m^2) on the water surface at the exposed site. Estimates based on rate of active ingredient applied (0.495 kg/ha).

Estimate	**Chlorpyrifos deposit on water surface µg/m^2**
Estimated environmental deposit based on 10% spray drift	4950
Estimate based on AgDRIFT™ simulation	163
Estimate based on water sensitive paper results	2.9
Mean measured deposit (± SE)	*338 (± 28)*

Comparisons with AgDRIFT™ simulations

AgDRIFT™ utilises a three-tier approach. Tier I is designed to "yield conservative exposure estimates for downwind deposition values...as a preliminary screen for aerial, ground and orchard airblast spraying" (Teske et al, 1997). Tier II and Tier III permit increasing access to more model details for aerial spraying only. Input data concerning application, meteorology and the environment can be included. As the level increases, the level of input data required increases.

For airblast applications AgDRIFT™ models three orchard scenarios with different canopy structures: normal (stone and pomefruit, vineyard), dense (citrus, tall trees) and sparse (young, dormant trees). Figure 9.5 shows a comparison of measured ground deposits with AgDRIFT™ simulations for these three orchard scenarios. The deposits shown are the mean horizontal deposits measured on filter papers located beneath the drift towers. The data collected in the Huon Valley orchard correlates reasonably with the AgDRIFT™ simulation for pomefruit orchards (normal simulation in Figure 9.5). Some variation between model and field measurements would be expected because downwind drift profiles are influenced by the prevailing meterological conditions, release height, initial droplet spectra and formulation (Dorr *et al.*, 1998).

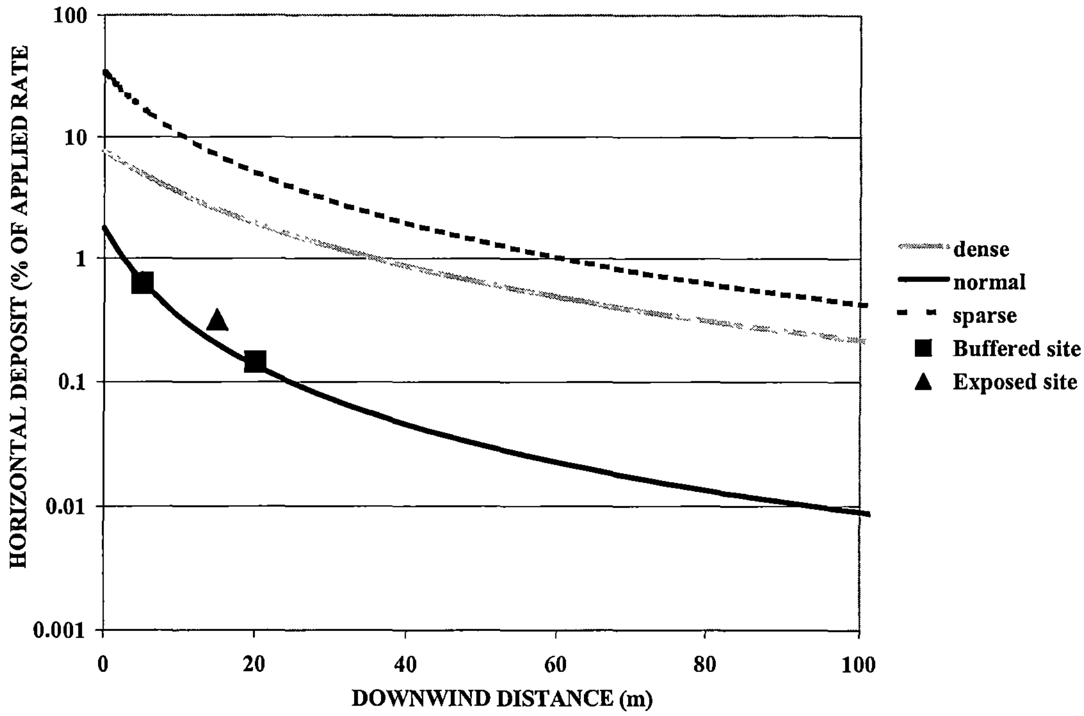


Figure 9.5 Comparisons of measured aerial drift with AgDRIFT™ simulations.

Further assessment of the AgDRIFT ™ model in orcharding systems was undertaken by comparing simulations with field data collected under similar conditions. The most comprehensive monitoring of spray drift in orcharding has been conducted by Ganzelmeier *et al.* (1995, 2000), and the field measurements for that work correlate well with the pomefruit scenario modeled by AgDRIFT™ simulations (Figure 9.6). The downwind deposit curves from the data were closer to the sparse or dense curve than the normal curve but these are such that 95% of the values are less than the value given whereas AgDRIFT™ would be closer to the mean.

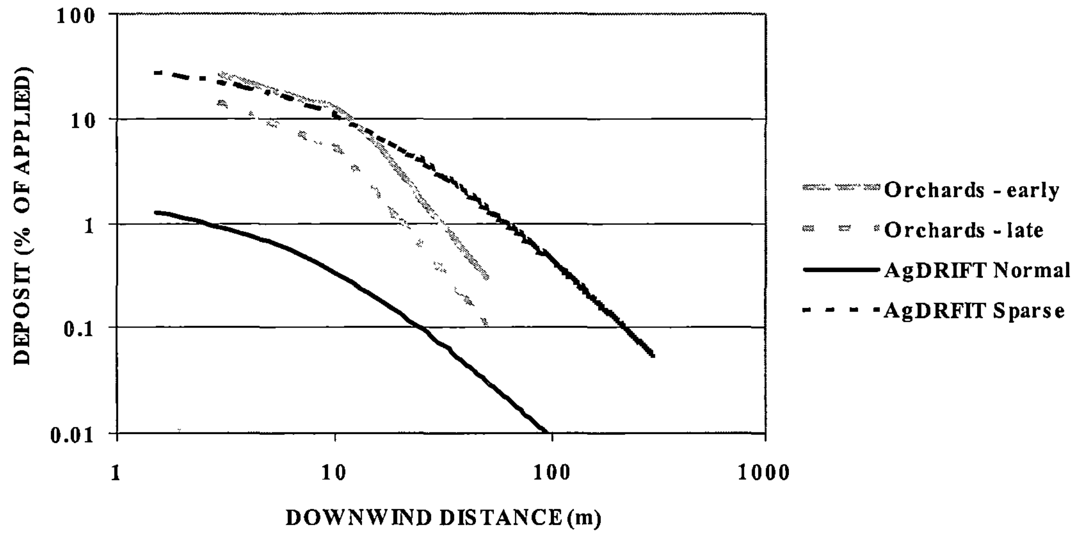


Figure 9.6 Comparison of AgDRIFT™ simulations with data collected by Ganzelmeier (1995).

DISCUSSION

The environmental regulatory authority in Australia currently uses a drift factor of 10% in their risk assessments (Holland, 1999). In Mountain River conservative drift estimates calculated using a standard percentage drift of 10% overestimated off-target deposition approximately 15 times. This has implications for any Tier 1 hazard quotient risk assessments conducted using a drift factor of 10%. The results from this study indicate that adoption of AgDRIFT™ as a tool for use in pesticides risk assessments in orcharding districts would generate more realistic exposure concentrations for aquatic organisms.

Considerable variability in the efficiency of different drift collection techniques has been previously reported (e.g. Grover *et al.*, 1978; Parkin and Merritt, 1988; Miller *et al.*, 1989) and the results from this experiment confirm that the results from field measurements must be considered in terms of the limitations of the sampling technique. For example, water sensitive papers have limited use for gaining quantitative data but they are useful for providing an estimate of droplet size.

Protection of aquatic environments is one of the main goals of spray drift mitigation. There is a range of mitigation practices from equipment specifications, meteorological restrictions and site modifications which can reduce spray drift from airblast applications, but only drift mitigation using buffer zones between the sprayed orchard and nearby watercourses was considered in this paper.

The Aquatic Risk Assessment and Mitigation Dialogue Group (1994) recommends buffers are one of the most effective risk mitigation options for achieving a quantifiable reduction in off-site movement, and the data collected in this study confirmed that vegetation buffers can significantly reduce off-target movement of chlorpyrifos.

The results for the drift tower deposits show that there was a statistically significant reduction in drift as a result of the vegetation buffer at the Huon Valley orchard site. The average transmission ratio for the buffered was 0.15 compared to 0.27 at the exposed site indicating that at this particular site the effect of the buffer was to decrease by half the amount of spray moving off site. These results are consistent with fieldwork conducted by Dorr *et al.* (1998) who did 26 studies measuring airborne spray concentration in front and behind a series of tree lines. They found that the net effect of the vegetative barrier was to effectively reduce the airborne spray drift by about 50%. The porosity of the vegetative buffers used in these studies ranged from 10-20%. The porosity of the buffer in the Huon Valley orchard was in the same range so the results are directly comparable.

Recent work by Raupach *et al.* (2000) has found a useful correlation between the optical porosity of a vegetative buffer and its effectiveness in entrapping particles. The optical porosity is the seen fraction visible through a buffer, from a viewpoint directly facing the buffer. It can be easily assessed by eye in the field. The fraction of particles transmitted through a windbreak (transmission ratio) approximates the *optical porosity*, and the fraction entrapped by the filtration of the airflow is about *(1-optical porosity)* (Raupach *et al.*, 2000).

For maximum effect the buffer must be dense enough to absorb particles efficiently, but sparse enough to allow some particles to flow through and be trapped. Raupach *et al.*

(2000) found an optical porosity of around 0.2 resulted in maximum total deposition within the buffer. The optical porosity of the Huon Valley orchard buffer was approximately 0.2 and this intercepted approximately 50% of spray drift. The results from Raupach *et al.* (2000) results indicate that this is about the maximum interception that can be expected.

Generally tree species with fine foliage have been found to be best at trapping drift particles. Tree species along waterways in the Huon Valley include a mixture of native and introduced species. Willow trees, which currently constitute a large percentage of streamside vegetation in the Huon Valley, make efficient spray buffers due to their height and fine foliage. A campaign to eradicate willows from watercourses is currently underway, but it is possible to replace willows with native species such as tea-tree and black wattle which are also effective at trapping spray drift.

In addition to air movement through the buffer, air movement over the top of the buffer is also a consideration. Due to the action of turbulence on the dispersion of a spray cloud, a vegetative buffer must be higher than the release height of the spray. The greater the density of the buffer (the lower the porosity), the higher a barrier needs to be in relation to the spray release height (Dorr *et al.*, 1998). Studies in wind tunnels have found that the minimum height of a buffer should be one and a half (1.5) times the release height of the spray for a 50% porosity buffer. If the porosity is reduced to 40% the minimum height of the barrier increases to double (2.0) the release height. For a solid barrier the required height approaches infinity so solid barriers are unsuitable (Dorr *et al.*, 1998).

The release height in apple orchards is the height of orchard trees. In the Pink Lady orchard block sprayed in this study the tree height was up to 4 m. Using the assumption that the minimum height of the buffer should be double the release height this means that a suitable buffer for this orchard block would be at least 8 m high. The existing buffer contains species growing at up to 25m with an approximate average height of 10 m which is adequate according to this height specification.

Raupach *et al.* (2000) found there was a decreasing localised effect of a vegetative buffer with distance from the buffer. This implies that vegetative buffers should be sited immediately adjacent to waterways in order for maximum mitigation effectiveness. At some localities in the Huon Valley streamside vegetation has been cleared, and this trend may increase in the future with concerted efforts to remove weeds and willows which are choking local waterways. In these instances, even if waterways are not rehabilitated with native vegetation, it is still possible to reduce spray drift onto the waterway if there is a large open area (pasture) which can act as a buffer. Based on AgDRIFT™ simulations the distance required for a halving of the spray deposit to levels equivalent with those behind the buffer is approximately 20 m i.e. if there is no vegetative spray buffer an open area of ground at least 20 m is needed between the orchard and the waterway in order to achieve an equivalent reduction in spray drift. The main disadvantage of large, unvegetated buffers compared with vegetation buffers is the potential economic impact associated with taking land out of production.

Recognition of the environmental benefits of vegetative buffer strips can help to reduce the impact of pesticides to the aquatic environment (de Snoo and de Wit, 1998). In some instances, the presence of a vegetative buffer may mean the difference between an acceptable and unacceptable level of risk to the aquatic environment. Monitoring of aquatic chlorpyrifos concentrations at the Mountain River site (Chapter 6) showed that when a vegetative buffer was absent, chlorpyrifos concentrations in the water were high enough to pose an unacceptable risk to aquatic species in Mountain River (Figure 9.7). When a vegetative buffer was present chlorpyrifos concentrations were less, and the risk to the aquatic environment was reduced to within an acceptable range.

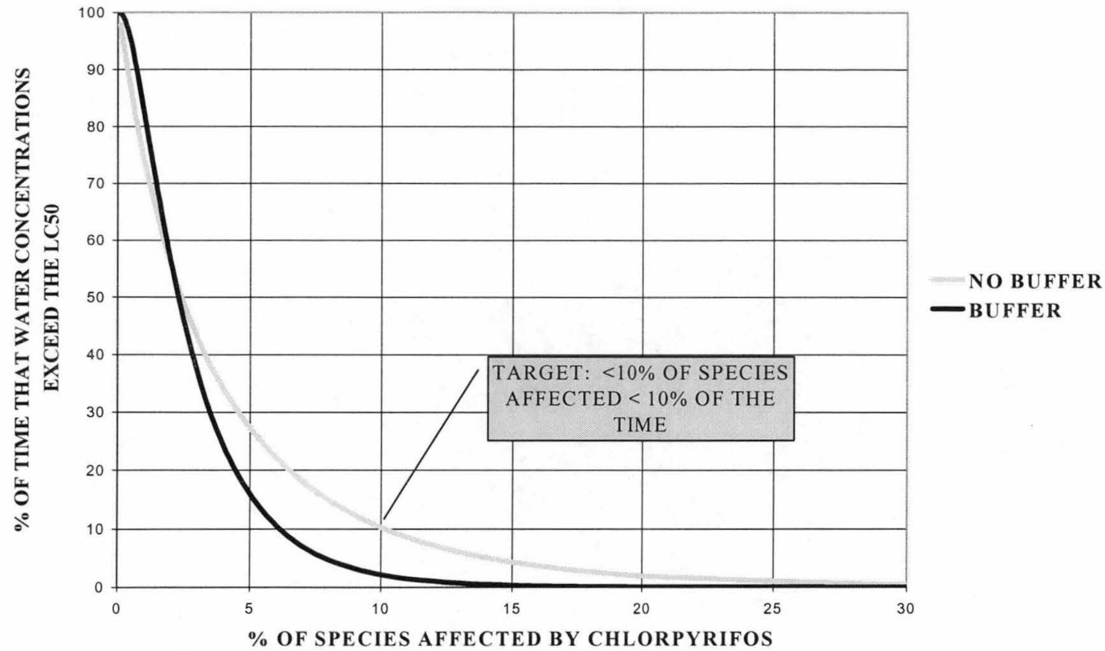


Figure 9.7 Data from an ecological risk assessment for the study site illustrating how the presence of a vegetative buffer can reduce risk to aquatic invertebrates (sensitive to chlorpyrifos). With a vegetative buffer present, the risks to aquatic invertebrates from chlorpyrifos sprays are considered acceptable; without a vegetative buffer present chlorpyrifos sprays pose an unacceptable risk to aquatic invertebrates. The level of risk deemed acceptable is 'not more than 10% of species affected more than 10% of the time'. This is the risk criterion used by the Aquatic Mitigation and Dialogue Group (1994).

A vegetative buffer, with the properties described above (Figure 9.8), provides an economical means of mitigating against spray drift and requires no changes in spray application equipment or production practices. The benefits of vegetative buffers for drift mitigation have been recognised in the cotton industry (RIRDC, 1999), and it is recommended that the environmental benefits of vegetative buffers be promoted in the orcharding industry.

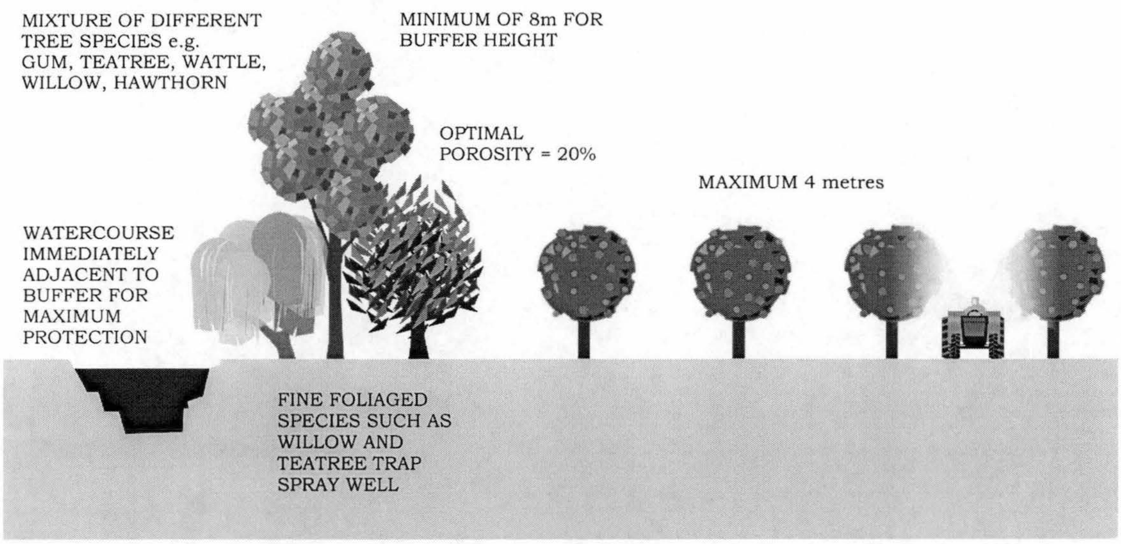


Figure 9.8 Schematic illustration of an effective spray buffer for protection of waterways in orcharding regions.

THESIS SYNTHESIS

CHAPTER 10. DISCUSSION

Chapter Background: This chapter comprises an integration of research outcomes, discussion on interpretation of outcomes and a critique of the different ecological risk assessment methods applied in this project.

SUMMARY OF RESEARCH FINDINGS

The objective of this project was to understand the probability and significance of effects of chlorpyrifos on aquatic ecosystems in the Mountain River catchment using ecological risk assessment methods. Given the limited research that has been conducted with chlorpyrifos in Australia, there was no basis for judging the levels of chlorpyrifos contamination that could be expected in Huon Valley waterways. At the commencement of fieldwork, it was not known whether chlorpyrifos would be detected in any water samples collected from Mountain River. Detections during seasonal sampling showed that chlorpyrifos was a pesticide of potential concern to the aquatic environment. This confirmed the outcomes of a Tier 1 risk assessment (Chapter 4). Seasonal data showed that chlorpyrifos was intermittently detected in waterways in orcharding areas, and that the magnitude and frequency of detections was related to the surrounding intensity of orcharding (Chapter 6).

Seasonal sampling was inadequate to characterise true environmental exposures because peak pulse concentrations were generally not measured – the maximum concentration detected during seasonal sampling was 0.08 μg/L, while the maximum concentration detected during pulse sampling was 0.163 μg/L. Sampling at the time of spraying provided unique field data describing the magnitude and duration of pulse exposures at a site directly exposed to spray drift. Although characterisation of pulse exposures in Mountain River was logistically difficult, the results obtained were central to the subsequent risk assessment.

Collection of field data specific to the application of chlorpyrifos in Huon Valley orchards meant that the risk outcomes were directly applicable to local production practices. The comprehensive risk assessment of chlorpyrifos conducted by Giesy *et al.* (1999) assumed that maximum instantaneous concentrations persisted for 48 hours. The fieldwork described in Chapter 6 indicated that this would have been a grossly conservative assumption to make for Mountain River. Characterisation of the pulse exposure indicated that detectable concentrations lasted for only three hours. The discrepancy between duration of field exposures and duration of laboratory exposures used in toxicity testing has been discussed by many authors (e.g. Crossland et al., 1982; Jarvinen et al., 1988; Siefert *et al.*, 1989; Suter, 1993; Geisy et al., 1999;). Studies such as this serve to reinforce the demand for toxicity laboratory testing using exposure durations comparable to those occurring in the field.

The probabilistic approach used in this study was conservative because it was based on the LC50/EC50 data of organisms exposed to continuous concentrations of pesticide for at least 48 hours. The mode of action of chlorpyrifos is by enzyme inhibition (Chapter 5), the process is reversible, and effects are transient if exposure is short. For the probabilistic assessment, the 10^{th} centile of fish and insect sensitivities was compared with exposure distributions. Probabilistic outcomes indicated that fish were unlikely to show chronic or acute responses to seasonal or pulse chlorpyrifos exposures.

To validate the outcomes of the probabilistic risk assessment, field studies on acute and chronic effects in fish were conducted (Chapter 8). There were no significant changes in respiratory physiology or brain cholinesterase activity, indicating that acute effects in the field were unlikely. Results from tissue residues, histology and biomass data were difficult to interpret because of confounding factors. Chronic responses seen in fish were indicative of exposure to various anthropogenic stressors, not just exposure to chlorpyrifos. Environmental stressors impacting on fish communities in the Huon Valley were considered in Chapter 3.

Risk mitigation using riparian vegetation as a spray buffer was considered. Riparian vegetation at the pulse exposure sampling site was shown to reduce off-target drift by approximately 50% (Chapter 9). Spray buffers are recommended as a simple and effective mitigation option in orchards. Aquatic concentrations and drift measurements for orchard spray applications were consistent with maximum values predicted using the spray drift model AgDRIFT™. The data collected in this study indicated that AgDRIFT™ is an appropriate model to use for assessments of pesticide contamination resulting from orchard spray drift (Chapter 6, Chapter 9).

LIMITATIONS ON THE INTERPRETATION OF RESULTS

Uncertainties in the characterisation of exposure and effects data have been discussed in preceding chapters. Many of the uncertainties encountered in this project are typical constraints that limit the interpretation of outcomes from all risk assessments. However, there are some constraints that are pertinent to this project, and these are outlined below.

Lack of field studies for effects on invertebrates

It is acknowledged that, in order to fully characterise risks to aquatic species in Mountain River catchment, field studies should have been undertaken for aquatic invertebrates as well as fish. However, due to time and resource constraints no field investigations of pesticide impacts on invertebrate populations were undertaken. Field surveys of invertebrates have been used to assess the condition of rivers in Tasmania (Read and Kranksi, 1998) using the AUSRIVAS approach.

AUSRIVAS (Australian River Assessment System) is a prediction system used to assess macroinvertebrate communities. The AUSRIVAS model predicts the aquatic macroinvertebrate fauna expected to occur at a site in the absence of environmental stress, such as pollution or habitat degradation, to which the fauna collected at a site can be compared (AUSRIVAS, 1994). AUSRIVAS predictive models have been developed for each state and territory for the main habitat types found in Australian river systems, including riffle, edge, pool and bed habitats. The AUSRIVAS approach could be a suitable model to assess whether invertebrate populations in streams in orcharding/agricultural areas differ from those in reference streams. However, it should be kept in mind that the AUSRIVAS approach is broad in scope, and lacks the resolution to detect subtle changes in populations.

Single chemical, single stressor

Apple pesticides are generally applied as mixes, with insecticides, fungicides and foliar treatments commonly mixed in the spray tank. In addition, pesticides are often applied at similar times within the same catchment and may be present simultaneously in local waterbodies. There is potential for synergistic toxic effects on aquatic organisms exposed to chemical mixes. In previous studies, chlorpyrifos has been shown to have additive acute toxicity with the organophosphorous pesticide, diazinon, to *Ceriodaphnia dubia*. (Bailey *et al.*, 1997). Atrazine and chlorpyrifos have been shown to have synergistic toxicity to larvae of the midge *Chironomus tentans* (Belden and Lydy, 2000).

When toxic substances are known to act additively, it is possible to use the toxic equivalents or toxic unit approach (Solomon and Giddings, 2000), however research into synergistic effects of pesticides is limited, particularly for Australian species. If laboratory toxicity testing facilities were available for future research it would be recommended to commence a study of synergistic effects using those pesticides identified as contaminants of potential environmental concern in Chapter 4. Azinphos-methyl, parathion-methyl and carbaryl are all anti-cholinesterase compounds and there is potential for synergistic effects with chlorpyrifos. However, it was beyond the scope of this project to assess risks from synergistic effects.

Also beyond the scope of this project was the consideration of multiple stressors acting on aquatic ecosystems. Benson *et al.*, (2000) note that a significant shortfall in current ecological risk assessment approaches is to focus simply on chemical stressors rather than all stressors, both chemical and non-chemical. Nutrient enrichment of waterways in agricultural areas may have implications for interaction with pesticide stressors. Cuppen *et al.* (1995) suggested that chlorpyrifos contamination of freshwater ecosystems may enhance the adverse effects of eutrophication by reducing the top-down (consumer) control of algal biomass, at least as long as non-arthropod grazers permit this to occur. However, their results are based on a 35 μg/L nominal dosing of chlorpyrifos, which is far higher than any concentration likely to occur in the Huon Valley.

Examples of non-chemical stressors, which could adversely impact aquatic ecosystems in the Huon Valley, are numerous and could include changes in hydrology due to the presence of willows, siltation from road runoff and shading effects from willows. Non-chemical stressors could also compound the effect of pesticides. For example, Macek *et al* (1969) found an increase of rainbow trout susceptibility to chlorpyrifos with an increase in water temperature.

While it is conceivable that some non-chemical stressors may be studied individually, it is unrealistic to imagine a study where both chemical and non-chemical stressors would be comprehensively assessed. The resources required for such a study are beyond those currently available for environmental research in Tasmania.

ACCEPTANCE OF RISK

The conclusion that chlorpyrifos sprays are not posing an unacceptable risk to aquatic environments in the Huon Valley is not absolute - it is entirely dependent on an individual's perception of risk. For example, when the project results were presented to community members at a Mountain River Landcare meeting, a number of individuals were skeptical of the outcomes and considered that any detection of chlorpyrifos in the aquatic environment constituted an unacceptable risk. For these people, the fact that there was uncertainty in the results was also unacceptable. Many people accept uncertainty in environmental decision-making as a realistic and valid approach, but critics of ecological risk assessment conclude that risk assessments are a tenuous basis for decision making. They believe that lack of data and knowledge hinders the application of risk assessment outcomes (Tal, 1997; American Chemical Society, 1998).

In addition to considerations of uncertainty, some environmental managers believe that the very process of risk assessment is flawed because it allows some level of risk to be considered acceptable (i.e. that a risk-benefit balance can be found) (American

Chemical Society, 1998). This may be unlawful under some statutes and may be perceived as unethical in some circumstances (American Chemical Society, 1998).

As noted by Baker (1998) it is necessary to build public confidence in the risk assessment process to narrow gaps between public perceptions of risks posed by pesticides and scientific perspectives of those same risks. Given the high public profile that pesticide contamination of the environment has received since the publication of Rachel Carson's *Silent Spring* (1963) it is not surprising that risks from pesticides are generally not objectively compared with risks associated with other human inputs to the environment. Good risk communication is essential so that risks are presented in a clear and realistic way.

RISKS VS. BENEFITS

The use of biologically active chemicals in modern society poses economic and health benefits, as well as potential adverse effects when off-target residues reach levels that may impact ecosystems (Woodburn, 2000). In this study, only the environmental implications for pesticide use in Huon Valley orchards were considered. It was beyond the scope of this project to undertake a cost-benefit analysis of pesticide use in apple orchards. A risk trade-off analysis is difficult, but it highlights the risks associated with alternatives (e.g. Gray and Hammit, 2000).

Management and regulatory decisions based on risk assessments with extreme safety factors and "worst-case" assumptions are of limited applicability. There are economic, practical and social implications for regulating false positives. This has been demonstrated in human health risk assessments for chlorpyrifos completed by Oliver *et al.* (2000). Their work showed that use of probabilistic methods resulted in decreased aggregated risk and exposure for human health risk assessments, and that probabilistic refinements provided more realistic indications of risk rather than using "worst-case" assumptions, and justifying the inherent inaccuracies as safety factors.

In the US, chlorpyrifos and other organophosphates have been the subject of intense scrutiny under the US Food Quality Protection Act. The recent push by the US EPA to ban chlorpyrifos has been controversial (Gori, 2000). The implications for production agriculture associated with the deregistration of organophosphates in USA have been reviewed in the horticultural industry journal, *Fruit Grower* (May 1998).

In Australia, chlorpyrifos use has recently been reviewed under the National Registration Authority's Existing Chemical Review program. The main environmental outcomes of this study were that chlorpyrifos is an occasional contaminant of surface waters, but can reach high levels on occasion. The use pattern of main concern with respect to high level surface water contamination was termite protection, which involves generally higher rates of application than agricultural treatments. Levels of contamination arising from agricultural uses of chlorpyrifos were considerably lower, generally below 1 µg/L. Chlorpyrifos was detected in Australian surface waters on rare occasions. The environmental assessment identified a need to strengthen labels to include measures to minimise spray drift and environmental contamination (NRA, 2000b).

CRITIQUE OF ECOLOGICAL RISK ASSESSMENT METHODS USED IN THIS PROJECT

Regional risk assessment

In retrospect, regional risk assessment represents a complex form of ecological risk assessment, and its application in this project was limited. Incorporating multiple stressors into a risk assessment is difficult and methods are still being developed. In this project, the Relative Risk Model was used to rank environmental stressors in the Mountain River catchment (Chapter 3). Although the *process* of conducting a relative risk ranking was useful, there were limitations on the interpretation of outcomes.

One property of the Relative Risk Model that is potentially misleading is the system for ranking of habitats. Habitats are ranked based on their occurrence within the region, so that a small area of one habitat is given a lower ranking than a large area of another. This system is flawed when endangered habitats form part of the region. For a rare habitat, it is not logical to conclude that because there is less land area of that habitat, the risks to it are less.

The major difficulty in conducting the regional risk assessment was establishing successful assessment endpoints. It may be easier to set good assessment endpoints in highly regulated and managed catchments, but Mountain River is typical of many catchments in Australia for which there is limited information available.

In conclusion, the Relative Risk Model is not recommended as a tool for catchment-scale risk assessments. One useful component of the Relative Risk analysis that was used in this project was GIS, which has great potential for risk assessment applications. GIS interpretations are recommended to identify study areas with the highest incidence of environmental stressors, and to focus fieldwork on 'environmental hotspots'.

Probabilistic risk assessment

Recently there has been debate about the application of probabilistic risk assessment techniques (Lee, 1999; Solomon and Giddings, 2000; de Vlaming, 2000; Benson *et al.*, 2000; Scholz and Collier, 2000; Woodburn, 2000). Probabilistic risk assessment has been criticised because it gives indirect predictions of impairments based on measurements of a single chemical rather than direct measurements of toxicity or biotic community impacts (de Vlaming, 2000). Considerations are not given to the multiple chemicals or stressors or to toxicant interactions and bioavailability of toxicants. Because the probabilistic approach is purely numerical, it cannot consider the ecological importance of the potentially affected organisms (Solomon and Chappel, 1998).

Despite its shortcomings, the probabilistic approach was very useful for the Mountain River risk assessment. The probabilistic approach would be applicable for other single chemical risk assessments where there is limited toxicity data available. While there is a scarcity of toxicology data available for Australian species, the use of probabilistic risk assessment techniques is one means by which to estimate ecological impacts of commonly used pesticides. Another advantage of probabilistic risk assessments methods is that risk analysis is independent of *a priori* selection of acceptable probabilities of exposure and response for the decision-making process (Giesy *et al.*, 1999). This makes probabilistic methods generically applicable to many situations where management and regulatory guidelines for pesticide effects have not been established. Probabilistic methods are highly recommended for pesticides risk assessments in Australia.

The Tiered Approach

Early tier risk assessments are based on conservative assumptions, such as maximum exposure and ecological sensitivity (US EPA, 1996), but they serve to highlight chemicals for which further investigation is important. Tier 1 risk assessment using the quotient method (Chapter 4) was an efficient and effective means of identifying which pesticides should be the focus of further investigations. Probabilistic risk assessment provided quantitative risk estimates that were validated using field investigations. The stepwise increment in resources and data requirements that typifies the tiered approach was very useful in this project, and the tiered approach is recommended as a basis for all pesticides risk assessments in Australia.

APPLICABILITY OF ECOLOGICAL RISK ASSESSMENT METHODS IN AUSTRALIA

The application of risk assessment methods in Australia is potentially restricted by the availability of environmental exposure data. In this project, considerable time was devoted to collection of chlorpyrifos exposure data. However, availability of toxicity data for endemic species is the fundamental restriction limiting risk assessments for Australian environments. Comprehensive risk assessments will require a significant level of funding to generate field exposure data and toxicity data. In situations such as this project, where there are limited resources available, it is recommended that probabilistic methods be adopted. The emphasis in resource allocation should be to the collection of field exposure data. Although not ideal, the use of exotic toxicity data in probabilistic assessments is generally indicative of risks to endemic species. Given the growing interest in ecological risk assessment within Australia, the next few years are likely to see instigation of projects designed to assess risks to endemic species in their natural habitats. There is tremendous potential for new and exciting research in this area.

REFERENCES

Abdullah AR Lim RP Chapman JC. 1993. Inhibition and recovery of acetylcholinesterase in *Paratya australiensis* exposed to the organophosphate insecticide chlorpyrifos. *Fresenius Environmental Bulletin* 2:752-757.

Adams G. 1997. Pers. comm. Technical Officer, Department of Primary Industries and Fisheries Grove Research Farm.

American Chemical Society. 1998. Understanding risk analysis. A short guide for health, safety, and environmental policy making. American Chemical Society.

ANZECC & ARMCANZ. In revision. Australian and New Zealand Guidelines for Marine and Fresh Water Quality (formerly ANZECC. 1992. 'Australian water quality guidelines for fresh and marine waters'. Australian and New Zealand Environment and Conservation Council, Canberra).

Apple and Pear News. December '91/January '92. Pesticide initiative a first for world. Australian Horticultural Corporation.

Aquatic Risk Assessment and Mitigation Dialogue Group. 1994. 'Final Report'. Society of Environmental Toxicology and Chemistry (SETAC) and SETAC Foundation for Environmental Education. Pensacola, Florida.

AUSRIVAS. 1994. [Online]. Available: http://ausrivas.canberra.edu.au/ (December 2000).

Australian Horticultural Corporation. 2000. 'The Australian Horticultural Statistics Handbook 1999-2000' . Canberra, Australia.

Bailey HC Krassoi R Elphick JR Mulhall A Hunt P Tedmanson L Lovell A. 2000. Whole effluent toxicity of sewage treatment plants in the Hawkesbury-Nepean watershed, New South Wales, Australia, to *Ceriodaphnia dubia* and *Selenastrum capricornutum. Environmental Toxicology and Chemistry* 19:72-81.

Bailey HC Miller JL Miller MJ Wiborg LC. 1997. Joint acute toxicity of diazinon and chlorpyrifos to *Ceriodaphnia dubia. Environmental Toxicology and Chemistry* 16:2304-2308.

Baker DB. 1998. Herbicides in drinking water: a challenge for risk communication. Ballantine LG McFarland JE Hackett DS. (eds). 'Triazines Herbicides: Risk Assessment'. ACS Symposium Series 683. American Chemical Society, Washington D.C.

Barnthouse LW Suter GWII Rosen AE. 1990. Risks of toxic contaminants to exploited fish populations:influence of life history, data uncertainty and exploitation intensity. *Environmental Toxicology and Chemistry* 9:297-311.

Barron MG Woodburn KB. 1995. Ecotoxicology of chlorpyrifos. *Reviews of Environmental Contamination and Toxicology* 144:1-93.

Barton JL Davies PE. 1993. Buffer strips and streamwater contamination by atrazine and pyrethroids aerially applied to Eucalyptus nitens plantations. *Australian Forestry* 56:201-210.

Batley GE Peterson SM. 1992. Fate of cotton pesticides in the riverine environment. Proceedings of The Impact of Pesticides on the Riverine Environment Workshop. Goondiwindi 20-21 May, 1992. Cotton Research and Development Corporation, Narrabri.

Belden JB Lydy MJ. 2000. Impact of atrazine on organophosphate insecticide toxicity. *Environmental Toxicology and Chemistry* 19:2266-2274.

Benson WH, Steevens JA, Summers JK. 2000. Reply to "The converging paths of ecological assessment and ecological risk assessment. *SETAC Globe* 1(5):30-31.

Berstein PL. 1996. 'Against the gods: the remarkable story of risk'. John Wiley and Sons, New York.

Bevelhimer MS Adams SM. 1996. Assessing contaminant distribution and effects in a reservoir fishery. *Proceedings of the Third National Reservoir Fisheries Symposium,* Multidimensional approaches to reservoir fisheries management, Chattanooga, Tennessee, USA, June 12-14, 1995, pp 119-132.

Bickford G Toll J Hansen J Baker E Keessen R. 1999. Aquatic ecological and human health risk assessment of chemicals in wet weather discharges in the Sydney region, New South Wales, Australia. *Marine Pollution Bulletin* 39:335-345.

Bidlack HD. 1977. Aerobic degradation of 3,5,6-trichloro-2-pyridinol in 15 agricultural soils. Agricultural Products Department, The Dow Chemical Company, Midland, Michigan. Unpub. Rep., April 19, 1977 cited in Marshall and Roberts (1978).

Bidlack HD. 1976. Degradation of 14C-labeled 3,5,6-trichloro-2-pyridinol in 15 select agricultural soils. Report GH-C 953. Dow Elanco, Indianpolis, cited and referenced in Giesy (1999).

Boone JS Chambers JE. 1996. Time course of inhibition of cholinesterase and aliesterase activities, and nonprotein sulfhydryl levels following exposure to organophosphorous insecticides in mosquitofish (Gambusia affinis). *Journal of Fundamental and Applied Toxicology* 29:202-207.

Bowmer K. 1993. Environmental chemistry and residue levels: some notes on selection of pesticides of highest priority. Proceedings of the Ecotoxicology Specialist Workshop. LWRRDC Occasional Paper No. 07/93.

Bradbury SP Carlson RW Niemi GJ Henry TR. 1993. Use of respiratory-cardiovascular responses of rainbow trout [*Oncorhynchus mykiss*] in identifying acute toxicity syndromes in fish: Part 4. Central nervous system seizure agents. *Environmental Toxicology and Chemistry* 10: 115-131.

Braun HE Frank R. 1980. Organochlorine and organophosphorous insecticides: their use in eleven agricultural watersheds and their loss to stream waters in southern Ontario, Canada, 1975-1977. *Science of the Total Environment* 15:169-192.

Brazner JC Kline ER. 1990. Effects of chlorpyrifos on the diet and growth of larval fathead minnows, Pimephales promelas, in littoral enclosures. *Canadian Journal of Fisheries and Aquatic Science* 47: 1157-1165.

Brock DA. 1977. Comparison of community similarity indices. *Journal of the Water Pollution Control Federation* 49:2488-2494.

Brown RP Landre AM Miller JA Kirk HD Hugo JM. 1997. Toxicity of sediment-associated chlorpyrifos with the freshwater invertebrates *Hyalella azteca* (amphipod) and *Chironomus tentans* (midge). DECO-ES-3036. Health and Environmental Research Laboratories, Dow Chemical Co., Midland, MI, USA In: Giesy *et al.* (1999).

Butcher JE Boyer MG Fowle. 1977. Some changes in pond chemistry and photosynthetic activity following treatment with increasing concentrations of chlorpyrifos. *Bulletin of Environmental Contaminatio and Toxicology* 17:752-758.

Calow P. 1992. Can ecosystems be healthy? Critical consideration of concepts. *Journal of Aquatic Ecosystem Health* 1:1-5.

Calow P. 1995. Risk Assessment: Principles and Practice in Europe. *Australasian Journal of Ecotoxicology* 1:11-13.

Cardwell RD Brancato MS Toll J DeForest D Tear L. 1999. Aquatic ecological risks posed by tributyltin in United States surface waters: pre-1989 to 1996 data. *Environmental Toxicology and Chemistry* 18:567-577.

Carson R. 1963. *Silent Spring.* Hamilton, London.

Chambers JE Chambers HW. 1989. An investigation of acetyl-cholinesterase inhibition and aging and choline acetyltransferase activity following a high level acute exposure to paraoxon. *Pesticide Biochemistry and Physiology* 33: 125-131.

Chapman JC Napier GM Sunderam RIM Wilson SP. 1993. The contribution of ecotoxicological research to environmental protection. *Australian Biology* 6:72-81.

CHAST (Centre for Human Aspects of Sciene and Technology) 1988. Chlorpyrifos. Hazardous Chemicals in the Environment Group of CHAST, Series Publication No. 1. University of Sydney.

Ciba-Giegy. 1985. Water-sensitive paper for monitoring spray distribution, Ciba-Giegy Limited, Basle, Switzerland.

Connell DW. 1988. Bioaccumulation behaviour of persistent organic chemicals with aquatic organisms. *Reviews of Environmental Contamination and Toxicology* 101:117-154.

Cook RB Suter GWII Riley Sain E. 1999. Ecological risk assessment in a large river-reservoir: 1. Introduction and background. *Environmental Toxicology and Chemistry* 18:581-588.

Cox DN Ooi SG Friebel EM. 1999. Development of risk-based guidelines for assessing and managing petroleum hydrocarbon sites. Conference Proceedings. EnviroTox'99. Australasian Society for Ecotoxicology.

CPAS (Centre for Pesticide Application and Safety). 2000. 'Draft national guidelines for spray drift reduction'. Standing Committee for Agriculture and Resource Management. Canberra.

Crook D Sanger A. 1997. 'Recovery plan for the Peddar, Swan, Clarence, Swamp and Saddled Galaxias'. Inland Fisheries Commission Report, Hobart, Australia.

Crossland NO Shires SW Bennett D. 1982. Aquatic toxicology of cypermethrin. III. Fate and biological effects of spray drift deposits in freshwater adjacent to agricultural land. *Aquatic Toxicology* 2: 253-270.

Cuppen JGM Gylstra R van Beusekom S Budde BJ Brock TCM. 1995. Effects of nutrient loading and insecticide application on the ecology of Elodea-dominated freshwater microcosms. III. Responses of macroinvertebrates detritivores, breakdown of plant litter, and final conclusions. *Archiv fur Hydrobiologie* 134:157-177.

Curnow B Pitt I Thompson G. 1993. Ecotoxicological research for pesticide regulation in Australia. Proceedings of the Ecotoxicology Specialist Workshop. LWRRDC Occasional Paper No. 07/93.

Davies JB. 1988. 'Land systems of Tasmania: South, East and Midlands; Region 6'. Department of Agriculture, Hobart, Tasmania, Australia.

Davies PE Cook LSJ Barton JL. 1994. Triazine herbicide contamination of Tasmanian streams: sources, contamination and effects on biota. *Australian Journal of Marine and Freshwater Research* 45:209-226.

Davies PE. 1984. Chlorothalonil: its environmental fate, toxicology and metabolism in fish. Department of Zoology PhD thesis. University of Tasmania.

Davies PE Cook LSJ. 1993. Catastrophic macroinvertebrate drift and sublethal effects on brown trout, *Salmo trutta*, caused by cypermethrin spraying on a Tasmanian stream. *Aquatic Toxicology* 27:201-224.

Davies PE Cook LSJ Goesnarso D. 1994. Sublethal responses to pesticdes of several species of Australian freshwater fish and crustaceans and rainbow trout. *Environmental Toxicology and Chemistry* 13:1341-1354.

de Snoo GR de Wit PJ. 1998. Buffer zones for reducing pesticide drift to ditches and risks to aquatic organisms. *Ecotoxicology and Environmental Safety* 41, 112-118.

de Vlaming V. 2000. More on probabilistic risk assessments - a magic bullet for all situations, they are not. *SETAC Globe* 1(3):27-28.

Dilling WL Lickly LC Lickly TD Murphy PG McKellar RL. 1984. Organic photochemistry. 19. Quantum yields for O,O-diethyl-O-(3,5,6-tricholor-2-pyridyl) phosphorothioate (chlorpyrifos) and 3,5,6-trichloro-2-pyridinol in dilute aqueous solutions and their environmental phototransformation rates. *Environmental Science and Technology* 18:540-543.

Dorr G Woods N Craig IP. 1998. Buffer zones for reducing drift from the application of pesticides. 1998 International Conference on Engineering in Agriculture. Paper No. SEAg 98/008.

DPIF (Department Primary Industries and Fisheries). 1999. Code of practice for orchard spraying in Tasmania. *Agriculture Tasmania* 3, 20-21.

Dushoff J Caldwell B. Mohler CL. 1994. Evaluating the environmental effect of pesticides: a critique of the environmental impact quotient. *American Entomologist*, Fall, 1994.

Ellman GL Courtney KD Andres V Featherstone RM. 1961. A new and rapid colorimetric determination of actetylcholinesterase activity. *Biochemical Pharmocology* 7, 88-95.

Environmental Systems Research Institute, Inc. 1998. *ArcView® Version 3.1.* Redlands, CA, USA.

Ernst WR Julien GR. 1984. Effects on brook trout (*Salvelinus fontinalis*) feeding behaviour and brain cholinesterase activity of experimental fenitrothion and aminocarb formulations containing Triton® X-100 and Cyclosol® 63. Environment Canada. Surveillance Report EPS-5-AR-84-9 Atlantic Region.

Felsot A Dahm PA. 1979. Sorption of organophosphorous and carbamate insecticides by soil. *Journal of Agriculture and Food Chemistry* 27:557-563.

Fischhoff B Lichtenstein S Slovic P Derby SL Keeney RL. 1981. *Acceptable Risk.* Cambridge University Press, Cambridge.

Foster S Thomas M Korth W. 1998. Laboratory derived acute toxicity of selected pesticides to Ceriodaphnia dubia. *Australasian Journal of Ecotoxicology* 4:53-59

Frank R Braun HE Ripley BD Clegg BS. 1990. Contamination of rural ponds with pesticide, 1971-85, Ontario, Canada. *Bulletin of Environmental Contamination and Toxicology* 44:401-409.

Ganzelmeier H Rautmann D Spangenberg R Streloke M Hermann M Wenzelburger HJ Walten HF. 1995. 'Studies on the spray drift of plant protection products.' BlackwellWissenschafts-Verlag, Berlin.
Ganzelmeier H Rautmann D. 2000. Drift, drift reducing sprayers and sprayer testing. *Aspects of Applied Biology* 57, 1-10.
Gibson JR Ludke JL Ferguson DE. 1969. Sources of error in the use of fish-brain acetylcholinesterase activity as a monitor for pollution. *Bulletin of Environmental Toxicology and Chemistry* 4:
Giddings JM Biever RC Racke KD. 1997. Fate of chlorpyrifos in outdoor pond microcosms and effects on growth and survival of bluegill sunfish. *Environmental Toxicology and Chemistry* 16:2353-2362.
Giddings JM Gall LW Solomon KR. 2000. Ecological risks of diazinon from agricultural use in the Sacramento-San Joaquin River Basins, California. *Risk Analysis* 20:545-572.
Giesy JP Solomon KR Coats JR Dixon KR Giddings JM Kenaga EE. 1999. Chlorpyrifos: Ecological risk assessment in North American aquatic environments. *Reviews of Environmental Contamination and Toxicology* 160:1-129
Gori GB. 2000. Turning point for EPA? Washington Times, Friday June 23, 2000.
Goss D, Wauchope RD. 1990. The SCS/ARS/CES pesticide properties database: II Using it with soils data in a screening procedure. In 'Pesticides in the Next Decade: The Challenges Ahead'. Virginia Water Resources Research Centre, Blacksburg, VA, USA, pp 471-493.
Gray GM. Hammitt JK. 2000. Risk/risk trade-offs in pesticide regulation: An exploratory analysis ofthe public health effects of a ban on organophosphate and carbamate pesticides. *Risk Analysis* 20:665-680.
Grover R Kerr LA Maybank J Yoshida K. 1978. Field measurement of droplet drift from ground sprayers. 1. Sampling, analytical and data integration techniques. *Canadian Journal of Plant Science* 58, 611-622.
Haimes YY Barry T Lambert JH. 1994. When and how you can specify a probability distribution when you don't know much? *Risk Analysis* 14:661-706.
Havens PL Cryer SA Rolston LJ. 1998. Tiered aquatic risk refinement: case study -at plant application of granular chlorpyrifos to corn. *Environmental Toxicology and Chemistry* 17:1313-1322.
Heckman WC. 1981. Long-term effects of intensive pesticide applications on the aquatic community in orchard drainage ditches near Hamburg, Germany. *Archives Environmental Contamination and Toxicology* 10:393-426.
Holland J. 1999. Current methodology of risk assessment for regulatory purposes in Australia. *Workshop Program Notes*, Ecological risk assessment of pesticides in the aquatic environment, Canberra, NSW, Australia, May 12-14, 1999.
Horticultural Research and Development Corporation (HRDC). 1998. An evaluation of the Australian Apple and Pear Growers Association/Horticultural Research and Development Corporation investment in research and development relating to integrated pest and disease management.
Hughes DN Boyer MG Papst MH Fowle. 1980. Persistence of three organophosphorous insecticides in artificial ponds and some biological implications. *Archives of Environmental Contamination and Toxicology* 9:269-279.
Hulbert SH. 1975. Secondary effects of pesticides on aquatic ecosystems. *Resid. Rev.* 57:81-148.
Hunsaker CT Graham RL Suter GWII, O'Neill RV Jackon BL Barnthouse LW. 1989. *Regional ecological risk assessment: Theory and demonstration.* ORNL/TM-11128. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
HHRP (Huon Healthy Rivers Project). 1997. *Huon Valley Catchment Management Plan.* Huon Valley Council, Tasmania.
Iwata Y O'Neal JR Barkley JH Dinoff TM Dusch E. 1983. Chlorpyrifos applied to California citrus: residue levels on foliage and in fruit. *Journal of Agriculture and Food Chemistry* 31:603-610.
Jarvinen AW Tanner DK Kline ER. 1988. Toxicity of chlorpyrifos, endrin , or fenvalerate to fathead minnows following episodic or continuous exposure. *Ectoxicology and Environmental Safety* 15:78-95.

Johnson WW Finely MT. 1980. Handbook of acute toxicity of chemicals to fish and aquatic invertebrates. Resource Publ 137. U.S. Fish and Wildlife Service, Washington D.C. USA.

Jones DS Barnthouse LW Suter GWII Efroymson RA Field JM Beauchamp JJ. 1999. Ecological risk assessment in a large river-reservoir: 3. Benthic invertebrates. *Environmental Toxicology and Chemistry* 18:599-609.

Jury WA Spencer WF Farmer WJ. 1984. Behaviour assessment model for trace organics in soil. II. Application of screening model. *Journal of Environmental Quality* 13:573-579.

Kenega EE. 1971. Some physical, chemical, and insecticidal properties of some *O,O*-dialkyl *O*-(3,5,6-trichloro-2-pyridyl)phosphates and phosphorothioates. *Bulletin of the World Health Organisation* 44:225-228.

Kersting K van den Brink PJ. 1997. Effects of the insecticide Dursban®4E (active ingredient chlorpyrifos) in outdoor experimental ditches: responses of ecosystem metabolism. *Environmental Toxicology and Chemistry*16:251-259.

Knuth ML Heinis LJ. 1992. Dissipation and persistence of chlorpyrifos within littoral enclosures. *Journal of Agriculture and Food Chemistry* 40:1257-1263.

Kookana RS Correll RL Simpson BW. 1998. Assessing risk at catchment or regional level through a Pesticide Impact Ranking Index (PIRI). Minimising the impact of pesticides on the riverine environment: key findings from research with the cotton industry. Conference Proceedings July 1998. LWRRDC Occasional Paper 23/98.

Korth W Bowmer KH Thomas M Foster S Napier G McCorkelle G. 1994. River pollution with agricultural chemicals. Final Report. CSIRO Division of Water Resources, Griffith, NSW, Australia.

Kovach J Petzoldt C Degni J Tette J. 1992. A method to measure the environmental impact of pesticides. *New York's Food and Life Sciences Bulletin* 139, 1-8.

Kreuger J. 1995. Monitoring of pesticides in subsurface and surface water within an agricultural catchment in southern Sweden. In Walker A Allen R Bailey SW Blair AM Brown CD Gunther P Leake CR Nicholls PH. (eds). 'Pesticide Movement to Water'. British Crop Protection Council Monograph No 62, Farnham, Surrey, United Kingdom, pp 81-96.

Landis WG Matthews GB Matthews RA Sergeant A. 1994. Application of multivariate techniques to endpoint determination, selection and evaluation in ecological risk assessment. *Environmental Toxicology and Chemistry* 13:1917-1927.

Landis WG Wieger JA. 1997. Design considerations and a suggested approach for regional and comparative ecological risk assessment. *Human and Ecological Risk Assessment* 3:287-297.

Landis WG, Markiewicz AJ, Matthews GB, Roze MJ, Matthews RA. 1998. Case study #2:An exploration of uncertainty in the determination of environmental toxicity. In Warren-Hicks WJ, Moore DRJ. (eds). 'Uncertainty analysis in ecological risk assessment'. SETAC Press, Pensacola, FL, USA, pp 226-236.

Landis WG. Yu MH. 1999. 'An Introduction to Environmental Toxicology: Impacts of Chemicals on Ecological Systems'. Second Edition. Lewis Publishing, Boca Raton, FL.

Landis WG McLaughlin JF. 2000. Design criteria and derivation of indicators for ecological position, direction and risk. *Environmental Toxicology and Chemistry* 19, 1059-1065.

Landis WG Luxon M Bodensteiner LR. in press. Design of a relative rank method regional-scale risk assessment with confirmational sampling for the Willamette and McKenzie River, Oregon In:Price FT Brix KV Lane NK (eds). 'Ninth Symposium on Environmental Toxicology and Risk Assessment: Recent Achievements in Environmental Fate and Transport' ASTM STP1381, West Conshohocken, PA, American Society for Testing and Materials.

Lee GF Jones-Lee A. 1999. The single chemical probabilistic risk assessment approach is inadequate for OP pesticide aquatic life toxicity. *SETAC News* 19(6):20-21.

Leeuwangh P. 1994. Comparison of chlorpyrifos fate and effects in outdoor aquatic micro- and mesocosms of various scale and construction. In: Hill IR Heimback F Leeuwangh P Matthiessen P (eds). 'Freshwater Field Tests for Hazard Assessment of Chemicals'. Lewis, Boca Raton, FL, pp 217-248.

Leonard RA. 1990. Movement of pesticides into surface waters. In: 'Pesticides in the Soil Environment'. Cheng HH (ed.) Lewis, Boca Raton, FL.

Liess M Schulz R Liess MH-D Rother B Kreuzig R. 1999. Determination of insecticide contamination in agricultural headwater streams. *Water Resources* 33:239-247.

Ludwig PD Dishburger HJ McNeill JC Jr. Miller WO Rice JR. 1968. Biological effects and persistenceof Dursban insecticide in a salt-marsh habitat. *Journal of Economic Entomology* 61:626.

Lundgren RE McMakin AH. 1998. 'Risk Communication - a handbook for communicating environmental, safety and health risks'. Second edition. Battelle Press. Columbus, Ohio, USA.

LWRRDC (Land and Water Resources Research and Development Corporation). 1998. Minimising the impact of pesticides on the riverine environment: key findings from research with the cotton industry. LWRRDC Occasional Paper 23/98. Canberra.

Macalady DL Wolfe NL. 1985. Effects of sediment sorption and abiotic hydrolysis. 1. organophosphorothioate esters. *Journal of Agriculture and Food Chemistry* 33:167-173.

Macek KJ Hutchinson C Cope OB. 1972. The effects of temperature on the susceptibility of bluegills and rainbow trout to selected pesticides. *Bulletin of Environmental Contamination and Toxicology* 4:174-183.

Mackay D Paterson S Shroeder WH. 1986. Model describing the rates of transfer processes of organic chemicals between atmosphere and water. *Environmental Science and Technology* 20:810-816.

Mackay D. 1994. Fate models. In: Calow P. (ed). 'Handbook of ecotoxicology'. Vol 2. Blackwell Scientific Publications, Oxford, pp 348-367.

Mallat J. 1985. Fish gill structural changes induced by toxicants and other irritants - a statistical review. *Canadian Journal of Fisheries and Aquatic Science* 42:630-648.

Marshall WK Roberts JR. 1978. Ecotoxicology of chlorpyrifos. NRCC 16079. Technical Report. National Research Council of Canada, Ottawa, Ontario, Canada.

McCall PJ Oliver GR McKellar RL. 1984. Modeling the runoff potential and behaviour of chlorpyrifos in a terrestrial-aquatic watershed. DowElanco, Indianapolis (unpublished report) In Racke KD. 1993. Environmental fate of chlorpyrifos. *Reviews of Environmental Toxicology and Chemistry* 131: 1-154.

McCarty LS Power M. 1997. Environmental risk assessment within a decision-making framework - letter to the editor. *Environmental Toxicology and Chemistry* 16:122-123.

Miller PCH Walklate PJ Mawer CJ. 1989. A comparison of spray drift collection techniques. Brighton Crop Protection Conference - Weeds - 1989. Farnham, Surrey, UK. pp.81-96

Moghissi AA. 1984. Risk management - practice and prospects. *Mechanical Engineering* 106:21-23.

Morton A. 1998. Distribution and habitat use of fish species within the Mountain River catchment, Tasmania. School of Zoology Thesis, University of Tasmania.

Murphy PG Lutenske NE. 1986. Bioconcentration of chlopryrifos in rainbow trout [*Salmo gairdneri* Richardson]. DowElanco, Indianapolis, IN, USA In: Giddings JM Biever RC Racke KD. 1997. Fate of chlorpyrifos in outdoor pond microcosms and effects on growth and survival of bluegill sunfish. *Environmental Toxicology and Chemistry* 16, 2353-2362.

Muschal M. 1997. Central and North West Regions Water Quality Program 1996/7 Report on Pesticides Monitoring. CNR97.03. Department of Land and Water Conservation, Centre for Natural Resources, Parramatta, NSW, Australia.

Nabholz JV. 1991. Environmental hazard and risk assessment under the United States Toxic Substances Control Act. *Science of the Total Environment* 109/110: 649-665.

Natale OE Gomez CE Penchen de D'Angelo A Soria CA. 1988. Waterborne pesticides in the Negro River Basin (Argentina). In: Abbou R (ed). 'Hazardous Waste: Detection, Control, Treatment.' Elsevier Science Publishers B.V. Amersterdam, Netherlands. pp 879-907.

National Registration Authority. 2000a. Pubcris Database. [Online]. Available: http://www.dpie.gov.au/nra/pubcris.html (July 2000).

National Registration Authority. 2000b. Chlorpyrifos draft review. National Registration Authority Series 00.2. January 2000. [Online]. Available: http://www.dpie.gov.au/nra/publications.html (April 2000).

National Residue Survey. 2000. Report on the Australian National Residue 1 January to 30 June 1999 Results. Department of Agriculture, Fisheries and Forestry - Australia, Canberra.

Newman MC Dixon PM Looney BB Pinder JE. 1989. Estimating mean and variance for environmental samples with below detection limit observations. *Water Resources Bulletin* 25:905-916.

Ng JC Kratzmann SM Qi LX Crawley H Chiswell B Moore MR. 1998. Speciation and absolute bioavailability: risk assessment of arsenic-contaminated sties in a residential suburb in Canberra. *Analyst* 123: 889-892.

Nowak B. 1996. Relationship between endosulfan residue level and ultrastructural changes in the liver of catfish, Tandanus tandanus. Archives of Environmental Contamination and Toxicology 30:195-202.

Nowak B. 1997. Biological significance of xenobiotic residues in fish. *Toxicology and Ecotoxicology News* 4:149-155.

NRC (National Research Council). 1983. 'Risk assessment in the federal government: managing the process'. National Academy Press, Washington, DC.

O'Brien RD. 1960. 'Toxic Phosphorous Esters'. Academic Press, New York.

OCED (Organisation for Economic Co-operation and Development) Environment Committee and Water Management Policy Group. 1986. Water pollution by fertilisers and pesticides. OCED.

Office for Pesticide Programs. 2000. About the Office of Pesticide Programs. [Online]. Available: http://www.epa.gov/pesticides/about.htm (November 2000).

Olima C Pablo F Lim RP. 1997. Comparative tolerance of three populations of the freshwater shrimp (Paratya australiensis) to the organophosphate pesticide, chlorpyrifos. *Bulletin of Environmental Contamination and Toxicology* 59:321-328.

Oliver GR Bolles HG Shurdut BA. 2000. Chlorpyrifos: probabilistic assessment of exposure and risk. *NeuroToxicology* 21:203-208.

Ooi SG Clarey P Mok S Cox DN. 1999. Ecological and health risk assessment – a tool for the development of site-specific remediation goals for contaminated sites (a case study). Conference Proceedings EnviroTox'99. Australasian Society for Ecotoxicology.

Palisade Corporation. 1996. *@Risk Ver 3.5d*. Newfield, NY, USA.

Palisade Corporation. 1996. *BestFit® Ver 2.0c*. Newfield, NY, USA.

Parkhurst BR Warren-Hicks W Etchison T Butcher JB Cardwell RD Volison J. 1995. Methodology for aquatic ecological risk assessment. Water Environment Research Foundation Report No. RP91-AER. Final Report prepared for the Water Environment Research Foundation. Alexandria, VA, USA.

Parkhurst BR Warren-Hicks W Etchison T Butcher JB Cardwell RD Volison J. 1994. Draft Final Report Methodology for Aquatic Ecological Risk Assessment. Contract No. RP91-AER-1. The Cadmus Group, Laramie, WY, USA.

Parkhurst BR Warren-Hicks W Etchison T Butcher JB Cardwell RD Volison J. 1995. Methodology for aquatic ecological risk assessment. Final Report prepared for the Water Environment Research Foundation. Alexandria, VA: Water Environment Research Foundation. Report No. RP91-AER.

Parkin CS Merritt CR. 1988. The measurement and prediction of spray drift. *Aspects of Applied Biology* 17:351-361.

Paustenbach DJ (ed). 1990. 'The Risk assessment of environmental and human health hazards: A Textbook of Case Studies'. John Wiley & Sons, New York.

Pedigo LP. 1996. 'Entomology and Pest Management'. 2nd Edition. Prentice Hall, Upper Saddle River, NJ.

Penrose LJ Thwaite WG Bower CC. 1994. Rating index as a basis for decision making on pesticide use reduction and for accreditation of fruit produced under integrated pest management. *Crop Protection* 13:146-152.

Perring FH Mellanby D. (eds). 1977. 'Ecological effects of pesticides'. Linnean Society Symposium Series No. 5. Academic Press, London.

Perry SF McDonald DG. 1993. Gas exchange In: Evans DH (ed). 'The physiology of fishes'.CRC Press Inc., Boca Raton Florida. pp 251-278.

Pesticides Manual. 1994. Tomlin C. (ed). 'The Pesticide Manual (incorporating the Agrochemicals Handbook)'. Tenth edition. British Crop Protection Council and the Royal Society of Chemistry, Crop Protection Publications. London.

Pusey BJ Arthington AH McLean J. 1994. The effects of a pulsed application of chlorpyrifos on macroinvertebrate communities in an outdoor artificial stream. *Ecotoxicology and Environmental Safety* 27:221-250.
Racke KD. 1993. Environmental fate of chlorpyrifos. *Reviews of Environmental Toxicology and Chemistry* 131:1-154.
Racke KD Steele KP Yoder RN Dick WA Avidov E. 1996. Factors affecting the hydrolytic degradation of chorpyrifos in soil. *Journal of Agriculture and Food Chemistry* 44:1582-1592.
Racke KD. 1997. Fate of chlorpyrifos in outdoor pond microcosms and effects on growth and survival of bluegill sunfish. *Environmental Toxicology and Chemistry*16:2353-2362.
Raupach MR Leys JF Woods N Dorr G Cleugh HA. 2000. Modeling the effects of riparian vegetation on spray drift and dust: The role of local protection. CSIRO Land and Water Technical Report 29/00.
Read M Kranski T. 1998. Assessing river health: progress in Tasmania. *Rivers for the Future* 6:30-33.
Renner R. 1996. Ecological risk assessment struggles to define itself. *Environmental Science and Technology* 30: 172-174A.
Richard RP Baker DB 1998. Triazines in waters of the midwest: exposure patterns. In Ballantine LG McFarland JE Hackett DS. (eds). 'Triazine Herbicides: Risk Assessment', ACS Symposium Series 683. American Chemical Society, Washington, D.C.
Richards RP Baker DB. 1993. Pesticide concentration patterns in agricultural drainage networks in the Lake Erie Basin. *Environmental Toxicology and Chemistry* 12:13-26.
Ritter AM Shaw JL Williams WM Travis KZ. 2000. Characterizing aquatic ecological risks from pesticides using a diquat dibromide case study. I. Probabilistic exposure estimates. *Environmental Toxicology and Chemistry* 19:749-759.
Roberts TR, Hutson DH. 1999. 'Metabolic Pathways of Agrochemicals. Part 2: Insecticides and Fungicides'. The Royal Society of Chemistry, Cambridge, United Kingdom.
Robson B. 1995. Habitat complexity, spatial scale and grazing interactions in a temperate river. PhD Thesis. University of Tasmania, Hobart, Tasmania, Australia.
Rowe D. 1999. The relevance of risk and uncertainty. *Risk.* December 1999.
Ruckelhaus WD. 1983. Science, risk and public policy. *Science* 221:1026-1028.
Rural Industries Research and Development Corporation (RIRDC) (1999) Growing trees on cotton farms. RIRDC, Canberra, Australia.
Samuels WB Ladino A. 1983. Calculation of seabird population recovery from potential oilspills in the mid-Atlantic region of the United States. *Ecological Modelling* 21:63-84.
Schaefer CH Dupras EF Jr. 1970. Factors affecting the stability of Dursban in polluted waters. *Journal of Economic Entomology* 63:701.
Scholz NL Collier TK. 2000. Endangered salmon and probabilistic assessments for organophosphate pesticides. *SETAC Globe* 1(6): 32-33.
Shukla BS. 1996. 'Transport of pesticides from watershed by volatilisation, infiltration and runoff (models and applications)'. Environmental Research and Publications, Hamilton, Canada.
Simon D Helliwell S Robertson D. 1995. The impact of chlorpyrifos on an enclosure system in a shallow billabong. *Australasian Journal of Ecotoxicology* 1:137-142.
Smith GN Watson BS Fischer FS. 1967. Investigations on Dursban insecticide: uptake and translocation of [36Cl] *O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate and [14C] *O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate by beans and corn. *Journal of Agriculture and Food Chemistry* 15:127-131.
Snelson JT. 1979. 'Pesticides and the Australian environment: public safety and consumer protection'. Australian Government Publishing Service. Canberra.
Soivio A Nyholm K Westman K. 1975. A technique for repeated blood sampling of the blood of individual resting fish. *Journal of Experimental Biology* 62: 207-217.
Solomon KR Baker DB Richards RP Dixon KR Klaine SJ La Point TW Kendall RJ Weisskopf CP Giddings JM Giesy JP Hall LW Williams WM. 1996. Ecological risk assessment of atrazine in North American surface waters. *Environmental Toxicology and Chemistry* 15:31-76.
Solomon KR Chappel MJ. 1998. Triazine herbicides: ecological risk assessment in surface waters. In: Ballantine LG McFarland JE Hackett DS. (eds). 'Triazine Herbicides: Risk Assessment'. ACS Symposium Series 683. American Chemical Society, Washington, D.C, USA, pp 357-368.

Solomon KR Giddings JM. 2000. Understanding probabilistic risk assessment. *SETAC Globe* 1(1):34-35.
Spalding RF Snow DD. 1989. Stream levels of agrichemicals during a spring discharge event. *Chemosphere* 29:1129-1140.
Spray Drift Task Force (SDTF). A summary of airblast application studies. [Online]. Available http://www.agdrift.com/orchard/orchard_main.htm (July 2000).
SRC (Syracuse Research Corporation) CHEMFATE environmental fate database. [Online]. Available: http:esc-plaza.syrres.com/efdb/Chemfate.htm (July, 2000).
SRC (Syracuse Research Corporation) Interactive LogKow database. [Online]. Available: http:esc-plaza.syrres.com/interlow/kowdemo.htm (July, 2000).
Srivastava SK Tiwari PR Srivastav AK. 1990. Effects of chlorpyrifos on the kidney of freshwater catfish, Heteropneustes fossilis. *Bulletin of Environmental Toxicology and Chemistry* 45:748-751.
Stapley JH. 1969. 'World crop protection'. CRC Press, Cleveland.
Steel BS List P Shindler B. 1994. Conflicting values about Federal forests: a comparison of national and Oregon Publics. *Society and Natural Resources* 7:137-153.
Steffert RE Lazano SJ Brazner JC Knuth ML. 1989. Littoral enclosures for aquatic field testing of pesticides: effects of chlorpyrifos on a natural system. In: Voshell JR. (ed). 'Using mesocosms to asses the aquatic ecological risk of pesticides: theory and practice'. Entomological Society of America, Boston, MA, USA, pp 57-73.
Stephen CE. 1977. Methods for calculating an LC50. In; Mayer FL Hamelink JL (eds). 'Aquatic Toxicology and Hazard Evaluation'. ASTM STP 634, American Society for Testing and Materials, pp. 65-84.
Stephens CG. 1935. 'The apple growing soils of Tasmanian. Part 1 - A general investigation of the soils'. Council for Scientific and Industrial Research. Bulletin No. 92. Melbourne, Australia.
Sturm A Wogram J Segner J Liess M. 2000. Different sensitivity to organophosphates of acetylcholinesterase and butyrlcholinesterase from three-spined stickleback [*Gasterosteus aculeatus*]: application in biomonitoring. *Environmental Toxicology and Chemistry* 19:1607-1615.
Sunderam RIM Cheng DMH Thompson GB. 1992. Toxicity of endosulfan to native and introduced fish in Australia. *Environmental Toxicology and Chemistry* 11: 1469-1476.
Suter GW.II. 1990. Endpoints for regional ecological risk assessments. *Environmental Management* 14:9-23.
Suter GWII. 1993a. 'Ecological Risk Assessment'. Lewis Publishers, Chelsea, Michigan, USA.
Suter GWII. 1993b. A critique of ecosystem health concepts and indexes. *Environmental Toxicology and Chemistry* 12:1533-1539.
Suter, G.W. 1998. In defense of ecorisk assessment - letter to editor. *Environmental Science and Technology* March 1, 1998: 116-117A.
Suter GWII. 1999a. Developing conceptual models for complex ecological risk assessments. *Human and Ecological Risk Assessment* 5:375-396.
Suter, G.W.,II. 1999b. A framework for assessment of ecological risks from multiple activities. *Human and Ecological Risk Assessment* 5:397-413.
Suter GWII Barnthouse LW Efroymson RA Jager J. 1999. Ecological risk assessment in a large river-reservoir: 2. Fish community. *Environmental Toxicology and Chemistry* 18:589-598.
Tal A. 1997. Assessing the environmental movement's attitudes toward risk assessment. *Environmental Science and Technology* 31:470-476.
Tasmanian Apple and Growers Association. 1998. A profile of the Tasmanian apple industry. Department of Primary Industries and Fisheries and Tasmanian Apple and Pear Growers Association, Hobart, Tasmania.
Tasmanian Apple and Growers Association. 1999. Pers. comm. from Information Officer.
Taylor JK Stephens CG. 1935. 'The apple growing soils of Tasmanian. Part 2 - A soil survey of part of the Huonville district'. Council for Scientific and Industrial Research. Bulletin No. 92. Melbourne, Australia.
Taylor AW Spencer WF. 1990. Volatilisation and vapour transport processes. In: 'Pesticides in the Soil Environment'. Cheng HH (ed.) Lewis, Boca Raton, FL.
Teske ME Bird SL Esterly DM Ray SL Perry SG. 1997. A users guide for AgDRIFT™ 1.0:A tiered approach for the assessment of spray drift of pesticides. C.D.I. Technical Note No. 95-10, Spray Drift Task Force, Missouri, USA.

Thiegs BJ. 1966. Degradation of [14C] Dursban in soil. DowElanco, Indianapolis. Cited in Racke (1993).
Thirugnanam M Forgash AJ. 1977. Environmental impact of mosquito pesticides: toxicity and anticholinesterase activity of chlorpyrifos to fish in a salt marsh habitat. *Archives of Environmental Toxicology and Chemistry* 5:415-425.
Thoma K Nicholson BC. 1989. Pesticide losses in runoff from a horticultural catchment in South Australia and their relevance to stream and reservoir water quality. *Environmental Technology Letters* 10:117-129.
Thomas C Warne M Lim R. 1999. Toxicity of deltamethrin to Australian riverine organisms: a preliminary risk assessment. Conference Proceedings EnviroTox'99. Australasian Society of Ecotoxicology.
Tucker VA. 1967. Method for oxygen content and dissociation curves on microliter blood samples. *Journal of Applied Physiology* 23:410-414.
U.S. Environmental Protection Agency. 1986. Ambient water quality criteria for chlorpyrifos - 1986. EPA 440/5-86-005. Office of Water Regulations and Standards, Washington, D.C.
U.S. Environmental Protection Agency. 1989. Registration standard (second round review) for the registration of pesticide product containing chlorpyrifos as the active ingredient. OMB 2070-0057. Washington, DC.
U.S. Environmental Protection Agency. 1992a. A framework for ecological risk assessment. EPA/630/R- 92/001. Risk Assessment Forum, Washington, D.C.
U.S. Environmental Protection Agency. 1992b. National study of chemical residues in fish. EPA/823/R/92/008a. Office of Science and Technology (WH-551), US EPA, Washington D.C.
U.S. Environmental Protection Agency. 1994. AQUIRE (Aquatic toxicity information retrieval). Office of Research and Development. National Health and Environmental Effects Research Laboratory, Mid-Continental Ecology Division, Duluth, Minnesota, USA.
U.S. Environmental Protection Agency. US EPA. 1996. Proposed Guidelines for Ecological Risk Assessment. EPA/630/R-95/002B. Risk Assessment Forum. Washington, D.C.
U.S. Environmental Protection Agency. 1998. Guidelines for Ecological Risk Assessment. EPA/630/R-95/002F. Risk Assessment Forum, Washington, D.C.
U.S. Environmental Protection Agency Office for Pesticide Programs. 2000. About the Office of Pesticide Programs [Online]. Available: http://www.epa.gov/pesticides/about.htm
Urban DJ Cook NJ. 1986. Hazard Evaluation Division Standard Evaluation Procedure Ecological Risk Assessment. United States Environmental Protection Agency, Office of Pesticide Programs, EPA 540/9-85-001, Washington, D.C.
van Dam RA Camilleri C Markich SJ. 1999. Ecological risk assessment of the herbicide tebuthiuron in northern Australian wetlands. Conference Proceedings EnviroTox'99. Australasian Society of Ecotoxicology.
Ware GW. 'The pesticide book'. 5th Edition. 2000. Thomson, California
Warne MStJ. 2000. Presidents Report. *Endpoint - Newsletter of the Australasian Society for Ecotoxicology* 7:5-6.
Warne MStJ Westbury AM Sunderam RIM. 1998. A compilation of data on the toxicity of chemicals to species in Australia Part 1: Pesticides. *Australasian Journal of Ecotoxicology* 4:93-144.
Wauchope RD Butler TM Hornsby AG Augustijn-Beckers PWM Burt JP. 1992. The SCS/ARS/CES Pesticide Properties Database for Environmental Decision-Making. *Reviews of Environmental Toxicology and Chemistry* 123: 1-164.
Weber JB. 1977. The pesticide scorecard. *Environmental Science and Technology* 11:756-761.
Weiss CM. 1961. Physiological effect of organophosphorous insecticides on several species of fish. *Transactions of the American Fisheries Society* 90:230-236.
Wiegers JK Feder HM Mortensen LS Shaw DG Wilson VJ Landis WG. 1998. A regional multiple-stressor rank based ecological risk assessment for the Fjord of Port Valdez, Alaska. *Human and Ecological Risk Assessment* 4:1125-1173.
Woodburn KB. 2000. In defence of the use of probabilistic risk assessment. *SETAC Globe* 1(3):28-30.
Woods N Craig IP Dorr G. 1999. Aerial Transport - spray application and drift *In* Minimising the impact of pesticides on the riverine environment Conference Proceedings, Canberra, 1998. LWRRDC Occasional Papers 23/98, Canberra, pp 19-22.

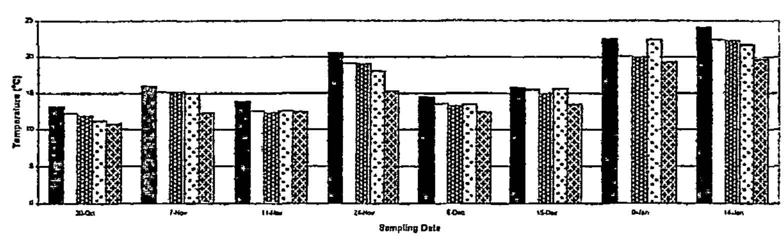
Wu R. 1996. Ecotoxicology: Problems and challenges in Australia. *Australasian Journal of Ecotoxicology* 2: 1-2 (Editorial).
Zinkl JG Shea PJ Nakamoto RJ Callman J. 1987. Technical and biological considerations for the analysis of brain cholinesterase of rainbow trout. *Transactions of the American Fisheries Society* 116:570-573.

APPENDICES

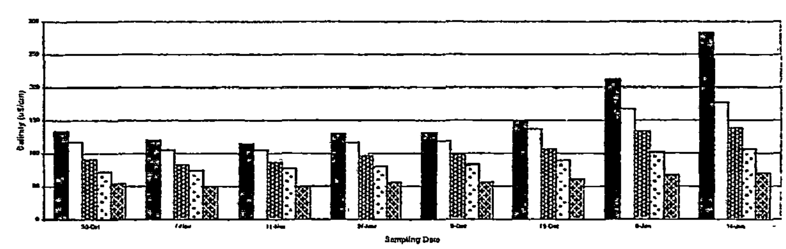
APPENDIX I

Water quality data for Mountain River (1997) collected from five sites. Sites are described in Chapter 6.

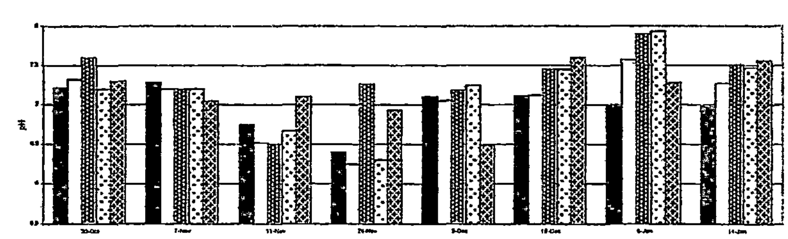
Water temperatures in Mountain River (1997 summer)



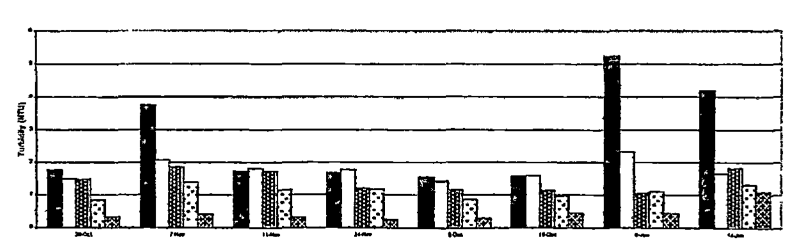
Salinity in Mountain River (1997 summer)



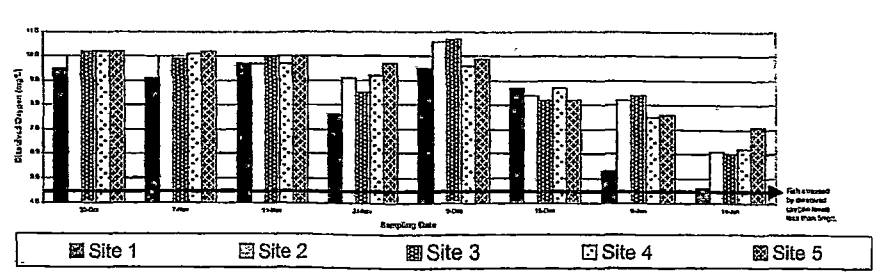
pH in Mountain River (1997 summer)



Turbidity in Mountain River (1997 summer)



Dissolved oxygen in Mountain River (1997 summer)



POISON

KEEP OUT OF REACH OF CHILDREN

READ SAFETY DIRECTIONS BEFORE OPENING OR USING

Dow AgroSciences

Lorsban* 750 WG

Insecticide

ACTIVE CONSTITUENT: 750 g/kg CHLORPYRIFOS (an anticholinesterase compound)

For control of certain insect pests in FRUIT and OTHER SITUATIONS as specified in the Directions For Use Table.

IMPORTANT: READ THE ATTACHED BOOKLET BEFORE USE.

WATER SOLUBLE PACKAGING. KEEP DRY

PRIMARY PACK CONTAINS 9 X 333g MEASURE PACKS WHICH IT IS ILLEGAL TO SELL SEPARATELY

Dow AgroSciences Australia Limited A.C.N. 003 771 659
20 Rodborough Road FRENCHS FOREST NSW 2086

CUSTOMER SERVICE TOLL FREE 1-800 700 096

Net Contents: 3 Kg

*Trademark of Dow AgroSciences

NRA Approval No. 51211/0499
GMID

STORAGE AND DISPOSAL

- Store in closed, original container in a dry, cool, well-ventilated area out of direct sunlight.
- Do not dispose of undiluted chemicals on site.
- Puncture or shred and bury empty containers in a local authority landfill. If no landfill is available, bury the containers below 500 mm in a disposal pit specifically marked and set up for this purpose clear of waterways, desirable vegetation and tree roots.
- Empty containers and product should not be burnt.

SMALL SPILL MANAGEMENT

If the water soluble bag is ruptured and a spill occurs, wear protective equipment (See SAFETY DIRECTIONS). Remove granules from surfaces and sweep up residual material Place in a container that will prevent further dispersion of the granules If spilled inside a building, wash contaminated surface to deactivate the chlorpyrifos with a solution of bleach (sodium hypochlorite) prepared according to the bleach label instructions Prevent entry of spilled chemical or damaged containers into drains, dams or waterways.
If the liquid spray mix is involved, apply absorbent material such as earth, sand, clay granules or cat litter to the spill. Sweep up material when absorption is completed and contain in a refuse vessel for disposal in the same manner as for containers (See Storage and Disposal Section).

SAFETY DIRECTIONS

- Product is poisonous if absorbed by skin contact, inhaled or swallowed. Repeated minor exposure may have a cumulative poisoning effect.
- Avoid contact with eyes and skin. Avoid inhaling spray mist.
- When opening the container, preparing the spray or using the prepared spray, wear cotton overalls buttoned to the neck and wrist, a washable hat, elbow-length PVC gloves and a face shield or goggles.
- If product on skin immediately wash area with soap and water.
- After use and before eating, drinking or smoking wash hands, arms and face thoroughly with soap and water
- After each day's use wash gloves, face shield or goggles, contaminated clothing

FIRST AID

- If poisoning occurs, contact a Doctor or Poisons Information Centre. (Ph: 13 1126)
- If swallowed, give one Atropine tablet every 5 minutes until dryness of the mouth occurs
- If poisoned by skin absorption or through lungs, remove any contaminated clothing, wash skin thoroughly and give atropine tablets as above.
- Get to a doctor or hospital quickly.
- If in eyes, hold eyes open, flood with water for at least 15 minutes and see a doctor.

MATERIAL SAFETY DATA SHEET

Additional Information is listed on the Material Safety Data Sheet for Lorsban 750 WG Insecticide which is available from Dow AgroSciences on request. Call Customer Service Toll Free on 1-800 700 096

NOTICE

Seller warrants that the product conforms to its chemical description and is reasonably fit for the purposes stated on the label when used in accordance with directions for use No warranty of merchantability or fitness for a particular purpose express or implied, extends to the use of the product contrary to label instructions, or under off-label permits not endorsed by Dow AgroSciences or under abnormal conditions

EMERGENCY RESPONSE
1-800 033 882
(LOCAL CALL FEE ONLY)

Barcode for stock identification

UN3077
ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.
(contains Chlorpyrifos 75%)

P.G. III
HAZCHEM 2X

CROP	INSECT PEST	STATE	RATE	CRITICAL COMMENTS
Container plants in soil or other growing media	Argentine ants (*Iridomyrmex humilis*)	Tas only	167g/25L water (1 measure pack per 50L water)	To meet requirements to enter Tasmania, treat the base of plants and the surface of growing media. A white deposit will remain.
Grapevines	Light brown apple moth	All States	33g/100L water (1 measure pack per 1000L water) OR 333g/ha (1 measure pack per ha)	Apply initial spray just after berry set. Later schedule spray should be made as required.
Kiwi fruit	Light brown apple moth	All States	33g/100L water (1 measure pack per 1000 L water) OR 666g/ha (2 measure packs per ha)	Apply the first application at green-tip, pre-blossom or post-blossom, after bees have been removed. The second application should be 14 days then every 21 to 28 days as required. Apply at least 10 days after dormant lime sulphur application.
Macrocarpa hedges	Dumpling bug (*Niastama punctaticollis*)	Tas only	33g/100L water (1 measure pack per 1000L water) OR 333g/ha (1 measure pack per ha)	Spray hedges adjacent to orchards in late winter to early spring to prevent adults entering the orchard.
Passion fruit	Queensland fruit fly (*Bactrocera tryoni*)	NSW and Qld only	80g plus 600mL yeast hydrolysate per 30 L water (1 measure pack plus 2.5 L yeast hydrolysate per 122 L water)	Apply 30L of spray mixture per hectare in a strip along the bottom of the vines. Repeat every seven to ten days during periods of fruit fly susceptibility. **AVOID CONTACT WITH FRUIT.** This treatment is preferred in integrated pest management (IPM) programmes where the use of cover sprays would be too disruptive.
Pears	Light brown apple moth	NSW, SA, Tas, Vic and WA only	33g/100L water (1 measure pack per 1000L water)	Commencing after petal fall, apply as full cover spray at intervals of two weeks. This rate will also suppress mealy bug populations present at spraying (not in Tasmania).
Stone fruit	Light brown apple moth	Tas and WA only	33g/100L water (1 measure pack per 1000L water)	Commencing after petal fall, apply as full cover spray at intervals of two weeks. This rate will also suppress mealy bug populations present at spraying (not in Tasmania).
	Queensland fruit fly (*Bactrocera tryoni*)	NSW and Qld only	80g plus 600mL yeast hydrolysate per 30 L water (1 measure pack plus 2.5 L yeast hydrolysate per 122 L water)	Use 50 to 100mL of mixture/tree as a strip or patch low on the tree every seven days. Use as an alternative to cover sprays, especially as an aid to integrated pest management, particularly integrated mite control **AVOID CONTACT WITH FRUIT.**

DIRECTION FOR USE
Restraints: DO NOT apply if bees are actively foraging.

CROP	INSECT PEST	STATE	RATE	CRITICAL COMMENTS
Apples	Apple dimpling bug	NSW, QLD, SA, Vic and WA only	67g/100 L water (1 measure pack per 500 L water	Apply up to late pink (balloon stage) Re-apply at the end of the flowering, if necessary. DO NOT apply for a minimum of three days before bees are actively foraging.
	Light brown apple moth	All States	33g/100L water (1 measure pack per 1000L water)	Commencing after petal fall, apply as a full cover spray at intervals of two weeks. This rate will also suppress mealy bug populations present at spraying (not in Tasmania)
Avocado	Queensland fruit fly (*Bactrocera tryoni*)	NSW and Qld only	80g plus 600mL yeast hydrolysate per 30 L water (1 measure pack plus 2.5 L yeast hydrolysate per 122 L water)	Use 50 to 100mL of mixture/tree as a strip or patch low on the tree every seven days **AVOID CONTACT WITH FRUIT.**
Bananas	Banana scab moth	Qld only	167g/125L water (1 measure pack per 250L water) OR 0.67kg or 1.33kg/ha (2 or 4 measure packs per ha)	Apply from the first appearance of flowers and repeat as populations indicate until fingers are exposed. **Air Blast:** Use 500 to 1000L water/ha. Use the high rate with onset of wet weather and for high insect numbers.
	Banana weevil borer	NSW and Qld only	333g/100L water (1 measure pack per 100L water) OR 333g/4kg sand (1 measure pack per 4kg sand)	Remove trash and apply 600mL of spray or 30g sand mixture as a 30cm band around the base of the plant. Apply one application at maximum weevil activity in spring (October to November) and in autumn (March to April). **NOTE:** Complete season's control is dependent on timely application.
Citrus	Queensland fruit fly (*Bactrocera tryoni*)	NSW and Qld only	80g plus 600mL yeast hydrolysate per 30 L water (1 measure pack plus 2.5 L yeast hydrolysate per 122 L water)	Use 50 to 100mL of mixture/tree as a strip or patch low on the tree Use every seven to ten days during periods of crop susceptibility. **AVOID CONTACT WITH FRUIT.**

PROTECTION OF LIVESTOCK

- Dangerous to bees. DO NOT spray any plants in flower while bees are foraging.

PROTECTION OF WILDLIFE, FISH, CRUSTACEANS, AND ENVIRONMENT

- Dangerous to fish.
- DO NOT contaminate streams, rivers or waterways with the chemical, used containers or containers used for mixing or holding treated seed.
- Only treat target plants. DO NOT allow spray to drift.

PRECAUTIONS

- Grapevine leaves treated with Lorsban 750 WG must not be used for human consumption.

STORAGE AND DISPOSAL

- Store in closed, original container in a dry, cool, well-ventilated area out of direct sunlight.
- Do not dispose of undiluted chemicals on site.
- Puncture or shred and bury empty containers in a local authority landfill. If no landfill is available, bury the containers below 500 mm in a disposal pit specifically marked and set up for this purpose clear of waterways, desirable vegetation and tree roots
- Empty containers and product should not be burnt.

SMALL SPILL MANAGEMENT

If the water soluble bag is ruptured and a spill occurs, wear protective equipment (See SAFETY DIRECTIONS). Remove granules from surfaces and sweep up residual material Place in a container that will prevent further dispersion of the granules. If spilled inside a building, wash contaminated surface to deactivate the chlorpyrifos with a solution of bleach (sodium hypochlorite) prepared according to the bleach label instructions. Prevent entry of spilled chemical or damaged containers into drains, dams or waterways.
If the liquid spray mix is involved, apply absorbent material such as earth, sand, clay granules or cat litter to the spill. Sweep up material when absorption is completed and contain in a refuse vessel for disposal in the same manner as for containers (See Storage and Disposal Section).

WITHHOLDING PERIODS

Apples, bananas, citrus, grape vines, kiwi fruit, passion fruit, pears, stone fruit: DO NOT harvest for fourteen days after application.

Avocado: DO NOT harvest for seven days after application.

GENERAL INSTRUCTIONS

MIXING:

SPRAY MIX

- One third fill the spray tank with water and add the required number of water soluble pre-packs to the strainer/sieve. Complete filling allowing the remaining water to run over the bags The bags will completely dissolve in a few minutes.

OR

- Add the required number of pre-packs to a mixing bucket and add enough water to completely cover the bags. Stir until the bags are completely dissolved and pour the pre-mix into the spray tank. Triple rinse the bucket and stirring implement, adding the rinse water to the spray tank.
- Agitate continuously to ensure thorough mixing before and during application. Only mix sufficient chemical for each day's work.
- Tank mixtures: Lorsban 750 WG should be added to the partially full spray tank first, followed by other dry flowables, suspension concentrates (flowables), aqueous concentrates and then emulsifiable concentrate formulations.

COMPATIBILITY

- Lorsban 750 WG is compatible with benomyl, carbendazim, dicofol, dinocap, dodine, fenarimol, mancozeb, propargite, superior oils, tetradifon, thiram, thiophanate-methyl, ziram.

APPLICATION

- Unless specified, it is essential to apply Lorsban 750 WG in sufficient water to obtain thorough coverage
- Apply through accurately calibrated equipment.

CLEANING SPRAY EQUIPMENT

Rinse water should be discharged onto a designated disposal area or, if this is unavailable onto unused land away from homes and water courses.

- After using Lorsban 750 WG, empty the spray equipment completely and drain the whole system. Quarter fill the spray equipment with clean water and circulate through the pump, line, hoses and nozzles. Drain and repeat procedure twice.

SAFETY DIRECTIONS

- Product is poisonous if absorbed by skin contact, inhaled or swallowed. Repeated minor exposure may have a cumulative poisoning effect.
- Avoid contact with eyes and skin. Avoid inhaling spray mist.
- When opening the container, preparing the spray or using the prepared spray, wear cotton overalls buttoned to the neck and wrist, a washable hat, elbow-length PVC gloves and a face shield or goggles.
- If product on skin immediately wash area with soap and water.
- After use and before eating, drinking or smoking wash hands, arms and face thoroughly with soap and water
- After each day's use wash gloves, face shield or goggles, contaminated clothing

FIRST AID

- If poisoning occurs, contact a Doctor or Poisons Information Centre (Ph.: 13 1126)
- If swallowed, give one Atropine tablet every 5 minutes until dryness of the mouth occurs.
- If poisoned by skin absorption or through lungs, remove any contaminated clothing, wash skin thoroughly and give atropine tablets as above.
- Get to a doctor or hospital quickly
- If in eyes, hold eyes open, flood with water for at least 15 minutes and see a doctor.

MATERIAL SAFETY DATA SHEET

Additional information is listed on the Material Safety Data Sheet for Lorsban 750 WG Insecticide which is available from Dow AgroSciences on request.
Call Customer Service Toll Free on 1-800 700 096

APPENDIX III

Wind data collected during orcharding spraying experiment described in Chapter 9.

	TIME (hrs)	WIND SPEED (m/sec) OVER 5 min INTERVAL AVERAGE	MAXIMUM	MINIMUM	DIRECTION (degrees)
	1300	0.62	1.16	0.08	70
	1305	0.10	0.73	0.00	30
	1310	0.33	0.60	0.00	60
	1315	0.11	0.73	0.00	65
Spraying started	1320	0.02	0.22	0.00	10
	1325	0.02	0.08	0.00	355
	1330	0.23	0.64	0.00	40
	1335	0.63	1.03	0.00	360
	1340	0.03	0.22	0.00	30
	1345	0.23	0.73	0.00	10
	1350	0.06	0.45	0.00	90
	1355	0.13	0.60	0.00	320
	1400	0.09	0.41	0.00	20
	1405	0.40	0.98	0.00	70
	1410	0.18	0.64	0.00	100
	1415	0.40	0.86	0.00	350
Spraying finished	1420	0.22	0.94	0.00	90
	1425	0.66	1.03	0.00	330
	1430	0.01	0.04	0.00	360
	1435	0.08	0.60	0.00	40
	1440	0.00	0.04	0.00	260
	1445	0.16	0.45	0.00	340
	1450	0.01	0.08	0.00	340
	1455	0.01	0.04	0.00	290
	1500	0.02	0.08	0.00	270

0 degrees = Magnetic North = 360 degrees

Appendix iv

Chlorpyrifos extraction efficiencies for quality control (QC) spiked water samples (Chapter 6).

	Extraction efficiency from QC spiked water samples (%)
	85
	39
	68
	93
	83
	56
	48
	105
	80
	76
	45
	102
	97
	74
Average	75.07
Standard Deviation	21.42

	Extraction efficiency from QC spiked sediment samples (%)
	68
	35
	37
	64
	40
	52
	37
Average	47.57
Standard Deviation	13.82