REVIEW OF THE POTENTIAL FOR AGROCHEMICALS USED IN VITICULTURE TO IMPACT ON THE ENVIRONMENT

A Review Report

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Grape and Wine Research and

Development Corporation

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Executive Summary

The Australian wine industry is under increasing international pressure to meet regulatory obligations and market, public, and investor demands. The current Grape and Wine Research and Development Corporation (GWRDC) 5-year plan, highlights the industry's need to meet production protocols and quality assurance parameters related, in particular, to the environmental impact of production processes. The State Governments are also engaging in activities to assess the sources and impacts of pollutants in the environment. Consequently, the project CRV01/04*, "Retaining the 'Clean and Green' image of Australian viticulture: minimising the effects of agrochemicals on the environment"*, has been funded by GWRDC and Department of Natural Resources and Environment (NRE) in Victoria.

This project aims to provide the Australian wine industry with knowledge and tools to enable growers to select and use chemicals to minimise the risk of environmental impact from production processes. To achieve this we need to:

- Understand the potential risk to the environment posed by viticultural agrochemicals and the circumstances that contribute to this risk,
- Assess the presence and movement of agrochemicals within and beyond vineyards,
- Predict, across a wide range of possible vineyard situations, whether there will be an off-target impact of agrochemicals, and
- Identify Best Management Practices, and in some cases find policy or engineering solutions to reduce potential risks.

We reviewed published literature and concurrent research relating to:

- The legislation to minimise impacts of agrochemicals on the environment,
- Breakdown, movement and impacts of agrochemicals within the environment,
- Properties and risks of agrochemicals,
- Assessment of environmental risk,
- Models that predict agrochemical behaviour,
- Methods for measuring agrochemical in air/soil/water,
- Biological significance of chemical levels,

We also established numerous linkages with Australian and overseas scientists and researchers.

Based on the review, the following conclusions and recommendations were made:

Australian policy to prevent or minimise environmental degradation

- Environment Australia conducts hazard assessments of agrochemicals before they are registered, to ensure that proposed uses will not lead to unacceptable impact.
- Most of the viticultural chemicals were registered prior to introduction of the current environmental risk assessment process.
- Various Acts in each state provide guidelines for protection of water, air and soil, but few prescribe acceptable concentrations of agrochemicals.
- The National Water Quality Guidelines provide detailed reference information on environmental concentrations based on ecological impacts, but few of the agrochemicals used in viticulture are included in the guidelines.
- It is recommended that, for grapegrowers to comply with the various acts and policies, they need firstly to know what concentrations of agrochemical are acceptable in the environment and secondly to know whether they are exceeding acceptable levels.

Overview of breakdown, movement and impact of agrochemicals in the environment

- Photolysis, hydrolysis, oxidation, bacteria and fungi are primarily responsible for the breakdown of agrochemicals.
- Agrochemicals break down in the environment, forming new chemicals usually less toxic than the original chemical. The original agrochemical and the breakdown products can redistribute within the application site or move off site.
- Water solubility and adsorption to soil are important in determining an agrochemical's tendency to move through the soil profile with infiltrating water, and over the soil with run-off.
- Leaching property of an agrochemical is not necessarily connected to water solubility of the chemical. Some agrochemicals such as glyphosate, diquat and paraquat are highly soluble in water but also highly adsorbed by the soil. On the other hand some agrochemicals such as captan and triadimenol are either insoluble or emulsifiable in water, but can move through the soil profiles at a moderate rate.
- The degree of accumulation or persistence of a particular agrochemical in soils depends on the percentage of organic matter and clay contents present in the soil. The accumulation will be higher in soil with higher percentage of organic matter and clay contents.
- While the fate and movement of agrochemicals can be predicted to some extent, predictions are not precise because the environment is very complex. Predictions are no substitute for monitoring.

Properties and potential hazards of agrochemicals used in Australian viticulture

- Growers are being provided with protocols for Best Practices for environmental management, and now need reference material for decision making that enables then to comply with such protocols, for example with respect to selection and use of low risk chemicals.
- The environmental data reviewed by the National Registration Authority and Environment Australia when chemicals are registered is not public domain and can be very hard to access. Information for comparing chemicals is very difficult for growers to interpret and the data in many cases is incomplete.
- Ranking of chemicals based on leaching or persistence in soil (Table 4-1 and Table 4-2) provides a practical starting point for identifying chemicals with highest potential to leach or accumulate in vineyard soils. However such rankings are not an adequate basis for risk assessment of chemicals in Australian viticulture, as there are many other factors that influence risk.
- To gauge the potential hazards, or risk quotients, of agrochemicals and their uses in viticulture we need some measurement of environmental concentrations to compare against known toxic concentrations.
- There are many systems that build risk quotients into algorithms to assess or rank risks more broadly. The various systems include (and give different weighting to) different potential hazards. Of these systems, Pesticide Impact Risk Index (PIRI) (see 4.2.8) and Soil Plant Atmosphere System Model (SPASMO) are useful tools to compare risks of particular practices, and Viticare Environmental Risk Assessment (VERA) (see 4.2.11) is a decision making tool that will help growers to ask appropriate questions when evaluating environmental risks.
- It is suggested that the grape industry will be able to justify chemical choices and uses, and confirm reductions in environmental impacts, when field data exists to support Estimated Environmental Concentrations, in air, soil and water in and around vineyards, associated with different practices.

Models for predicting the risk of off-target exposure to agrochemicals

- Various models have been developed internationally to predict movement of pesticides and estimate environmental concentrations in air, soil and water. The models are being continuously validated and improved, but all have limitations.
- Predictions by modelling are no substitute for field data collected by monitoring.
- Drift models describing vineyard spraying contain limited data but are being improved, as field data becomes available. The inclusion of any spray drift data generated in this project into the Agdrift model has been discussed with members of the Spray Drift Task Force.
- The available leaching models present a trade-off between simplicity and accuracy and few leaching models make predictions relevant to Australian soils. The inclusion of Australian soil data into PestRisk has been discussed with HortResearch, New Zealand.
- Models, by definition, include assumptions and work from limited data sets. In the case of agrochemical modelling in soil, the data sets come from standardised laboratory tests and very limited field monitoring.
- It is recommended that we compare field data collected in this project with the estimates from PestRisk or SPASMO (leaching) and Agdrift (spray drift), to see whether the models are suitable for predicting off target agrochemical movement across the grape growing regions in Australia.

Measuring agrochemical levels in air, soil and water in Australia

- Trials to measure agrochemicals in air, water or soil should be designed so that the data can be used and incorporated into existing data sets used in various models being developed.
- There are clear protocols for drift and water quality sampling, however there are no clear protocols for soil sampling.
- Passive samplers are increasingly being used to extract agrochemicals from soil and water, although their use at this stage is limited to extraction of metals from soil or water, or of polar compounds from water. The residues collected in passive samplers are analysed using conventional, costly techniques.
- Analytical methods preferred in standard protocols are laboratory based and expensive.
- Cheap and simple-to-use tools such as Enzyme Linked Immuno-Sorbent Assays (ELISA) and photometers are available and come with assurance of a high degree of accuracy. They seem an attractive alternative to conventional analytical methods.
- It is recommended that the suitability and accuracy of cheap and simple-to-use tools such as ELISA kits and the photometer for measuring agrochemicals in soil and water from vineyards must be tested before they should be used or recommended as an industry option.

Assessing biological impacts of agrochemical use

- The standard tests for assessing toxicity involve exposing a narrow range of test species to toxicants under controlled conditions.
- The sensitivities of different species to any particular toxicant vary, and ecological impact of agrochemicals depends on the role played by each exposed species in supporting the ecosystem.
- Interactions between agrochemicals can alter their toxicity.
- Most toxicity data submitted to Australian regulatory authorities relates to test species that do not occur in Australia.
- Australian and New Zealand data are being accumulated in a database with other available toxicity data and the database is available for use by this project.

- The Australian Guidelines for Water Quality Monitoring and Reporting describe various approaches to assessing the health of aquatic systems. The Guidelines are quite prescriptive in recommending sampling water, sediment and aquatic organisms, site selection and analysis.
- It is recommended that the limitations of standard tests must be recognised when interpreting data.

Current Australian research

- Monitoring of waterways for agrochemicals has revealed the presence of herbicides, fungicides and insecticides, sometimes at levels that exceed trigger values of environmental concern.
- Various programs are currently underway across Australia to monitor environmental impacts of agrochemicals. Of these, the leaching trials at Yalumba vineyards in the Coonawarra and the sediment quality study by SA EPA/CSIRO in the Adelaide Hills are very relevant and have the potential to provide very good, site specific data about agrochemicals in water moving off vineyards.
- In general, the concentrations of agrochemicals in water that have been measured in existing monitoring programs cannot be related to the agrochemical inputs at the farm level. They cannot be identified as coming from single, inappropriate uses (point sources) or seasonal use across a region by growers who are complying with label recommendations and using standard practices (diffuse sources).
- Generic data about environmental risk of 'average' practices does not relate to the risk associated with an individual grower' s local situation or practices because the concentrations of agrochemical entering and persisting in the environment vary according to conditions and usage at the individual vineyard. Adoption and refinement of Best Practices will be greater if growers can monitor agrochemicals in and near their own vineyards.
- It is recommended that the wine industry needs to measure environmental concentrations of agrochemicals, and equate these to toxic concentrations, in order to substantiate that Best Practice recommendations do lead to reductions in environmental impacts.

Consultation, communication and networking

- Project development, methods, grower participation, site selection, technical information and data and sampling infrastructure have been discussed with researchers, natural resource managers, equipment manufacturers, consultants and growers in Australia and overseas (Section 9).
- The research team has developed an effective network with national and international scientists.

Identified information gaps

- What is the environmental damage potential of a particular agrochemical used in Australian viticulture?
- Do biologically significant amounts of agrochemical move within or beyond vineyards?
- What management practices should be used to minimise the risks of off-target impact of agrochemicals?

Recommended research

- Predict spray behaviour from nozzles in wind tunnel experiments and model the spray plume using Gaussian diffusion model.
- Measure distribution of spray drift in vineyards by collecting drift samples from collectors on towers and on the ground. The combination of four nozzles and two nozzle pressures will be investigated using 'worst', 'average' and 'best' spray applicators. Relative risks of drift versus soil contamination from spraying will be determined.

- Monitor the movement of agrochemicals with high leaching potential (for example simazine or metalaxyl) through soil profile at two depths under drip and overhead sprinkler irrigation systems in sandy and clay soils.
- Collect soil samples from a number of vineyards in different grape growing regions to determine whether copper levels are linked to history of use of agrochemicals containing copper and whether the bioavailable concentrations are approaching levels known to impact on soil organisms.

Project outputs proposed in the original project proposal

- Review report and industry workshop.
- Recommendation of models suited to predicting drift or leaching in viticulture at the end of the project.
- Checklist of potential environmental impacts of common viticultural chemicals across different grape growing regions, and protocols for On-Farm Trials.
- Modifications to best management practices for chemical use, based on research data, and recommendations for mitigating environmental impacts
- Grower friendly kit for monitoring drift and soil-water contamination.
- Training of extension personnel.
- Policy recommendations.

Summary of Industry Reference Group recommendations regarding project directions and priorities

- The proposed research is appropriate.
- All practices used in the research trials must reflect current grower practices for the project to have credibility across the industry.
- The emphasis needs to be on the research objectives rather than extension or on providing tools for growers to conduct their own monitoring. For this reason the last three ‘Project Outputs’ should be removed.

Background

Consumers in our key overseas and local markets have questioned the "Clean and Green" image of Australian viticultural practices. Little is known about the actual, or potential, off-target movement or environmental impacts of viticultural chemical usage, however it is estimated that each year 4.1 million litres (before dilution) of agrochemicals will be applied to Australian vineyards. The Australian viticulture industry is keen to ensure that its agrochemical choice and usage does not impact adversely on the environment and that this concern is recognised by overseas and domestic consumers, and by the rural communities in viticultural regions. Also, to help consolidate a defensible position as a 'clean and green' industry, the Australian wine industry is developing Best Management Practices (BMPs) for chemical use in vineyards.

Concerns about agrochemicals can be catalysts that inflame community concerns. Fears from consumers and communities in North America and Europe over potential off-target impacts of viticulture have been exacerbated by, for example, the detection of agrochemicals in waterways. Increasingly, Europe is restricting agrochemical use in vineyards, for example copper is restricted to reduce its impact on soil organisms, and tunnel sprayers are being encouraged to minimise pesticide drift and run-off onto soil. Drift classifications for vines and other crops (Ganzelmeier and Rautmann 2000) and drift modelling (Hewitt 2000; Ganzelmeier et al. 1995) have resulted in prescribed buffer zones (eg 35 m) in Europe and USA.

This publication has been prepared to provide the industry with a clear review describing:

- Current knowledge of known or potential environmental impacts of key agrochemicals used in Australian viticulture,
- Techniques to predict impacts and to predict and measure movement of pesticides, and
- Recommendations for further research.

Objectives

The objectives of this review were to:

- Review the published literature and databases to understand the chemical properties (solubility, volatility, sorption, degradation, persistence in soil) of agrochemicals commonly used in Australian viticulture,
- Rank agrochemicals according to leaching potential and hazards in particular to aquatic life and soil organisms,
- Assess models that predict agrochemical movement, through soils or as spray drift, and select appropriate models to compare predictions with field collected data,
- Identify information gaps in the national and regional Environmental Best Practice Protocols,
- Develop networks with relevant research groups in Australia and overseas, and
- Provide industry with recommendations for ongoing research directions.

This information will be provided to industry as a comprehensive report on existing information, information sources, relevant models, critical information deficiencies, key linkages, detail and justification for proposed research methods for years two to four of this project.

Definitions

Acute toxicity: Acute toxicity is the amount of chemical that is immediately lethal to one-half (50%) of experimental animals (adopted from EXTOXNET 2002). Acute toxicity can be expressed as acute dermal (irritation or sensitisation observed in skin tests), oral or exposure toxicity. See also LC_{50} and LD_{50}.

Agrochemical: Chemicals that are used in agricultural industries, in particular for crop protection are known as agrochemicals or the synonym agrichemicals.

Aquatic life: The biological life (eg. algae, fish, frogs etc.) in fresh, marine or estuarine surface waters (adopted from Howard 1991).

Bioaccumulation – the increase in concentration of a chemical in animal or plant tissue compared to the environment. Bioaccumulation tends to occur with chemicals that are more soluble in lipids and organics (lipophilic) than in water (hydrophilic) (Landis and Yu 1999), for example organochlorine insecticides are stored and accumulate in animal fat.

Biodiversity: Biodiversity is the variety of all living things; it includes all types of plants, mammals, fish, birds, insects and microorganisms. Australia is one of the most biologically diverse countries in the world, with a large portion of its species found nowhere else in the world (Environment Australia 2002a).

Biodegradation: Biodegradation is the process that breaks a pesticide or other compound into a simpler form. Ultimately the biodegradation of organic pesticides results in the release of CO_2 and H_2O into the environment (Landis and Yu 1999).

Biotransformation: After a chemical is introduced into a living organism, the organism may metabolise and transform the chemical into other materials, reducing or altering the toxicity of the chemical.

Chronic toxicity: Chronic toxicity refers to any level of toxicity that is apparent after an organism is exposed to the chemical, through oral, dermal or inhalation, over a period of time (adopted from EXTOXNET 2002). The oral doses are expressed as mg of chemical per kg of animals body weight per day (mg/kg/day). Doses applied to aquatic species are expressed as an amount (mg) of chemical present per litre of water.

Degradation or breakdown of chemical: In the environment, chemicals breakdown via biotic and abiotic degradation. Biotic degradation is caused by soil microorganisms, especially bacteria and fungi, while abiotic degradation occurs due to acids, UV radiation, temperature, oxidation etc. (adopted from U.S. National Library of Medicine 2002).

EC_{50}, EC_{10}, and EC_5: Concentrations at which 'an effect' is observed in 50, 10 or 5 percent of a test population, respectively.

Emulsifiable chemicals: Chemicals that do not dissolve in water but disperse (blend) in water are known as emulsifiable chemicals.

Environmental hazard: Anything with the potential to cause injury, illness and damage to living and non-living things within the environment.

A danger posed to the environment, whether imminent or otherwise, resulting from any activities, practices, the location, storage or handling of any substance having toxic, corrosive, flammable, explosive, infectious or otherwise dangerous characteristics (adopted from the Environment Protection Act 1970 (Vic), Section 4).

Environmental impact: Any impact on plants, animals or the environment caused by human activities is an environmental impact. Impacts may be reversible or irreversible, minor or major, affect a whole ecological community or only a few individuals.

Environmental impact assessment: Environmental impact assessment (EIA), also called ecological risk assessment (ERA), is the practice of measuring or estimating the nature and likelihood of effects

of an action (eg the application of pest control products or practices) on one or more environmental parameters (Levitan 1997; SETAC 1997). EIAs may simply be methods for identifying changes in the environment, or they may also evaluate the magnitude and significance of these changes.

Environmental risk: An environmental risk will be presented by an environmental hazard. Risk and hazard are often used interchangeably but a hazard is the action, practice or event, and risk is the measure of danger associated with the hazard. Environmental risk is the product of the consequences and probability of an action, practice or event that has potential to disrupt established environmental processes.

Environmental risk is commonly expressed as the ratio between the estimated environmental concentration and the predicted no-effect concentration. Risk is also described as Toxicity × Exposure.

Gaussian diffusion model: This model predicts the downwind distribution of particles settling from a diffusing cloud created by a sprayer moving through a crosswind. The model assumes a uniform but manipulable atmosphere. The rate of diffusion is essentially controlled by turbulence, which affects the shape of the downwind deposition profile (Craig, Hugo and Cregan 2001).

Half-life: Time taken for half of the initial amount of a pesticide to break down.

Henry's Law constant: Henry's Law constant (air/water partition coefficient), H, is a non-dimensional value relating the chemical concentration in the gas phase to its concentration in the water phase (Howard 1991). The dimensional H can be determined by dividing the vapour pressure in atmospheres by the water solubility in mole/m^3 to give H in atm-m^3/mole.

Hydrolysis: Decomposition by chemical reaction with water.

LC_{50}: The lethal concentration fifty, or LC_{50}, is that concentration of a chemical in air or water that kills half of the experimental animals exposed to it for a set period of time (EXTOXNET 2002). For example, the 96-hour LC_{50} for rainbow trout is 32 mg/L of paraquat.

LD_{50}: The lethal dose fifty, or LD_{50}, is that amount of a chemical that when ingested kills half of the experimental animals exposed to it for a set period of time, expressed as mg per kg of the animals' body weight (EXTOXNET 2002).

LOEC: Lowest observed effect concentration.

Metabolism: Metabolism is a process in living organisms by which nutritive material is built up into living matter, or is a process that breaks down complex substances into simpler substances.

Metabolites: The breakdown or degraded products of a metabolic process are known as metabolites.

Mobility of chemicals in soil: Mobility or leaching of a chemical through a soil profile is the ability of the chemical to percolate through the soil profile. The mobility of the chemical depends on adsorption ability of the soil which is affected by a numerous soil properties such as organic carbon content, particle size, clay mineral composition, pH, cation-exchange capacity (adopted from Howard 1991). The chemical properties and water solubility of the chemical can also influence its mobility. The measured or estimated soil adsorption coefficients (see below) are used to determine the likelihood of leaching through soil or adsorbing to sediments (Swann et al. 1983).

NOEC: No observed effect concentration.

Oxidation: Decomposition by chemical reaction with oxygen.

Photolysis: Breakdown from the energy of sunlight.

Risk: see 'environmental risk'

Soil adsorption: Soil adsorption is where molecules of a liquid, solute or gas are held by the surface of soil particles. Numerous soil properties, such as organic carbon content, particle size, clay mineral composition, pH, and cation-exchange capacity affect sorption. However, organic carbon content is the most important factor that influence soil adsorption. Chemicals that form cations at ambient pH conditions are generally thought to sorb strongly on clay material. The adsorption coefficient is calculated from experimental soil or sediment partition coefficients using the Freundlich equation

(adopted from Howard 1991). Occasionally the experimental adsorption coefficients are reported on a soil-organic matter basis and these are converted to the organic content (Koc) by multiplying by 1.724 (Lyman et al. 1990).

Suspension of a chemical in water: Some chemicals do not dissolve in water but their fine particles disperse in water to form suspensions.

Vapour pressure: Vapour pressure of a substance is the pressure of vapour in connection with its liquid or solid form. The volatilisation of a chemical from water is dependent upon the vapour pressure and water solubility (Howard 1991). Vapour pressure is expressed in mm mercury (Hg) at or as close as possible to 25°C.

Volatilisation: Volatilisation is a process of rapid evaporation. The Henry's Law constant (H) can give qualitative indications of the importance of volatilisation. Chemicals with H values less than 10-7 atm-m^3/mole are less volatile than water and as water evaporates their concentration will increase. Chemicals with H values around 10^{-3} atm-m^3/mole will volatilise rapidly (Howard 1991).

Water solubility: The degree of dissolving in water.

Wetland: Wetlands include swamps, billabongs, lakes, salt-marshes, mudflats and mangroves. Wetlands are areas that have acquired special characteristics from being wet on a regular or semi-regular basis. The term also applies to depressions in the landscape of our more arid regions that only occasionally hold water but which, when they do, teem with life and become environmental focal points (Environment Australia 2002d).

1 Introduction

Based on available information, the Australian wine industry is exploring management systems that reduce environmental impacts (CRCV 2002, NRE 2002). With respect to chemical use, the current recommendations are very general. They lack regional relevance and growers have no means to assess the subtle impacts of chemical application. Prioritising and recommending viticultural chemicals according to the risk they pose to the environment will be valid and defensible where existing information is coupled with field validation of predicted behaviours of agrochemicals. Adoption of Best Management Practices (BMPs) for chemical use will be accelerated if growers can monitor the need for and quantify the benefits of impact reduction measures.

Following is a review of existing information on agrochemical properties, predicted behaviours in and around vineyards in air, soils and soil-water, and decision support systems (models, risk quotients, sampling techniques) for assessing the impact of agrochemicals.

2 Australian policy to prevent or minimise environmental degradation

Consumers and communities, particularly in Australia, USA, UK and Europe are becoming increasingly conscious of the potential impacts of agri-industries on the environment. Increasingly, in many countries, Environmental Management Systems (EMS) are being adopted to encourage best practices with regard to agrochemical use. Best practice protocols and auditing systems have been widely adopted by the wine industries in New Zealand and South Africa, and such systems help to reassure customers that the wines have been produced in an environmentally responsible way.

2.1 Assessing the hazards of agrochemicals used in Australia

Environment Australia (EA) undertakes hazard assessments for new agrochemicals submitted for registration in Australia and for registered agrochemicals undergoing review. The assessment considers hazard to aquatic and terrestrial life of proposed uses.

EA uses a hazard assessment process based on that adopted by the US EPA, whereby Expected Environmental Concentrations (EEC) of the agrochemical are compared against the toxicity of the product to derive a *risk quotient* (see 4.2.4). EA requires companies proposing registration of a new agrochemical to provide data showing EECs in air, soil and water, based on simple formulae. EA also requires data showing the toxicity of the chemical to a range of test species that represent the various fauna that may be exposed to the chemical. The test species are not required to be Australian species, and the data is not required to be Australian data. Most environmental toxicity data submitted to Environment Australia to support agrochemical registration applications is from predictive models and laboratory trials conducted in the USA.

Environmental hazard assessments of agrochemicals registered earlier than the 1990s did not require the complexity of data that are now required. The National Registration Authority's *Existing Chemical Review Program* (ECRP) reviews agrochemicals that were registered prior to the introduction of current requirements for health and safety, environmental hazard and residue data, however the ECRP is slow to progress through all the chemicals.

Of the agrochemicals registered for use in viticulture, most were registered prior to introduction of current requirements for environmental hazard data. Only a small proportion (notably parathion, endosulfan, vinclozolin and methidathion) has been reviewed, and endosulfan and vinclozolin are no longer available to viticulture as a consequence of their review.

2.2 Regulating agrochemical use

The activities of Australian grape growers are overseen by several acts of policies or codes of practice related to agricultural practices including chemical use, for example at a National level the suitability and supply of agricultural chemicals is covered by the Agricultural and Veterinary Chemicals Code Act 1994 Act No. 47 of 1994. Each state has its own series of regulations related to chemical use. Some of the relevant Acts in Victoria are:

- Clean Waters Act 1970 - controls 'point source' pollution by determining the appropriate water quality criteria for both wastewater and receiving waters.
- Agricultural and Veterinary Chemicals (Victoria) Act 1994 (Act No. 73/1994) - controls use of chemicals in Victoria. The preamble to this Act recognises that the protection of the health and safety of humans, animals and the environment is essential to the well-being of society, and that a regulatory system is required to ensure that the use of pesticides today will not impair the prospects of future generations (http://www.dms.dpc.vic.gov.au/).
- Agricultural and Veterinary Chemicals (Control of Use) Regulations 1996 S. R. No. 71/1996 - prescribes the records farmers must keep as users of agricultural chemicals; testing and

maintenance of spraying equipment; prohibition of certain chemical products; requirements for labels; and reasons for requiring produce to be residue tested (http://www.dms.dpc.vic.gov.au/)

- Water Act 1989, Act No. 80/1989 is, among other things, to provide formal means for the protection and enhancement of the environmental qualities of waterways and their in-stream uses (http://www.dms.dpc.vic.gov.au/).
- Soil Conservation Act 1938 includes gazetted watercourses, wetlands and land under threat of degradation from farming activities.
- The Australia New Zealand Food Authority (ANZFA) set limits to the amount of pesticide residues permitted in foods (maximum residue limits) (http://www.anzfa.gov.au/draftfoodstandards/Chapter1/Part1.4/1.4.2.htm)
- The Environmental Protection Act 1970 allows the EPA to prosecute for the off-target contamination of soil, plants, water and air.

The remainder of this chapter describes policy initiatives that indirectly influence agricultural development and farming practices. For the various legislations and policies summarised here to achieve their common goal of arresting environmental degradation, the primary industry sectors need a better understanding of the environmental impacts of practices including agrochemical use.

2.3 Local politics and community

Issues: Urban encroachment is causing conflict between farmers and urban residents regarding noise, dust, odour, spray-drift, night-lights etc. Consequently, the "right to farm working party" and the Victorian Farmers Federation (VFF) are recommending measures be put in place to satisfy both primary producers and urban residents.

Actions: Actions recommended by both the VFF and "right to farm working party" include:

- Amendment to the nuisance provisions of the Health Act.
- Disclosure notices relating to purchasing land in a rural zone.
- Dispute resolution mechanisms to encourage mediation between conflicting parties.
- Education to enhance awareness of the importance of primary production to the economy.
- Rural Disputes Settlement Centre (RDSC) to be established as part of the Dispute Settlement Centre of Victoria, administered by the Department of Justice.
- Mediators familiar with farming practices be trained and employed in a fee-for-service position.

2.4 Summary of environmental legislation and policy

Table 2-1: Summary of legislation and policy related to environmental protection (courtesy of Tony Smith, NRE).

Environmental Aspect	International	Commonwealth	State (Victoria selected as an example)	Local
Biodiversity	• Convention on Biological Diversity 1992 – Ratified 1993	• Environment Protection and Biodiversity Conservation Act 1999 • National Strategy for Conservation of Australia's Biological Diversity • Natural Heritage Trust	• Flora and Fauna Guarantee Act 1988 • Victoria's Biodiversity Strategy – 1997 (Our living wealth, Sustaining our living wealth, Directions in management).	• Regional Catchment Strategies
Native Vegetation	• Framework Convention on Climate Change	• Environment Protection and Biodiversity Conservation Act 1999 • ANZECC National Framework for the Management and Monitoring of Australia's Native Vegetation • Bushcare: The National Vegetation Initiative • Natural Heritage Trust	• Planning and Environment Act 1987 • Victorian Planning Provisions – Native Vegetation Retention Controls • Victoria's Draft Native Vegetation Management Framework 2000	• Regional Native Vegetation Plans • Local Govt. Planning Schemes
Wildlife	• Convention on Migratory Species – Bonn Convention • Japan-Australia Migratory Bird Agreement JAMBA • China-Australia Migratory Bird Agreement CAMBA • CITES Convention on International Trade in Endangered Species of Wild Fauna and Flora	• Environment Protection and Biodiversity Conservation Act 1999 • Environment Protection and Biodiversity Conservation Amendment (Wildlife Protection) Act 2001 • Natural Heritage Trust	• Wildlife Act 1975 • Flora and Fauna Guarantee Act 1988	• Action Statements – prepared under FFG Act 1988
Wetlands	• Convention on Wetlands of International Importance - Ramsar Convention 1971	• Environment Protection and Biodiversity Conservation Act 1999 • Wetlands Policy of the Commonwealth Government of Australia 1997 • National Wetlands Program • MDB Ministerial Council - Floodplain Wetlands Management Strategy • Natural Heritage Trust	• Water Act 1989 • Environment Protection Act 1970 • State Environment Protection Policies (Waters & Groundwaters of Victoria) • Victoria's Biodiversity Policy	• Wetland Operational Plans

Convention on Migratory Species (Bonn Convention) and international treaties such as the Japan-Australia and China-Australia Migratory Bird Agreements (JAMBA and CAMBA) will be met through the four program areas under the Natural Heritage Trust — Phase Two. The four areas are: Rivercare, Bushcare, Landcare and Coastcare. Natural Heritage Trust is the Commonwealth environmental policy.

2.5 Biodiversity

Issues: Australia is one of the most biologically diverse countries in the world, with a large portion of its species found nowhere else in the world (Environment Australia 2002a). At the national level there are over 1,100 native species listed on the Endangered Species Protection Act 1992 as either endangered or vulnerable, and 109 as presumed extinct (Environment Australia 2002a). The most significant impediment to the conservation and management of biodiversity is our lack of knowledge about it and the effects of human population and activities on it.

Actions: The National Strategy for the Conservation of Australia's Biological Diversity provides a framework for protecting Australia's biodiversity (Environment Australia 2002a). The Strategy's stated aim is: "to bridge the gap between current activities and those measures necessary to ensure the effective identification, conservation and ecologically sustainable use of Australia's biological diversity".

2.6 Native vegetation

Issues: The depletion and degradation of native vegetation communities threatens the long-term health and productivity of Australian landscapes. Destruction of native vegetation is the greatest contributor to loss of biodiversity; it is a primary cause of land degradation, salinity and declining water quality; and contributes substantially to our net greenhouse gas emissions (Environment Australia 2002b).

Actions: The Commonwealth, State and Territory Governments committed themselves, through the Natural Heritage Trust, to the national goal of reversing the decline in the quality and extent of Australia's native vegetation cover by June 2001. The commitment included agreement to halt clearing of endangered ecological communities, clearing that changes the conservation status of a vegetation community, and any clearing which is inconsistent with the sustainable management of biodiversity at a regional scale.

2.7 Water quality

Issues: Over the years salt, nutrients, sediments, agrochemicals, heavy metals, bacteria, protozoa, toxic algae, viruses etc. have contributed to deteriorating water quality in Australia.

Actions: The National Water Quality Management Strategy (NWQMS) was introduced in 1992 as a response to community concerns over the condition of Australia's water bodies and the need to manage them in an environmentally sustainable manner (Environment Australia 2002c). The objectives of the NWQMS are to:

- Achieve sustainable use of the nation's water resources by protecting and enhancing their quality while maintaining economic and social development,
- Involve the community to work with government to set and achieve local environmental values and water quality objectives for water bodies.
- Develop management plans for catchments, aquifers, estuarine areas, coastal waters or other water bodies.
- Develop national guidelines covering issues across the whole of the water cycle - ambient and drinking water quality, monitoring, groundwater, rural land uses and water quality, stormwater, sewerage systems and effluent management for specific industries.

The guidelines are to help the community, catchment managers, environment protection agencies and water authorities manage water quality including developing local action plans. A total of 19 guideline documents have been released and two more are being prepared (Environment Australia 2002c). The general categories for the water quality guidelines are a) Guidelines for aquatic ecosystems, b) Guidelines for primary industries, c) Guidelines for human health values, and d) Guidelines for monitoring and assessment.

Prior to 2000, and as part of the pesticide registration process the National Registration Authority (NRA) determined the safe level of exposure to chemicals for humans and this in turn led to formulation of guideline levels for pesticides in drinking water [Australian drinking water quality guidelines (Environment Australia 2002c)]. For pesticides that are not approved for use in water or water catchment areas the guideline value is set at or about the limit of determination (LOD). If a pesticide is detected at or above the guideline value, steps should be taken to determine the source and to stop further contamination.

Table 2-2: Upper limit concentration (*Trigger Values*) in freshwater systems, of chemicals registered for use in viticulture (ANZECC and ARMCANZ 2000b). The trigger values aim to ensure protection of aquatic species.

Chemical	**Trigger values for freshwater (µg/L) Level of protection of species (% species)**			
	99%	**95%**	**90%**	**80%**
Metals				
Copper[H]	1.0	1.4	1.8[C]	2.5[C]
Zinc[H]	2.4	8.0[C]	15[C]	31[C]
Insecticides				
Chlorpyrifos[B]	0.00004	0.01	0.11[A]	1.2[A]
Diazinon	0.00003	0.01	0.2[A]	2[A]
Dimethoate	0.1	0.15	0.2	0.3
Malathion	0.002	0.05	0.2	1.1[A]
Parathion	0.0007	0.004[C]	0.01[C]	0.04[A]
Methomyl	0.5	3.5	9.5	23
Herbicides				
Amitrole	ID	ID	ID	ID
Diquat	0.01	1.4	10	80[A]
Diuron	ID	ID	ID	ID
Glyphosate	370	1200	2000	3600[A]
Paraquat	ID	ID	ID	ID
Simazine	0.2	3.2	11	35
Trifluralin[B]	2.6	4.4	6	9[A]
Fungicides				
Thiram	0.01	0.2	0.8[C]	3[A]

ID = insufficient data
[A] = figure may not protect key test species from acute and chronic toxicity
[B] = chemicals for which possible bioaccumulation and secondary poisoning effects should be considered.
[C] = figure may not protect key test species from chronic toxicity
[H] = the values have been calculated using a hardness effects of 30 mg/l $CaCo_3$. These should be adjusted to site specific hardness.

Few of the agrochemicals registered for use in viticulture in Australia are listed in the tables of trigger values outlined by ANZECC and ARMCANZ (2000a). Acceptable concentrations of at least some additional chemicals used in the industry are listed in the Australian Drinking Water Guidelines (NHMRC 1996) (Table 2-3).

Table 2-3: Guidelines for concentrations of viticultural chemicals in drinking water, extracted from the Australian Drinking Water Quality Guidelines (NHMRC 1996).

Chemical	Guideline value (mg/L) (usually based on limit of determination)	Health value (mg/L) (usually = 10% of the Acceptable Daily Intake)
Metals		
Copper	1.0	
Insecticides		
Aldicarb	0.001	0.001
Carbaryl	0.005	0.03
Chlorpyrifos		0.01
Maldison		0.05
Methidathion		0.03
Methiocarb	0.005	0.005
Parathion-methyl	0.0003	0.1
Trichlorfon		0.005
Herbicides		
Diquat	0.0005	0.005
Glyphosate	0.01	1
Naproamide	0.001	1
Norflurazon	0.002	0.05
Oryzalin		0.3
Paraquat	0.001	0.03
Pendimethalin		0.3
Simazine	0.0005	0.02
Trifluralin	0.0001	0.05
Fungicides		
Benomyl		0.1
Chlorothalonil	0.0001	0.03
Fenarimol	0.001	0.03
Thiophanate		0.005
Thiram		0.003
Triadimefon	0.1	0.002

According to the drinking water guidelines, guideline values are set at or about the limit of determination (LOD) for pesticides that are not approved for use in water or water catchment areas (NHMRC 1996).

Table 2-4: Agrochemicals registered for use in viticulture but omitted from the Australian Drinking Water Quality Guidelines (NHMRC 1996) or from the environmental impact trigger values for chemicals in freshwater systems (ANZECC and ARMCANZ 2000b).

Insecticides, snail/slug killer, repellents and pheromones	**Herbicides**	**Fungicides**
Alpha-cypermethrin	2,2-DPA-sodium	Azoxystrobin
Azinphos-methyl	Amitrole	Benalaxyl + Mancozeb
Bacillus thuringiensis	Bromoxynil + Diflufenican	Captan
Dicofol	Carfentrazone-ethyl	Carbendazim
Endosulfan	Dichlobenil	Cyprodinil + Fludixonil
Esfenvalerate	Diuron	Dimethomorph
Fenamiphos	Fluazifop-P	Dimethomorph + Mancozeb
Fenitrothion	Glufosinate-ammonium	Dithianon
Fenthion	Haloxyfob-R methyl ester	Fenhexamid
Indoxacarb	Oxyfluorfen	Flusilazole
Iron EDTA complex	Quizalofop-P-ethyl	Hexaconazole
Metaldehyde		Hydroxyquinoline sulphate
Petroleum oil		Iprodione
Prothiofos		Mancozeb
Spinosad		Mancozeb + Metalaxyl
Sulfur (elemental)		Mancozeb + Petroleum oil
Sulfur (polysulfide)		Metalaxyl + Copper hydroxide
Tebufenozide		Metalaxyl + Copper oxychloride
Tetradecadienyl acetate + tetradecenyl acetate		Metiram
		Myclobutanil
		Oxadixyl + Mancozeb
		Oxadixyl + Propineb
		Penconazole
		Phosphorous acid
		Procymidone
		Pyrimethanil
		Quinoxyfen
		Spiroxamine
		Sulfur (elemental)
		Sulfur (polysulfide)
		Triadimenol
		Trifloxystrobin
		Zineb
		Ziram

2.8 Wetlands

Issues: The Wetlands Policy of the Commonwealth Government of Australia states that wetlands are ecologically, economically and socially important for the following reasons (Environment Australia 2002d).

- Biodiversity conservation;
- Nursery and breeding grounds, especially for fish and waterbirds;
- Improved water quality;
- Biological productivity;
- Aesthetic, cultural and heritage values;
- Recreation;
- Nutrient cycling;

- Flood mitigation through water storage and retention;
- Water storage;
- Ground water recharge;
- Scientific research;
- Education;
- Foreshore protection from wave action and erosion;
- Soil and water conservation; and
- Grazing, forestry and cropping.

It is estimated that since European settlement approximately 50% of Australia's wetlands have been converted to other uses. In some regions the rate of loss has been even higher. For example, on the Swan Coastal Plain of Western Australia 75% of the wetlands have been filled or drained and in southeast South Australia 89% have been destroyed (Environment Australia 2002d).

Actions: The Wetlands Policy of the Commonwealth Government of Australia, and the strategies it details, seek to promote the conservation, ecologically sustainable use and where possible enhancement, of wetland functions. To achieve the goal of the Wetlands Policy, the Commonwealth Government has set the following objectives (Environment Australia 2002d).

- Conserve Australia's wetlands particularly through the promotion of their ecological, cultural, economic and social values;
- Manage wetlands in an ecologically sustainable way and within a framework of integrated catchment management;
- Achieve informed community and private sector participation in the management of wetlands through appropriate mechanisms;
- Raise community and visitor awareness of the values, benefits and range of types of wetlands;
- Develop a shared vision between all spheres of Government and promote the application of best practice in relation to wetland management and conservation;
- Ensure a sound scientific and technological basis for the conservation, repair and ecologically sustainable development of wetlands; and
- Meet Australia's commitments, as a signatory to relevant international treaties, in relation to the management of wetlands.

2.9 Key issues

- Concern among consumers and the community about the impacts of agrochemicals is increasing.
- Environment Australia conducts hazard assessments of agrochemicals before they are registered, to ensure that proposed uses will not lead to unacceptable impact.
- Most of the viticultural chemicals were registered prior to introduction of the current environmental risk assessment process.
- Various Acts in each state provide guidelines for protection of water, air and soil, but few prescribe acceptable concentrations of agrochemical.
- The National Water Quality Guidelines provide detailed reference information on environmental concentrations based on ecological impacts, but few of the agrochemicals used in viticulture are included in the guidelines.

- For grapegrowers to comply with the various acts and policies, they need firstly to know what concentrations of agrochemical are acceptable in the environment and secondly to know whether they are exceeding acceptable levels.

3 Introductory overview of breakdown, movement and biological impacts of agrochemicals in the environment

Agrochemical residues in the environment result from the widespread use and disposal of agrochemicals. Over time, agrochemical residues may

- Breakdown,
- Be redistributed within the application site,
- Move off site, including movement to groundwater, run-off, into plants and the atmosphere, or
- Persist in the environment.

Breakdown and movement occur simultaneously and are the primary determinants of agrochemical dissipation at the point of measurement. The factors that determine the quantity and extent of agrochemical distribution to air, soil, water, plants and animals include the:

- Weather during application,
- Method of application (amount, timing, frequency and placement),
- Formulation of the agrochemical
- Edaphic factors (topography, vegetation type and density, soil conditions (temperature, soil type, organic matter, moisture, pH, aeration, and microbial activity), and
- Proximity of water bodies

This section covers breakdown, redistribution, movement and persistence of agrochemicals. This section also introduces methods to predict movement and the impacts of agrochemical residues on the environment.

3.1 Breakdown of agrochemicals

All agrochemicals react in the environment to form new chemicals. There can be many transformations in the chemistry before mineralisation (complete breakdown) occurs. The rate at which they react and the toxicity of products formed varies; transformation products are generally less toxic than the parent agrochemical, but may be of similar or greater toxicity. Pesticides most often react with oxygen (oxidation) or water (hydrolysis) and all agrochemicals are subject to breakdown in the presence of sunlight (EXTOXNET FAQ Team 1998). In soil and sediments, microorganisms (bacteria, fungi, etc.) are primarily responsible for agrochemical breakdown. Some agrochemicals may enter animals or plant roots or foliage and break down via plant metabolism or be excreted (EXTOXNET FAQ Team 1998). The rate at which agrochemicals breakdown, depends on their reactivity in each media (air, soil, water, plants, animals). Each agrochemical has unique properties that determine reactivity. Some agrochemicals are sensitive to acidic and/or basic conditions (pH), others are sensitive to sunlight, microbial attack, or plant and animal metabolism (EXTOXNET FAQ Team 1998).

3.2 Movement of agrochemicals offsite - ground water and run-off

Agrochemicals that are applied directly or injected into the soil may be washed off the soil into nearby bodies of surface water or may percolate through the soil to lower soil layers and groundwater (Oregon State University 1993).

Water solubility and adsorption to soil are important in determining an agrochemical's tendency to move through the soil profile with infiltrating water, and over the soil with run-off. Most agrochemicals that have low water solubility also tend to sorb strongly to soil, but there are exceptions. The more strongly an agrochemical sorbs to soil, the lower the tendency to move with infiltrating water (EXTOXNET FAQ Team 1998). Soil properties are also important, as each soil has

a characteristic ability to adsorb agrochemicals. Soils high in clay and organic matter have better sorption than sandy soils low in organic matter (EXTOXNET FAQ Team 1998). Soil structure is also important as it determines the infiltration rate. Rapidly infiltrating water may move agrochemicals on the surface deeper into the soil because they have less time for sorption. Soils that weakly adsorb agrochemicals and have a rapid infiltration rate are more likely to contribute to groundwater pollution than soils that strongly adsorb agrochemicals and have a slow infiltration rate.

Soil sorption and infiltration rates also determine agrochemical loss in run-off. Soils with slow infiltration rates may be more prone to run-off, as more water will remain on the surface. Agrochemicals sorbed to soil will not be lost to run-off. However, if run-off results in soil erosion, agrochemicals sorbed to surface soil will also move with run-off. To understand the potential for agrochemical movement toward groundwater or in run-off, agrochemical properties, application factors, soil and site conditions must be evaluated. Rainfall, irrigation practices, and evapotranspiration will also significantly influence the potential for agrochemical movement in water.

3.3 Movement of agrochemicals offsite - uptake by plants

Plant uptake can be important to agrochemical movement. Agrochemicals that are taken up by plants are not available for movement into the atmosphere, or movement into ground or surface water. However, if the plants are harvested some agrochemical may move from the site with the crop (EXTOXNET FAQ Team 1998).

3.4 Persistence of agrochemicals in the environment

Agrochemical persistence is often expressed in terms of half-life. This is the time required for one-half the original quantity to break down. Agrochemicals can be divided into 3 categories based on half-lives: non-persistent --less than 30 days; moderately persistent -- 30 to 100 days; and persistent -- greater than 100 days (Oregon State University 1993; EXTOXNET FAQ Team 1998). Because half-life values can vary considerably depending on environmental conditions, they are often reported as a range for each medium.

3.5 Prediction of agrochemical movement

Considering the above factors it is possible to predict in a general sense how an agrochemical will behave in the environment. However, more precise prediction is extremely difficult because the environment itself is very complex. There are, for example, huge numbers of soil types varying in the amount of sand, organic matter, metal content, acidity, etc. All of these soil characteristics influence the behaviour of an agrochemical so that an agrochemical that might be anticipated to contaminate groundwater in one soil may not do so in another. Similarly, surface waters vary in their properties, such as acidity, depth, temperature, clarity (suspended soil particles or biological organisms), flow rate, and general chemistry. These properties and others can affect agrochemical movement and fate.

With such great complexity, scientists cannot determine exactly what will happen to a particular agrochemical once it has entered the environment. However, they can divide agrochemicals into general categories with regard to, for example, persistence and potential for groundwater contamination and they can also provide some idea as to where the released agrochemical will most likely be found at its highest levels. Thus, it is possible to gather information to help make informed decisions about what agrochemicals to use in which situations and what possible risks are posed by a particular mode of use.

3.6 Ecological impacts of agrochemicals that move into the environment

Introducing a stressor, such as an agrochemical, into an environment can cause a range of effects. The effects may be brief or lasting, reversible or irreversible, they may impact on one or many individuals in a community. Detail on mammalian toxicity and toxicity to some invertebrates (especially bees) or aquatic species (eg. fish, crustacea) have long been required to support agrochemical registrations but

research into the more subtle ecological impacts of agrochemicals is relatively recent and complex to assess. The extent of an impact depends on:

- Physical and chemical characteristics of the chemical.
- Any bioaccumulation, biotransformation or biodegradation that occurs when the chemical is introduced to an ecosystem.
- The sites of action of the chemical in organisms, for example a compound may alter nerve synapsing, thus altering behaviour, or it may move into cellular membrane and so change the characteristics of the cell membrane (Landis and Yu 1999). The site of action influences whether the effect is broad or specific, and whether it is lethal or recoverable.
- Biochemical changes occurring in organisms in response to the chemical (production of stress proteins, changes to metabolism, suppression of the immunological system, changes to nerve receptors (anticholinesterase inhibition) (Woods and Kumar 2001; Landis and Yu 1999), changes in the conversion of sugars to energy (ATP cycle).
- Physiological and behavioural changes to the organisms in response to the chemical (chromosomal damage, lesions and necrosis, tumours and teratogenic effects, reproductive success, behavioural alterations, mortality, compensatory behaviours) (Landis and Yu 1999).
- Population parameters (population size, density, movement, recovery, adaptation)
- Community parameters (roles of each impacted species within the community)
- Ecosystem effects (resilience of the ecosystem to withstand local changes in communities)

3.7 Key issues

- Agrochemicals breakdown in the environment, forming new chemicals usually less toxic than the original chemical. The original agrochemical and the breakdown products can redistribute within the application site or move off site. Water solubility and adsorption to soil are important in determining an agrochemical's tendency to move through the soil profile with infiltrating water, and over the soil with run-off.
- Some agrochemicals persist in the environment.
- While the fate and movement of agrochemicals can be predicted to some extent, predictions are not precise because the environment is very complex. Predictions are no substitute for monitoring.
- The sensitivities of different species to any particular toxicant vary, and ecological impact of agrochemicals depends on the role played by each exposed species in supporting the ecosystem.

4 Review of the properties and potential environmental hazards of 24 agrochemicals used in Australian viticulture

Information on which to base comparisons of the available chemicals certainly exists within the data packages submitted by chemical companies when they are registering new chemicals, and some is available on material safety data sheets for chemicals. The information reviewed by the NRA and EA when chemicals are registered is not public domain and can be very hard to access. Moreover information about chemical properties or toxicity can be difficult to interpret and the data in many cases is incomplete.

Meanwhile national and regional protocols for Environmental Management Best Practices recommend that growers select chemicals based on a low potential to leach, and a low persistence in soil (CRCV 2002, NRE 2002). Grape growers attending *Research to Practice™ - Spray Application in Viticulture* workshops are shown Figure 4-1 to facilitate discussion about developing an 'awareness zone' of potentially sensitive areas within or around their vineyards. This provides a starting point to developing operating procedures that reduce the environmental impacts of agrochemical application. In Figure 4-1 the vineyard poses obvious risks to the organic grower, the nearby school, the holiday cottages, aquatic life in the creek, residents of the house on the vineyard, and to the commercial bees. There are other less obvious threats to the environment posed by agrochemical use in the vineyard example in Figure 4-1. Agrochemical use will affect non-target insects in the vineyard, may alter the availability/palatability of food for wildlife harbouring in the shelterbelts, and may affect invertebrates in the vineyard dam.

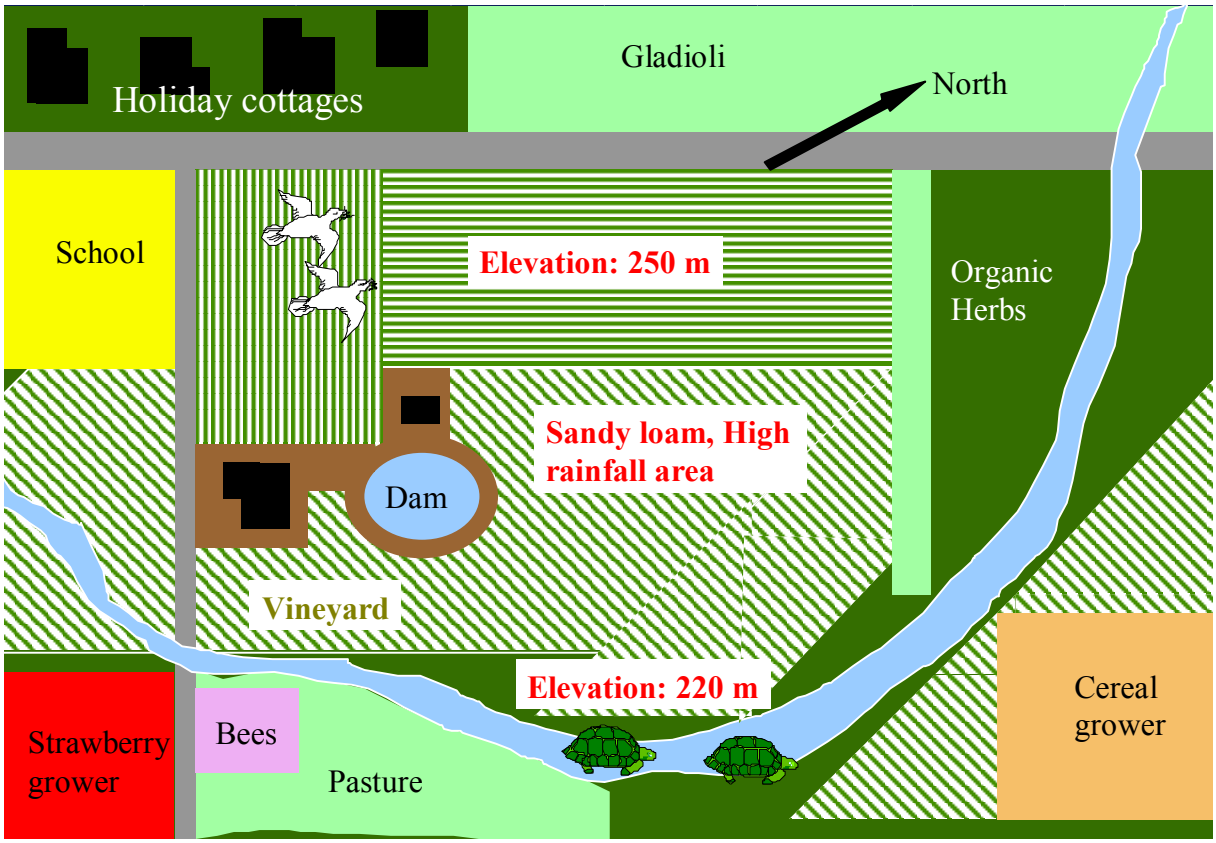

Figure 4-1: Hypothetical situation presented to grower participants attending *Research to Practice™ - Spray Application in Viticulture* workshops to facilitate discussion of 'Awareness Zones' around vineyards. Image courtesy of Research to Practice™.

For grape growers to adopt Best Management Practices that reduce environmental impacts, they need to make informed choices about the relative risks associated with agrochemicals and various management practices. In the draft Best Practices documents being prepared nationally and regionally, growers are advised to:

- " Chose the chemical ... least toxic to .. the environment…"
- "Check label ... on toxicity to non-target organisms …"
- " Check persistence and leachability …"

These well-intentioned recommendations are not enactable without reference material to support growers' decisions. In many cases the information on which growers would base choices is not readily accessible. Adjustments to management of application of chemicals that address and minimise risks can be costly and in any one year a grower may make very few adjustments, so adjustments must be prioritised. The most valuable adjustments are those that reduce risk from an unacceptable to an acceptable level, rather than from an already acceptable level to different but also acceptable level, or one unacceptable to another unacceptable level.

Towards making information more accessible, detailed information on the fate and potential impacts of 24 key agrochemicals used in Australian viticulture (fungicides, insecticides and herbicides) is presented in Appendix A. The information in Appendix A is drawn from a large number of disparate sources and covers physical and chemical properties, metabolites, factors that influence degradation, impacts on aquatic and soil organisms, birds and bees.

Biological information in Appendix A has been limited to birds and bees as there is data regarding these for all the chemicals. It is intended that Appendix A will eventually include data describing toxicity to a much broader range of species, extracted from the CD-Rom of eco-toxicity compiled by Micheal Warne (NSW EPA) as part of the National Water Quality Management Strategy (ANZEEC and ARMCANZ 2000).

4.1 Properties of agrochemicals commonly used in Australian viticulture

Table 4-1 to Table 4-3 below summarise the key information from Appendix A into a form designed to help viticulturists select chemicals. The tables summarise the properties (solubility, volatility, sorption, degradation and persistence in soil) of 24 agrochemicals commonly used in Australian viticulture, and potential risks to aquatic life, soil microorganisms, birds and bees.

It is important to notice that Table 4-1 to Table 4-3 are not sufficient alone to be the basis for decisions about relative risks of chemicals in Australian viticulture. These tables provide information for comparing the likelihood of chemicals leaching or accumulating in soils and designate values to the risks to aquatic life and soil organisms. The ranking system is based on published information and is useful for macro sorting of agrochemicals, ie to gauge which we are likely or unlikely to find moving into water or being accumulated in soil. The half-lives of each agrochemical in soil, and influences of various environmental factors on agrochemical degradation, are also presented. The ranking will not predict when or how far a chemical will move.

Halfon et al. (1996) used a similar approach to compare the risks of leaching of 50 chemicals used in Italian agriculture, based on half-life, water solubility, volatility and usage (tonnes per year). They confirmed that these parameters were suitable for assessing relative risks, because seven out of eight pesticides ranked as most hazardous (most persistent in soil, highest solubility, lowest volatility) were subsequently detected in river water samples. After comparing the relative importance of each criterion, Haflon et al. (1996) concluded that all the criteria were equally relevant to determining the risk of leaching into water.

While the behaviour of an agrochemical in soil depends on the properties of the chemical, it is influenced by properties of the soil (organic carbon content, particle size, clay mineral composition, pH, cation-exchange capacity). Leaching potential of an agrochemical does not necessarily depend on water solubility of the chemical. A soil that is high in organic carbon will strongly adsorb

agrochemicals that consist of organic structures, limiting leaching of these compounds. Soils that are high in clay will strongly adsorb agrochemicals that form cations at the pH of that soil (Howard 1991). Some agrochemicals are highly soluble in water (eg glyphosate, diquat, paraquat) but also highly adsorbed by soils with organic matter and so have low leaching potential. On the other hand chemicals that are either insoluble or emulsifiable in water (eg captan and triadimenol) can move through the soil profile.

Photolysis, hydrolysis, oxidation, bacteria and fungi are primarily responsible for the breakdown of agrochemicals. The metabolites or breakdown products of the agrochemicals reviewed are similar or less toxic than the initial chemical.

Table 4-1: Ranking, according to leaching potential, of 24 agrochemicals used in Australian vineyards.

Active constituents	Solubility in water	Volatility	Soil sorption	Half-life (days)	Leaching property	The potential effects of agrochemicals on:			
						Aquatic life	Birds	Bees	Soil micro-organisms
Metalaxyl	5	2	1	70	5	2	2	2	2
Captan	1	2	3	56	3	5	2	2	2
Carbaryl	3	2	3	28	3	3	2	5	2
Simazine	2	2	2.5	91	3	2	2	0	2
Triadimenol	1	1	3	400	3	4	?	2	5
Azoxystrobin	2	1	3	28	2	4	2	2	2
Benomyl	1	2	5	365	2	5	3	2	5
Chlorothalonil	1	1	3	90	2	5	2	2	3
Copper hydroxide	1	0	5	45	2	5	2	5	5
Diuron	2	1	2.5	330	2	4	2	2	2
Glyphosate	5	1	5	174	2	1	2	0	1
Iprodione	2	1	3	60	2	3	2	0	1
Mancozeb	1	1	3	56	2	3.5	2	0	2
Myclobutanil	3	1	4	66	2	3.5	2	2	2
Penconazole	0	1	4	45	2	3	2	2	2
Pyrimethanil	1	4	4	?	2	5	1	0	?
Sulphur- elemental	0	0	4	176	2	1	0	0	2
Teufenozide	0	2	4	115	2	3	?	2	2
Ziram	3	2	3	30	2	3	2.5	?	4
Chlorpyrifos	1	3	5	120	1	5	5	5	2
Copper oxychloride	0	1	5	45	1	4	2	2	5
Diquat	5	1	5	1000	1	2.5	2.5	0	2
Fenarimol	1	2	4	365	1	4	?	2	2
Paraquat	5	1	5	1000	1	3	3	2	2

Keys: 0= None; 1= Very low; 2= Low; 3= Medium; 4= High; 5= Very high; and ?= No specific data available
The half-life presented reflects the maximum reported value in soil.

Table 4-2: Ranking according to soil sorption, of 24 agrochemicals used in Australian vineyards.

Active Constituents	Solubility in water	Volatility	Soil sorption	Half-life-persistence in soil (days)	Leaching property	The potential effects of agrochemicals on:			
						Aquatic life	Birds	Bees	Soil micro-organisms
Benomyl	1	2	5	365	2	5	3	0	5
Chlorpyrifos	1	3	5	120	1	5	5	5	2
copper hydroxide	1	0	5	45	2	5	2	5	5
copper oxychloride	0	1	5	45	1	4	2	0	5
Diquat	5	1	5	1000	1	2.5	2.5	0	2
Glyphosate	5	1	5	174	2	1	2	0	1
Paraquat	5	1	5	1000	1	3	3	2	2
Fenarimol	1	2	4	365	1	4	?	2	2
Myclobutanil	3	1	4	66	2	3.5	2	2	2
Penconazole	0	1	4	45	2	3	2	2	2
Pyrimethanil	1	4	4	?	2	5	1	0	?
sulphur- elemental	0	0	4	176	2	1	0	0	2
Teufenozide	0	2	4	115	2	3	?	2	2
Azoxystrobin	2	1	3	28	2	4	2	2	2
Captan	1	2	3	56	3	5	2	0	2
Carbaryl	3	2	3	28	3	3	2	5	2
Chlorothalonil	1	1	3	90	2	5	2	0	3
Iprodione	2	1	3	60	2	3	2	0	1
Mancozeb	1	1	3	56	2	3.5	2	0	2
Triadimenol	1	1	3	400	3	4	?	2	5
Ziram	3	2	3	30	2	3	2.5	?	4
Diuron	2	1	2.5	330	2	4	2	2	2
Simazine	2	2	2.5	91	3	2	2	0	2
Metalaxyl	5	2	1	70	4	2	2	0	2

Keys: 0= None; 1= Very low; 2= Low; 3= Medium; 4= High; 5= Very high; and ?= No specific data available
The half-life presented reflects the maximum reported value in soil.

Table 4-3 Influence of environmental factors on degradation rates of 24 agrochemicals commonly used in Australian vineyards.

Active Constituents	Half-life-persistence in soil (days)	Influence of environmental factors on degradation rates of agrochemicals						
		Water (hydrolysis)	Vegetation (plant metabolism)	Increasing Soil pH	Soil micro-organisms	Sunlight (photolysis)	Increasing temperature	Increasing concentration of active constituents
Azoxystrobin	28	0	2	?	3	4	?	2
Benomyl	365	4	2	2	3	0	increase	3
Captan	56	5	4	4	2	2	increase	2
Carbaryl	28	4	4	4	4	4	increase	4
Chlorothalonil	90	3	2	3	4	0	increase	2
Chlorpyrifos	365	4	2	4	5	2	increase	2
copper hydroxide	45	3	2	2	1	2	increase	2
copper oxychloride	45	0	2	2	1	0	increase	2
Diquat	1000	3	0	4	5	5	increase	2
Diuron	330	2	4	0	4	4	increase	2
Fenarimol	365	2	?	?	1	4	none	0
Glyphosate	174	2	3.5	2	5	2	increase	4
Iprodione	60	5	5	4	4	5	increase	0
Mancozeb	7	5	5	2	1	2	increase	4
Metalaxyl	70	3	3	5	3	4	increase	4
Myclobutanil	66	0	4	0	4	4	?	?
Paraquat	1000	2	0	2	4	4	none	2
Penconazole	45	1	2	2	3	5	increase	?
Pyrimethanil	?	1	2	3	?	2	none	?
Simazine	91	2	3	2	3	2	increase	?
sulphur- elemental	176	?	2	4	4	2	increase	4
Teufenozide	115	2	?	?	4	4	increase	0
Triadimenol	400	2	1	?	1	4	increase	?
Ziram	30	2	4	2	2	2	none	2

Keys: 0= None; 1= Very low; 2= Low; 3= Medium; 4= High; 5= Very high; and ?= No specific data available The half life presented reflects the maximum reported value in soil

4.2 Systems for assessing the environmental risks of agrochemical use

The rankings above show the likelihood that agrochemicals will leach (Table 4-1) or be absorbed by the soil. Leaching does not pose substantial risk unless the leachate contains ecologically significant concentrations of toxicant. A further assessment is therefore required to estimate whether leaching, for example, will cause an environmental impact.

Risk assessments of agrochemicals and their proposed uses are conducted by regulatory agencies, such as the National Registration Authority and Environment Australia, when agrochemicals are being registered or reviewed. Various agricultural industries or researchers have developed systems to assess or rank the risks associated with agrochemicals, and are working towards enabling users to select those of lowest risk.

4.2.1 Measures of Risk and Risk Assessment

Risk is estimated from the relationship between exposure and effects, ie Risk = Toxicity × Exposure (SETAC 1997). Environment Australia uses the Quotient Method (Urban and Cook 1986) for risk assessment, in which toxicity (LD50 or LC50) is divided by the expected environmental concentration (EEC). The Urban and Cook (1986) Quotient Method is also used by the US EPA.

A variant on these definitions is the *Relative Risk Ratio* where the predicted environmental concentration (PEC) of chemical is compared against the concentration that is predicted to have no environmental effect (PNEC). ie Risk = PEC:PNEC (Van Straalen and Van Rijn 1998, Herrchen, Klein and Lepper 1995).

Many regulatory agencies adopt a tiered approach. The initial risk calculations are based on one of the above, or similar, approaches, and if risk exceeds a certain level they enter into increasingly complex analyses to manipulate estimates of exposure or consider toxicity to additional species.

Estimates of exposure can take into account measured concentrations of agrochemical in water or air or soil or diet, or rates and frequency of chemical applications on farms, or proportions of land being exposed. There are various models that simulate the behaviour of agrochemicals in the environment and are used for estimating exposure. Some of these are described in Chapter 5.

Estimates of effect may take into account any changes observed in an individual, or a species, or a whole ecological community, as a consequence of exposure to the agrochemical. Estimates of effects need to be based on biological data, which can be quite limited. As the quantity, quality and consistency of biological data improve, there is greater opportunity to develop models to estimate biological effects (see 4.2.7).

Potential for recovery of an affected ecological community can be included in a risk assessment, by combining persistence of the agrochemical into the Risk = PEC:PNEC quotient (Van Straalen and Van Rijn 1998). Wang, Edge and Wolff (2001) showed that recovery of whole populations after exposure to pesticide depended on the density of the population, with smaller populations recovering less predicably. This has important implications when an ecological community being exposed to agrochemicals includes rare and endangered species.

Some risk assessment systems derive a cumulative score for each pesticide based on risk ratios or quotients associated with several parameters (risk to human health plus risk to aquatic organisms plus risk of groundwater contamination, etc).

4.2.2 Limitations of Risk Assessment

Risk assessment systems may derive scores for particular chemicals and uses based on research data showing or predicting pesticide fate and toxicity of each chemical to particular vulnerable end points. We will call these ‘primary assessments. They are particularly important in the evaluation of new pesticides by regulatory agencies.

Lack of biological data means that toxicity information in primary assessments has frequently been restricted to analysis of LD_{50} values from laboratory experiments, using a very narrow range of standard test species and limited test conditions. Computer modelling is sometimes used to simulate impacts, using existing data for chemicals with similar properties. The quantity and quality of biological data for making primary assessments has increased dramatically in the last decade but there remain enormous gaps, particularly regarding sub-lethal effects, chronic toxicity, whole-of-system impacts of chemicals, and toxicity of the metabolites that form when agrochemicals are breaking down.

Primary assessments provide the support information for 'secondary assessments that rank or compare potential management options, for example to help growers select between chemicals or use patterns. The accuracy or relevance of rankings from secondary assessments depends heavily on the quality and relevance of the original data used to make the primary assessments of risk.

In a review of pesticide impact assessment systems for the OECD, Levitan (1997) illustrated the importance of selecting relevant parameters when making risk assessments, showing that the relative risk values for several pesticides are quite different when they were assessed using different ranking systems. Reus et al. (2002) compared eight risk assessment systems being used for evaluating pesticides in Europe, as part of a project to harmonise the different European systems (Table 4-4). They noted that most of the systems provided similar scores for individual components (risks for surface water, or soil, or groundwater) when scores were based on toxicity (although when application rates were added to the equations, the correlation between the rankings by different systems were lost). Consistent with Levitan (1997) however, Reus et al. (2002) also showed that the eight systems arrived at quite different scores for total environmental risk for 15 pesticides used in the comparison. Such differences are due to different levels of importance being given to certain parameters, for example leaching potential, or fate of metabolites, or occupational hazard, or surface run-off are weighted differently in the various scoring systems.

Table 4-4: Parameters considered by eight European systems for assessing environmental risk of pesticides, summarised from Reus et al. (2002), Tables 1 – 4, pages 179-180.

System	Acronym	Country	Effects included	Method
Environmental Yardstick	EYP	Netherlands	GWS(H)AqSo	Risk ratios
HD	HD	Denmark	GWSAqSo	Relative ranking
SYNOPS-2	SYNOPS-2	Germany	WS(A)AqSo	Risk ratios
Environmental performance indicator of pesticides	p-EMA	UK	GW(S)(A)HaqBaB	Relative scoring tables
Pesticide environmental impact indicator	Ipest	France	GWAHAq	Expert system
Environmental potential risk indicator for pesticides	EPRIP	Italy	GWSAHAqSo	Risk ratios
System for predicting the environmental impact of pesticides	SyPEP	Belgium	GW(H)Aq	Risk ratios
Pesticide environmental risk indicator	PERI	Sweden	GSAAqSoBaB	Relative scoring tables

G=groundwater W=surface water S=soil A=air
H=human health Aq=aquatic organisms So=soil organisms Ba=bioaccumulation B=bees
( ) letter in brackets means the effect is partly taken into account.

Risk assessments will become more accurate and relevant to particular situations as the quality and consistency of biological data and modelling improves, and as the complexity of interactions within ecosystems is better understood.

There are strong arguments for 'regionalisation' of environmental risk assessments and use of crop specific scenarios (Herrchen, Klein and Lepper 1995, Ramos et al. 2000) because risk assessments based on worst case scenarios may not reflect the risks of exposure across different regions or from different crops. Environmental concentrations of agrochemicals are influenced by local soil type and depth, topography, proximity of a sprayed site to surface water, local climatic conditions, portion of land under agricultural use, and typical pesticide programs for the region (including rates and frequency). Some risk assessment systems do give consideration to at least some of these variables (see 4.2.8).

Risk assessment is hampered by lack of published information on persistence and on No Observed Effect Concentrations (NOEC) of breakdown products (metabolites) from agrochemical degradation. Some metabolites are more toxic or have greater potential to leach than their parent agrochemical (Belfroid et al. 1998). While they found that there was little available, reliable data showing physico-chemical properties or toxicity of metabolites, Belfroid et al. (1998) concluded that, in general, metabolites of triazines and carbamates pose a greater ecological risk than their parent compounds (these groups include simazine, carbaryl and methomyl, used in Australian viticulture). Metabolites of organophosphates and dithiocarbamates, in general, pose less overall ecological risk than their parent compounds although tended to pose an increased risk to aquatic organisms (Belfroid et al. 1998) (these groups include chlorpyrifos and mancozeb, used in Australian viticulture).

4.2.3 Using Risk Assessment systems

In a review of pesticide risk assessment systems, Levitan (1997) describes three categories:

- Research and policy tools generated and used in government, industry and academia
- "Ecolabeling" systems (also called "green labels") designed to influence consumer opinion and market behaviour
- Decision aids used by farmers, farm advisers and resource managers in choosing among pest control options and evaluating the impacts of their choices.

Some examples of systems used for assessing environmental risk, and examples of how they are being applied, are described below:

4.2.4 Urban and Cook (1986)

The US EPA and Environment Australia have adopted the risk quotient method described by Urban and Cook (1986) to assess the risk associated with particular use patterns of a chemical, as part of the pesticide registration process. The risk quotient Q is an expression of estimated environmental concentrations (EEC) relative to the toxicity of the agrochemical. If the EEC in, for example, a 15 cm depth of water, exceeds the concentration that would be toxic to a relevant species, then $Q>1$. The Urban and Cook (1986) risk quotient model for risk assessment has been widely adopted by regulatory agencies internationally.

The NRA (1997) considers $Q<0.5$ to be an acceptable hazard. The quotient can be manipulated by altering the estimated environmental concentration, for example by reducing the amount expected to drift to water by extending the minimum distance between spraying and the nearest waterway, or by reducing the application rate, or by reducing the frequency of applications. The NRA (1997) recommends that if Q is between 0.1 and 0.5, then some additional risk management might be imposed to further reduce Q. The NRA (1997) considers that $Q<0.1$ is low risk and no mitigating management is required. This would appear to be a conservative approach, except that the NRA does not stipulate whether the toxic concentration in the quotient is based on LD_{50}, a Lowest Observed Effect Concentration (LOEC) or the No Observed Effect Concentration (NOEC), nor the species that

should be considered in the quotient. Thus the value for Q is not always conservative and is not a constant.

Examples of how to derive the EEC are provided by the National Registration Authority in their *Agricultural Requirements Series,* the guidelines for registering agrochemicals (NRA 1997).

The Australian viticulture industry could use the Quotient Method to compare predicted and actual risk, if concentrations of agrochemicals were first measured in air, soil and water in and around vineyards. The quotient method could then provide an indication of the suitability of recommended best practices for minimising environmental risk from agrochemicals.

4.2.5 Environmental Impact Quotient (Kovach et al. 1992)

A widely cited method for comparing pesticides is the "Environmental Impact Quotient" (EIQ), designed by Kovach et al. (1992) to help horticulturists in New York State choose low impact pest-control options. The EIQ is an example of a system that ranks cumulative risk values of pesticides by adding the risk quotients (toxicity of the compound plus extent of exposure, after Urban and Cook (1986). In this case each of eight environmental parameters are used: the hazard to spray operators, to pickers, to consumers, groundwater, fish, birds, bees, and beneficial arthropods.

The Kovach system would allow the viticulture industry to rank and select preferred pesticides according to a range of parameters.

4.2.6 Dutch Environmental Yardstick (Reus and Leendertse 2000)

In the Netherlands, the agencies managing water provided incentive payments to growers who used the Dutch Environmental Yardstick (Reus and Leendertse 2000) developed by the Centre for Agriculture and Environment for assessing and reducing environmental impacts. Like the EIQ (Kovach et al. 1992), the Yardstick is also a points-based system, but gives three separate output values: acute risk to water organisms, risk of groundwater contamination, and acute and chronic risk to soil organisms. Points for each use scenario are based on chemical properties of the active ingredients and principal metabolites, dose rates, organic matter content of soil, time and method of application and distance to surface water. Users can calculate their scores online (www.agralin.nl/milieumeetlat, however, a password is required and the information is in Dutch).

The Yardstick is used as a decision tool by Dutch farmers, as a tool for setting standards in ecolabelling, and as a policy evaluation tool (Reus and Leendertse 2000). Growers using the Netherlands eco-label *Milieukeur* must use pesticides that score <100 for water organisms, soil organisms and groundwater. This has resulted in an estimated 95% reduction in the environmental impact of potato growers producing under the *Milieukeur* label (Reus and Leendertse 2000). The Yardstick has also been combined with GIS information to identify high risk crops and pesticide uses at a regional level, and now needs to aims to incorporate models predicting pesticide emissions and behaviour, and include air, sub lethal effects to aquatic systems, and human health (Reus and Leendertse 2000). The Dutch Yardstick is an example of a sophisticated points system.

4.2.7 PERPEST

Most risk assessment models continue to rely on limited available biological data. Alterra Green World Research, Netherlands is developing the model PERPEST to predict ecological risks of agrochemicals in freshwater ecosystems when there is insufficient biological data. PERPEST predicts the effects of particular concentrations of pesticide on various ecological communities, dealing with data gaps by using existing data from the literature for compounds with similar chemistry under similar conditions and uses (Paul van den Brink, pers. comm.). In this regard PERPEST is quite different from the EIQ, Dutch Yardstick or Risk Quotient, and may have some usefulness to Australian situations where biological data on relevant species is scarce. This type of model is of most use to regulatory agencies rather than an agri-industry. PERPEST will be available later in 2002 from the Alterra web site (Paul van den Brink, pers. comm.).

4.2.8 Pesticide Impact Risk Index (PIRI)

The Pesticide Impact Risk Index (PIRI), by Kookana, Correll and Miller at CSIRO Land and Water, was developed for the Australian cotton industry to estimate the contamination of waterways attributable to agrochemicals. PIRI considers leaching, surface water run off, movement of pesticide in soil erosion and spray drift, and includes various conditions (soil types, irrigation, rainfall etc.). PIRI makes an assessment of the risk (high, medium, low) of aquatic impact based on these estimates, together with limited biological impact data. PIRI is useful for macro sorting of pesticides, ie to gauge which we are likely or unlikely to find moving into water, and which are most likely to impact on different trophic levels (crustacea, fish, algae etc.). It will not predict when or how far chemical will move. PIRI is an extremely valuable tool for Australian agriculture, and will become very useful to viticulture once soil, climate and irrigation data for viticultural districts are included in the software.

4.2.9 New Zealand Pesticide Rating System (Walker et al. 1997) and Environmental Scorecard (Jordan 1997)

Walker et al. (1997) developed a simple points-based model based on Kovach et al. (1992) for classifying agrochemicals used on fruit in New Zealand. They used a semi-quantitative rating system to compare the impact of horticultural industries, and to assess and compare the environmental impacts associated with farming by 'conventional' methods, versus integrated pest management, versus certified 'Organic' systems. Growers can also use the rating system to assist when making decisions about chemical use. This secondary assessment system can be used to compare practices but relies on risk values for pesticides that have already been calculated elsewhere in primary risk assessments.

It is worth noting that Walker et al. (1997) found that on average the scores from New Zealand grape producers compared favourably against the other fruit crops.

In 1996, the Winegrowers of New Zealand developed a scorecard system to evaluate the sustainability of the wine industry (Jordan 1997). Like the system by Walker et al. (1997), the scorecard does not rank or assess risk, instead using existing risk ratings as the basis for assessing compliance with preferred chemical use, fertiliser use and irrigation practices. The scorecard was subsequently developed into a system to guide growers towards more sustainable practices and for growers to aim for and self assess continuous improvement. Use of the scorecard and compliance with various practices have become a basis for membership of the Integrated Wine Production scheme in New Zealand, which now encompasses the majority of crop grown in New Zealand (David Jordan, pers. comm.). The success of the scorecard indicates that growers appreciate more detailed information on which to base their own risk assessments than is provided on chemical labels.

The pesticide rating system is being merged with New Zealand software that predicts the potential for agrochemical to leach through New Zealand soils (PestRisk – see 5.2.1), providing a new model SPASMO (Soil Plant Atmosphere System Model). The aspect of the pesticide rating system relating to risk to consumers has been omitted from SPASMO, priority instead given to more complex environmental assessment by evaluating the risks of leaching and other parameters at a regional level.

4.2.10 Ecological Relative Risk (EcoRR) (Sanchez, Baskaran and Kennedy 2001)

Ecological Relative Risk (EcoRR) was developed to predict and rank the potential ecological impacts of several chemicals applied to a small area for example a single farm. EcoRR ranks risk components to provide a total risk score of high, medium, low or no risk. EcoRR is based on the standard risk assessment frameworks used by the US EPA (ie exposure versus toxicity). EcoRR was used by the Australian cotton industry to assess risk of 36 agrochemicals, highlighting four insecticides that scored as high risk and ten chemicals that were medium risk. It was useful in identifying the environmental areas most at risk (Sanchez, Baskaran and Kennedy 2001).

4.2.11 Australian *Viticare Environmental Risk Assessment* (VERA) Tool

Viticare Environmental Risk Assessment (VERA) (CRCV unpub.) is a spreadsheet-based decision tool that takes a grower through six steps in order to produce a simple Environmental Action Plan for his or her business. The steps are:

1. Preliminary planning
2. Identification of potential risks (eg. pesticide use, water use, soil management, equipment, waste management etc.).
3. Assessment of potential environmental risks (derived by multiplying an exposure rating and a consequence (eg toxicity) rating, using scales provided)
4. Consideration of the legal dimension of environmental risks
5. Preparation of a prioritised list of potential environmental risks
6. Develop an Environmental Action Plan

In preliminary planning the user needs to answer 9 questions from his or her perspectives regarding the community concerns, environmental issues, involvement with environmental activities, water source, other land use in the area etc. The user can also consider the views of external stakeholders like Government.

VERA asks the user to rate the probability and consequence of contamination of land, surface water and ground water, impacts upon on-site and off-site flora and fauna, and health and social impacts of drift by the application of pesticides. At the moment these ratings can only be based on individual users' perceptions of environmental contamination by particular agrochemicals, as it is very difficult for a grower to access relevant data on which to base such risk assessments. Australian data is rare. Accessing and interpreting overseas data can be very difficult.

VERA will be a good tool for assessing environmental risk of agrochemicals once information becomes available to growers indicating the potential environmental risks and impacts associated with agrochemicals used in Australian viticulture.

4.3 Key issues

- Growers are being provided with protocols for Best Practices for environmental management, and now need reference material for decision making that enables them to comply with such protocols, for example with respect to selection and use of low risk chemicals.
- The environmental data reviewed by the NRA and EA when chemicals are registered is not public domain and can be very hard to access. Information about the environmental risks of chemicals is very difficult for growers to interpret or compare and in many cases there is no relevant data as most of the chemicals used in viticulture were registered prior to the introduction of the current regulatory framework for risk assessment.
- Ranking of chemicals based on leaching or persistence in soil (Table 4-1 and Table 4-2) provides a practical starting point for identifying chemicals with highest potential to leach or accumulate in vineyard soils. However such rankings are not an adequate basis for risk assessment of chemicals in Australian viticulture, as there are many factors that influence risk.
- The most cited method for assessing risk of a single compound in a single situation is the Risk Quotient method of Urban and Cook (1986). The risk quotient compares environmental concentrations with toxic concentrations. To gauge the potential hazards, or risk quotients, of agrochemicals and their uses in viticulture we need some measurement of environmental concentrations to compare against known toxic (or LOEC, or NOEC) concentrations.
- There are many systems that build risk quotients into algorithms to assess or rank risks more broadly. The various systems include (and give different weighting to) different potential hazards. Of these systems, PIRI and SPASMO are useful tools to compare risk of particular practices, and

VERA is a decision making tool that will help growers to ask appropriate questions when evaluating environmental risks.

- The grape industry will be able to justify chemical choices and uses, and confirm reductions in environmental impacts, when field data exists to support Estimated Environmental Concentrations, in air, soil and water in and around vineyards, associated with different practices.

5 Models for predicting the risk of off-target exposure to agrochemicals

This section reviews several of the available models to predict the distribution and movement of agrochemicals.

5.1 Models to predict drift of agrochemicals

5.1.1 AgDrift

The AgDrift model for predicting spray drift (Teske et al. 2000, cited in Hewitt 2000) was developed by the Spray Drift Task Force (SDTF), with membership of 40 chemical companies. The model includes aerial spray drift, drift from ground rigs and from orchard/vineyard sprayers. The AgDrift model has three tiers. Tier I provides very basic predictions, based on assumed worst case situations. Tiers II and III allow for more variables to be manipulated.

AgDrift was constructed primarily to address drift from aerial applications. Ground spraying and orchard/vineyard spraying were later additions and the data for vineyard spraying that supports the model is very limited (only 8 studies, limited to three sprayers, all producing fine droplets: Andrew Hewitt, SDTF, pers. comm.). Tier I of AgDrift became available on the Internet for a short time in mid 2001, however the Internet version was not suited to predicting drift from vineyard sprayers.

Early 2001, Environment Australia (EA) was considering using AgDrift, for evaluating the risk of drift from orchard sprayers, as part of the agrochemical registration review process (Risk assessment and spray drift workshop, prelude to Ecotox 2001, 11th February 2001, Canberra). However, EA is now using the German drift values (Ganzelmeier and Rautmann 2000) (Darryl Murphy, EA, pers. comm.).

The AgDrift model includes very little orchard or vineyard field data, and is not reliable at this stage for simulating vine spraying. There is discussion amongst the developers regarding the inclusion of additional data sets into the AgDrift model, in particular Australian data (from CPAS, Nicholas Woods), the German drift models by Heinz Ganzelmeier and New Zealand drift data (Andrew Hewitt, SDTF, pers. comm.; J-P Praat, Lincoln Ventures, pers. comm.). Inclusion of the larger data sets, and in particular data derived from trials using Australian and New Zealand vines, sprayers and conditions, would make the AgDrift model more applicable to Australian viticulture.

5.1.2 German drift models

Ganzelmeier and Rautmann (2000) derived basic 'drift values' from a series of 77 vineyard trials conducted in Germany during the 1990s. The drift patterns were reasonably consistent, and are summarised below. The drift values are aimed to assist in calculating a concentration of chemical likely to be measured on the surface of a still water body at various distances from the sprayer, specifically for predicting risk to aquatic species. .

Table 5-1: Basic drift values derived from 77 drift trials (Ganzelmeier and Rautmann 2000).

Distance from field edge (m)	Spray drift deposition (% of application rate)	
	Grapevine early stage	Grapevine late stage
3	3.6	6.78
5	1.63	3.43
7.5	0.87	2.00
10	0.55	1.36
15	0.29	0.79
20	0.19	0.54
30	0.1	0.31
40	0.06	0.21
50	0.05	0.16

It is important to be clear that the Ganzelmeier and Rautmann (2000) models are not a measure of sprayer efficiency, and that they show the proportion of spray that settles out at each respective distance from the crop, not the total proportion of spray that drifts. If the values in Table 5-1 are considered cumulatively, such that the proportion settling at 3 metres is added to the proportion that settles at 5 metres etc up to 50 metres from the crop, drift settling in a 50 metre zone beyond sprayed, late-stage vines accounts for just over 15% of the sprayed volume. This is without including the drift settling at intermediate distances in the cumulative total.

Note that the levels reported by Ganzelmeier and Rautmann (2000) are much less than drift measured from U.K. apple orchards by Richardson, Walklate and Baker (2002).

5.1.3 SprayCan

The SprayCan model (Maber, Dewer and Praat 2002) predicts drift onto neighbouring properties based on a property map (ortho-photo image), and nozzle type, pressure, fan speed, sprayer type, wind direction, wind speed, chemical and positions of wind breaks. SprayCan also rates the hazard associated with each prediction scenario based on the sensitivity of neighbouring enterprises to particular chemicals. Maber, Dewer and Praat (2002) based the SprayCan model on the AgDrift model plus further New Zealand spray trial data.

5.2 Models to predict leaching of agrochemicals through soil or into water

Various models have been developed to predict the movement of agrochemicals through soil into groundwater or across soil into surface water. The models contain soil physical and hydrological parameters (for example water retention, soil temperature, bulk density, stone fraction, % carbon). Assumptions within the models can limit their application to Australian irrigated viticulture, for example soil pH is not always considered although this will dramatically influence half-life. The leaching models do not include a measure of biological activity by organisms, although these play a significant role also in degrading agrochemical.

5.2.1 PestRisk

PestRisk was developed by Steve Green and Brent Clothier of HortResearch, NZ to assess the risk of pesticides entering groundwater in horticultural areas. It draws on a database of site/soil/pesticide characteristics (PESTPRO) that predicts the potential of agrochemicals leaching beyond the root zone into the groundwater. PestRisk was developed to provide a detailed assessment of risk under various soil and management scenarios.

PestRisk considers a wide range of soil parameters, but makes certain assumptions. For example it assumes a constant half-life for each pesticide, whereas the half-lives vary in different soils, and there is no function for considering soil pH, which also influences degradation.

PestRisk is currently being further refined by HortResearch to include additional data relating to chemical hazard, the pesticide rating system (Walker et al. 2000) and data for 22 different crops and 7 different regions in NZ. The refined version is called the Soil Plant Atmosphere System Model (SPASMO) (see 4.2.9).

5.2.2 LEACHM

The LEACHM model (Hutson and Wagenet 1992) and the LEACHP version of LEACHM, predicts the persistence and leaching of agrochemicals through soil profiles. It is a complex model, requiring detailed inputs, including biological data.

LEACHM provided good predictions of leaching for sulfonylurea herbicides and tracer in Australian alkaline soils under rainfall, but not under rainfall plus irrigation (Sarmah, Kookana and Alston 2001).

5.2.3 PESTSCRN 3

PESTSCRN 3 (Aylmore and Di 2002) is a leaching model designed to screen out or identify those pesticides that are likely to cause groundwater contamination, at a catchment or individual farm level. While many leaching models assume constant recharge rates, PESTSCRN 3 aims particularly to address situations where groundwater recharge occurs at a variable rate.

5.2.4 PRZM-3 and EXAMS

The US EPA recommends that companies seeking agrochemical registration use the Pesticide Root Zone Model (PRZM-3) or Exposure Analysis Modelling System (EXAMS) to assess exposure of surface water to agrochemicals.

PRZM3 predicts pesticide transport and transformation down through the crop root and unsaturated zone (US EPA 2002a). The Exposure Analysis Modelling System (EXAMS) is for evaluating the fate, transport, and exposure concentrations of synthetic organic chemicals including pesticides, industrial materials, and leachates from disposal sites. (US EPA 2002b).

Lin, Hetrick and Jones (undated) provide a simple overview of the two models. Both EXAMS and PRZM-3 can be downloaded from the US EPA website. Like all models they have limitations. For example they are not suited to predicting movement of agrochemical from controlled release formulations or granules (Cryer and Laskowski 1998).

5.3 Models combining exposure by drift, run-off and leaching

Huber, Bach and Frede (2000) combined various existing models that estimated leaching using PELMO (Klein 1995), surface run off using GLEAMS (Leonard et al. 1987), and drift using drift values by Ganzelmeier et al. (1995). They predicted that of the pesticides applied in Germany in 1994, 14 tonnes were lost into surface waters via run-off, tile drains and drift. Surface run-off was estimated to contribute more than drift or leaching, due in particular to the steep land farmed in Germany. The modelled estimates compared favourably with monitoring data collected from various catchments in Germany.

5.4 Modelling biological impacts of agrochemicals in water or soil

Various groups are developing models to predict the biological impacts of agrochemicals and other pollutants. The models are designed to address particular questions regarding biological impacts.

At the lowest scale of impact, models such as the biotic ligand model or the free-ion activity model (McLaughlin, 2002) estimate the proportion of total metal concentration that is available to soil biota or aquatic organisms (bio-available). Measuring the bioavailable concentration of metal is important because total metal concentrations in soil or water do not relate directly to their toxicity. It is only the bio-available portion that is able to impact on organisms.

At a higher level of impact, models are being developed to predict the risk that agrochemical concentrations will impact on ecosystems. The PERPEST model (see 4.2.7) is a risk assessment tool that uses existing data from the literature to estimate the effects on biota of compounds with similar chemistry (Paul van den Brink, pers. comm.).

AUSRIVAS is a prediction system for assessing the biological health of Australian rivers (http://ausrivas.canberra.edu.au/). The AUSRIVAS software was developed by the CRC for Freshwater Ecology, under the National River Health Program. AUSRIVAS is based on British models that predict the species expected to occur at a pristine site, for comparison with species actually collected at a site. The comparison indicates overall ecological health of a site. AUSRIVAS predictive models have been developed for each state and territory for the main habitat types found in Australian river systems. Reference sites for condition assessments are scarce in some areas, for example for the Murray near Mildura (Leon Metzeling, EPA Vic, pers. comm.).

5.5 Key issues

- Various models have been developed internationally to predict movement of pesticides and estimate environmental concentrations in air, soil and water. The models are being continuously validated and improved, but all have limitations.
- Models, by definition, include assumptions and work from limited data sets. In the case of agrochemical modelling in soil, the data sets come from standardised laboratory tests and very limited field monitoring.
- The available leaching models present a trade-off between simplicity and accuracy and few leaching models make predictions relevant to Australian soils. The inclusion of Australian soil data into PestRisk has been discussed with HortResearch, New Zealand.
- Drift models describing vineyard spraying contain limited data but are being improved, as field data becomes available. The inclusion of any spray drift data generated in this project into the Agdrift model has been discussed with members of the Spray Drift Task Force.
- Predictions by modelling are no substitute for field data collected by monitoring.
- We plan to compare field data collected in this project with the estimates from PestRisk or SPASMO (leaching) and Agdrift (spray drift), to see whether the models are suitable for predicting off target agrochemical movement across the grape growing regions in Australia.

6 Measuring pesticide levels in air, soil and water in Australia

6.1 Agrochemicals in air

International standards have been developed to assist in the standardisation of testing spray application technologies, and further standards are being developed (Herbst and Ganzelmeier 2002). Although the standards are preliminary at this stage (Nicholas Woods, CPAS, pers. comm.), the components are outlined below with more detail in Section 10.2. Spray drift field trials conducted in Australia have focussed on herbicide drift, and drift from aerial applications. Field assessments of drift have rarely been conducted in vineyards or orchards in Australia.

Drift trials are generally conducted to assess the proportions and concentrations of agrochemical that either remain airborne, or land at various distances from the sprayed canopy, on soil within the sprayed area, or on nearby sensitive areas including waterways.

Drift is often expressed as a proportion (%) of the applied rate that drifts to various distances from the edge of a sprayed swath (for example see Table 5-1). Expressing drift as a proportion enables comparisons to be made of the propensity of spray plumes to drift, but does not provide information about the concentration of the chemical or the hazard it poses. Estimated Environmental Concentrations (EEC) in water bodies (see 4.2.4) can be extrapolated from drift data expressed as proportion of the applied rate, and this is commonly the approach used by regulatory agencies during risk assessment.

Drift is heavily influenced by

- Density of grapevine canopy (Praat et al. 2000; Ganzelmeier and Rautmann, 2000),
- Volatility of the agrochemical being sprayed (Praat et al. 2000),
- Atmospheric conditions, which change dramatically between and even during commercial spraying operations,
- Formulation of the agrochemical (Butler-Ellis and Bradley 2002),
- Addition of adjuvants (Jamie Nichols, pers. Comm.), And
- Equipment, such as drift reducing nozzles now available from many nozzle manufacturers.

6.1.1 Defining the spray plume

A preliminary requirement in spray drift assessment is definition of the spray plume. This is typically carried out in a wind tunnel and the proportion of droplets within each droplet size in the spray cloud are measured by projecting a laser beam into the spray plume and assessing the defraction pattern of the plume. The wind tunnel at the Centre for Pesticide Application and Safety, University of Qld, Gatton has been hailed as world class by members of the Spray Drift Task Force (Andrew Hewitt, SDTF, pers. comm.).

Once the spray plume has been described, the behaviour of that plume under a range of conditions (temperature, wind speeds, release heights, humidity can be predicted using diffusion models (Craig, Hugo and Cregan 2001).

6.1.2 Field trials to measure spray drift

Field trials are critical to understanding the behaviour of spray drift, because entrainment of spray plume by the sprayer and around the vines will inevitably interfere with the pattern of spray movement. This means that the plume behaviour will differ from that predicted by diffusion model and wind tunnel results. There is data to show that drift is affected by the presence of a grapevine canopy (Praat et al 2000; Ganzelemier and Rautmann 2000), but the data are inconsistent in showing whether drift is greatest from dense or thin canopies.

6.1.2.1 Tracers to simulate spray deposits in field trials

For occupational health and safety reasons, tracers, rather than pesticide, are used for making field measurements of drift. The main tracers used by researchers exploring nozzle performance and drift are soluble fluorescent dyes, although various other tracers are available.

The most common tracer used is fluorescein sodium dye. Taylor (2002) used fluorescein sodium at 0.2% (w/v) and Agral (0.1% v/v). The tracer was extracted from individual collector lines by washing in 250 ml of buffered water solution. Samples were kept in the dark and then measured on a filter fluorometer (Perkin Elmer LS2).

Weisser, Landfreid and Koch (2002) also used fluorescein sodium at 50 g/ha in 200 L water. It offers a high sensitivity with a limit of detection on a leaf surface of approx 0.02 ng/cm^2. They sampled 4-6 replicates per position and each sample contained enough leaves to make up approximately 100 cm^2 area as the sampling unit. The leaves were sampled directly into 100 ml plastic bottles that were placed in the dark immediately after sampling. In the lab, the tracer was washed off the leaves and the concentration measured in a fluorometer at excitation wavelength of 484 nm and emission wavelength of 512 nm. After measuring leaf area, the tracer was expressed in ng/cm^2 leaf surface.

Cilgi and Jepson (1992) used fluorescein tracers (Acid yellow 73, Aldrich) to measure the amount of spray deposit landing on insects (pinned to leaves within a crop). Tracer was washed from the insects, and surface areas of foliage and insects were calculated to compare the amount of tracer deposited per area.

Resin based fluorescent pigments, commonly used in Australian viticulture to assess and compare deposits in vine canopies (Furness 2000) can be used as a qualitative measure (presence or absence) of drift at various distances downwind but cannot be interpreted quantitatively.

EDTA chelates of cobalt, copper, manganese or zinc (approx 1.0 g/L plus non-ionic wetter (0.1%) in water) have also been used as tracers (Richardson, Walklate and Baker 2002).

Tartrazine (food dye) was used in Sunraysia in the 2000-01 season by Alison MacGregor (NRE) and David Manktelow (HortResearch, NZ) to compare pesticide deposits throughout vine canopies. They used spectrophotometric analysis of the soluble food dye, rinsed from known leaf areas from within various parts of the vine canopy. The analysis was rapid and very cheap, used a standard spectrophotometer and was suited to making comparative measures of deposition in the canopy. However to use this tracer for drift work, it would need to be formulated to ensure that the surface tension of droplets is comparable to that of standard spray solutions. The detection limits for this marker are unlikely to be as low as those for fluorescein.

Of the methods described, the simplest tracer to source, easiest to analyse, plus most readily detectable at very low levels, is fluorescein sodium and will thus be used in this research.

6.1.2.2 Samplers to collect drift

Methods for collecting airborne drift include hair curlers, pipe cleaners, plastic rods, narrow pipes, simple aspirated air samplers, photographic papers, petri dishes, woollen line, filter papers, bridal veil, alpha-cellulose and strings (Cooper, Smith and Dobson 1996; Craig, Woods and Dorr 2000; Richardson, Walklate and Baker 2002; Praat et al. 2000). Water sensitive cards have been used for drift collection (Klein and Johnson 2002) but in that case the drift assessment was based primarily on measuring plant kill and the cards were only used to provide data on droplet size and number. Taylor (2002) used chromatography paper sprayed with fluorescein sodium to assess spray deposits close to nozzles. For collecting spray deposits landing on the ground, Richardson, Walklate and Baker (2002) used Whatman glass filter papers (6 cm diameter glass micro-fibre GF/A filters) placed in the base of 88 mm diameter x 15 mm high petri dishes.

Cooper, Smith and Dobson (1996) compared the efficiencies of a battery powered rotary sampler, which collects drops upon a moving surface, and a passive sampler of synthetic wool yarn. Collection efficiencies of fluorescein droplets (10-25 micron range) varied from 40-100% for the yarn and from 1% to 70% for the rotary sampler. There is little other data available on collection efficiencies of the

various collectors. However, poor collection efficiency means that there can be a significant disparity between the amount of spray, either in drops or volume, passing through unit vertical area in unit time (true flux) and amount collected on samplers (apparent flux). The efficiency of collectors is influenced by the directional nature of the collecting surface, so that the choice of collectors depends on the purpose of the sampling. For example flat ribbons will measure deposits from a single direction, while woollen yarn with fine hairs will collect deposits from all directions (Cooper, Smith and Dobson 1996). In typical field drift trials, drift collectors are mounted on towers up to 20 m tall or placed on the ground. Some authors (Richardson, Walklate and Baker 2000; Nicholas Woods, pers. comm.) describe making three or four passes past the towers with drift samplers so that the average deposit from the four passes can be used to overcome small temporal variations in the wind gusts.

6.1.2.3 Analysis of tracers from drift collectors

Fluorescein dye is soluble, and typically rinsed off collectors and measured as a concentration in the rinsate using a fluorometer. Tartrazine is similarly rinsed off collectors and the depth of colour in the rinsate measured by spectrometer.

6.1.3 Characterising the equipment, canopy and weather

Meteorological data, operational records of the spray equipment and characterising of the canopy structures are necessary for meaningful interpretation of spray drift results.

Parameters related to the sprayer that must be defined include nozzle types, pressures, and flow rates, spray release heights, travel speeds, formulations and distance between nozzles and the canopy.

Characterisation of the canopy includes row spacing, vine spacing, vine height, vine width, tree row volume index, mean area index and mean area density (Richardson, Walklate and Baker 2002).

At the time of spraying, wind speeds and direction, temperature and humidity must be measured within the trial site so that they can be accounted for in the analysis of drift or run off.

6.2 Agrochemicals in soil

6.2.1 Bioavailability of agrochemical concentrations in soil

The biological significance of agrochemical levels in soils is influenced by soil characteristics, such as pH and soil temperature, because these influence the availability of agrochemical contaminant to organisms. While measuring total concentrations of agrochemicals is a cost-effective way to conduct initial screening, agrochemical levels must be considered in a context of the availability of the contaminant to affect organisms (bioavailability).

This is particularly evident in the case of metals (eg copper and zinc). Bioavailability of metals is affected by the forms in which the metal ions occur (Howell, 2002 - abstract in Warne and Hibbert, 2002). The forms in which the metal ions occur are influenced by pH, organic matter content and cation exchange capacity. These soil characteristics caused copper to vary in toxicity to potworm (*Enchytraeus albidus)* by more than two orders of magnitude (Lock and Janssen 2001). The age of contaminant in soil also influences the degree of binding of chemicals to soil and affects toxicity of agrochemicals (Pedersen, Kjaer and Elmegaard 2000).

Copper levels in soil can also influence retention and toxicity of other compounds. Morilla et al. (2000) found that copper enhanced the adsorption of glyphosate to soil. Copper also increased the persistence of atrazine in soil, perhaps because copper is toxic to bacteria that normally degrade the herbicide (Mallavarapu et al. - abstract in Warne and Hibbert, 2002).

The type of organic matter present influences the bioavailability of agrochemicals. For example Kookana et al. (2002 - abstract in Warne and Hibbert 2002) found that the proportion of black carbon in soil influenced the sorption and therefore bioavailability of carbaryl.

Analytical methods are being developed to improve the assessment of bioavailable rather than total metals in soil and water (Howell, 2002; McLaughlin et al 2002, abstracts in Warne and Hibbert 2002).

6.2.2 Sampling to measure agrochemicals in soil

There appear to few prescriptions for sampling soil for agrochemicals. Samples taken from the soil surface, soil cores, and composite samples are common.

6.2.2.1 Extraction of bioavailable chemical

The choice of soil sampling method does depend on whether total concentrations or bioavailable concentrations are to be measured.

There is much recent interest in using thin gradient diffuse samplers (DGT) to extract chemical in-situ from surrounding contaminated soil. The DGT passive samplers developed by Lancaster University, U.K., extract bioavailable chemical from soil (Nolan et al (2002 - abstract in Warne and Hibbert 2002).

6.2.2.2 Extraction of pore water from soil samples

Pore water testing is used to assess toxicity of the water versus solid-phase in sediments in aquatic systems. Pore water testing may also assist with the comparison of mobile pesticide with pesticide fixed onto soil particles in a vineyard soil profile. Carr et al. (2001) provide a comparison of in situ methods (pore water stored in the soil and collected just prior to analysis using samplers (peepers) or suction) and ex situ methods (pore water separated from soil by centrifuge or pressure and stored at 4°C or frozen to await analysis).

6.3 Agrochemicals in water

6.3.1 Sampling to measure agrochemicals in water

Detailed methods for routine monitoring or sampling of water and sediment quality are prescribed in the *Australian guidelines for water quality monitoring and reporting* (ANZECC and ARMCANZ 2000). The guidelines provide a comprehensive reference for designing and conducting trials to assess contamination by agrochemicals of groundwater, fresh or marine water and sediments. They provide detail on trial designs, selection of sampling sites, sampling frequency, equipment, analytical techniques, data analyses and data interpretation.

6.3.1.1 Sources of contamination influence sampling method

Design of sampling methods must take into account the likely sources of contamination, for example whether the agrochemicals are entering aquatic systems from point or diffuse sources, or whether the contamination occurs as distinct pulses or occurs uniformly. Point sources in viticulture could include drainage outfalls carrying leachates, or run-off or leaching from hazardous waste disposal sites. Point sources, once identified, are relatively easy to monitor if the timing of discharges can be identified, for example associated with irrigation or rainfall events. Diffuse sources of agrochemicals include run-off from vineyard soils, erosion of vineyard soils, spray drift and airborne contaminated soil. Origin, timing or amounts of diffuse discharges can be very difficult to identify.

6.3.1.2 Frequency and time of exposure influence sampling method

When agrochemicals enter the environment as a discrete event, perhaps at a biologically significant concentration but only over a brief period, it is referred to as a pulse exposure. The compound may only last at toxicological concentrations for a matter of minutes or hours, but when repeated within some critical interval, the repeated brief exposures may be enough to have major ecological impact. Routine monitoring programs that rely on monthly or weekly sampling are not suited to situations where contamination is occurring as pulse exposures. Walker, Brown and Dorr (2001) measured

chlorpyrifos contamination of surface water in Mountain River, Tasmania, adjacent to an apple orchard during and after spraying. While a ten minute sampling interval indicated that concentrations of chemical in the water remained low despite evidence on drift collectors of spray drift, a two minute sampling interval revealed a biologically significant pulse of insecticide.

While chemicals with low leaching potential are likely to be released gradually or relatively uniformly into irrigation drainage, timing of pulse exposures, if present, needs to be identified before monitoring irrigation drainage water for agrochemicals with high leaching potential.

6.3.1.3 Equipment and methods

Having characterised the contamination, sampling design can be planned and appropriate samplers can be chosen.

Samplers recommended in the water quality monitoring guidelines (ANZECC/ARMCANZ, 2000) include:

- Discrete water samples collected into containers by hand (grab samples),
- Sample collection using pumps,
- Discrete water samples collected using automatic samplers,
- Samplers that collect and integrate samples over a period of time,
- Automated real time measurements of, for example pH, EC, temperature,
- Remote sensing, or
- Field observations of water quality, for example turbidity,
- Grab samples are suited to situations where contamination level and/or water quality (pH, turbidity etc) are static. Grab sampling is not suited to groundwater sampling.

Samples can be pumped from depths down to 10 m in a surface water body. Pumping is not suitable for sampling very low concentrations of contaminants as the extraction tube from the pump can adsorb the contaminant.

Automatic samplers consist of a pump system, a controller and an array of sample bottles within a housing. Automatic sampling reduces the labour required, so that samples can be collected frequently. This method is suited to some measurement parameters, but while samples are stored in an automatic sampler located in a field situation there is likely to be degradation of any agrochemical within the sample.

Integrated samplers collect samples over a period of time, providing cumulative measure of contamination, which is useful when contaminants are likely to vary with time. The most commonly used integrated samplers are the passive semipermeable membrane samplers. These are most simply described as a bag with a semipermeable membrane that allows molecules of agrochemical, for example, to transfer into the bag where they are then bound, and accumulate, on a resin, lipid or other medium in the bag, to await extraction (Prest et al. 1995). The first examples of passive semipermeable membrane samplers appeared in the late 1980s when Södergren (1987, cited in Prest et al. 1995) used hexane inside a dialysis tube to extract the film microlayer from a surface to understand its chemical composition. Södergren (1990) then used the hexane filled dialysis membranes to accumulate organochlorines from water. A range of passive samplers are being used in Australia for various applications (Nolan et al. 2002; Ross Hynes NSW EPA pers. comm, Leo Duivenvoorden Central Qld Univ. pers comm., Anu Kumar, CSIRO Land and Water pers. comm.).

The passive semipermeable membrane samplers are suited to sampling for some metals (eg copper) and non-polar chemicals but at this stage may not suit some of the more polar agrochemicals used in viticulture. There is potential to use passive samplers in field monitoring of irrigation drainage water coming from vineyard areas, or in water bodies near vineyards, to measure metals (eg copper, arsenic) and a limited number of agrochemicals. Hyne et al. (2002 - abstract in Warne and Hibbert 2002)

modelled the kinetics of pesticide uptake and release from passive samplers in flowing water. Uptake by passive samplers of pesticides with K_{ow} >3.5 is linear and independent of pesticide concentration in water. Pesticides with K_{ow} <3.5 have lower uptake rates.

6.4 Analysis of soil and water samples

Before selecting an analytical technique for measuring agrochemicals in soil or water, the following must be considered:

- The required detection limit,
- The precision of potential methods,
- The phase in which the analyte is present in the sample (eg complexed with other compounds or as free ions),
- Whether the total amount present or only the bioavailable portion needs to be measured, and
- Occupational health and safety issues associated with handling, extracting and analysing the sample.

The *Australian guidelines for water quality monitoring and reporting* (ANZECC and ARMCANZ 2000) recommend that for greatest accuracy organic agrochemicals are analysed using gas chromatography (GC) or high pressure liquid chromatography (HPLC) and that metals are analysed using ICPMS, ICPAES or AAS.

There is an international effort to develop rapid and simple test methods for bioavailable copper. CSIRO Land and Water (Mike McLaughlin) is participating in this effort and has offered to assist the wine industry by providing guidance and bench space for bioavailable copper analyses at CSIRO Land and Water in Adelaide.

Gas chromatography (GC) is recommended for analysis of organophosphate insecticides and the majority of the fungicides used in viticulture. High performance liquid chromatography (HPLC) is recommended for analysis of carbamates (eg carbaryl, iprodione).

GC and HPLC are very precise methods, with low limits of detection. The guideline levels recommended for water quality (ANZECC and ARMCANZ 2000) in many cases correspond to the limits of detection achieved by GC and HPLC. The disadvantage of GC and HPLC is that they are costly, laboratory based analyses requiring elaborate sample preparation and expensive equipment, which limits the number of samples that are affordable.

Enzyme-linked immunosorbent assays (ELISA) are available for rapid analysis of water samples for a range of agrochemicals (chlorpyrifos, metalaxyl, simazine, paraquat). ELISA assays are relatively cheap and easy to use, do not require elaborate equipment or a highly skilled operator, and according to the manufacturer (EnviroLogix, USA) measure pesticide concentrations as low as parts per billion (ppb). EnviroLogix claim accuracy to parts per million or parts per billion, depending on the compound, but our experience with ELISA assays for rapid analysis of agrochemicals on grape foliage and bunches (Skerritt 1997, Riches et al. 2000) indicates that the accuracy of the analyses are variable.

Metal ions can be measured in water samples simply and cheaply using a photometer which assesses colour depth of reagent in the presence of metal ions.

6.4.1 Bioavailability of agrochemical concentrations in water

As already discussed in section 6.2.1 with respect to soil, not all of a chemical concentration measured in water is necessarily bioavailable or therefore toxic. For example the toxicity of a given concentration of agrochemical can vary with the pH of the water, for example Wilde et al. (2002 - abstracted in Warne and Hibbert 2002) found that copper and zinc accumulation and toxicity in freshwater algae decreased as pH decreased. Patra et al. (2002 - abstracted in Warne and Hibbert 2002) observed that the toxicity of chlorpyrifos to fish increased at increasing temperatures.

6.5 Key issues

- Trials to measure agrochemicals in air, water or soil should be designed so that the data can be used and incorporated into existing data sets used in various models being developed.
- There are clear protocols for drift and water quality sampling, however there are no clear protocols for soil sampling.
- Passive samplers are increasingly being used to extract agrochemicals from soil and water, although their use at this stage is limited to extraction of metals from soil or water, or of polar compounds from water. The residues collected in passive samplers are analysed using conventional, costly techniques.
- Analytical methods preferred in standard protocols are laboratory based and expensive.
- Cheap and simple-to-use tools such as the ELISA kits and the photometer are available and come with assurance of a high degree of accuracy. They seem an attractive alternative to conventional analytical methods, but their suitability and accuracy for measuring agrochemicals in soil and water from vineyards must be tested before they should be used or recommended as an industry option.

7 Assessing biological impacts of agrochemical use

7.1 Toxicity testing as part of risk assessment

7.1.1 Standard measures of biological impact

The traditional way of describing the potential biological impact of a compound has been to explore its toxicity to one or a series of test species. The standard measures are LC_{50} (concentration of toxicant, in air or water, lethal to 50% of test population when exposed) or LD_{50} (dose (mg toxicant/kg body weight) lethal to 50% of test population when ingested), lowest observed effect concentration (LOEC) and no observed effect concentration (NOEC). More recently, and more relevantly, sub lethal endpoints are being described. These include the EC_{50}, EC_{10}, EC_5, concentrations at which 'an effect' is observed in 50, 10 or 5 percent of the test population, respectively.

Van Strallen and van Rijn (1998), using published data on pesticide toxicities to soil fauna to test a risk assessment model, found that EC_{10} and EC_5 were only reported in the literature by proportionally few authors. Sub lethal endpoints are probably more important than LC_{50}, but the studies that describe sub lethal endpoints are not easily compared - for example studies describing effects on reproduction cannot be compared with studies describing effects on feeding behaviour or growth.

Some examples of sublethal tests include numbers of microorganisms per g soil, nitrification of ammonium from soil, and oxygen consumption (Tu 1991). Samu and Vollrath (1992) used web building behaviour of spiders (web size, building accuracy) to compare the side effects of a range of fungicides and insecticides, including triadimenol.

7.1.2 Standard test conditions

The standard tests for assessing toxicity involve exposing test species to toxicants under controlled conditions in a laboratory. The impact of a given concentration of pesticide or metal to a particular species is influenced by the age of the population, presence of other species, pH of water or soil, dissolved organic matter, cations and anions in water, light regimes and temperature. To overcome these influences most testing follows standard laboratory controlled methods, under conditions outlined in various protocols (summaries are provided by Landis and Yu 1999). Protocols prescribe light intensity, photoperiod, pH, temperatures, the size of test chambers, humidity, exposure frequencies and duration. Standard tests have advantages and disadvantages. By standardising conditions and methods, the data sets from different tests are comparable and tests can be repeated. Results can be assessed against standard criteria, and can be compiled into larger data sets (Landis and Yu 1999). The limitations of standard tests must be recognised when interpreting data. For example although toxicity is only assessed in a narrow range of soil types in standard tests, the tolerances of algae to copper levels vary between soils collected from different sites in Australia (Mallavarapu et al. - abstract in Warne and Hibbert, 2002).

7.1.3 Test species

Toxicity testing typically includes a narrow range of test species. These are intended to represent the range of trophic levels that would be exposed to the chemical, and represent the behaviours of the species in each trophic level. Most toxicity data submitted to Australian regulatory authorities relates to test species that do not occur in Australia. Australian and New Zealand data are being accumulated in a database with other available toxicity data (Michael Warne, pers. comm.), available as a CD-ROM with the ANZECC and ARMCANZ Water Quality Guidelines (ANZECC and ARMCANZ 2000b). As the toxicity database is expanded it will become an increasingly important resource for providing context to environmental concentrations of agrochemicals from viticulture.

7.1.4 Microcosm and mesocosm tests

Standard toxicity tests are usually developed to answer specific questions, and are not suited to asking broader questions about impacts, or understanding interactions. Increasingly researchers are using multispecies tests to account for the changes to feeding and other behaviours of species when more than one species is present in a system, and the effect that this has on toxicity. Results of multispecies tests are sometimes not repeatable and, depending on the analyses used, the tests may not be comparable, but they provide useful information about the impact of agrochemicals on the interactions between species. Multispecies tests, using fungi, bacteria, algae and small invertebrates, can be conducted in the laboratory in artificial media, in dishes or glass flasks (microcosms), or on a larger scale in the field under less controlled but more natural conditions (mesocosms), which seeks to simulate a natural setting. For example, a stream may be simulated by diverting a local watercourse, with its inherent pH, organic matter, temperatures, cation/anion content, through tanks to simulate streams or ponds. Mesocosm experiments can take a long time to establish, are expensive to run, difficult to analyse and interpret, and the results may not be consistent with results of other similar experiments because the conditions are not easily controlled or manipulated and because of the interactions that occur.

Landis and Yu (1999), in a review of typical toxicity tests, provide the caution that standard tests are often extrapolated to situations or to ask questions that the toxicity test was not designed to answer.

7.1.5 Interactions between agrochemicals can alter their toxicity

The impact of co-contaminants is not considered in standard toxicity testing, yet the combined toxicity of pollutants can vary from the toxicity of each single pollutant. For example a reduction in the diversity of algae species in the presence of copper was further reduced when copper was present in combination with atrazine (Mallavarapu et al. - abstract in Warne and Hibbert, 2002). Synergistic effects of co-contamination, for example between organic pesticides and metals (eg a triazine herbicide and copper or cadmium, Kookana pers. comm.) may be due to the metal being toxic to organisms that break down organic pesticides, so that the persistence of the organic pesticide increases.

Changes in the persistence and therefore toxicity of co-contaminants may also be due to altered chemistry. For example the enhanced persistence of glyphosate in soil in the presence of copper is probably due to complexing of the glyphosate with copper, increasing its ability to be adsorbed onto soil (Morilla et al. 2000).

Woods, Kumar and Correll (2001) assessed changes in toxicity of three insecticides, chlorpyrifos, endosulfan and profenfos when used in two-way and three-way mixtures. They found that mixtures of chlorpyrifos plus profenfos were more acutely and chronically toxic to their test species (the water flea *Ceriodaphnia dubia)* than the sum of the toxicity of the individual compounds. There was a similarly synergistic effect, of profenfos plus endosulfan, and the three-way mixture. However, the mixture of chlorpyrifos plus endosulfan was antagonistic (less toxic than either of the two individual compounds). They also compared the toxicities of the three insecticides individually and in combinations against a frog species (*Xenopus laevis*) (Woods and Kumar 2001) finding that the different combinations led variously to synergistic, additive or antagonistic effects.

7.2 Monitoring environmental health

7.2.1 Water monitoring guidelines

The Australian Guidelines for Water Quality Monitoring and Reporting (ANZECC and ARMCANZ 2000a) describe various approaches to assessing the health of aquatic systems. These include:

- Descriptive studies of undisturbed ecosystems, ie baseline studies.

- Studies that measure change include BACI (before-after, control-impact) designs and those that infer impact from evidence of changes over time or space. These studies would evaluate the effects of particular input or disturbance.
- Studies that lead to a greater understanding of the processes within ecosystems, and to show causes and effects.

The Guidelines are quite prescriptive in recommending sampling design, site selection and analysis.

AUSRIVAS (see 5.4) is a rapid method for assessing the ecological health of freshwater by biological monitoring and habitat assessment. 6000 sites will be sampled across Australia over three years (ANZECC and ARMCANZ 2000a). More than 1500 minimally disturbed sites have been sampled across Australia to establish the reference data. Methods for sampling water, sediment and aquatic organisms are clearly outlined in the Guidelines (ANZECC and ARMCANZ 2000a).

7.3 Key issues

- The standard tests for assessing toxicity involve exposing a narrow range of test species to toxicants under controlled conditions. The traditional way of describing the potential biological impact of a compound is LC_{50} or LD_{50}, LOEC and NOEC.
- Most toxicity data submitted to Australian regulatory authorities relates to test species that do not occur in Australia.
- Australian and New Zealand data are being accumulated in a database with other available toxicity data and the database is available for the use of this project.
- The limitations of standard tests must be recognised when interpreting data.
- Interactions between agrochemicals can alter their toxicity.
- The Australian Guidelines for Water Quality Monitoring and Reporting describe various approaches to assessing the health of aquatic systems. The Guidelines are quite prescriptive in recommending sampling water, sediment and aquatic organisms, site selection and analysis.

8 Current Australian research investigating the movement or impacts of agrochemicals relevant to viticulture

Various state agencies and research organisations have implemented programs to monitor agrochemicals in water. Some examples are provided here:

The Central and North West Regions Water Quality (CNWRWQ) Program was developed to address concerns about impacts of irrigated agriculture on ecosystem health in NSW rivers and streams (Poletika, Muschal and Hughes 2001). As part of this program, Dow AgroSciences together with NSW Department of Land and Water Conservation took weekly samples from streams exposed to cotton pesticides during the 2001 summer.

The Australian Cotton Industry has invested heavily in identifying and manages risks associated with agrochemical use in cotton. They were involved in the CNWRWQ program, funded development of the PIRI risk index (see 4.2.8) and funded research on vegetative buffers to reduce the movement of spray drift and on spray application (Nick Woods, pers comm).

As an adjunct to the CNWRWQ program NSW Department of Land and Water Conservation and the Ecotoxicology Section of the NSW EPA assessed the hazard and risk posed by agrochemicals to riverine organisms in NSW, using the risk quotient method (see 4.2.4). Chlorpyrifos, diuron and two others (non-viticultural) posed an unacceptable hazard to the environment (Muschal and Warne, 2001).

NSW EPA requires that irrigation drainage water entering waterways from the Wentworth/Coomealla irrigation area is sampled for agrochemicals and other contaminants (Anthony Couroupis pers. comm.). The monitoring has highlighted that paraquat, copper, zinc and other contaminants have been detected entering the Murray River in irrigation drainage outfalls.

The Department of Water Resources (DWR), SA screened drainage water from Cobdogla and Berri district for agrochemicals in 2000 (Tony Herbert, Tiffany Ingliss pers. comm). None of the pesticides included in the screen were detected in the initial water samples (Tony Herbert pers. comm.). In 2001 CSIRO Land and Water ran a risk analysis using PIRI (see 4.2.8) that highlighted priority pesticides for the DWR sampling program (bromacil, chlorpyrifos, copper sulphate, copper oxychloride, diuron, metalaxyl and sulphur) and in the 2001/2002 season DWR tested drainage water for these pesticides. Running water from drainage outfalls and standing water from the drainage basin were sampled once per month. Sampling was not timed to coincide with applications, so while at any one time there was likely to have been a recent application, soluble pesticide from any one property on a sampling day may have been massively diluted.

CSIRO Land and Water and the EPA in SA are conducting a case study to assess sediment quality in a catchment in the Adelaide Hills (Kumar et al 2002 - abstract in Warne and Hibbert, 2002). The same CSIRO team is also working on a case study with Yalumba Wine company to assess leachates from a vineyard in the Coonawarra.

As part of the AUSRIVAS stream health monitoring program (see 5.4), macroinvertebrate sampling is being conducted in Central Queensland (Leo Duivoordenen, Central Queensland University) and North-East Victoria (Golam Kibria, Goulburn Murray Water).

The Centre for Environmental Stress and Adaptation Research (CESAR) at LaTrobe University is investigating impacts of management practices on biodiversity in vineyards and development of invertebrate bioindicators of vineyard sustainability (Ary Hoffmann and Linda Thomas). CESAR are also using mesocosms to assess water quality for other industries.

Table 8-1 summarises some of the recent findings of current Australian research on environmental impacts of agrochemicals that are also used in viticulture.

8.1 Key issues

- Monitoring of waterways for agrochemicals has revealed presence of herbicides, fungicides and insecticides and sometimes at levels that exceed trigger values of environmental concern.
- Various programs are currently underway across Australia to monitor environmental impacts of agrochemicals. Of these, the leaching trials at Yalumba vineyards in the Coonawarra and the sediment quality study by SA EPA/CSIRO in the Adelaide Hills are very relevant and have the potential to provide very good, site specific data about agrochemicals in water moving off vineyards.
- In general, the concentrations of agrochemicals in water that have been measured in existing monitoring programs cannot be related to the agrochemical inputs at the farm level. They cannot be identified as coming from single, inappropriate uses (point sources) or seasonal use across a region by growers who are complying with label recommendations and using standard practices (diffuse sources).
- Generic data about environmental risk of 'average' practices does not relate to the risk associated with an individual grower' s local situation or practices because the concentrations of agrochemical entering and persisting in the environment vary according to conditions and usage at the individual vineyard. Adoption and refinement of Best Practices will be greater if growers can monitor agrochemicals in and near their own vineyards.
- The wine industry needs to understand environmental concentrations of agrochemicals, and equate these to toxic concentrations, in order to substantiate that Best Practice recommendations do lead to reductions in environmental impacts.

Table 8-1: Summary of relevant Australian studies reported in 15 minute contributed oral abstacts at Interact 2002 conference, Sydney July 2002 (Warne and Hibbert 2002). Authors cited in this table are not listed in the reference section as the proceedings of the conference only include brief abstracts and some detail in the table exceeds the content of the abstract. The descriptions of each study reflect the title of the abstract in the proceedings (see Warne and Hibbert 2002 for the full citation).

Study	Observations	Group	Authors
Effect of pH on the toxicity and accumulation of Cu and Zn in freshwater algae	Toxicity may decrease with decreasing pH.	Environment Division, Australian Nuclear Science and Technology Organisation	Wilde et al. (2002)
Effects of temperature on acute toxicity of chlorpyrifos to fish	Observed that the toxicity of chlorpyrifos increased at increasing temperatures	Ecotoxicology Section, NSW EPA, UTS Sydney UTS/EPA Centre for Ecotoxicology CSIRO Div Land and Water, Qld.	Patra et al. (2002)
Developing a model to predict the kinetics of pesticide uptake and release from passive samplers in flowing water.	Uptake by passive samplers of pesticides with K_{ow} >3.5 is linear and independent of pesticide concentration in water. Pesticides with K_{ow} <3.5 have lower uptake rates.	Ecotoxicology Section, NSW EPA UTS Sydney UTS/EPA Centre for Ecotoxicology	Hyne et al. (2002)
Influence of black carbon content of soils on the sorption and bioavailability of carbaryl.	Sorption affinity of carbaryl to soil was affected by the type of carbon in the soil	CSIRO Land and Water	Kookana et al. (2002)
Environmental effects of pesticide use in Australia.	Organochlorine pesticides have been measured in fish, sediments and birds. Chlorpyrifos has been measured in oysters, diuron measured in sea grass, and so on.	NSW EPA on behalf of the Academy of Science Technologies and Engineering.	Chapman and Osborne (2002)
Impacts of co-contaminants on soil biota	The toxicity of combined toxicants can exceed the toxicities of the individual compounds. Soil algae were good indicators of bioavailable copper, and more algal species were sensitive to 50 ppm copper when it was present with atrazine. Copper increased the persistence of atrazine, perhaps because the metal was toxic to bacteria that normally degrade the herbicide.	CSIRO Land and Water.	Mallavarapu et al. - abstract in Warne and Hibbert, 2002
Interactive effects of pesticide mixtures to freshwater shrimp	Toxicity of pesticide combinations is frequently additive, particularly if they have similar modes of action. Some interactions are synergistic, although the degree of the interactive effect can be time, species, chemical and concentration dependent.	School of Environmental Engineering, Griffith University.	Chapman (2002)
Total versus bioavailable copper	Metal speciation affects the availability of metals in sediment and water. Total metal concentrations are a cost-effective way to conduct initial screening, this must be considered in context of bioavailability.	URS Australia Pty Ltd	Howell (2002)

Table 8-1 continued.

Study	Observations	Group	Authors
Assessment of metal availability in contaminated soils using passive samplers.	Regulations indicating permitted levels of metals are based on total concentrations, not bioavailable concentrations. The DGT passive sampler method and metal uptake by wheat seedlings are being assessed and compared as ways of measuring bioavailable metal ions.	CSIRO Land and Water Lancaster University, UK	Nolan et al. (2002)
Determining copper toxicity in aquatic systems	Copper toxicity in aquatic systems was monitoring using sensitivity tests, biological monitoring and chemical speciation techniques. Copper measured by chemical speciation was usually a good predictor of toxicity.	Centre for Advanced Analytical Chemistry, CSIRO Energy Technology Catholic University Chile	Stauber et al. (2002)
Comparison of speciation methods for estimating copper toxicity in water	Copper levels measured using DGT passive samplers, Chelex columns or anodic stripping were compared with copper toxicity to bacteria. The chelex column was the easiest method for assessing copper toxicity.	Centre for Advanced Analytical Chemistry, CSIRO Energy Technology	Bowles et al. (2002)
Effects of tebufenozide (Mimic™) on macroinvertebrates in artificial stream mesocosms.	Tebufenozide was detected 330 days after treating an artificial stream, due to being slowly released from sediments. It affects moulting of Lepidotera but also affects the fecundity of insects, flatworms, pond snails. Recovery of the populations in the mesocosms was complete after 65 days. Effects on invertebrates occurred at concentrations that would exceed any likely environmental concentrations.	UTS Sydney Ecotoxicological Section, NSW EPA UTS/EPA Centre for Ecotoxicology	Colville et al. (2002)
Sediment quality assessments: A South Australian catchment as a case study	Sediment cores taken from streams were classified according to their exposure to run-off from viticulture, vegetables, orchards, urban or reference areas. Samples variously contained heavy metals, organochlorines and organosphates, in some cases exceeding water quality guideline levels. Based on biological assessments using caged yabbies, pollution from horticulture > viticulture > urban development > reference areas.	CSIRO Land and Water EPA SA School of Pharmaceutical, Molecular and Biomedical Sciences, Univ SA.	Kumar et al. (2002)
Estrogenic compounds in soil-water systems: occurrences and implications – A review.	Until recently estrogenic compounds were assumed to be present at concentrations too low to have ecological impact, but now with increasing observations of endocrine disruption, eg the feminisation of male fish, US Govt are now very focussed on monitoring and understanding endocrine disruptors.	Landcare Research, NZ.	Sarmah (2002)

Table 8-1 continued

Combining direct toxicity tests macroinvertebrate sampling and passive samplers in the field in ecological risk assessment.	Recent research funded by DPI, MDBC, LWRRDC and others have identified unacceptable levels of pesticides in rivers downstream of cotton irrigation areas. Passive samplers are now being used to monitor pesticides in streams, and residues related to health of caged shrimps. macroinvertebrates are being sampled according to the AUSRIVAS program.		Duivenvoorden et al. (2002)
Ratios of copper to zinc in gills of rainbow trout as a predictor of copper exposure	Plasma and Na in fish gills may be a good biomarker for assessing Cu exposure. In presence of elevated Cu and Zn, the Cu in gills increased relative to Zn levels.	School of Aquaculture, Univ. Tasmania	Daglish et al. (2002)
In-situ sediment toxicity testing using a benthic microalga	Toxicity of metals in sediments can be tested using microalga placed in situ to avoid problems associated with disturbing sediments in transport and storage.	Centre for Advanced Analytical Chemistry, CSIRO Energy Technology	Adams et al. (2002)
Role of piperonyl butoxide in the toxicity of chlorpyrifos to *Daphnia* and a frog species	Chlorpyrifos (highly toxic to *Daphnia*, LD_{50} 0.05 μg/L) was much less toxic to *Daphnia* when in combination with piperonyl butoxide.	School of Pharmaceutical, Molecular and Biomedical Sciences, University of SA.	El-Merhibi et al. (2002)
Algal bioassays with time varying contaminant concentrations	Standard algal bioassay procedures typically result in 10-40% loss in metal (eg Cu) and up to 100% loss in other agrochemicals which leads to an underestimation of EC_{50} and no observed effect concentrations (NOEC).	Centre for Advanced Analytical Chemistry, CSIRO Energy Technology. Chalmers Univ, Sweden CSIRO Land and Water, WA.	Simpson et al. (2002)

9 Linkages with other organisations and people aiming to reduce environmental impacts of agrochemicals

Project development, research methodology, technical information, sampling infrastructure, grower participation, and site selection have been discussed with the research, policy or industry groups in Table 9-1.

Table 9-1: Research, policy or industry groups working on relevant aspects of the off-target movement and impacts of agrochemicals.

Organisation/Group	Contact	Role	Topic on which the organisation has been consulted as part of this review
Alterra Green World Research, Netherlands	Paul van den Brink	Modelling	Access to the PERPEST model for estimating ecological risk
ANZECC and ARMCANZ	Michael Warne and John Chapman (NSW EPA/UTS)	Research, policy, guidelines	Guidelines on water quality and toxicity database
Aristotle University of Thessaloniki, Greece	Zisis Vryzas	Research	Sampling of soil-water using ceramic cups
Australia New Zealand Food Authority	Steve Crossley	Regulation	Pesticides monitoring and evaluation
Australian Cotton Industry	Various	Extension, implementation	Biological Impact of Cotton Pesticides
BAA, Germany	Heinz Ganzelmeier	Research, Policy	Modelling drift from vineyards, use of buffers and sampling and assessment techniques
Central Qld University	Leo Duivoordenen	Research, monitoring	National program for macroinvertebrate monitoring in aquatic systems. Passive samplers for monitoring pesticides in water, relating levels to macroinvertebrate populations
CESAR, LaTrobe University	Ary Hoffmann	Research	Research methodology
Cornell University	Lois Levitan	Policy and Pesticide Risk Indicators	Risk assessment
CPAS, University of Queensland, Gatton	Nick Woods, Jamie Nichols, Bill Gordon, Gary Dorr	Research	Spray plume definition, Spray drift modelling, field trials
Cranfield University UK Silsoe campus	Sabine Beulke, Fabrice Renaud, Richard Godwin and Colin Watt	Ecochemistry, modelling and Engineering	Chemical fate and exposure modelling, lysimeter, field trials
CRC for Freshwater Ecology Lower Basin Laboratory	Ben Gawne	Aquatic Research	Assessment of ecological impacts of drainage and ground water on aquatic species, in the Murray River and wetlands
CRC Fresh Water Ecology, University of Canberra		Modelling	*No direct contact yet*
CSIRO energy and technology	Graeme Battely, Cathy King, Jenny Stauber	Research	*No direct contact yet*

Table 9-1 continued

Organisation/Group	Contact	Role	Topic on which the organisation has been consulted as part of this review
CSIRO Land and Water	Rai Kookana, Ray Correll	Research, Consultancy	Using PIRI to index risks of agrochemicals contaminating surface and soil water. Impacts of agrochemical inputs into waterways. Methods for measuring pesticides.
CSIRO Land and Water	Mike McLaughlin	Research	Metals, measurement methods, bioavailability
CSIRO Land and Water	Anu Kumar	Research	Toxic effects on species using the concept of mesocosms
Department of Land and Water, SA.	Tony Herbert, Tiffany Ingliss	Research and extension	Monitoring pesticides in drainage water from Cobdogla and Berri district
DuPont	Harry Strek	Crop protection	Method for determination of the soil sorption of pesticides
Environment Australia	Darryl Murphy, Greg Rippon (ex EA), Gary Fan	Policy and Guidelines	Assessment of environmental risk and predicting drift of agrochemicals from vineyards using AgDrift models and Ganzelmeier charts.
Flinders University	John Hutson	Modelling	LEACHM model for predicting movement of agrochemicals though soil profiles.
Goulburn Murray Water	Golam Kibria	Monitoring	Similarities between objectives of our project and proposed sampling in Goulburn Murray area.
Hawkes Bay Regional Council, NZ	Dan Bloomer	Policy, water quality monitoring	Recommending pesticide choices for vineyard areas with different susceptibilities to ground water contamination
Horticulture Research International, Wellesbourne, Warwick, CV35 9EF, UK	Jerry Cross, Oliver Price	Research (spray drift)	Drift assessment and spatial variation in pesticide degradation rate in field soils.
HortResearch, Palmerston North NZ	Brent Clothier, Steve Green, Tessa Mills	Modelling and research re leaching of pesticides in soils.	Lysimeters. Incorporation of Australian soil and weather data sets into the PestRisk model, to predict leaching of agrochemicals through Australian soil profiles. Further development of the Soil Plant Atmosphere System Model (SPASMO) and relevance to Australia.
HortResearch, Hawkes Bay	Sarah Gurnsey and David Manktelow	Research	Defining sustainable use patterns of copper, sulphur and phosphorus acid in vineyard, vegetable and orchard systems in NZ
	David Jordan	Consultant	Integrated Wine Production program
NZ Wine Growers	Philip Manson	Policy and extension	Integrated Wine Production program
Crawthron Institute, Nelson, NZ	Pat Holland	Research	Established a recipe for stream health, including reference to pesticides.

Table 9-1 continued

Organisation/Group	Contact	Role	Topic on which the organisation has been consulted as part of this review
Institut Fresnius Ag, Germany	Tina Butzbach	Research	Design and procedure for a hydrological monitoring study on a fine textured soil in vineyard.
Lincoln Ventures	Jean Paul Praat, John Maber	Modelling	New drift model (SprayCan) and spray drift research.
Lower Murray Darling Catchment Management Board	Bill Tatnell, John McLaughlin, Lesley Palmer	Policy making and monitoring	Current activity within the NSW catchment areas to sample water for agrochemicals.
Mallee Catchment Management Authority	Damien Wells, Trent Wallis, Ian Ballantyne	Policy making and monitoring	Use of CMA water auto-sampler, groundwater bores, test-wells, drainage, current drainage water sampling program.
NRA	Various	Policy	*No direct contact yet*
NRE Catchment and Agriculture Services	Ben Keir, Maxine Schache	Research	Instrumentation, data samplers, data available from different projects on Mallee Catchment 8.
NRE Chemical Standards Branch	Alan Roberts	Chemical standards	Monitoring for compliance with Victorian legislation regarding agrochemical use.
NRE Knoxfield	David Riches	Research (development of ELISA rapid test kits)	Sample analysis using conventional and ELISA analysis of soil and water samples.
NRE Stats Info	Mark Taylor and Caren Omachen	Statistics	Statistical information on irrigated horticulture in Mallee and North-West of Victoria
NRE, Ellinbank	David Nash	Research	Agrochemical sampling in surface and soil-water.
NSW DLW	Anthony Couroupis	Policy and monitoring	Routine monitoring of irrigation drainage to meet NSW EPA requirements
NSW EPA/UTS Centre for Ecotoxicology	Ross Hyne	Ecotoxicology research	Water quality monitoring using passive samplers and suitability for compounds with low polarity
RCC, Switzerland	Manfred Mirbach, Alexander Krainz, Wolfgang Volkel, Ulrich Memmert	Contract research	Environmental chemistry and ecotoxicology
Red Cliffs Catchment 8	Growers	Grape growing	Project aims and proposed activities and to develop their interest in participating in monitoring of irrigation drainage water.
RMIT	Dayanthi Nugegoda	Ecotoxicology research	Potential relevance of projects by RMIT to the wine industry
SA EPA	Katherine Serneckis	Water quality monitoring	*No direct contact yet*
Silsoe Research Institute	Paul Miller	Research and policy	LERAP and other solutions to minimise spray drift

Table 9-1 continued

Organisation/Group	Contact	Role	Topic on which the organisation has been consulted as part of this review
Sinclair Knight and Mertz	Kylie Braszell, Kym Boyle	Water quality monitoring	Maps of Catchment 8 drainage bores
State Chemistry Laboratory	Fawzia Tawfik	Sample analysis (GLC, HPLC)	State Chemistry Laboratory (Fawzia Tawfik) regarding sample analysis using conventional and ELISA analysis of soil and water samples.
SunRise 21	Sue Argus	Ortho-photo mapping Sunraysia horticultural properties	Property and land use maps for Catchment 8 and other regions.
Syngenta	Various	Crop protection	Biological research, lysimeter, pond studies (mesocosms)
Technical Committee of the Vineyard Association of Tasmania	Richard Richardson	Grower	Interest among Tasmanian growers in the project.
University of Queensland	Heather Chapman	Ecotoxicological research	*No direct contact yet*
University of Reading	Miles Marshall	Research	Pesticide leaching
University of Technology, Sydney, Centre for Ecotoxicology.	John Chapman	Research	Pesticide monitoring and assessing biological impacts
Victorian EPA	Alex Leonard	Monitoring	Use of passive samplers for water quality monitoring in Gippsland Lakes
	Leon Metzeling	AUSRIVAS program	Modelling using AUSRIVAS and availability of reference data for environmental health assessments.
Yalumba Wine Company	Cecil Camilleri and Ashley Ratcliff	Technical managers	Program to reduce environmental impacts of viticulture.

10 Recommendations for research

10.1 Aims

1) To provide scientific and user-friendly information to Australian grape growers regarding vineyard chemical use and their potential impacts on the environment.
2) Provide a mass balance (or accounting) of the proportions of agrochemicals persisting in the vineyard soil, captured by the vine canopy, or leaving the vineyard as spray drift, in irrigation drainage water or in surface run-off.
3) Test the suitability of a range of sampling and residue or drift monitoring equipment to enable industry to adopt some protocols for sampling as part of compliance with Best Practice recommendations.

10.2 Experiment 1 – Mass balance of the agrochemical applied to a vineyard

10.2.1 Hypothesis

Of the total spray volume applied to a vineyard, the proportions leaving the vineyard as spray drift or dripping from the canopy onto the ground can be biologically significant (published information), and can be reduced by careful spray delivery (nozzles, pressure, airspeed of machine).

10.2.2 Materials and methods

Drift sampling protocols have been provided by the Centre for Pesticide Application and Safety (CPAS), University of Queensland, complying with international standards for drift trials. Drift data will be extrapolated to a range of chemicals of similar particle size to the tracers used in the experiments. Following the CPAS protocols will ensure that data from drift trials will be suitable for incorporating into current drift models.

Treatments for spray drift monitoring will be applied as controlled trials, using both hydraulic nozzle (coarse atomisation) and air shear (fine atomisation) spray equipment. Drift trials will be conducted using tracers rather than agrochemical.

The design recommended by CPAS for drift experiments follows.

10.2.2.1 Description of the spray plumes from typical nozzles used in axial fan and air shear sprayers

To interpret drift readings it is necessary to understand the droplet spectrum produced by the nozzle in question. A Malvern 2600 (laser defraction reader) in the wind tunnel at CPAS will be used to measure the droplet spectrums for a range of hydraulic and air shear nozzles used on vineyard sprayers.

The Gaussian diffusion model (Craig et al. 2001) will be used to predict the behaviours of the droplet spectrum profile released by each tested nozzle, under a range of temperatures and wind speeds, so we can assess and rank the likelihood of drift from each nozzle. In a vineyard, entrainment of spray plume by the sprayer and around the vines inevitably interferes with the pattern of spray movement, and Gaussian diffusion will not predict the actual fate of the spray plume. The profiles do however assist in predicting a mass balance for the total spray volume from each nozzle: the proportions likely to end up on the ground as run off, the proportions likely to be retained by canopy, and the proportions likely to drift.

Experimental factors:

Several different hydraulic nozzles, and one air shear nozzle, will be run at various pressures and air speeds in the wind tunnel at Gatton. The level of replication will reflect that typically used for nozzle experiments in the wind tunnel.

Data analysis:

Droplet data will be analysed using Gaussian diffusion model, by Gary Dorr of CPAS. Various wind speeds and ambient temperatures will be used in the model to reflect the range of conditions under which growers' spray.

10.2.2.2 Mass balance field trials to measure the proportions of drift and run-off from a range of typical sprayers in vineyards

The mass balance field trial is an accounting exercise, to compare the relative proportions of drift, run-off (dripping) due to overspray, and retained spray when commercial spray equipment is used under typical conditions (wind speeds, temperature and humidity) in a vineyard. In this pilot drift study we will select four types of spray equipment set up according to the manufacturers' specifications. The nozzle choices and pressures will reflect the extremes of drift potential predicted from the wind tunnel work at CPAS.

Experimental factors

Each treatment includes one sprayer operated at one setting (nozzle type and pressure). There will be four sprayers and each will run at two settings, providing eight treatments.

- Axial fan airblast sprayer (no ducts)
- Axial fan with ducts
- Airshear sprayer (eg Silvan Turbomiser)
- Multi headed sprayer (eg Quantum Mist, Greentech or SARDI fan)

Each treatment will include three passes across the plots to override the extreme effects of very localised changes to wind speeds and directions. Dividing the total measured deposits by three will provide an average deposit for a single application of agrochemical.

Each treatment will be replicated four times over four consecutive days.

Tracer dye:

Sprayer tanks will contain fluorescein sodium and Agral.

Collectors:

The drift and run-off will be measured using tracers (eg fluorescein sodium and wetter). Run-off will be collected on papers (Richardson, Walklate and Baker 2002) and bridal veil (Craig et al. 2000) and drift will be collected on strings (Nicholas Woods, pers. comm.).

Four towers (each 20 m tall) with collectors will be placed at 6 metres out from the last sprayed row. Each tower will be 30 metres apart down the row. Each tower will have two (sub samples) vertical strings for drift collection. Each string will be sectioned into 50 cm heights across the entire 20 m of string length.

Collectors would also be placed on the ground at 2-5 m intervals across 20 m (10 m on each side of the vine row sprayed) to collect drift that falls out under gravity.

Quantifying the drift collected on samplers

Fluorescein tracer will be rinsed off collectors and the concentration of tracer in rinsate measured in a filter fluorometer on loan from CPAS, Gatton.

Extra data recording

We will record meteorological conditions during spray drift trials - wind speed, temperature and humidity at the vineyard edge and up to 5 m above the ground, using an anemometer and temperature and humidity probes mounted on a weather station (as per Richardson, Walklate and Baker 2002)

We will also record those parameters necessary to allow our monitoring data to be compared against the various drift and leaching models (eg bulk density, porosity, organic fraction, %clay, temperature, pH, irrigation volumes).

10.2.3 Deliverables

- Definition of the droplet spectrums produced by a range of nozzles reflecting those used commonly in the Australian wine industry, required to interpret drift readings from subsequent field trials.
- Predictions of the relative drift potential for each treatment.
- A mass balance of spray deposits in the air, landing on the ground, within the vineyard and landing in canopy, from the range of nozzles included in the wind tunnel experiments. These experiments will show the relative proportions of, and therefore relative risk associated with, run-off and drift.
- Evidence related to the extent of drift from the range of vineyard sprayers representing good and bad practice.
- Demonstrate ways that growers can assess the drift and run-off from their own spraying.
- The concentrations and associated hazards of various agrochemicals will then be extrapolated from the measured drift of tracers.

10.3 Experiment 2 – Contamination of soil-water

10.3.1 Hypothesis

Leaching of agrochemical is greatest in sandy loam vineyards and least in clay loam vineyards, and the quantity of leachate can be reduced by selecting alternative chemical (if possible) and modifying irrigation scheduling or irrigation type.

10.3.2 Materials and methods

10.3.2.1 Core experimental site for leaching experiments– Red Cliffs, Victoria

In the Lower Murray area, 77,740 hectares of irrigated horticulture (Statistical Information Services 2002) are estimated to receive 2.2 million litres (before dilution) of agrochemical per year. Irrigation drains in the Lower Murray area carry pollutants including agrochemicals from perched water tables to the river and disposal basins. A proportion of irrigation water with pollutants also permeates into ground water. In the Sunraysia district this proportion is estimated to be as high as 40% (Mallee CMA pers. Comm.).

Red Cliffs Catchment 8 within the Sunraysia Irrigation District has been selected as the core experimental site for monitoring agrochemicals in soil, drainage water and ground water. As Red Cliffs Catchment 8 is a small, contained catchment (129 hectares, mostly vineyards) the agrochemical/nutrient/water inputs to the vineyards can be matched with measured outflows from drains. Detailed ortho-photo images and soil survey maps of the properties are available. Movement of

water, salt and nutrients within and from the catchment has been studied in two previous projects. Monitoring began in 1993 as part of a Murray Darling Basin Commission funded project "*Integrated Policy Mapping for Sustainable Irrigation and Management*" and continued until 1998/99 under the Soil Water and Nutrient (SWAN) project. A data logger, an auto-sampler, property drain access, test wells, tensiometers, a small weir through which total drainage from the catchment passes, and ground water bores are all already installed throughout the Catchment 8 area. Growers in the area are also interested in participating in the trials. The catchment is less than 15 km from the Sunraysia Horticultural Centre, which will allow researchers to collect comprehensive data cost-effectively, and visit the site frequently and, as necessary, out of normal working hours.

10.3.2.2 Experimental plot:

Each experimental plot will be made up of an area of vines under common management, on a particular soil type, with drainage collecting into one sampling point. The size of the plot and vine varieties within the plot may be irrelevant providing that the whole area is sprayed and irrigated as one unit, because only the concentration of the chemical will be measured in water sample not the total quantity.

Control plots will be the same plots as those sprayed with agrochemical but the soil-water will be collected during the irrigation that is scheduled prior to the spray treatment. This is likely to be a fortnight earlier than the collection of irrigation drainage water associated with the irrigation following the spraying treatment.

10.3.2.3 Experimental factors

- Two chemicals (metalaxyl and simazine) will be used in the first year. If no metalaxyl or simazine are detected we will monitor for chlorpyrifos and paraquat as these can be analysed cheaply using ELISA kits. Others such as captan and carbaryl may be measured in subsequent seasons.
- Two soil types (sandy loam and clay loam with high organic matter).
- Two irrigation volumes (overhead sprinkler irrigation and drip irrigation)
- Two soil depths within the root zone, for suction cup sampling - (about 50 cm and at the bottom of the root zone or near the drain depth)
- Three replications each treatment (no replication for control).

Each plot will be sprayed with the chemical and irrigation applied after three hours of spraying. This is to simulate the worst case scenario, ie the event of a rainfall after spraying.

10.3.2.4 Sampling

After spraying and prior to irrigation, a composite sample of surface soil (20 cm) from the sprayed part of each vineyard will be collected to determine the background level of agrochemical present.

The soil-water samples will be collected from each plot at 50 cm depth and depth of the drain using ceramic or teflon cups. At each sampling point in each plot samples will be sucked from the cups at 12 minutes (10 minutes suction and 2 minutes change over) intervals and transferred into vials. All samples will be kept at about 4°C in ice and in dark before analysing them to prevent the breakdown of chemical.

Sampling from control blocks will be the same as for experimental blocks. This is to determine the level of agrochemical existing in the soil prior to the treatments.

10.3.2.5 Residue analysis in water samples

Total copper in water samples will be measured at SHC using a C 200 Series Multiparameter Photometer (Hanna Instruments 2002). The photometer can detect copper at concentrations less than

0.25 ppm. Bioavailable copper will be analysed at CSIRO Land and Water in Adelaide under the guidance of, and using techniques developed by, Mike McLaughlin.

Metalaxyl, simazine, chlorpyrifos and paraquat in water can be measured at SHC using enzyme-linked immuno-sorbent assay (ELISA) kits from EnviroLogix, USA.

Some duplicate samples will also be sent to the State Chemistry Laboratory, Victoria, to confirm the accuracy or develop calibration graph for photometer and the ELISA kits.

10.3.3 Deliverables

- Evidence that the high leaching potential of a chemical can translate to measurable quantities of chemical in soil-water.
- A method that can be used in further research to measure concentrations of other pesticides in soil-water.

10.4 Experiment 2.1 - Contamination of ground water

10.4.1 Hypothesis

The concentration of agrochemical in ground water will be below the limit of detection, and the ones detected will represent only a narrow group of compounds compared to residues in water from irrigation drains.

10.4.2 Method

Two ground water bores are positioned at the edges of Catchment 8 in Red Cliffs and are maintained and monitored for salt by Sinclair Knight Mertz under contract to NRE. We will collect water samples from these bores monthly during the growing season and analyse the water samples for those agrochemicals predicted by PestRisk or LEACHM to leach through the alkaline Blanchetown Clay and into the Parilla Sand.

Residues in water samples will be analysed as per previous section.

10.4.3 Deliverables

- Evidence that the high leaching potential of a chemical can translate to measurable quantities of chemical in ground-water.

10.5 Experiment 3 - Accumulation of copper in vineyard soils

Agrochemicals containing copper are used frequently in vineyards. Copper has low leaching potential and high toxicity to invertebrates and microorganisms.

Levels of copper will be measured in vineyard soils with 1-2 years of copper use up to 60 years of copper use. This will test for a relationship between history of copper usage and the levels of copper in the soil. This relationship will be used to determine when, if ever, copper approaches levels that are considered toxic to earthworms or phytotoxic.

10.5.1 Hypothesis

Levels of copper in vineyard soils are correlated positively with the duration of use of copper-containing agrochemicals and approach biologically significant levels after 10 years.

10.5.2 Method

10.5.2.1 Development of soil sampling technique

- Sampling techniques will be tested on three sites. The sites will be a) approximately 5 year old vines planted on virgin soil, b) vines recently replanted (eg new variety) on 30 year old vineyards and c) vineyards with 60 year old original vines will be chosen for trial sites.
- Samples will be taken randomly recording the soil type and the position (undervine, inter row, under drip line etc) in the vineyard. Vertical soil cores will be bored to 40 cm with sub samples taken at 0-10 cm, 10-20 cm, 20-30 cm and 30–40 cm following methods described for sampling agrochemical residues in vineyards soils by Frank et al. (1976). This will help us to determine the importance of position and depth (surface soil or at a depth where inter rows are ploughed and vineyard has been redeveloped) of sampling.
- From each of the samples (ie 50 per vineyard) of soil, a pair sample will be placed into a composite sample bucket. This is to ensure that composite sampling from vineyards does not distort the results compared to the averaging of the 50 individual samples.

10.5.2.2 Soil sampling from vineyards in different regions

After establishing the sampling protocol, soil samples from a number of vineyards (approx. 100) of all ages from different grape growing regions will be collected for analysis.

Storage, transport and preparation of the soil samples will be in accordance with the NRE protocol for contaminated soils residue testing (Fawzia Tawfik, SCL, pers. comm., Alan Roberts, pers. comm.).

10.5.2.3 Copper analysis in soil samples

Copper in water samples can be measured at SHC using a C 200 Series Multiparameter Photometer (Hanna Instruments 2002). The photometer detects copper at concentrations less than 0.25 ppm. Extraction of copper from soils into solution, so that it can be measured with the photometer, provides a measure of total soil copper. A number of soil samples will be analysed at the State Chemistry Laboratory, Victoria.

Bioavailable copper will also be assessed, in Adelaide using a technique developed by Mike McLaughlin at CSIRO Land and Water (Mike McLaughlin pers. comm.). In exchange for assistance with measuring bioavailable copper, CSIRO Land and Water are interested in having access to the data from this vineyard copper survey.

10.5.3 Deliverables

- Data on copper levels in Australian vineyard soils.
- Relationship between copper in soils and the period of time that land has been a vineyard.
- Comparison of bioavailable copper with levels known to affect soil microorganisms and invertebrates present in the top 40 cm of vineyard soils.

10.6 Sites across a range of grape growing regions

In the 2004/05 seasons, methods tested at the Red Cliffs Catchment 8 site and other sites in Sunraysia will have been refined and adapted ready for implementation in other regions.

The intended regions are:

- Coonawarra
- McLaren Vale
- Hunter Valley

- Yarra Valley

These sites will be used to further ground-truth the various models that predict agrochemical behaviour and fate.

10.7 Statistical analysis of data and interpretation of results

Data will be analysed using Genstat 4 Release 3, statistical software package. NRE's chief biometrician, Dr John Reynolds will help with trial design, data analysis and interpretation of results.

Sampling results will be discussed in the context of a) concentrations known to affect species representing various trophic levels, b) the Australian Drinking Water Guidelines (NHMRC, 1996), c) influence of management practices on the measured levels, and d) implications for Best Practice recommendations.

10.8 Reporting

We will provide an interpretation of the biological relevance of our sampling results, based on the availability of existing biological data.

The overall aim of this project is to assist the industry to ensure that off-target effects of agrochemical use are minimised. Therefore if the results of monitoring show a potential risk of off-target impacts, those results plus resolution of the issues will be discussed immediately within the steering committee and the outcomes communicated to the CRCV.

The progress of the project will be reported twice a year through progress reports required by CRCV. Key outcomes (good news stories, solutions) will be presented to the industry through industry journals, seminars, conference and field days.

A final report will be prepared at the completion of the project and submitted to NRE, GWRDC and CRCV.

11 Proposed project outputs

11.1 Review report and industry workshop

This review report presents the findings of the first year review of published literature, concurrent research, various models and agrochemical risk rankings. This document was presented to an industry workshop on 27 August 2002. The recommended research approach to achieve the objectives of the project was also presented to the workshop. The implications and benefits of the project were also discussed amongst the stakeholders through facilitated discussion. Minutes from the review workshop are presented in Appendix B.

11.2 Recommendation of models suited to predicting drift or leaching in viticulture

This review report has described the merits or relevance of several models that predict leaching or drift of agrochemicals from vineyards, in particular the data requirements for each, the sophistication of the modelling and the extent to which each have been validated in Australian or irrigated soils.

At the end of the project we will recommend to industry those models that are suited to predicting drift or leaching across the viticultural regions of Australia.

11.3 Checklist of potential environmental impacts of common viticultural chemicals across different grape growing regions, and protocols for On-Farm Trials

Levels of off target chemical predicted or measured in each region will be interpreted in terms of their biological relevance, and the interpretation provided to the industry with a simple checklist for growers to self-audit their potential environmental impacts.

The checklist will help growers to measure and compare practices.

11.4 Modifications to best management practices for chemical use, based on research data, and recommendations for mitigating environmental impacts

Research trial results will provide a sound basis for Best Management Practice recommendations for chemical use, for example we will provide information on which growers can base their chemical choice:

- In districts with high erosion potential, where growers may need to avoid the chemicals that have high persistence, high sorption coefficients and high aquatic toxicity. Conversely there may be no evidence of movement of these pesticides with erosion.
- In vineyards with drains that flow during irrigations, growers may need to minimise the risk of agrochemicals that are highly mobile in soil and may enter waterways.

Research results and models should enable us to recommend the priorities that growers in different regions should place on striving for particular outcomes, eg reducing droplet size from sprayers to reduce soil contamination, or to increasing droplet size to reduce drift.

Biological data from the literature will also help us to propose chemical choice to minimise impacts on soil organisms and soil management to enhance degradation of pesticide.

We hope to find that a majority of practices pose little environmental risk, and will be able to endorse those practices.

As a component of the Best Practices we will recommend techniques growers can use to mitigate potential environmental impacts.

11.5 Grower friendly kit for monitoring drift and soil-water contamination

In the original proposal we suggested that simple kits for sampling, analysing and interpreting spray drift and water samples could be prepared and made available to growers and consultants. As a consequence of discussions with the industry reference group in August 2002 (see Appendix B), this is no longer proposed as a project deliverable.

11.6 Training of extension personnel

In the original proposal we suggested that we would provide at least one training session in each state for departmental extension staff by June 2005. A training 'roadshow' to explain the project findings to extension staff in EMS, OFT and BMP projects would be completed by June 2005. As a consequence of discussions with the industry reference group in August 2002 (see Appendix B), this is no longer proposed as a project deliverable.

11.7 Policy recommendations

The array of products being used by growers in the next decade will change as new chemicals are introduced into the wine industry and old chemicals undergo retesting by the NRA. Growers will need to know the potential risks associated with each new product. The steering committee and industry reference group may consider it appropriate to summarise some examples of trial data for the National Registration Authority (NRA) and Environment Australia together with recommendations about the environmental data that should be required of chemical companies submitting new agrochemicals for registration in viticulture. The NRA's readiness to incorporate wine industry issues into the registration process was evident when results from pesticide residue trials in GWRDC project DAV92/94 (MacGregor et al. 1995, MacGregor 1998) catalysed the NRA to include specific grape data protocols in chemical registration submissions (NRA 1997).

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Appendix A. Details of the properties and potential hazards of 24 agrochemicals used in Australian viticulture

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1. Active constituent: **azoxystrobin** (controls powdery mildew, downy mildew and botrytis bunch rot)

Some registered products: Amistar WG

Mode of Metabolism: Photolysis (photodegradation) and microbial processes (Pilling, Earl and Joseph 1996)

Common metabolites: R230310, R234886, R401553 and R402173 (U.S. EPA 1997a).

Time taken for half of the initial amount of a pesticide to break down (half-life): 1 to 4 weeks in the field (Pilling, Earl and Joseph 1996).

Water solubility: Low. Water solubility of azoxystrobin is 6.0 mg/L (U.S. EPA 1997a).

Soil adsorption/mobility: Moderate / Low. Azoxystrobin and its metabolites demonstrate low mobility in soil (Pilling, Earl and Joseph 1996). Field and laboratory studies showed that azoxystrobin is moderately mobile and relatively non-persistent in soils (U.S. EPA 1997a).

Volatility: Very low. The vapour pressure of azoxystrobin is very low, 1.1×10^{-13} kPa @ 25°C (U.S. EPA 1997 a) indicating that the volatility of azoxystrobin is very low.

Influence of environmental factors on degradation rates:

Water	None. Azoxystrobin is stable in aquatic environments (U.S. EPA 1997a).
Vegetation	Low. Foliar uptake of azoxystrobin is low with no accumulation recorded at leaf tips or margins of leaves (Pilling, Earl and Joseph 1996).
Increasing Soil pH	No specific information available.
Soil microorganisms	Medium. After photodegradation the dissipation of azoxystrobin depends on microbial metabolism (U.S. EPA 1997a).
Concentration of active constituent	Low. Concentration may not influence the breakdown. After fermentation, azoxystrobin was present in wine at the same concentration as on the grapes (Cabras and Angioni 2000).
Sunlight	High. The dissipation of azoxystrobin is predominantly dependent on photodegradation (U.S. EPA 1997a).
Temperature	No specific information available. Schirra et al. (2002) treated grapefruit with different concentrations of azoxystrobin at different temperatures to control storage decay. Storage of treated grapefruits at 8°C for three weeks and another two weeks at 20°C did not affect the amount of azoxystrobin residues in the fruit. This may indicate that temperature (at least up to 20°C) has no influence on degradation of azoxystrobin.

General Information:

Azoxystrobin is the first of a new class of pesticidal compounds called β-methoxyacrylates, which are derived from the naturally occurring strobilurins. Their biochemical mode of action is inhibition of electron transport.

Toxicity to humans:

Azoxystrobin is of low acute and chronic toxicity to humans (U.S. EPA 1997a, Cornell University 2001a).

Toxicity to other mammals:

Azoxystrobin is of low acute and chronic toxicity to mammals (U.S. EPA 1997a, Cornell University 2001a). The acute oral toxicity study in rats of technical azoxystrobin resulted in a LD_{50} of 5,000 mg/kg for both male and female rats (Cornell University 2001a). In a two-year feeding study of rats fed diets containing 0, 60, 300, and 750/1,500 ppm (males/females), the systemic toxicity "no observed adverse effect level" was 18.2 mg/kg/day for males and 22.3 mg/kg/day for females. The acute inhalation of azoxystrobin by rats resulted in a LC_{50} of > 4.67 mg/L for both males and females (U.S. EPA 1997a).

Toxicity to non-mammalian species:

Aquatic organisms: High. Azoxystrobin is highly toxic to freshwater fish, freshwater invertebrates, and estuarine/marine fish, and extremely toxic to estuarine/marine invertebrates (U.S. EPA 1997a). The azoxystrobin metabolite R234886 is practically nontoxic to rainbow trout and daphnids, while metabolites R402173 and R401553 may be slightly toxic to daphnids. Azoxystrobin is not a carcinogen.

Birds: Low. Azoxystrobin is of low acute and chronic toxicity to birds (U.S. EPA 1997a).

Other species: Azoxystrobin is of low acute and chronic toxicity to bees (U.S. EPA 1997a).

2.	**Active constituent:**	**benomyl** (controls botrytis bunch rot)
	Some registered products:	Benlate WP
	Mode of Metabolism:	Acid-catalysed hydrolysis (WHO 1994). Benomyl in soil is easily hydrolysed to methylbenzimidazole-2-ylcarbamate (carbendazim; MBC) (Howard 1991).
	Common metabolites:	Carbendazim; MBC and 2-aminobenzimidazole (2-AB) (Howard 1991; Liu and Hsiang 1994; WHO 1994). Benomyl is metabolised to various compounds including ring-opening products of the benzimidazole ring to produce ortho-phenylenediamine, ortho-aminobenzonitrile, methoxycarbonylguanidine, and methoxycarbonylurea. In mammals, metabolites include hydroxylated products at the 4, 5 and 6 positions of the phenyl ring of benzimidazole (U.S. National Library of Medicine 2002a).
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		When applied to turf, it has a half-life of 3 to 6 months and, when applied to bare soil the half-life is 6 to 12 months (U.S.D.A. 1984, Howard 1991, U.S. National Library of Medicine 2002a).
	Water solubility:	Very low. 3.8 mg/L (Howard 1991; U.S. National Library of Medicine 2002a).

Soil adsorption/mobility:	Very high / Low. Benomyl is strongly bound to soil (Howard 1991; Wauchope et al. 1992; U.S. National Library of Medicine 2002a). An estimated soil adsorption coefficient (Koc), using a water solubility of 3.8 ppm, is 2100 (Howard 1991; U.S. National Library of Medicine 2002a). In a field study on the fate of benomyl applied to bare soil and to turf, benomyl and its degradation products showed little or no downward movement through the soil (Howard 1991; U.S. National Library of Medicine 2002a).
Volatility:	Low. One study estimated that in excess of 3.5 to 6.5 kg benomyl/ha/year would vaporise from a loam soil at 25°C under annual rainfall of 150 cm (Howard, 1991; U.S. National Library of Medicine 2002a).

Influence of environmental factors on degradation rates:

Water	High. Benomyl completely degrades to carbendazim within several hours in acidic or neutral water. The half-life of carbendazim is 2 months (Kidd and James 1991).
Vegetation	Low. Because benomyl is a systemic fungicide, it is absorbed by plants, where it accumulates in veins and at the leaf margins (U.S.D.A. 1984). The metabolite carbendazim seems to be the fungicidally active agent. Benomyl residues are quite stable in vegetation, with 48 to 97% remaining as the parent compound 21 to 23 days after application (U.S.D.A. 1984).
Increasing Soil pH	Low. Benomyl persisted longer in alkaline soils than in acid soils (Gupta and Bhattacharjee 1987).
Soil microorganisms	Medium. Soil microorganisms enhance biodegradation of benomyl (Gupta and Chatrath 1979; Howard 1991; Aharonson and Katan 1993; Odeyemi, Salami and Ugoji 1998; Boyle 1995).
Concentration of active constituent	Medium. The degraded compound, methyl-2-benzimidazole carbamate, of benomyl adsorbed by soil varied, depending on fungicide concentration and soil type (Liu and Hsiang 1994).
Sunlight	None. Stable to light (WHO 1994). It may photodegrade in water. Mixed cultures from water were able to use benomyl as a sole carbon source but the degradation rate was slow (Howard 1991).
Temperature	Positive relationship. Benomyl degraded more rapidly at higher temperature (20 and 25°C) and persisted longer at lower temperature (5, 10 and 15°C) (Gupta 1988).

General Information:

Benomyl is a systemic, broad spectrum benzimidazole carbamate fungicide (WHO 1994; Oregon State University 1996a).

Toxicity to humans:

For humans, Acute toxicity is low, and there is no evidence of accumulation. It is only mildly irritant to skin and eyes, but sensitises skin (WHO 1994). Skin irritation may occur for workers exposed to benomyl.

Toxicity to other mammals:

Benomyl is of such a low acute toxicity to mammals that it has been impossible or impractical to administer doses large enough to firmly establish an LD_{50}. Thus the LD_{50} is greater than 10,000 mg/kg in rats and greater than 3400 mg/kg in rabbits (using a 50% wettable powder formulation). Because of its high LD_{50} there is a low risk for acute poisoning from this compound (Kidd and James 1991). Skin

reactions have been seen in rats and guinea pigs, and sensitisation can occur. Benomyl is readily absorbed into the body by inhaling the dust, but there are no reports of toxic effects to humans by this route of exposure. The inhalation LC_{50} in rats is greater than 4 mg/L (WHO 1994).

Inhalation and oral exposure reduced spermatogenic activity in laboratory animals (WHO 1994).

Toxicity to non-mammalian species:

Aquatic organisms: Very high. Benomyl is highly to very highly toxic to fish. Increasing in susceptibility to benomyl are catfish, bluegill, rainbow trout, and goldfish. The LC_{50} values for the compound in fish are 0.05 mg/L to 14 mg/L in adults, and 0.006 mg/L in catfish fry (U.S. National Library of Medicine 1995). The main breakdown product, carbendazim, had the same order of toxicity as benomyl. Crayfish have an LC_{50} greater than 100 mg/L. The estimated bioconcentration factor ranges from 159 in rainbow trout up to 460 in bluegill sunfish, indicating that benomyl does not tend to concentrate significantly in living tissue (Howard 1991; U.S. National Library of Medicine 1995; U.S. National Library of Medicine 2002a).

Birds: Low. In bobwhite quail and mallard ducks, the 5-day dietary LC_{50} for benomyl is greater than 10,000 ppm. In redwing blackbirds, the LD_{50} value is 100 mg/kg, which indicates that benomyl is moderately toxic to this species (Cummings et al. 1992).

Other species: A single application of benomyl to turf grass can substantially reduce some soil dwelling organisms. The compound is very lethal to earthworms at low concentrations over a long time period. The 7-day LC_{50} in earthworms is 1.7 mg/L and the 14-day LC_{50} is 0.4 mg/L (U.S.D.A. 1984). Benomyl is not toxic to bees (WHO 1994).

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3. Active constituent: **captan** (controls black spot, downy mildew and botrytis bunch rot)

Some registered products: Crop Care Captan WG

Mode of Metabolism: Captan readily hydrolyses in water, it will probably also hydrolyse in soil depending upon the pH (Howard 1991; U.S. National Library of Medicine 2002b).

Common metabolites: Mainly tetrahydrophthalimide -96.5%(Alary et al. 1995).

Time taken for half of the initial amount of a pesticide to break down (half-life):

Captan has a half-life of 1 to 10 days in most soil environments (Oregon State University 1996b). Depending on soil pH, type and moisture content, the half-life of captan in different soils ranged from 3 to 56 days (Howard 1991; U.S. National Library of Medicine 2002b). These studies indicate that captan will not be persistent in soil under most conditions.

Water solubility: Very low. 0.5 mg/L at 20°C (Howard 1991). Practically insoluble in water (U.S. EPA 1988a).

Soil adsorption/mobility: Medium /Medium. The Koc values for captan estimated in different studies ranged from 20 to 196 indicating that captan will be moderately mobile in soil (Howard 1991; U.S. National Library of Medicine 2002b).

Volatility: Low. Estimated Henry's Law constant for captan is 5.9×10^{-6} atm-m^3 /mole, indicating that the volatilisation of captan may be low. Volatilisation will be unimportant under most conditions both in soil and water compared to other abiotic

processes (Howard 1991; U.S. National Library of Medicine 2002b).

Influence of environmental factors on degradation rates:

Water	Very high. Captan is rapidly degraded in near neutral water. Half-lives of 23 to 54 hours and 1 to 7 hours have been reported at various acidities and temperatures (USDA 1984). The effective residual life in water is 2 weeks (Chemical Information Systems Inc. 1988).
Vegetation	High. Captan is taken up through leaves and roots and translocated throughout the plant. Residual fungitoxicity remains for 23 days after application on potato leaves, but residues were below the detection limit within 40 days after application (USDA 1984).
Increasing Soil pH	High. Captan persisted longer in acid than in alkaline soils (Gupta and Bhattacharjee 1987; U.S. EPA 1988a).
Soil microorganisms	Low. In captan-treated (1000 ppm) soils, total count of fungi, bacteria and actinomycetes decreased significantly (Banerjee and Banerjee 1987). This implies that degradation of captan by soil microorganisms is low. Abiotic degradation rather than microbial metabolism is assumed (Schoen and Winterlin 1985).
Concentration of active constituent	Low. Degradation of captan was much lower at the 1000 ppm than at 100 ppm level of fortification (Schoen and Winterlin 1985).
Sunlight	Low. Direct photolysis of captan is unimportant compared to hydrolysis. However, substances in water that sensitise oxygen formation, such as methylene blue and chlorophyll may accelerate photolysis (Howard 1991; U.S. National Library of Medicine 2002b).
Temperature	Positive relationship. Captan degraded more rapidly at higher temperature (20 and 25ºC) and persisted longer at lower temperature (5, 10 and 15ºC) (Gupta 1988).

General Information:

Captan is a non-systemic phthalimide fungicide used to control diseases of many fruit, ornamental, and vegetable crops (Oregon State University 1996b).

Toxicity to humans:

Swallowing can result in nausea and diarrhoea (Crop Care Australia Pty Ltd 1995a). Contact with skin will result in severe irritation. Corrosive to eyes; contact can cause corneal burns. Contamination of the eyes can result in permanent injury.

Repeated or prolonged skin contact may lead to allergic contact dermatitis. Not generally expected to be a skin irritant. Can cause sensitisation. Inhalation of dust or spray mist will result in respiratory irritation.

Toxicity to other mammals:

The rat oral LD_{50} for captan ranges from 8400 to 15,000 mg/kg, indicating very low acute toxicity (Chemical Information Systems Inc. 1988). The mouse LD_{50} is 7000 mg/kg. Sheep showed no effect at doses of 200 mg/kg, but deaths occurred at 250 mg/kg. The acute inhalation LC_{50} in rat is 5.8 mg/L (males) and 8.9 mg/L (females) (U.S. EPA 1988a). The inhalation LC_{50} (2-hour) in mice is 5.0 mg/L (US National Library of Medicine 1995). Rabbits showed little or no skin sensitisation to captan, while guinea pigs were moderately sensitive (USDA 1984).

No deaths occurred in pigs given as much as 420 to 4000 mg/kg/day in the diet for 12 to 25 weeks, however, cattle given six doses of 250 mg/kg experienced varied toxic effects, including death (USDA 1984).

Toxicity to non-mammalian species:

Aquatic organisms: Very high. Captan is highly toxic to fish. The LC_{50} (96-hour) for technical captan ranges from 0.056 mg/L in cutthroat trout and chinook salmon to 0.072 mg/L in bluegill (Kidd and James 1991). The LC_{50} for captan in the aquatic invertebrate *Daphnia magna* is 7 to 10 mg/L, indicating that the compound is moderately toxic to this and other aquatic invertebrates (US National Library of Medicine 1995). Captan has a low to moderate tendency to accumulate in living tissue.

Birds: Low. Captan is practically nontoxic to birds. The LD_{50} is greater than 5000 mg/kg in mallard ducks and pheasants. The LD_{50} is 2000 to 4000 mg/kg in bobwhite quail (Kidd and James 1991). High doses administered for 90 days to chickens caused an 80% reduction in the number of eggs produced, but had no effect on the fertility or hatchability of the eggs produced (USDA 1984).

Other species: Captan is not toxic to bees when used as directed (Kidd and James 1991).

4.	**Active constituent:**	**carbaryl** (controls lightbrown apple moth and grapevine moth, and grape leaf blister mite)
	Some registered products:	Bugmaster Flowable, Carbaryl 500, Carbaryl 800 WP, Flowable Carbaryl 500
	Mode of Metabolism:	Release to soil will result in photolysis at the soil surface at a rate dependent upon soil water content. Hydrolysis is expected to be rapid in neutral and basic soil but fairly slow in acidic soil. Biodegradation in soil has been shown to be significant (Howard 1991; U.S. National Library of Medicine 2002c).
	Common metabolites:	Methylocarbaryl (major), 4-hydroxy-1-naphthyl methylcarbamate, 5-hydroxy-1-naphthyl methylcarbamate, and 1-naphthyl methylcarbamate (Zhong et al. 1995)
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		Carbaryl has a half-life of 7 to 14 days in sandy loam soil and 14 to 28 days in clay loam soil (Oregon State University 1996c).
	Water solubility:	Medium. 32 mg/L at 20°C (Howard 1991) to 120mg/L (U.S. National Library of Medicine 2002c).
	Soil adsorption/mobility:	Medium / Medium. Carbaryl has a low persistence in soil. It is bound by organic matter and can be transported in soil run-off. Soil sorption coefficient (Koc) values ranging from 104 to 390 were determined from a variety of techniques (Howard 1991; U.S. National Library of Medicine 2002c). These Koc values indicate that carbaryl is expected to be moderately mobile in soil and may leach to ground water.
	Volatility:	Low. Considerable differences exist in the reported vapour pressure and water solubility and consequently the Henry's Law constant for carbaryl. The volatilisation half-life from a water body was estimated over 3000 days (Howard 1991). Therefore, volatilisation may not be an important factor.

Influence of environmental factors on degradation rates:

Water	High. In surface water, carbaryl is broken down by bacteria and through hydrolysis. Evaporation is very slow. Carbaryl has a half-life of about 10 days in water of neutral pH. The half-life varies greatly with water acidity (Howard 1991).
Vegetation	High. Degradation of carbaryl in crops occurs by hydrolysis inside the plants. It has a short residual life of less than 2 weeks (Oregon State University 1996c).
Increasing Soil pH	High. In neutral and alkaline soils carbaryl is expected to hydrolyse rapidly (Howard 1991). Increases in soil pH increased soil bound residues of carbaryl (Murrthy and Raghu 1991).
Soil microorganisms	High. Soil microorganisms readily degrade carbaryl (Yang and See 1990; Howard 1991; Kuo and Regan 1992; Regan 1994)
Concentration of active constituent	High. Soils that had been treated with multiple applications of carbaryl degraded the compound more rapidly than those with single application (Rajagopal et al. 1983). This may imply that carbaryl with high concentration degrade more rapidly than carbaryl with low concentration.
Sunlight	High. Release to soil will result in photolysis at the soil surface at a rate dependent upon soil water content (Howard 1991).
Temperature	Positive relationship. The half-life of carbaryl is temperature dependant (Uyanik and Ozdemir 1999). The breakdown of carbaryl is strongly dependent on acidity and temperature (U.S. National Library of Medicine 1995).

General Information:

Carbaryl is a wide-spectrum carbamate insecticide that controls over 100 species of insects. Carbaryl works whether it is ingested into the stomach of the pest or absorbed through direct contact.

Toxicity to humans:

Most animals, including humans, readily break down carbaryl and rapidly excrete it in the urine and faeces. Workers inhaling carbaryl dust excreted 74% of the inhaled dose in the urine in the form of a breakdown product (U.S. EPA 1987b). The metabolism of up to 85% of carbaryl occurs within 24 hours after administration (U.S.EPA 1987b). The metabolites of carbaryl have lower toxicity to humans than carbaryl itself (U.S. National Library of Medicine 1995).

Toxicity to other mammals*:*

The acute oral LD_{50} for the rat is 850 mg/Kg, and the acute dermal LD_{50} is 4,000 mg/Kg. Acute inhalation LC_{50} (rat, 4hr): 2.5 mg/L. In 2 years of feeding trials, rats receiving a diet containing 200 mg/Kg suffered no ill effects (Chemspray Pty Limited 1996).

Toxicity to non-mammalian species:

Aquatic organisms: Medium. Carbaryl is moderately toxic to aquatic organisms, such as rainbow trout (LC_{50} of 1.3 mg/L), and bluegill (LC_{50} of 10 mg/L) (Kidd and James 1991). Some accumulation of carbaryl can occur in catfish, crawfish, and snails, as well as in algae and duckweed. Residue levels in fish were 140-fold greater than the concentration of carbaryl in water. In general, due to its rapid metabolism and rapid degradation, carbaryl should not pose a significant bioaccumulation risk in alkaline waters. However, under conditions below neutrality, it may be significant (Kidd and James 1991).

Birds: Low. Carbaryl is practically nontoxic to wild bird species. The LD_{50} values are greater than 2000 mg/kg in mallards and pheasants, 2230 mg/kg in quail, and 1000 to 3000 mg/kg in pigeons (Kidd and James 1991).

Other species: Carbaryl is lethal to many non-target insects, including bees and beneficial insects (Kidd and James 1991).

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5. Active constituent: **chlorothalonil** (controls botrytis bunch rot)

Some registered products: Barrak 720, Bravo 720, Check-Out 500 SC, Check-Out 720, Chlorothalonil 500 SC, Crotp 720, Echo 500 SC, Echo 720, Elect 500, Elect 720, Elect 750, Fung-O-Nil, Whack

Mode of Metabolism: In moist alkaline soils, hydrolysis probably takes place in conjunction with biodegradation (U.S. National Library of Medicine 2002d). Other studies suggests that modes of metabolism are microbial and chemical (Sato and Tanaka 1987; Takagi and Wada 1990; Katayama, Isemura and Kuwatsuka 1991; Mori et al. 1996; Motonaga, Takagi and Matumoto 1996; Katayama, Mori and Kuwatsuka 1995)

Common metabolites: One grab sample test indicates rapid biodegradation of chlorothalonil in soil to: isophthalonitrile, mono-, di- and tri-chlorinated isophthalonitriles, 2,5,6-trichloro-4-hydroxyisophthalonitrile and 2,5,6-trichloro-4-methoxyisophthalonitrile (U.S. National Library of Medicine 2002d). In moist alkaline soils, hydrolysis produced hydroxy-chlorothalonil and chloride anion (Pas et al. 1999; Motonaga, Takagi and Matumoto 1996)

Time taken for half of the initial amount of a pesticide to break down (half-life):

In aerobic soils, the half-life is from 1 to 3 months (Oregon State University 1996e). According to all available data in the U.S. Department of Agriculture's Pesticide Properties Database, a degradation half-life of 30 days was estimated for chlorothalonil in soil (U.S. National Library of Medicine 2002d).

Water solubility: Very low. 0.6 mg/L at 25°C (Oregon State University 1996e).

Soil adsorption/mobility: Medium / Low. Chlorothalonil is moderately persistent. Chlorothalonil has high binding and low mobility in silty loam and silty clay loam soils, and has low binding and moderate mobility in sand (U.S. EPA 1987a). Chlorothalonil was not found in any of 560 groundwater samples collected from 556 U.S. sites (U.S. EPA 1987a). The adsorption coefficient, Koc is about 1380 (Oregon State University 1996e). A Koc value of 1,800 has been experimentally determined based on adsorption isotherms of chlorothalonil on 3 black soils and 1 clay mineral, Na-bentonite soil (U.S. National Library of Medicine 2002d). According to a suggested classification scheme, this Koc value indicates that chlorothalonil will have low soil mobility.

Volatility: Very low. This vapour pressure value 1.3 mPa at 40°C (Oregon State University 1996e) suggests that chlorothalonil will exist in both the vapour- and the particulate-phases in the ambient atmosphere. Vapour-phase chlorothalonil is very slowly degraded in the ambient atmosphere by reaction with photochemically formed hydroxyl radicals; the half-life for this reaction in air can be estimated to be about 7 yrs.

According to a suggested classification scheme, the value of Henry's Law constant for chlorothalonil indicates that chlorothalonil will be essentially nonvolatile from water (U.S. National Library of Medicine 2002d).

Influence of environmental factors on degradation rates:

Water	Medium. In very basic water (pH 9.0), about 65% of the chlorothalonil was degraded into two major metabolites after 10 weeks. Chlorothalonil was found in one surface water location in Michigan at 6.5 mg/L (U.S. EPA 1987a).
Vegetation	Low. Residues of chlorothalonil may remain on aboveground crops at harvest, but will dissipate over time. Chlorothalonil is a fairly persistent fungicide on plants, depending on the rate of application. Small amounts of one metabolite may be found in harvested crops (Vettorazzi, 1979).
Increasing Soil pH	Medium. No aqueous hydrolysis of chlorothalonil occurred at pH 7 or lower; however, at pH 9 (temperature was not reported), chlorothalonil hydrolysed to 4-hydroxy-2,5,6-trichloroisophthalo-nitrile and 3-cyano-2,4,5,6-tetrachlorobenzamide (U.S. National Library of Medicine 2002d).
Soil microorganisms	High. A number of studies suggest microbial degradation of chlorothalonil in soils (Sato and Tanaka 1987; Takagi and Wada 1990; Katayama, Isemura and Kuwatsuka 1991; Mori et al. 1996; Motonaga, Takagi and Matumoto 1996). However, a later study has claimed chlorothalonil is toxic to beneficial microorganisms and earthworms (Cox 1997).
Concentration of active constituent	Low. Chlorothalonil degraded faster in soils treated with 1 µg/g chlorothalonil compared with soils treated with 10 µg/g chlorothalonil (Balasubramanian and Mathan 1996). It implies that rate of chlorothalonil degradation depends on its concentration.
Sunlight	None. Chlorothalonil is not degraded by sunlight on the soil surface (U.S. National Library of Medicine 1995).
Temperature	Positive relationship. Increased temperature increases chlorothalonil degradation (Oregon State University 1996e).

General Information:

Chlorothalonil is an aromatic halogen compound, a member of the chloronitrile chemical family. It is a greyish to colourless crystalline solid that is odourless to slightly pungent (U.S. National Library of Medicine 1995). It is a broad-spectrum organochlorine fungicide.

Toxicity to humans:

Chlorothalonil is rapidly excreted, primarily unchanged, from the body. It is not stored in animal tissues (Oregon State University 1996e). No adverse effects are expected, however large amounts may cause general depression, diarrhoea and irritation of the mouth, oesophagus and stomach (Crop Care Australia Pty Ltd 2000a). Chlorothalonil may be an eye irritant and may cause conjunctivitis and corneal opacity. Contact with the skin may result in irritation, and may cause skin sensitisation in sensitive individuals. Inhalation of mists or aerosols may produce respiratory irritation. Available evidence indicates that repeated or prolonged exposure to chlorothalonil may cause kidney disorders (Crop Care Australia Pty Ltd 2000a). Very high doses may cause a loss of muscle coordination, rapid breathing, nose bleeding, vomiting, hyperactivity, and death. Dermatitis, vaginal bleeding, bright yellow and/or bloody urine, and kidney tumours may also occur (U.S. National Library of Medicine 1995).

Toxicity to other mammals:

The oral LD_{50} is greater than 10,000 mg/kg in rats and 6000 mg/kg in mice (Kidd and James 1991; U.S. National Library of Medicine 1995). The acute dermal LD_{50} in both albino rabbits and albino rats is 10,000 mg/kg (Kidd and James 1991; U.S. National Library of Medicine 2002). In albino rabbits, 3 mg of chlorothalonil applied to the eyes caused mild irritation that subsided within 7 days of exposure (U.S. EPA 1987a).

Toxicity to non-mammalian species:

Aquatic organisms: Very high. Chlorothalonil and its metabolites are highly toxic to fish, aquatic invertebrates, and marine organisms. Fish, such as rainbow trout, bluegill, and channel catfish are noticeably affected even when chlorothalonil levels are low (less than 1 mg/L). The LC_{50} is 0.25 mg/L in rainbow trout, 0.3 mg/L in bluegills, and 0.43 mg/L in channel catfish (Kidd and James 1991). Chlorothalonil does not store in fatty tissues and is rapidly excreted from the body. Its bioaccumulation factor is quite low (U.S. National Library of Medicine 1995).

Birds: Low. Chlorothalonil is practically nontoxic to birds. The LD_{50} in mallard ducks is 5000 mg/kg (Kidd and James 1991). Most avian wildlife are not significantly affected by this compound (U.S. National Library of Medicine 1995).

Other species: The compound chlorothalonil is nontoxic to bees (Kidd and James 1991).

6.	**Active constituent:**	**chlorpyrifos** (controls lightbrown apple moth and grapevine moth)
	Some registered products:	Bar 500 EC, Chlorpyrifos, Chlorpyrifos 500, Chlorpyrifos 500 EC, Chlorpyrifos 500 LO, Chlorpyrimax 500, Lorsban 500 EC, Lorsban 750 WG, Pyrinex 500 WP, Strike-Out 500 EC, Voodoo 500
	Mode of Metabolism:	When released to soil, chlorpyrifos can degrade by a combination of chemical hydrolysis and microbial degradation (Howard 1991). Microbial degradation may be significant in various soils as indicated by significantly faster degradation rates in non-sterile versus sterile soil (Howard 1991). The main modes of metabolism are microbial and hydrolytic (Racke et al.. 1996).
	Common metabolites:	The principal degradation product 3,5,6-trichloro-2-pyridinol (TCP), occurs in both dry and moist soils (Howard 1991). TCP adsorbs weakly to soil particles and appears to be moderately mobile and persistent in soils (U.S. EPA 1989).
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		The half-life of chlorpyrifos in soil is usually between 60 and 120 days, but can range from 2 weeks to over 1 year, depending on the soil type, climate, and other conditions (Howard 1991;Wauchope et al.. 1992).
	Water solubility:	Low. 1.12 mg/L in water at 24°C (Howard 1991).
	Soil adsorption/mobility:	Very high / Very low. Koc values for chlorpyrifos range from 995 to 13,000 (Howard 1991). In laboratory studies using a sandy loam soil, chlorpyrifos was determined to be relatively immobile (Howard 1991; U.S. National Library of Medicine 2002e). Chlorpyrifos is moderately persistent in soils. Chlorpyrifos adsorbs strongly to soil particles and it is not readily soluble in water (Wauchope et al.. 1992 and U.S. EPA

1989). It is therefore immobile in soils and unlikely to leach or to contaminate groundwater (Racke 1992).

Volatility: Medium. Chlorpyrifos was found to be moderately volatile from moist mineral soil as determined by fumigant activity on insects. Volatilisation of chlorpyrifos from potted soil treated with 5 ppm of the compound was sufficient to kill 50% of houseflies contained near the soil over an 11-hour period (Howard 1991). The Henry's Law constant for chlorpyrifos is 2.9×10^{-6} atm-m^3/mole, indicating that chlorpyrifos is expected to volatilise from water and moist soil surfaces (U.S. National Library of Medicine 2002e).

Influence of environmental factors on degradation rates:

Water	High. If released to water, chlorpyrifos partitions significantly from water column to sediments. The measured hydrolysis half-life at 25°C is 35-78 days (Howard 1991; U.S. National Library of Medicine 2002e). The concentration and persistence of chlorpyrifos in water will vary depending on the type of formulation. For example, a large increase in chlorpyrifos concentrations occurs when emulsifiable concentrations and wettable powders are released into water. Because the pesticide adheres to sediments and suspended organic matter, concentrations decline rapidly. In water, the increase in the concentration of insecticide is not as rapid for granules and controlled release formulations, but the resulting concentration persists longer (U.S. EPA 1986a).
Vegetation	Low. Chlorpyrifos may be toxic to some plants, such as lettuce (McEwen and Stephenson 1979). Residues remain on plant surfaces for approximately 10 to 14 days. Data indicate that this insecticide and its soil metabolites can accumulate in certain crops (U.S. Public Health Service 1995).
Increasing Soil pH	High. The hydrolysis rate is relatively independent of pH from pH 1to pH 7, but increases significantly under alkaline conditions (Howard 1991). Chlorpyrifos hydrolysis was much slower in acidic soils (pH <= 7) compared with alkaline soils (Racke et al.. 1996).
Soil microorganisms	Very high. Adsorbed chlorpyrifos is subject to degradation by UV light, chemical hydrolysis and by soil microbes (Oregon State University 1996d not listed).
Concentration of active constituent	Low. Experiments in several soils that displayed rapid chlorpyrifos hydrolysis at 10 µg/g provided evidence that the hydrolytic reaction was inhibited at higher concentration, 1000 µg/g (Racke et al. 1996).
Sunlight	Low. Adsorbed chlorpyrifos is subject to degradation by UV light, chemical hydrolysis and by soil microbes (Oregon State University 1996d).
Temperature	Positive relationship. Research suggests that this insecticide is unstable in water, and the rate at which it is hydrolysed increases with temperature, decreasing by 2.5- to 3-fold with each 10°C drop in temperature (Howard 1991).

General Information:

Chlorpyrifos is a broad-spectrum organophosphate insecticide (Oregon State University 1996d).

Toxicity to humans:

Chlorpyrifos is moderately toxic to humans (U.S.EPA 1989). Chlorpyrifos is readily absorbed into the bloodstream through the gastrointestinal tract if it is ingested, through the lungs if it is inhaled, or through the skin if there is dermal exposure (U.S. Public Health Service 1995). In humans, chlorpyrifos and its principal metabolites are eliminated rapidly (Gallo and Lawryk 1991).

Chlorpyrifos is eliminated primarily through the kidneys (U.S. Public Health Service 1995). Poisoning from chlorpyrifos may affect the central nervous system, the cardiovascular system, and the respiratory system. It is also a skin and eye irritant (Gallo and Lawryk 1991; Nufarm Ltd 1996). Symptoms of acute exposure to organophosphate or cholinesterase-inhibiting compounds may include the following: numbness, tingling sensations, uncoordination, headache, dizziness, tremor, nausea, abdominal cramps, sweating, blurred vision, difficulty breathing or respiratory depression, and slow heartbeat (Gallo and Lawryk 1991; Nufarm Ltd 1996). These symptoms are typical of repeated or prolonged exposure to organophosphates (Nufarm Ltd 1996).

Toxicity to other mammals:

The oral LD_{50} for chlorpyrifos in rats is 95 to 270 mg/kg (Gallo and Lawryk 1991, Kidd and James 1991). The LD_{50} for chlorpyrifos is 60 mg/kg in mice, 1000 mg/kg in rabbits, 32 mg/kg in chickens, 500 to 504 mg/kg in guinea pigs, and 800 mg/kg in sheep (Gallo and Lawryk 1991; Kidd and James 1991; Gosselin, Smith and Hodge 1984). The dermal LD_{50} is greater than 2000 mg/kg in rats, and 1000 to 2000 mg/kg in rabbits (Gallo and Lawryk 1991; Kidd and James 1991).

Toxicity to non-mammalian species:

Aquatic organisms: Very high. Chlorpyrifos is extremely toxic to freshwater fish, aquatic invertebrates and estuarine and marine organisms (U.S. EPA 1989). Cholinesterase inhibition was observed in acute toxicity tests of fish exposed to very low concentrations of this insecticide. Concentrations as low as 11.2 g of active ingredient per hectare may cause fish and aquatic invertebrate deaths (U.S. EPA 1989). Chlorpyrifos toxicity to fish may be related to water temperature. The 96-hour LC_{50} for chlorpyrifos is 0.009 mg/L in mature rainbow trout, 0.098 mg/L in lake trout, 0.806 mg/L in goldfish, 0.01 mg/L in bluegill, and 0.331 mg/L in fathead minnow (U.S. EPA 1986a). Chlorpyrifos accumulates in the tissues of aquatic organisms. Studies involving continuous exposure of fish during the embryonic through fry stages have shown bioaccumulation values of 58 to 5100 (Racke 1992). Smaller organisms appear to be more sensitive than larger ones (U.S. EPA 1986a).

Birds: Chlorpyrifos is moderately to very highly toxic to birds (U.S. EPA 1989). Its oral LD_{50} is 8.41 mg/kg in pheasants, 112 mg/kg in mallard ducks, 21.0 mg/kg in house sparrows, and 32 mg/kg in chickens (U.S. Public Health Service 1995; Kidd and James 1991; U.S. EPA 1989). The LD_{50} for a granular product (15G) in bobwhite quail is 108 mg/kg (Kidd and James 1991; U.S. EPA 1989). At 125 ppm, mallards laid significantly fewer eggs (U.S. EPA 1989). There was no evidence of changes in weight gain, or in the number, weight, and quality of eggs produced by hens fed dietary levels of 50 ppm of chlorpyrifos (U.S. Public Health Service 1995).

Other species: Aquatic and general agricultural uses of chlorpyrifos pose a serious hazard to wildlife and honeybees (Kidd and James 1991; U.S. EPA 1984).

7.	**Active constituent:**	**copper hydroxide** (controls downy mildew)
	Some registered products:	Blue Shield DF, Coppit-OH, Coppit-OH DF, Country Copper Hydroxide 500 WP, Flo-Bordo, Kocide, Kocide Blue, Kocide Liquid Blue
	Mode of Metabolism:	Decomposition (Robert Bryce & Co Ltd 1997; U.S. National Library of Medicine 2002f).
	Common metabolites:	Copper oxide and water (Robert Bryce & Co Ltd 1997)
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		Total copper deposits decreased after application of copper hydroxide on orange and bean leaves with a half-life of 45 days for navel orange and 35 days for bean leaves (Menkissoglu and Lindow 1991).

Water solubility:	Very low. 2.9 mg/L at 25°C and pH 7 (U.S. National Library of Medicine 2002f). Disperses in water to form a suspension. Copper hydroxide is insoluble in cold water and decomposes in hot water (Griffin Corporation Australia 1998). Forms slurries in water (Robert Bryce & Co Ltd 1997).
Soil adsorption/mobility:	Very high / Low. Because copper is an element it will persist indefinitely. Copper is bound, or adsorbed, to organic materials, and to clay and mineral surfaces. The degree of adsorption to soils depends on the acidity or alkalinity of the soil (Oregon State University 1996f). Copper leaching from 2.3 litre containers was greater with the combination of applied solution of pH 6.5 and bark-sand-peat medium than with the combination of applied solution of pH 8.0 and bark-sand medium (Arnold et al.. 1997). This may indicate that copper is less bound in acidic soil. However, because of its binding capacity and insolubility in water, its leaching potential is low in all but sandy soils (U.S. National Library of Medicine 1995).
Volatility:	None. There is no volatile compound in copper hydroxide (Robert Bryce & Co Ltd 1997).

Influence of environmental factors on degradation rates:

Water	Medium. Disperses in water to form a suspension. Copper hydroxide is insoluble in cold water and decomposes in hot water (Griffin Corporation Australia 1998).
Vegetation	Low. One of the limiting factors in the use of copper compounds is their serious potential for phytotoxicity (U.S. EPA 1986b). Copper toxicity can kill plants by disrupting photosynthesis. This may indicate that degradation of copper compounds in plants is low.
Increasing Soil pH	Low. Copper leaching from 2.3 litres containers treated with copper hydroxide was greater with the combination of applied solution of pH 6.5 and bark-sand-peat medium than with the combination of applied solution of pH 8.0 and bark-sand medium (Arnold et al.. 1997). This may indicate that copper hydroxide decomposes faster in acidic soils than in alkaline soils.
Soil microorganisms	Very low. Most animal life in soil, including large earthworms, have been eliminated by the extensive use of copper containing fungicides in orchards (Pimentel 1971). This may imply that degradation of copper compound by soil microorganisms is very low.
Concentration of active constituent	Low. Copper is taken up by tomato plants from potting soils containing various levels of copper hydroxide (Rhoads, Olson and Manning 1989). The level of copper concentration in plant tissue depended on copper concentration in soil and soil pH.
Sunlight	Low. Copper hydroxide decomposes at above 60°C (Griffin Corporation Australia 1998). Therefore, in summer copper hydroxide may decompose under sunlight.
Temperature	Positive relationship. Copper hydroxide decomposes into copper oxide and water at above 60°C (Griffin Corporation Australia 1998).

General Information:

Copper hydroxide is light blue granule and is used as agricultural fungicide.

Toxicity to humans:

Copper hydroxide is harmful if swallowed (Griffin Corporation Australia 1998) and may be toxic if ingested in large quantities. Ingestion of large doses of copper salts may result progressively in irritation of the gastrointestinal tract, nausea, vomiting, salivation, gastric pain, haemorrhagic gastritis, diarrhoea, capillary damage, liver and kidney damage, and central nervous system stimulation followed by depression. Jaundice, pain in the liver, and haemolytic anaemia has been reported following acute human poisoning. Acute oral LD_{50} = 646 mg/kg.

Copper hydroxide is severely irritating to the eyes. Direct contact may cause destruction of eye tissue. May be corrosive to the eyes if not washed immediately.

Copper hydroxide is a slight skin irritant. Excessive exposure, especially if prolonged, may produce skin irritation. Repeated exposure may cause allergic contact dermatitis. Acute dermal LD_{50} = > 5000 mg/kg.

Copper hydroxide is harmful by inhalation. Irritating to the respiratory system. Excessive exposure may cause coughing, mucous production, shortness of breath, reflecting metal fume fever. Exposure to copper fumes may result in metallic taste, nausea, vomiting and metal fume fever with chills, fever, aching muscles, dry throat and headache. Excessive exposure to copper by inhalation may result in irritation of the upper respiratory tract which, if severe, may lead to perforation of the nasal septum after long periods of exposure.

Copper hydroxide has a low chronic toxicity unless excessive exposure is encountered.

Toxicity to other mammals:

Acute inhalation LC_{50} is 3.4 mg/L for rats over 4 hours. The oral LD_{50} for rats is 1000 mg/kg body weight.

The inhalation LC_{50} for rabbits is >1.303 mg /L (Griffin Corporation Australia 1998)

Toxicity to non-mammalian species:

Aquatic organisms: Very high. This product is very toxic to fish and aquatic organisms (Griffin Corporation Australia 1998).

Birds: Low. Copper sulphate may be of comparable toxicity to copper hydroxide. Copper sulphate is practically nontoxic to birds (Oregon State University 1996f).

Other species: Copper sulphate mixture may be of comparable toxicity to copper hydroxide, and harmful to bees. Most animal life in soil, including large earthworms, have been eliminated by the extensive use of copper containing fungicides in orchards (Oregon State University 1996f).

8.	**Active constituent:**	**copper oxychloride** (controls downy mildew)
	Some registered products:	Brycop, Copper Oxychloride, Rotam Copper Oxychloride WP, Copperoxy 500 WP, Coppox, Coppurite, Coppurite DF, Cuprox, Oxydul, Sipcam Copper Oxychloride 500 WP
	Mode of Metabolism:	Decomposition (U.S. National Library of Medicine 2002g; Chemspray Pty Limited 1997)
	Common metabolites:	Copper oxides and hydrogen chloride (U.S. National Library of Medicine 2002g)
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		Total copper deposits decreased after application of copper hydroxide (copper oxychloride may behave the same as copper hydroxide) on orange and bean leaves with a half-life of 45 days for navel orange and 35 days for bean leaves (Menkissoglu and Lindow 1991).

Water solubility:	None. Practically insoluble in water; less than 0.00001 mg/L at 20°C in neutral water (U.S. National Library of Medicine 2002g).
Soil adsorption/mobility:	Very high / Very low. Copper oxychloride is strongly absorbed by soils (Chemspray Pty Limited 1997). Therefore, the mobility of copper oxychloride through soil is expected to be very low.
Volatility:	Very low. Vapour pressure is negligible at 20°C (Chemspray Pty Limited 1997). Therefore, it is expected that the volatility of copper oxychloride will be very low.

Influence of environmental factors on degradation rates:

Water	None. Copper oxychloride is expected to behave the same as copper hydroxide. Copper hydroxide decomposes in hot water (Griffin Corporation Australia 1998) but is generally insoluble.
Vegetation	Low. One of the limiting factors in the use of copper compounds is their serious potential for phytotoxicity (U.S. EPA 1986b). Copper toxicity can kill plants by disrupting photosynthesis.
Increasing Soil pH	Low. The degradation by soil pH may be of comparable to that of copper hydroxide.
Soil microorganisms	Very low. Most animal life in soil, including large earthworms, have been eliminated by the extensive use of copper containing fungicides in orchards (Pimentel 1971). This may imply that degradation of copper compound by soil microorganisms is very low.
Concentration of active constituent	Low. Copper is taken up by tomato plants from potting soils containing various levels of copper hydroxide (Rhoads, Olson and Manning 1989). The level of copper concentration in plant tissue depended on copper concentration in soil and soil pH. Copper oxychloride is expected to be comparable to copper hydroxide.
Sunlight	None. Copper oxychloride decomposes on heating > 220°C (Chemspray Pty Limited 1997). Therefore, it is very unlikely that copper oxychloride will decompose under sunlight.
Temperature	Positive relationship. Copper oxychloride decomposes on heating > 220°C (Chemspray Pty Limited 1997).

General Information:

Copper oxychloride is a green powder with mild lignin sulphonate odour.

Toxicity to humans:

Copper oxychloride is highly toxic, and may be fatal if inhaled, swallowed or absorbed through skin (U.S. National Library of Medicine 2002g; Chemspray Pty Limited 1997). Swallowing of a quantity of copper oxychloride, eg 3 - 5 g, may result in symptoms of gastroenteritis. A larger dose, eg 5 - 8 g, may cause damage to capillaries and mucous membrane of digestive tract, signs of heavy metal poisoning, and loss of water and electrolytes. At higher doses, ie 8 - 12 g, death may occur.

Copper oxychloride may be an eye irritant, but is not expected to be harmful by skin absorption. Dusts generated during handling and use may cause irritation of the nose and upper respiratory passages.

Toxicity to other mammals:

Acute oral LD_{50} (rat): 700 - 800 mg/kg. Acute dermal LD_{50} (rat): > 2000 mg/kg. Acute inhalation LC50 (4hr) (rat): > 30mg/L (Chemspray Pty Limited 1997). Need full sentences for consistency with the rest of the document

Toxicity to non-mammalian species:

Aquatic organisms: High. Copper oxychloride is toxic to fish and aquatic organisms (Chemspray Pty Limited 1997). Acute toxicity LC_{50} (48hr) - carp: 2.2mg/L. Acute toxicity LC_{50} (24hr) - daphnia: 3.5mg/L.

Birds: Low. Copper sulphate may be of comparable toxicity to copper oxychloride. Copper sulphate is practically nontoxic to birds (Oregon State University 1996f).

Other species: Copper oxychloride is not toxic to bees (Chemspray Pty Limited 1997).

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9. Active constituent: diquat

Some registered products: Aquacide, Aquakill, Dextrone, Diquat, Reglone, Reglox, Reward,Tag, Torpedo, Vegetrole, and Weedtrine-D*Mode of Metabolism:* Biodegradation (Funderburk and Bozarth 1967; Simsiman and Chesters 1976), photodegradation (Funderburk and Bozarth 1967; Sanborn et al.. 1977) and hydrolysis (Fickle and Hiltibran 1971).

Common metabolites: After oral administration to rats, 77% of dose appeared in faeces as diquat, and 12% as metabolic products, almost half of which was monopyridone of diquat (Kearney and Kaufman 1975). Paraquat and diquat were metabolised to a limited extent in experimental animals. The principal oxidative metabolites which were excreted in small quantities by several species, were the mono- and dipyridone derivatives of the parent herbicides (Banks et al. 1986)

Time taken for half of the initial amount of a pesticide to break down (half-life):

Diquat dibromide is highly persistent, with reported field half-lives of greater than 1000 days (Wauchope. 1992). It is very well sorbed by soil organic matter and clay (Wauchope et al. 1992).

Water Solubility: Very high. Diquat dibromide (Synonym: diquat) is a highly water soluble compound (700,000 mg/L) (Verschueren 1983).

Soil adsorption/mobility: Very high / Very low. Although diquat is water-soluble (700g/L) (Wauchope et al. 1992; Verschueren 1983), its capacity for strong adsorption to soil particles suggest that it will not easily leach through the soil, be taken up by plants or soil microbes, or broken down by sunlight (photochemical degradation). Field and laboratory tests show that diquat usually remains in the top inch of soil for long periods of time after it is applied (Tucker 1980). Diquat is strongly adsorbed by humic substances by an ion exchange mechanism, the reaction being accompanied by a release of hydrogen ions (Choudry 1983).

Volatility: Very low. Diquat has a very low vapour pressure ($< 4x10^{-5}$ mm Hg (Royal Society of Chemicals 1983)) and will therefore not volatilise appreciably from water or soil (Howard 1991).

Influence of environmental factors on degradation rates:

Water	Medium. When diquat was intentionally applied to water to control aquatic weeds it disappeared from two experimental ponds within 14 and 30 days and was more persistent in the pond that had a lower average temperature of 18°C (Grzenda et al. 1966). The most reasonable explanation for the difference in persistence in the two ponds was a higher turbidity level and hence more adsorption in the pond from which the diquat disappeared the fastest (Grzenda et al. 1966).
Vegetation	None. Metabolic breakdown does not occur in plants (Weed Science Society of America 1979). Diquat dibromide is rapidly absorbed into the leaves of plants, but usually kills the plant tissues necessary for translocation too quickly to allow movement to other parts of the plant. The herbicide interferes with cell respiration, the process by which plants produce energy. Diquat dibromide is broken down on the plant surface by photochemical degradation (Weed Science Society of America 1994).
Increasing Soil pH	High. Diquat is stable in neutral or acid solutions; however, it hydrolyses in the presence of alkaline materials including alkaline waters (Weed Science Society of America 1979).
Soil microorganisms	Very high. A number of studies indicate that microorganisms are capable of degrading diquat (Funderburk and Bozarth 1967; Gillett 1970; Simsiman and Chesters 1976). Simsiman and Chesters (1976) found that following rapid weed kill, profuse prolification of microorganisms occurred, promoting degradation of diquat sorbed on the decomposing weeds.
Concentration of active constituent	Low. Response of the aquatic macrophyte hydrilla (Hydrilla verticillata) to diquat dibromide was studied in aquariums using the following measurements: dissolved oxygen concentration, chlorophyll a concentrations, and membrane permeability of hydrilla cells. Diquat was applied in doses of 0, 0.2, 0.5, 0.75, and 1.0 μg/ml diquat cation. The concentration of diquat initially followed an exponential decline; after day 3 the decline in concentration in the 3 highest treatments was less precipitous. By day 5, diquat was below the minimum detectable level of 0.05 μg/ml in all treatments (Cassidy and Rodgers 1989). This may indicate that degradation at higher concentrations is slower than the degradation at lower concentration.
Sunlight	Very high. Should diquat be released to the atmosphere during spraying operations, it would be associated with aerosols. It will be subjected to photolysis (half-life approximately 48 hrs) and gravitational settling. Diquat will photodegrade in surface layers of water in 1-3 or more weeks when not adsorbed to particulate matter (U.S. National Library of Medicine 2002h). Microbial degradation and sunlight play roles in the breakdown of diquat (Gillett 1970)
Temperature	Positive relationship. Diquat was intentionally applied to water to control aquatic weeds. Diquat disappeared from two experimental ponds within 14 and 30 days and was more persistent in the pond that had a lower average temperature of 18°C (Grzenda et al. 1966). A study on the influence of water temperature on the efficacy of diquat showed that the diquat efficacy was inhibited as water temperature decreased (Netherland et al. 2000). This may imply that diquat degrades more rapidly at higher temperature.

General Information:

Diquat dibromide is a nonselective, quick-acting herbicide and plant growth regulator, causing injury only to the parts of the plant to which it is applied. Diquat dibromide is referred to as a desiccant because it causes a leaf or an entire plant to dry out quickly. It is used to desiccate potato vines and seed crops, to control flowering of sugarcane, and for industrial and aquatic weed control. It is not

residual; that is, it does not leave any trace of herbicide on or in plants, soil, or water (Oregon State University 1996g).

Toxicity to humans:

Swallowing can result in nausea, vomiting, diarrhoea and abdominal pain within a few hours of swallowing. Ulceration of lips, mouth, throat and intestine may follow within 24-48 hours. Kidney failure and liver damage may occur at higher doses in severe cases circulatory collapse, coma and death from respiratory failure/cardiac arrest can occur (Crop Care Australia Pty Ltd 2000b).

Diquat is an eye irritant, it may lead to ulceration of corneal and conjunctival epithelium giving rise to secondary infection. Although healing may be slow, the injury is superficial and with proper medical care will be complete, even in severe cases. Highly toxic if inhaled, however, inhalation is unlikely because of the low vapour pressure of the material at ambient temperature. Nose bleeding and soreness of the throat may result from spray mist or dust trapped on the nasal mucosa (Crop Care Australia Pty Ltd 2000b).

Toxicity to other mammals:

Diquat dibromide is moderately toxic via ingestion, with reported oral LD_{50} values of 120 mg/kg in rats, 233 mg/kg in mice, 188 mg/kg in rabbits, and 187 mg/kg in guinea pigs and dogs (Kidd and James 1991). Cows appear to be particularly sensitive to this herbicide, with an oral LD_{50} of 30 to 56 mg/kg (American Conference of Governmental Industrial Hygienists. Inc 1991). The acute dermal LD_{50} for diquat dibromide is approximately 400 to 500 mg/kg in rabbits, indicating moderate toxicity by this route as well (Weed Science Society of America 1994).

Toxicity to non-mammalian species:

Aquatic organisms: Low - Medium. Diquat dibromide is moderately to practically nontoxic to fish and aquatic invertebrates. The 8-hour LC_{50} for diquat dibromide is 12.3 mg/L in rainbow trout and 28.5 mg/L in Chinook salmon (Pimentel 1971). The 96-hour LC_{50} is 16 mg/L in northern pike, 20.4 mg/L in fingerling trout, 245 mg/L in bluegill, 60 mg/L in yellow perch, and 170 mg/L in black bullhead (Johnson and Finley 1980; Simonin and Skea 1977). Research indicates that yellow perch suffer significant respiratory stress when herbicide concentrations in the water are similar to those normally present during aquatic vegetation control programs (Bimber 1976). There is little or no bioconcentration of diquat dibromide in fish (U.S. National Library of Medicine 1995).

Birds: Low – Medium. Diquat dibromide ranges from slightly to moderately toxic to birds (U.S. EPA 1986c). The reported acute oral LD_{50} in young male mallards is 564 mg/kg (U.S. National Library of Medicine 1995). The oral LD50 for diquat dibromide is 200 to 400 mg/kg in hens (U.S. National Library of Medicine 1995). The 5-day dietary LC_{50} is about 1300 ppm in Japanese quail (Hill and Camardese 1986).

Other species: Diquat dibromide is not toxic to honey bees (Kidd and James 1991).

10.	**Active constituent:**	**diuron** (controls weeds)
	Some registered products:	Diurex WG, Diurgranz, Diurmax Flowable, Diurmax Granules 900 WDG, Diuron WG, Diuron 500, Diuron 500 SC, Diuron 800, Diuron 900 DF, Diuron 900 WG, Flowable Diuron, Striker 500 SC
	Mode of Metabolism:	Oxidation (Masclet, Bardinet and Royer 1997; Rhone-Poulenc Geronazzo S.p.A. 1996). Soil microorganisms primarily degrade diuron (Cullington and Walker 1999; Howard 1991). Diuron absorbs light in the environmental spectrum and has the potential for direct photolysis (U.S. National Library of Medicine 2002i).

Common metabolites: Metabolites of microbial degradation include the major metabolite, 3,4-dichloroaniline, and also 3-(3,4-dichlorophenyl) urea and 3-(3,4-dichlorophenyl)-1-methylurea (Jury et al. 1984). Oxides of nitrogen and chlorine compounds may be produced on decomposition of product (Rhone-Poulenc Geronazzo S.p.A. 1996).

Time taken for half of the initial amount of a pesticide to break down (half-life):

Diuron is a highly persistent herbicide which when worked into the top 10 cm of land has a half-life of 330 days (Jury et al. 1984; U.S. National Library of Medicine 2002i).

Water solubility: Low. 37.3 mg/L at 25°C (Yalkowsky 1989)

Soil adsorption/mobility: Low – medium / Low. Diuron is a highly persistent and fairly immobile herbicide (Jury et al. 1984). The soil adsorption coefficient (Koc) values range from 224-879 indicating that diuron is expected to have low-to-moderate mobility in soil (U.S. National Library of Medicine 2002i).

Volatility: Very low. Diuron has a very low Henry's Law constant and therefore will not volatilise appreciably from water. Due to its low vapour pressure and high adsorption to soil, diuron will not volatilise appreciably from soil (Jury et al. 1984).

Influence of environmental factors on degradation rates:

Water	Low. Diuron is relatively stable in neutral water. Microbes are the primary agents in the degradation of diuron in aquatic environments (Howard 1991).
Vegetation	High. Diuron is readily absorbed through the root system of plants and less readily through the leaves and stems (Weed Science Society of America 1994).
Increasing Soil pH	None. A study by Reddy, Megh-Singh and Alva (1992) indicated that the sorption of diuron to soil was not influenced by soil pH.
Soil microorganisms	High. Soil microorganisms primarily degrade diuron (Cullington and Walker 1999; Howard 1991).
Concentration of active constituent	Low. Biological degradation in soil decreased with increasing concentration (U.S. National Library of Medicine 2002i).
Sunlight	High. Diuron absorbs light in the environmental spectrum and has the potential for direct photolysis (U.S. National Library of Medicine 2002i).
Temperature	Positive relationship. Biological degradation in soil increased with increasing temperature (U.S. National Library of Medicine 2002i; Madhun and Freed 1987; Majka and Lavy 1977).

General Information:

Diuron is a substituted urea herbicide used to control a wide variety of annual and perennial broadleaf and grassy weeds, as well as mosses. Diuron works by inhibiting photosynthesis. It may be found in formulations as wettable powders and suspension concentrates (Oregon State University 1996h).

Toxicity to humans:

Diuron is slightly toxic by oral route, is a mild eye irritant, and is slightly toxic by dermal route. Contact with the skin may result in irritation and may irritate mucous membranes of nose and mouth. No other known health effects (Rhone-Poulenc Geronazzo S.p.A. 1996). Diuron may irritate the skin, eye, or nose (U.S. National Library of Medicine 2002i). For humans, the only reported case of acute,

oral exposure to the herbicide produced no significant symptoms or toxicity (Weed Science Society of America. 1994; U.S. National Library of Medicine 1995).

Toxicity to other mammals:

Diuron is slightly toxic to mammals. The oral LD_{50} in rats is 3400 mg/kg. The dermal LD_{50} is greater than 2000 mg/kg (Weed Science Society of America 1994; U.S. National Library of Medicine 1995; Rhone-Poulenc Geronazzo S.p.A. 1996). Inhalation LC_{50} (4hr) for rats > 5mg/L. In 2-year feeding trials (technical), the no observed effect level (NOEL) for rats was 250mg/kg diet; for dogs 125mg/kg (Rhone-Poulenc Geronazzo S.p.A. 1996). Some signs of central nervous system depression have been noted at high levels of diuron exposure.

Toxicity to non-mammalian species:

Aquatic organisms: High. The LC_{50} (48 hour) values for diuron range from 4.3 mg/L to 42 mg/L in fish, and range from 1 mg/L to 2.5 mg/L for aquatic invertebrates. The LC_{50} (96-hour) is 3.5 mg/L for rainbow trout (Weed Science Society of America. 1994; U.S. National Library of Medicine 1995). Thus, diuron is moderately toxic to fish and highly toxic to aquatic invertebrates. The manufacturer of diuron states that it is dangerous to fish (Rhone-Poulenc Geronazzo S.p.A. 1996).

Birds: Low. Diuron is slightly toxic to birds. In bobwhite quail, the dietary LC50 is 1730 ppm. In Japanese quail and ring-necked pheasant, it is greater than 5000 ppm. The LC50 is approximately 5000 ppm in mallard ducks (Weed Science Society of America. 1994; U.S. National Library of Medicine 1995).

Other species: Diuron is low hazard to bees (Rhone-Poulenc Geronazzo S.p.A. 1996).

11.	**Active constituent:**	**fenarimol** (controls powdery mildew)
	Some registered products:	Rubigan 120 SC
	Mode of Metabolism:	Photolytic
	Common metabolites:	Carbon dioxide (major metabolite), carbon monoxide and smoke (Dow AgroSciences 2001).
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		Fenarimol has a half-life of approximately 12 hours in intensive sunlight (Dow AgroSciences 2001). If incorporated into the soil, fenarimol may persist for one year depending on soil conditions (Dow AgroSciences 2001).
	Water solubility:	Very low. Fenarimol has low water solubility, 0.137 mg/L at 25°C (Dow AgroSciences 2001).
	Soil adsorption/mobility:	High / Very low. Fenarimol has minimal leaching ability and usually remains in the top five to ten centimetres of the soil profile (Dow AgroSciences 2001).
	Volatility:	Low. No specific data, however expected to be low at 100°C (Dow AgroSciences 2001).

Influence of environmental factors on degradation rates:

Water	Low. Fenarimol will only decompose after boiling to dryness (Dow AgroSciences 2001).
Vegetation	No specific data available.
Soil pH	No specific data available.
Soil microorganisms	Very low. Fenarimol does not degrade in soil under aerobic or anaerobic conditions (Cornell University 2001b). In soil, fenarimol may persist for one year depending on soil conditions (Dow AgroSciences 2001).
Concentration of active constituent	None. Concentration may not influence the breakdown. After fermentation azoxystrobin was present in the wine at the same concentration as on the grapes (Cabras and Angioni 2000).
Sunlight	High. Fenarimol breaks down in intense sunlight (Dow AgroSciences 2001).
Temperature	None. Fenarimol is unlikely to decompose at temperatures normally achieved in a fire (Dow AgroSciences 2001).

General Information:

Fenarimol is a hazardous chemical. It is amber/pale brown liquid with an aromatic odour.

Toxicity to humans:

Fenarimol may cause severe eye irritation with corneal injury, resulting in permanent vision impairment or blindness (Dow AgroSciences 1998).

Toxicity to other mammals:

The oral LD_{50} (rat) is above 2000 mg/kg (low toxicity). The acute dermal LD_{50} (rabbit) is above 4000 mg/kg (low toxicity). The acute inhalation toxicity is low. (Dow AgroSciences 2001). Prolonged or repeated contact with the concentrate may cause slight irritation, drying or flaking of the skin (Dow AgroSciences 2001).

In animals, fenarimol has been shown to affect the liver and kidneys at high doses (Dow AgroSciences 2001). It did not cause cancer in long-term animal studies. Fenarimol did not cause birth defects in animal studies but nontoxic doses did reduce fertility, cause birth difficulties and reduce live born litter size. This effect is due to a hormonal mechanism that is not present in humans. Fenarimol does not cause genetic change and does not accumulate in the body.

Toxicity to non-mammalian species:

Aquatic organisms: High. Fenarimol is toxic to fish (Dow AgroSciences 1998 and 2001)

Birds: No specific data available.

Other species: Low hazard to bees and earthworms (Dow AgroSciences 1998 and 2001)

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12. Active constituent: **glyphosate** (controls weeds)

Some registered products: APL 360, Glyphosate 360, Glyphosate 450, Pestmaster Aqua-Tech, Pestmaster, Glyphosate CT, Roundup, Sanos 360, Sanos 450, Sanos CT Plus, Wipe-Out 360, Wipe-Out 450.

Mode of Metabolism: Microbes are primarily responsible for the breakdown of glyphosate in soils (Weed Science Society of America 1994; U.S. EPA 1990).

Common metabolites: Parent compound is N-methylated and degraded into three compounds at the initial metabolic sequence. These are further metabolised to N-methylated glycines and some phosphonic acids in plants, soil, and water (Aizawa 1982). Glyphosate's only significant metabolite is aminomethylphosphosphonic acid (AMPA), which also rapidly degrades in soil (Feng and Thompson 1990). The U.S. EPA (1990) has determined that the metabolite aminomethylphosphonic acid (AMPA) is formed on plants in amounts that can range as high as 28% of total residue in the plant.

Time taken for half of the initial amount of a pesticide to break down (half-life):

Glyphosate is moderately persistent in soil, with an estimated average half-life of 47 days (Kidd and James 1991; Wauchope et al. 1992). Reported field half-lives range from 1 to 174 days (Wauchope et al. 1992)

Water solubility: Very high. 12,000 mg/L at 25°C (Kidd and James 1991). Glyphosate is highly water-soluble (Nufarm Australia Limited 2000).

Soil adsorption/mobility: Very high / Low. Glyphosate is strongly adsorbed to most soils, even those with lower organic and clay content (Kidd and James 1991; Wauchope et al. 1992). Thus, even though it is highly soluble in water, field and laboratory studies show it does not leach appreciably. In addition to binding to organic matter and clay in soil, it may also form insoluble complexes with metal ions in the soil. Distribution data for glyphosate after spraying in a coastal forest ecosystem indicate that glyphosate is strongly adsorbed to the upper layers of soil and has a low propensity for leaching (Feng and Thompson 1990).

Volatility: Very low. Due to its ionic state in water, glyphosate would not be expected to volatilise from water or soil (U.S. National Library of Medicine 2002j).

Influence of environmental factors on degradation rates:

Water	Low. In water, glyphosate is strongly adsorbed to suspended organic and mineral matter and is broken down primarily by microorganisms (U.S. Department of Agriculture 1984). Its half-life in pond water ranges from 12 days to 10 weeks (U.S. EPA 1992).
Vegetation	Medium – High. Glyphosate may be translocated throughout the plant, including to the roots. It is extensively metabolised by some plants, while remaining intact in others (Kidd and James 1991).
Increasing Soil pH	Low. In the environmental pH range, 5 to 9, glyphosate has a net negative charge that increases with pH. The nitrogen atom is positively charged and both the carboxylic acid group and phosphonic acid group are deprotonated; above pH 5.6 the latter is predominantly doubly ionised and below pH 5.6 it is singly ionised (Spankle 1975). Experiments using sterile controls in biodegradability studies indicate that glyphosate does not chemically degrade in soil (Spankle 1975).
Soil microorganisms	Very high. Microbes are primarily responsible for the breakdown of glyphosate in soils (Weed Science Society of America 1994; U.S. EPA 1990). Glyphosate readily and completely biodegrades in soil (U.S. National Library of Medicine 2002j).

Concentration of active constituent	High. The photolytic half-life of glyphosate in deionised water exposed outdoors to sunlight was approximately 5 wk at 100 ppm and 3 wk at 2000 ppm (Lund-Hoie and Friestad 1986). This may indicate that the rate of degradation of glyphosate is higher at higher concentration.
Sunlight	Low. Glyphosate photodegrades when exposed to UV radiation, but not visible light (Lund-Hoie and Friestad 1986). Loss of glyphosate from photodecomposition is negligible (U.S. EPA 1990).
Temperature	Positive relationship. A study by Eberbach (1998) indicates that degradation of glyphosate in soil increased at 25°C compared with the degradation at 10°C.

General Information:

Glyphosate is a broad-spectrum, nonselective systemic herbicide used for control of annual and perennial plants including grasses, sedges, broad-leaved weeds, and woody plants. Glyphosate itself is an acid, but it is commonly used in salt form, most commonly the isopropylamine salt. It may also be available in acidic or trimethylsulfonium salt forms. It is generally distributed as water-soluble concentrates and powders (Oregon State University 1996i).

Toxicity to humans:

The glyphosate concentrate is mildly harmful by ingestion (Nufarm Australia Limited 2000), although acute oral toxicity is very low; ingestion of larger quantity may cause injury. Prolonged contact with the concentrate may cause non-permanent damage. No adverse respiratory effects are anticipated for this product as the vapour pressure of the active ingredient is very low and it is soluble in water

Toxicity to other mammals:

Glyphosate is practically nontoxic by ingestion, with a reported acute oral LD_{50} of 5600 mg/kg in the rat (Weed Science Society of America 1994; Monsanto Company 1985). The oral LD_{50} for the trimethylsulfonium salt is reported to be approximately 750 mg/kg in rats, which indicates moderate toxicity (Weed Science Society of America 1994). Oral LD_{50} values for glyphosate are greater than 10,000 mg/kg in mice, rabbits, and goats (U.S. National Library of Medicine 1995; Monsanto Company 1985). It is practically nontoxic by skin exposure, with reported dermal LD_{50} values of greater than 5000 mg/kg for the acid and isopropylamine salt (Weed Science Society of America 1994).

Toxicity to non-mammalian species:

Aquatic organisms: Very low. Technical glyphosate acid is practically nontoxic to fish and may be slightly toxic to aquatic invertebrates. The 96-hour LC_{50} is 120 mg/L in bluegill sunfish, 168 mg/L in harlequin, and 86 mg/L in rainbow trout (Weed Science Society of America 1994). The reported 96-hour LC_{50} values for other aquatic species include greater than 10 mg/L in Atlantic oysters, 934 mg/L in fiddler crab, and 281 mg/L in shrimp (Weed Science Society of America 1994). The 48-hour $LC_{50}$for glyphosate in Daphnia is 780 mg/L (Weed Science Society of America 1994). Glyphosate is moderately toxic to fish and other aquatic species, mainly due to surfactant (Nufarm Australia Limited 2000).

Birds: Low. Glyphosate is slightly toxic to wild birds. The dietary LC_{50} in both mallards and bobwhite quail is greater than 4500 ppm (Kidd and James 1991).

Other species: Glyphosate is nontoxic to honeybees (Nufarm Australia Limited 2000; Kidd and James 1991; Weed Science Society of America 1994). The reported contact LC_{50} values for earthworms in soil are greater than 5000 ppm for both the glyphosate trimethylsulfonium salt and Roundup (Weed Science Society of America 1994).

13. Active constituent: **iprodione** (controls botrytis bunch rot)

Some registered products: Civet Aquaflo, Rovral Aquaflo, Rovral Liquid

Mode of Metabolism: Microbial (Mercadier, Vega and Bastide 1997) and hydrolysis (Oregon State University 1996j). Iprodione will degrade in soil through microbial degradation and aqueous hydrolysis (U.S. National Library of Medicine 2002k).

Common metabolites: 3,5-dichloroaniline (Kidd and James 1991; Mitchell and Cain 1996), N-(3,5-dichlorophenyl)-2,4-dioxoimidazolidine and dichlorophenylurea acetic acid (Mercadier, Vega and Bastide 1997).

Time taken for half of the initial amount of a pesticide to break down (half-life):

The half-life of iprodione in soil ranges from less than 7 to greater than 60 days (Kidd and James 1991; Wauchope et al. 1992). A representative half-life in most soils is estimated to be 14 days (Wauchope et al. 1992).

Water solubility: Low. 13.9 mg/L at 25°C (Wauchope et al. 1992).

Soil adsorption/mobility: Medium / Low. Iprodione is slightly soluble and moderately to well sorbed by most soils (Wauchope et al. 1992). A reported Koc of 700 suggests that iprodione has low soil mobility (Wauchope et al. 1992).

Volatility: Very low. The value of Henry's Law constant for iprodione indicates that iprodione is essentially nonvolatile from water (Lyman et al. 1990).

Influence of environmental factors on degradation rates:

Water	Very high. The compound breaks down very rapidly in water under aerobic conditions; the rate is slower, but still rapid under near-anaerobic conditions (U.S. National Library of Medicine 1995).
Vegetation	Very high. The compound is rapidly broken down in the plant after is taken up by the roots and translocated (Kidd and James 1991). The main metabolite in plants is 3,5-dichloroaniline (Kidd and James 1991).
Increasing Soil pH	High. Degradation rates of iprodione vary with soil acidity, soil clay content, and history of the soil fungicide treatment (Oregon State University 1996j). In soils with pH ranging from 4.3 to 6.5, the rate of degradation of iprodione increased with increased soil pH (Walker 1987).
Soil microorganisms	High. Soil bacteria degrade iprodione (Mercadier et al. 1996; Mercadier, Vega and Bastide 1997; Athiel et al. 1995). Biological screening studies have demonstrated that iprodione can degrade much faster in non-sterile soil as compared to sterilised soil (Slade et al. 1992; Walker and Welch 1990).
Concentration of active constituent	None. Soils that had acquired full-enhanced degradation rapidly degraded iprodione applied at 30 times the recommended field rate (Mitchell and Cain 1996). In another study rapid degradation of iprodione was observed at high and low application rates (Mitchell et al. 1993).
Sunlight	Very high. The compound is readily degraded by UV light (Oregon State University 1996j).

Temperature	Positive relationship. Rapid degradation of iprodione and vinclozolin was observed in laboratory studies even at low temperatures, over a wide range of moisture conditions and at high and low application rates (Mitchell et al. 1993).

General Information:

Iprodione is a dicarboximide contact fungicide used to control a wide variety of crop diseases (Oregon State University 1996j).

Toxicity to humans:

Iprodione may irritate eyes, mucous membranes of nose and mouth. This product is not a skin irritant or sensitising agent (Aventis CropScience Pty Ltd 2000).

Toxicity to other mammals:

Iprodione is slightly toxic by ingestion, with reported oral LD_{50} values of 3500 mg/kg in rats, 4000 mg/kg in mice, and greater than 4400 mg/kg in rabbits (Kidd and James 1991; U.S. National Library of Medicine 1995). No dermal toxic effects were noted at 2500 mg/kg in the rat and at 1000 mg/kg in the rabbit, indicating slight toxicity by this route (Kidd and James 1991; U.S. National Library of Medicine 1995). Inhalation toxicity is also low for this compound. The 4-hour inhalation LC_{50} for iprodione is greater than 3.3 mg/L in the rat (U.S. National Library of Medicine 1995).

Rats given dietary doses of approximately 60 mg/kg/day over 18 months suffered no ill effects (Kidd and James 1991; U.S. National Library of Medicine 1995). Dogs fed approximately 60 mg/kg/day over 18 months also showed no adverse effects (Kidd and James 1991; U.S. National Library of Medicine 1995).

Toxicity to non-mammalian species:

Aquatic organisms: Medium. Iprodione is moderately toxic to fish species, with LC_{50} values ranging from 2.25 mg/L in the sunfish to 6.7 mg/L in the rainbow trout (U.S. National Library of Medicine 1995).

Birds: Low. Iprodione is slightly toxic to wildfowl. The reported acute oral LD_{50} in bobwhite quail is 930 mg/kg (Kidd and James 1991).

Other species: Iprodione is nontoxic to bees (Kidd and James 1991; Aventis CropScience Pty Ltd. 2000).

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14. Active constituent: **mancozeb** (controls black spot and phomopsis cane and leaf spot)

Some registered products: Dithane DF, Dithane M-45, Mancozeb DG, Mancozeb WDG, Mancozeb 750 DF, Mancozeb 800, Mancozeb 800 WP Penncozeb 750 DF

Mode of Metabolism: Acid-catalysed hydrolysis (Weissmahr and Sedlak 2000)

Common metabolites: Ethylenethiourea (ETU) –is the major metabolite and carbon disulfide is the minor metabolite (U.S. EPA 1988b). Ethyleneurea (EU), ethylenethiuram disulfide (ETD), ethylenethiuram monosulfide (ETM) (Kumar and Agarwal 1992).

Time taken for half of the initial amount of a pesticide to break down (half-life):

Mancozeb is of low soil persistence, with a reported field half-life of 1 to 7 days (Wauchope *et. al.* 1992)

Water solubility:	Very low. 6.0 mg/L (Wauchope et al.1991). Mancozeb is practically insoluble in water (Meister 1992).
Soil adsorption/mobility:	Medium / Low. Mancozeb is practically insoluble in water, therefore, it is unlikely to infiltrate groundwater (Meister 1992). The average Koc value for mancozeb is 1000 (Harris 1995). Other studies have shown mancozeb to have a Koc value ranging from 363-892 in silt loam, suggesting that mancozeb is expected to have low mobility in soil (U.S. National Library of Medicine 2002l). Studies do indicate that ETU, a metabolite of mancozeb has the potential to be mobile in soils (U.S.EPA 1987c; Cornell University. 2001c).
Volatility:	Very low. This Henry's Law constant indicates that mancozeb is expected to be essentially nonvolatile from water surfaces (Lyman et al. 1990).). Mancozeb's estimated Henry's Law constant indicates that volatilisation from moist soil surfaces will not occur. Mancozeb is not expected to volatilise from dry soil surfaces based upon its vapour pressure (U.S. National Library of Medicine 2002l).

Influence of environmental factors on degradation rates:

Water	Very high. Mancozeb rapidly and spontaneously degrades to ETU in presence of water and oxygen (U.S. EPA 1988b).
Vegetation	Very high. In plants, the principal metabolite is ethylenethiourea, which undergoes further metabolism. Ethylenethiuram monosulfide, ethylenethiuroum disulfide, and sulfur are also metabolites (Tomlin 1997). Mancozeb rapidly degraded to ETU, EU, ETD and ETM when applied on the foliage of eggplants (Kumar and Agarwal 1992).
Increasing Soil pH	Low. Mancozeb has a hydrolysis rate constant of 0.46, 0.30, and 1.04 per day at pH 5, 7, and 9, respectively, which equates to a half-life of 1.5, 2.3, and 0.7 days at pH 5, 7, and 9, respectively (U.S. Department of Agriculture 1999). Another source has suggested hydrolysis half-lives of 20 days at pH 5, 17 hrs at pH 7, and 34 hrs at pH 9 (Tomlin 1997). These indicate that mancozeb degrade rapidly in alkaline soils.
Soil microorganisms	Very low. Mancozeb is readily degraded by soil microorganisms, releasing its ethylene C-atoms as CO_2 (Lyman and Lacoste 1975).
Concentration of active constituent	High. The degradation of ethylenethiourea depends on the concentration in the water implying first order reaction kinetics (Jacobsen and Bossi 1997). The ethylenebisdithiocarbamate group includes maneb, zineb and mancozeb.
Sunlight	Low. Mancozeb has a photolysis rate constant of >5.5/day in air which equates to a half-life of <3 hrs (U.S. Department of Agriculture 1999). Other studies showed that mancozeb was stable to photolysis in soil (U.S. Department of Agriculture 1999). Mancozeb does not evaporate easily (Information Ventures Inc. 2001).
Temperature	Positive relationship. Mancozeb degrades more rapidly at soil temperature of 20°C or above (Gupta 1988).

General Information:

Mancozeb is a practically nontoxic ethylene bisdithiocarbamate (U.S. EPA toxicity class IV-practically nontoxic) (Oregon State University 2001a). It is a polymer of maneb combined with zinc (Cornell University 2001c). While it is relatively stable and noncorrosive under normal, dry storage conditions, it is decomposed at high temperatures by moisture and by acid.

Toxicity to humans:

Mancozeb is rapidly absorbed into the body from the gastrointestinal tract, distributed to various target organs, and almost completely excreted in 96 hours (Oregon State University 2001a).

Toxicity to other mammals:

The oral LD_{50} for mancozeb ranges from 4.500 to 11,200 mg/kg in rats. When applied to the skin of rabbits, its dermal LD_{50} is 5,000 to 15,000 mg/kg (Meister 1992). In a two-year study dogs were fed doses of 0, 0.625, 2.5 or 25 mg/kg of mancozeb. Lower iodine uptake was observed after 24 months in dogs fed the two highest doses, while no difference was observed between those dogs fed 0 and 0.625 mg/kg (Hayes and Laws 1990).

Toxicity to non-mammalian species:

Aquatic organisms: Medium – High. Mancozeb is moderately to highly toxic to fish and aquatic organisms. Reported 48-hour LC_{50} are 9 mg/L in goldfish, 2.2 mg/L in rainbow trout, 5.2 mg/L in catfish, and 4.0 mg/L in carp (U.S. National Library of Medicine 1995). The reported 72-hour LC_{50} for mancozeb in crayfish is greater than 40 mg/L; the 48-hour LC50 is 3.5 mg/L in tadpoles (DuPont de Nemours 1983).

Birds: Low. Mancozeb is slightly toxic to birds, with reported -day dietary LC_{50} values in bobwhite quail and mallard ducklings of greater than 10,000 ppm (DuPont de Nemours 1983). The 10-day dietary LC_{50} values of 6400 ppm and 3200 ppm are reported for mallard ducks and Japanese quail, respectively (U.S. National Library of Medicine 1995).

Other species: Mancozeb is not toxic to honeybees (U.S. National Library of Medicine 1995).

15.	**Active constituent:**	**metalaxyl + copper oxychloride** (controls downy mildew)
	Some registered products:	Axiom Plus, Ridomil Gold Plus
	Mode of Metabolism:	Acid-catalysed hydrolysis, photolysis (U.S.EPA 1988c).
	Common metabolites:	Acid metabolites (Droby and Coffey 1991).
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		Under field conditions, metalaxyl has a half-life of 7 to 170 days in the soil environment (Wauchope et al. 1992). A representative half-life in moist soils is about 70 days (Wauchope et al. 1992). Should be 170d in tables?
	Water solubility:	Very high. 7100 mg/L at 20°C (Kidd and James 1991).
	Soil adsorption/mobility:	Very low / Very high. It is poorly sorbed by soils and highly soluble in water (Wauchope et al. 1992). It readily leaches in sandy soil, although increased organic matter may decrease the rate of leaching (Kimmel, Casida, and Ruzo 1986). In a large-scale, national survey, metalaxyl was detected in the groundwater of several states at concentrations of 0.27 ug/L to 2.3 mg/L (Williams et al. 1988).
	Volatility:	Low. The biodegradation of ring-labelled [14C] metalaxyl in six Indian soils was examined. The total recovery of radioactivity from soil was 100 ± 6% of the applied radioactivity. Volatile organics and $14CO_2$ were detected at lower levels. This suggests that neither mineralisation nor volatilisation is a major route of metalaxyl dissipation (Sukul and Spiteller 2001).

Influence of environmental factors on degradation rates:

Water	Medium. At pH levels of 5 to 9 and temperatures of 20 to 30°C, the half-life of metalaxyl in water was greater than 4 weeks (U.S. EPA 1988c). However, exposure to sunlight reduced the half-life to 1 week (U.S. EPA 1988c)
Vegetation	Medium. Plants absorb foliar applications through the leaves and stems, and can translocate the compound throughout the plant. Metalaxyl is not absorbed directly from the soil by plants. The parent compound is the major residue in potato tubers and grapes, but in potato leaves and on lettuce, metabolites are the major product (FAO 1983).
Increasing Soil pH	Very high. Metalaxyl degraded rapidly in water of pH 10 (Sharom and Edgington 1982). Therefore, metalaxyl may degrade rapidly in alkaline soil.
Soil microorganisms	Medium. With single microorganisms, breakdown of metalaxyl ranged from 36 to 52% after 25 days, and up to 75% with mixtures of either different kind of fungi or bacteria (Bailey and Coffey 1986). Metalaxyl was stable in sterilised soils but degraded in unsterilised soils (Sharom and Edgington 1982).
Concentration of active constituent	High. Rate of biodegradation was higher for metalaxyl applied at higher concentration in soils (Droby and Coffey 1991). The rate of volatilisation of several compounds (methidathion, diazinon, isazophos, metolachlor fungicide metalaxyl) from soil increased with increasing pesticide concentration, temperature and airflow rate and with decreasing soil organic matter content (Burkhard and Guth 1981).
Sunlight	High. Increased sunlight may increase the rate of breakdown in the soil (Oregon State University 1996k). Long-time (65 h) irradiation under artificial sunlight in the presence of commercially available humic acid resulted in 65% degradation of metalaxyl (Sukul et al. 1992).
Temperature	Positive relationship. The rate of volatilisation of several compounds (methidathion, diazinon, isazophos, metolachlor fungicide metalaxyl) from soil increased with increasing pesticide concentration, temperature and airflow rate and with decreasing soil organic matter content (Burkhard and Guth 1981).

General Information:

Metalaxyl is a systemic, benzenoid fungicide used in mixtures as a foliar spray for tropical and subtropical crops, as a soil treatment for control of soil borne pathogens, and as a seed treatment to control downy mildews (Oregon State University 1996k).

Toxicity to humans:

Metalaxyl is slightly hazardous.

Toxicity to other mammals:

The oral LD_{50} in rats is 669 mg/kg and the dermal LD_{50} is greater than 3100 mg/kg (U.S. National Library of Medicine 1995), indicating slight toxicity by ingestion and dermal application. Rabbits exhibited slight eye and skin irritation, but guinea pigs displayed no sensitisation after metalaxyl exposure (Kidd and James 1991)

Toxicity to non-mammalian species:

Aquatic organisms: Low. Metalaxyl is practically nontoxic to freshwater fish. The 96-hour LC_{50} values in rainbow trout, carp, and bluegill are all above 100 mg/L (Kidd and James 1991). Freshwater aquatic invertebrates are slightly more susceptible to metalaxyl. *Daphnia magna*, has an LC_{50} of 12.5 to 28 mg/L, depending on the product formulation (U.S. EPA 1988c). This indicates that metalaxyl is slightly toxic to this organism. There is little tendency for metalaxyl to accumulate in the edible portion of fish. Metalaxyl did not accumulate beyond seven times the background concentration and it

was quickly eliminated after exposed fish were placed in fresh (metalaxyl-free) water (U.S. EPA 1988c).

Birds: Low. Metalaxyl is reported to be practically nontoxic to birds (U.S. EPA 1988c).

Other species: Metalaxyl is nontoxic to bees (Kidd and James 1991).

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16. Active constituent: **myclobutanil** (controls powdery mildew)

Some registered products: Mycloss

Mode of Metabolism: Photolysis (U.S. National Library of Medicine 2002m).

Common metabolites: Beta-(1,2,4-triazol-1-yl) alanine (Ikegami et al. 1990)

Time taken for half of the initial amount of a pesticide to break down (half-life):

In silt loam soil, myclobutanil has a half-life of about 66 days (Tomlin 1994).

Water solubility: Medium. 142 mg/L (Tomlin 1994). Myclobutanil emulsifies in water (Aventis CropScience Pty Ltd 2001).

Soil adsorption/mobility: High / Low. Based on the estimated Koc value of 950 myclobutanil is expected to have low mobility in soil (U.S. National Library of Medicine 2002m).

Volatility: Very low. The estimated values of Henry's Law constant, vapour pressure and water solubility for myclobutanil indicate that myclobutanil is expected to be essentially nonvolatile from water surfaces (Lyman et al. 1990). The Henry's Law constant for myclobutanil indicates that volatilisation from moist soil surfaces is not expected to occur (U.S. National Library of Medicine 2002m). Based on the measured vapour pressure of 1.6×10^{-6} mm Hg, myclobutanil is not expected to volatilise from dry soil surfaces (U.S. National Library of Medicine 2002m).

Influence of environmental factors on degradation rates:

Water	None. Based on the estimated Koc value of 950 myclobutanil is expected to adsorb to suspended solids and sediment in water (U.S. National Library of Medicine 2002m). Hydrolysis of myclobutanil was not observed after 28 days at pHs 5,7 and 9 at 28°C (Tomlin 1994).
Vegetation	High. Beta-(1,2,4-triazol-1-yl) alanine, an important metabolite of myclobutanil, was derived from O-acetyl-L-serine and 1,2,4-triazole by cysteine syntheses from pea seedlings and leaves of *Lathyrus latifolius* and *Leucaena leucocephala* (Ikegami et al. 1990). This may indicate that myclobutanil will be degraded by plants.
Increasing Soil pH	None. Hydrolysis of myclobutanil was not observed after 28 days at pHs 5,7 and 9 at 28°C (Tomlin 1994).
Soil microorganisms	High. Fungi in sandy loam soil were least affected by myclobutanil (Digrak and Ozcelik 1998). A large number of bacteria were capable of growing on pesticide-only media. Hence soil microorganisms may breakdown myclobutanil. No degradation was observed under anaerobic conditions (Tomlin 1994).
Concentration of active constituent	No specific data available.

Sunlight	High. The rate constant for the vapour-phase reaction of myclobutanil with photochemically-produced hydroxyl radicals has been estimated as 7.0 x 10^{-12} cm^3/molecule-sec at 25°C using a structure estimation method (Meylan and Howard 1993). This indicates vapour-phase myclobutanil will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 2.3 days (U.S. National Library of Medicine 2002m). Aqueous solutions of myclobutanil decompose on exposure to light with half-lives of 222 days in sterile water, 0.8 days in sensitised sterile water, and 25 days in pond water (Tomlin 1994).
Temperature	No specific data available.

General Information:

Myclobutanil is a member of the DMI group of fungicides. Myclobutanil is a hazardous chemical. It is yellow liquid with an aromatic odour (Aventis CropScience Pty Ltd 2001).

Toxicity to humans:

Myclobutanil irritates the eyes, nose, throat and skin and may cause serious damage to the eyes (Aventis CropScience Pty Ltd 2001). Occupational exposure to myclobutanil may occur through inhalation of mists or aerosols and dermal contact with this fungicide during or after its application and at workplaces where myclobutanil is produced (U.S. National Library of Medicine 2002m).

Toxicity to other mammals:

The oral LD_{50} in male rats is 1600 mg/kg and in female rats is 2290 mg/kg (Tomlin 1994).

Toxicity data by Aventis CropScience Pty Ltd (2001) are presented below:

Myclobutanil is harmful if swallowed. The oral LD_{50} (rat) is 2800 mg/kg. The dermal LD_{50} (male rat) is greater than 5000 mg/kg . Prolonged or repeated contact with the concentrate may cause slight irritation, drying or flaking of the skin. Myclobutanil is harmful by inhalation. No evidence of teratogenicity was observed in studies with myclobutanil in rats and rabbits. Embroyotoxicity was observed in the developmental studies with rats and rabbits.

Toxicity to non-mammalian species:

Aquatic organisms: Medium – High. Rainbow trout LC_{50} (96 h) 3.9 mg/L. Bluegill sunfish LC_{50} (96 h) 2.2 mg/L. Mysid shrimp LC_{50} (96 h) 240 µg/L. Eastern oyster LC_{50} (96 h) 0.72 mg/L. *Daphnia magna* LC_{50} (48 h) 10.2 mg/L (Aventis CropScience Pty Ltd 2001). Bioconcentration of myclobutanil in aquatic organisms is moderate to high (U.S. National Library of Medicine 2002m).

Birds: Low. Dietary LC_{50} mallard duck, bobwhite quail > 5000 ppm. Acute oral LD_{50} bobwhite quail 510 mg/kg (Aventis CropScience Pty Ltd 2001).

Other species: Low hazard to bees (Aventis CropScience Pty Ltd 2001).

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17. Active constituent: **paraquat** (used to control weeds)

Some registered products: Boa 250, Gramoxone 250, Maxitop 250, Nuquat 250, Country Paraquat 250, Shirquat 250, Spayquat 250, Spraytop 250

Mode of Metabolism: Ultraviolet light, sunlight, and soil microorganisms can degrade paraquat to products that are less toxic than the parent compound. The strong affinity for adsorption by soil particles and organic matter may limit the bioavailability of paraquat to plants, earthworms, and microorganisms

(Wauchope et al. 1992, Weed Science Society of America 1994).

Common metabolites: Degradation products isolated from plants sprayed with (14)C paraquat dichloride included 4-carboxyl-1-methyl-(14)C-pyridylium chloride and methlamine-(14)C-hydrochloride (U.S. National Library of Medicine 2002n). Several soil microorganisms have been isolated that will metabolise paraquat. There are indications that dealkylation occurs followed by ring scission with ultimate conversion to carbon dioxide (Casarett and Doull 1975).

Time taken for half of the initial amount of a pesticide to break down (half-life):

Paraquat is highly persistent in the soil environment, with reported field half-lives of greater than 1000 days (Wauchope et al. 1992, Weed Science Society of America 1994).

Water solubility: Very high. 700,000 mg/L at 20°C (Kidd and James 1991).

Soil adsorption/mobility: Very High / Very low. The Koc value for paraquat in soil is in the range 15,473-1,000,000 (Wauchope et al. 1992; Reinbold et al. 1979; Foster et al. 1991; Kenaga 1980). These high Koc values indicate that paraquat will be strongly bound and almost immobile in soil (Swann et al. 1983).

Volatility: Very low. The photolysis and volatilisation from soil are not important. The vapour pressure of paraquat is less than 1 x 10^{-7} mm Hg and the Henry's Law constant is less than 1 x 10^{-9} atm-m^3/mole (Seiber and Woodrow 1984) and based on these, volatilisation from dry soil and soil water solution should be negligible (Lyman et al. 1990; U.S. National Library of Medicine 2002n).

Influence of environmental factors on degradation rates:

Water	Low. Paraquat present in solution in the unadsorbed state may biodegrade easily in water (Calderbank and Slade 1976). But when paraquat is adsorbed to clay or organic matters in water, biodegradation will be very slow (Calderbank and Slade 1976). The hydrolysis of paraquat in water will not be important (Hance 1967)??. Paraquat will be bound to, suspended in, or precipitated from sediment in the aquatic environment, and may be even more highly persistent than on land due to limited availability of oxygen (Oregon State University 1996l).
Vegetation	None. It has been demonstrated that there is no metabolic breakdown of paraquat in tomato, broad bean, and maize plants. In sunlight, however, some photochemical breakdown occurs for paraquat that remains on the outside of treated plants. (U.S. National Library of Medicine 2002n).
Increasing Soil pH	Low. The hydrolysis of paraquat in water or soil at neutral and acidic pH is not an important loss process (Hance 1967). Hydrolysis is more important in basic pH, but it may not be important at a pH below 9 (Faust 1975). Since the pH of most natural water and soil is in the range 5-9, hydrolysis may not be important for paraquat (Hance 1967).
Soil microorganisms	High. If released to soil, paraquat will be slowly degraded due to biodegradation. It was demonstrated that paraquat (1,1'-dimethyl-4,4'-bipyridynium dichloride) sorbed to plant residues was degraded by natural microbial populations associated with plants and/or soil under laboratory conditions (Lee, Katayama and Kimura 1995).
Concentration of	Low. The photolysis of paraquat was found to be a first order process. However, the

active constituent	observed first order rate constant decreased from 0.0908 to 0.0141 per minute when the starting paraquat concentration was changed from 3.0 to 18.0 mg/L. This indicates that the rate of photolysis decreased at higher paraquat concentrations. (Nguyen and Zahir 1999)
Sunlight	High. Photochemical degradation of soil-bound paraquat by solar radiation is expected to be limited on soil surface, since penetration of light below the soil surface does not occur (Calderbank and Slade 1976). Available laboratory data show that photodegradation of paraquat in soil is not important (U.S. National Library of Medicine 2002n).
Temperature	None. In laboratory experiments the adsorption of paraquat by an organic soil, various humic fractions from that soil, model humic polymers, a polystyrene resin and ion exchange resins was studied. The adsorption reached equilibrium after about 3 to 48 hours for the soil and humic preparations and the more highly cross-linked materials respectively. Temperature changes from 20°C to 70°C did not affect the adsorption equilibrium and no decomposition of paraquat was observed. (Burns, Hayes and Stacey. 1973).

General Information:

Paraquat is a quaternary nitrogen herbicide widely used for broadleaf weed control. It is a quick-acting, nonselective compound that destroys green plant tissue on contact and by translocation within the plant (Oregon State University 1996l).

Toxicity to humans:

Paraquat can kill if swallowed and rapid treatment is essential. The immediate effects of poisoning depend on the dose of paraquat and diquat absorbed into the blood. Mild poisoning occurs at < 20 mg paraquat ion/kg body weight and the effects are vomiting and diarrhoea (Crop Care Australia Pty Ltd 2000c). Moderate to severe poisoning occurs at 20-30 mg paraquat ion/kg body weight and the effects are vomiting, abdominal discomfort, soreness and inflammation of the mouth, throat and oesophagus, difficulty in swallowing and, later, diarrhoea. Ulceration of lips, mouth, throat and intestine may follow within 24-48 hours. Kidney and liver damage may appear 1-3 days after exposure. Can cause death by a delayed proliferating fibrosis of the lung within 1-3 weeks. Lethal poisoning occurs at > 30 mg paraquat ion/kg body weight and the effects are nausea and vomiting, and can cause death by multi-organ failure and circulatory collapse within 48 hours (Crop Care Australia Pty Ltd 2000c). The minimum lethal dose of paraquat is stated to be about 35 mg/kg body weight for human beings (WHO 1984).

Toxicity to other mammals:

Paraquat is highly toxic via ingestion, with reported oral LD_{50} values of 110 to 150 mg/kg in rats, 50 mg/kg in monkeys, 48 mg/kg in cats, and 50 to 70 mg/kg in cows (Howard 1991; Stevens and Sumner 1991). The toxic effects of paraquat are due to the cation, and the halogen anions have little toxic effects (Stevens and Sumner 1991). The dermal LD_{50} in rabbits is 236 to 325 mg/kg, indicating moderate toxicity by this route (Weed Science Society of America 1994; Stevens and Sumner 1991).

Toxicity to non-mammalian species:

Aquatic organisms: Medium. Paraquat is slightly to moderately toxic to many species of aquatic life, including rainbow trout, bluegill, and channel catfish (Weed Science Society of America 1994; Howard 1991). The reported 96-hour LC_{50} for paraquat is 32 mg/L in rainbow trout, and 13 mg/L in brown trout (Weed Science Society of America 1994). The LC_{50} for the aquatic invertebrate *Daphnia pulex* is 1.2 to 4.0 mg/L (Howard 1991). In rainbow trout exposed for 7 days to paraquat, the chemical was detected in the gut and liver, but not in the meat of the fish. Aquatic weeds may bioaccumulate the compound. In one study, 4 days after paraquat was applied as an aquatic herbicide, weeds sampled

showed significant residue levels (Stevens and Sumner 1991). At high levels, paraquat inhibits the photosynthesis of some algae in stream waters (Stevens and Sumner 1991).

Birds: Medium. The compound is moderately toxic to birds, with reported acute oral LD_{50} values of 981 mg/kg and 970 mg/kg in bobwhite and Japanese quail, respectively (Weed Science Society of America 1994). The reported 5- to 8-day dietary LC_{50} value for the compound is 4048 ppm in mallards (Weed Science Society of America 1994).

Other species: Paraquat is nontoxic to honey bees (U.S. EPA 1987d).

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18. Active constituent: **penconazole** (controls powdery mildew)

Some registered products: Topas 100 EC

Mode of Metabolism: Photolysis (Schwack and Hartmann 1994).

Common metabolites: Photolysis in isopropanol and cyclohexane resulted in considerable formation of 1-(4-chloro-beta-propylphenethyl)-1H-1,2,4-triazole (Schwack and Hartmann 1994).

Time taken for half of the initial amount of a pesticide to break down (half-life):

No information is available for half-life in soil. However, a half-life of 45 days was estimated during fermentation of wines (Navarro *et. al.* 1997).

Water solubility: None. Emulsifiable in water (Syngenta Crop Protection Pty Ltd 2001b).

Soil adsorption/mobility: High / Low. A study on the adsorption and mobility of penconazole in 19 vineyards soils in the La Rioja region of NW Spain found that the vertical leaching of penconazole is low (Sanchez-Martin et al. 2000). The fungicide was adsorped by the organic matter fraction in the soils (Sanchez-Martin et al. 2000).

Volatility: Very low. Slightly volatile (Bateman et al. 1994)

Influence of environmental factors on degradation rates:

Water	Very low. In a solid phase extraction study of pesticides from water samples showed that the recovery of penconazole improved at basic pH (Baez et al. 1997). This may indicate that penconazole may degrade in acidic waters.
Vegetation	Low. In a survey on residues in olive oil from olives treated with penconazole found that the concentration of penconazole increased with time after the last treatment (Corda, Maddau and Marras 1993). This indicates that penconazole may not be degraded by plants.
Increasing Soil pH	Low. In a solid phase extraction study of pesticides from water samples showed that the recovery of penconazole improved at basic pH (Baez et al. 1997). This may indicate that penconazole may degrade in soils with low pH (acidic soils).
Soil microorganisms	Medium. There was no accumulation of penconazole in the soil after applying four times in an apple orchard in northeastern Switzerland (Rueegg and Siegfried 1996). This indicates that penconazole may be degraded by soil microorganisms.
Concentration of active constituent	No specific data available.

Sunlight	Very high. Sunlight will degrade pencanozle because photolysis is the mode of metabolism for penconazole (Schwack and Hartmann 1994).
Temperature	Positive relationship. The manufacturers suggests to store the chemical in a closed original container in a dry, well-ventilated place as cool as possible out of direct sunlight (Syngenta Crop Protection Pty Ltd 2001b). This indicates that penconazole may degrade at high temperature.

General Information:

Topas® 100 EC with active constituent of 100 g/L penconazole is a member of DMI group of fungicides (Syngenta Crop Protection Pty Ltd 2001b). This product is slightly hazardous (WHO Hazard Class III).

Toxicity to humans:

Penconazole may be harmful if swallowed and will irritate the eyes and skin.

Toxicity to other mammals:

Tests on rats indicated (Syngenta Crop Protection Pty Ltd 2001b):

A low toxicity following single doses of the undiluted product (LD_{50} > 4000 mg/kg). A low toxicity due to skin contact with the undiluted product (LD_{50} > 3000 mg/kg). A low toxicity due to inhalation of the undiluted product (product (LC_{50} (4 h) = 5294 mg/m^3).

Penconazole technical has been tested extensively on laboratory mammals and in test-tube systems to determine chronic toxicity. No evidence of mutagenic, carcinogenic, teratogenic or reproductive effects was obtained (Syngenta Crop Protection Pty Ltd 2001b). However, the fungicide penconazole has been listed as a potential endocrine disrupter by the German Federal Environment Agency, who report that it can affect thyroid, prostate and testes weight (ENDS 1998).

Toxicity to non-mammalian species:

Aquatic organisms: Medium. Medium toxicity to fish and aquatic invertebrates (Syngenta Crop Protection Pty Ltd 2001b).

Birds: Low. Practically nontoxic to birds (Syngenta Crop Protection Pty Ltd 2001b).

Other species: Low hazard to bees (Syngenta Crop Protection Pty Ltd 2001b).

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19. Active constituent: **pyrimethanil** (controls botrytis bunch rot)

Some registered products: Scala 400 EC

Mode of Metabolism: Oxidation (Tomlin 1994).

Common metabolites: Hydroxylated derivatives of pyrimethanil followed by conjugation (Tomlin 1994).

Time taken for half of the initial amount of a pesticide to break down (half-life):

The half-life of pyrimethanil in laboratory soil column experiments was reported in the range of 27-82 days (Tomlin 1997). The half-life in soils determined from field experiments was in the range of 7-54 days (Tomlin 1997).

Water solubility: Low. 0.121 g/L at 25°C (Tomlin 1997).

Soil adsorption/mobility: High / Low. Based the estimated Koc value of 835, pyrimethanil is expected to have low mobility in soil (U.S. National Library of Medicine 2002o).

Volatility: High. Volatilisation of pyrimethanil from moist soil surfaces is expected to be an important fate process given an estimated Henry's Law constant of 2.5 x 10^{-6} atm-m^3/mole (U.S. National Library of Medicine 2002o). Pyrimethanil is not expected to volatilise from dry soil surfaces (U.S. National Library of Medicine 2002o) based upon a vapour pressure of 1.65 x 10^{-5} mm Hg (Tomlin 1997).

Influence of environmental factors on degradation rates:

Water	Very low. If released into water, pyrimethanil is expected to adsorb to suspended solids and sediment in water. Volatilisation from water surfaces is expected to be an important fate process (U.S. National Library of Medicine 2002o).
Vegetation	Low. Little metabolism occurs on fruit (Tomlin 1994)
Increasing Soil pH	Medium. Pyrimethanil may partially exist in the protonated form in acidic waters (U.S. National Library of Medicine 2002o). This indicates pyrimethanil may degrade in soil with high pH.
Soil microorganisms	No specific data available.
Concentration of active constituent	No specific data available.
Sunlight	Low. Pyrimethanil may undergo direct photolysis in the environment, but the kinetics of this reaction are unknown (U.S. National Library of Medicine 2002o).
Temperature	None. Pyrimethanil is stable for 14 days at 54°C (Tomlin 1997). This indicates that the expected soil temperatures in the fields may not influence the degradation of pyrimethanil.

General Information:

Pyrimethanilan anilinopyrimidine fungicide belongs to a new chemical group that inhibits the secretion of fungal enzymes required for the infection process and blocks cell destruction and nutrient uptake. It thereby stops germ tube extension and mycelium growth. Scala acts both protectively and curatively by contact, translaminar mobility and vapour pressure (AgrEvo 1998).

Toxicity to humans:

Pyrimethanil has been classified as a group C- chemical (possible human carcinogen) in USA. However, U.S. EPA has a reasonable certainty that no harm will result from exposures to residues of pyrimethanil (U.S. EPA 1997b). Pyrimethanil is not classified as hazardous according to criteria of worksafe Australia (Hoechst Schering Agrevo Pty Ltd. 1997).

Toxicity to other mammals:

Pyrimethanil is of low acute oral toxicity in the rat. LD_{50} = 4,149 mg/kg (males) and 5,971 mg/kg (females); an acute dermal LD_{50} > 5,000 mg/kg for both sexes; an acute inhalation LC_{50} > 1.98 mg/L; slight eye irritation; no dermal irritation; and pyrimethanil is not a sensitiser (U.S. EPA 1997b).

Toxicity to non-mammalian species:

Aquatic organisms: Very high. Pyrimethanil may cause long-term adverse effects in the aquatic environment and it is harmful to aquatic organisms (Hoechst Schering Agrevo Pty Ltd. 1997). LC_{50} = 53 mg/L (96 h) for rainbow trout.

Birds: Very low. Pyrimethanil is of very low toxicity to birds (Hoechst Schering Agrevo Pty Ltd. 1997). Acute oral LD_{50} > 200 mg/kg; 8 day dietary LC_{50} > 5200 mg/kg in duck and quail.

Other species: Non toxic to bees (Hoechst Schering Agrevo Pty Ltd. 1997).

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20. Active constituent: **simazine** (used to control weeds)

Some registered products: Flowable Simazine, Gesatop 500 SC, Gesatop 600 SC, Gesatop Granules, Simagranz, Simamax Flowable, Simamax Granules, Simazine 500, Simazine 900 DF, Simazine Liquid .

Mode of Metabolism: Mainly soil-catalyzed hydrolysis (Burkhard and Guth 1981) and microbial breakdown (Tomlin 1997).

Common metabolites: N-Desethyl simazine and 2-chloro-4,6-bisamino-s-triazine were identified as metabolites (Ruedel et al. 1993).

Time taken for half of the initial amount of a pesticide to break down (half-life):

Half-lives of simazine in soil biometer studies ranged from 32 to 91 days (Ruedel et al. 1993). Simazine is moderately persistent with an average field half- been reported (Wauchope et al. 1992). Residual activity may remain for a year after application (2 to 4 kg/ha) in high pH soils (Oregon State University 1996m).

Water solubility: Low. 5 mg/L at 20°C (Kidd and James 1991)

Soil adsorption/mobility: Low – medium / Medium. Based on Koc values ranging from 78 to 3,559 (Scribner et al. 1992; Sukop and Cogge, 1992), indicate that simazine is expected to have high to slight mobility in soil. Increasing sorption has been observed with decreasing pH (Celis et al. 1997). Simazine is moderately to poorly bound to soils (Wauchope et al. 1992). It does, however, adsorb to clays. Its low water solubility, however, makes it less mobile, limiting its leaching potential (Weed Science Society of America 1994). Simazine has little, if any, lateral movement in soil, but can be washed along with soil particles in run-off (Oregon State University 1996m).

Volatility: Low. Volatilisation of simazine from moist soil surfaces is not expected to be important given an estimated Henry's Law constant of 3.4×10^{-9} atm-cu m/mole (U.S. National Library of Medicine, 2002p). Simazine is not expected to volatilise from dry soil surfaces based on a vapour pressure of 2.2×10^{-8} mm Hg (Tomlin, 1997).

Influence of environmental factors on degradation rates:

Water	Low. The average half-life of simazine in ponds where it has been applied is 30 days, with the actual half-life dependent on the level of algae present, the degree of weed infestation, and other factors (Weed Science Society of America 1994). Simazine may undergo hydrolysis at lower pH. It does not readily undergo hydrolysis in water at pH = 7 (Weed Science Society of America 1994).
Vegetation	Medium. Plants absorb simazine mainly through the roots, with little or no foliar penetration. From the roots, it is translocated upward to the stems, leaves, and growing shoots of the plant (Kidd and James 1991; Weed Science Society of America 1994). Resistant plants readily metabolise simazine. Plants that are sensitive to simazine accumulate it unchanged (Kidd and James 1991). It is possible that livestock or wildlife grazing on these plants could be poisoned.
Increasing Soil	Low. Simazine may undergo hydrolysis at lower pH. It does not readily undergo

pH	hydrolysis in water at pH = 7 (Weed Science Society of America 1994). The half-life for degradation of simazine in Hatzenbuhl soil at pH 4.8 was 45 days and Neuhofen soil at pH 6.5 was 100 days (Burkhard and Guth 1981).
Soil microorganisms	Medium. Microbial breakdown in soil results in degradation of simazine at very variable rates, half-lives range from 27 to 102 days (median 49 days); temperature and moisture are the main factors affecting the rates (Tomlin 1997).
Concentration of active constituent	No specific data available.
Sunlight	Low. Photolysis of simazine did not occur in methanol, ethanol, butanol and water at wavelengths > 300 nm (Pape and Zabik 1970). 1,3,5-Triazines, such as simazine, have UV absorption bands whose tail extends beyond 290 nm (Jordan et al. 1970), suggesting a potential for direct photolysis.
Temperature	Positive relationship. Estimated soil hydrolysis half-lives in Wongan Hills loamy sand at 9, 20, and 28°C were 144, 37, and 21 days, respectively (Walker and Blacklow 1994). This shows that degradation of simazine increases with high temperature.

General Information:

Simazine is a selective triazine herbicide. It is used to control broad-leaved weeds and annual grasses (Oregon State University 1996m).

Toxicity to humans:

This product is of low acute toxicity and is not considered a hazard.. Product dust in the eyes may cause irritation and possible abrasion (Nufarm Australia Limited 1997). Prolonged or repeated exposure may constitute a hazard to the lungs when in dry state. Avoid inhaling dust (Nufarm Australia Limited 1997).

Toxicity to other mammals:

Simazine is slightly to practically nontoxic. The reported oral LD_{50} for technical simazine in rats and mice is >5000 mg/kg (Kidd and James 1991; Weed Science Society of America 1994); its dermal LD_{50} is 3100 mg/kg in rats and > 10,000 mg/kg in rabbits (Kidd and James 1991; Weed Science Society of America 1994). The 4-hour inhalation LC_{50} in rats is greater than 2 mg/L (Kidd and James 1991). The formulated products, in most cases, are less toxic via all routes (Weed Science Society of America 1994). Simazine is nonirritating to the skin and eyes of rabbits except at high doses (Stevens and Sumner 1991). While many mammals may be insensitive to simazine (U.S. National Library of Medicine 2002p), sheep and cattle are especially sensitive (Stevens and Sumner 1991).

Toxicity to non-mammalian species:

Aquatic organisms: Low. Simazine is slightly to practically nontoxic to aquatic species (Kidd and James 1991; Weed Science Society of America 1994). The 96-hour LC_{50} for simazine is >100 mg/L in rainbow trout, 100 mg/L (wettable powder) in bluegill sunfish, 0.100 mg/L in fathead minnows. It may have greater toxicity to Daphnia and stoneflies (Johnson and Finley 1980). A 96-hour LC_{50} of >3.7 mg/L is reported in oysters (Weed Science Society of America 1994).

Birds: Low. Simazine is practically nontoxic to birds (Kidd and James 1991). The reported LD_{50} values in mallard and Japanese quail are >4600 mg/kg and 1785 mg/kg, respectively (Kidd and James 1991). The acute dietary LD_{50} values in hens and pigeons are both greater than 5000 ppm (Ware 1986). The 8-day dietary LC_{50} in bobwhite quail is >5260 ppm and in mallard ducks is >10,000 ppm (Kidd and James 1991; Weed Science Society of America 1994).

Other species: Simazine is nontoxic to bees (Kidd and James 1991; U.S. National Library of Medicine 2002p). A soil LC_{50} in earthworms of >1000 mg/kg has been reported (U.S. National Library of Medicine 2002p).

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21. Active constituent: **sulphur- elemental** (controls powdery mildew, bunch mite, grape leaf rust mite and grape leaf blister mite)

Some registered products: Brysulf 800 WG, Cosavet DF, Country Wettasul 800, Flowable Sulphur, Flosul-SC, Kumulus DF, Microsul DF, Microthiol, Rutec Sulphur, Scarf DF, Sipcam Sulphur DF, Sulphur Spray, Thiovit Jet, Top Wettable Sulphur, wettable Sulphur, Lime Sulphur

Mode of Metabolism: Oxidation

Common metabolites: Sulphate, sulphur dioxide and organic sulphur (Jaggi, Aulakh and Sharma 1996).

Time taken for half of the initial amount of a pesticide to break down (half-life):

The half-life ranged from 12 days to 176 days in two different soils (He et al. 1994).

Water solubility: None. Practically insoluble in water (Kidd and James 1991; Crop Care Australia Pty Ltd 1995b)

Soil adsorption/mobility: High / Low. Sulphur is first oxidised to sulphate and can leach depending on soil type. Most of the sulphate was lost from 45 cm of loamy sand after 180 days while the silty clay loam showed almost no sulphate movement (Rhue and Kamprath 1973). Elemental sulfur leaches in soil as sulfate at a slow rate (Oregon State University 1995).

Volatility: None. There is no volatile component in sulphur (Crop Care Australia Pty Ltd 1995).

Influence of environmental factors on degradation rates:

Water	No specific data available.
Vegetation	Low. There is slight oxidation of sulfur to the volatile oxide. Primarily microbial reduction in and on plants; partial incorporation into physiological substances (Kidd and James 1991). Plants take up sulphur as sulphate; degradation depends on how quickly soil microorganisms can convert sulphur into sulphate (Maples, Keogh and Sabbe 1976).
Increasing Soil pH	High. Oxidation of elemental sulphur was highest in alkaline soil (Jaggi, Aulakh and Sharma 1999 1996?).
Soil microorganisms	High. Elemental sulfur is slowly converted to sulfate in soil by the action of autotrophic bacteria (Oregon State University 1995). Alkaliphilic sulphur-oxidising bacteria can oxidise elemental sulphur at 7-11 pH (Sorokin, Robertson and Kuenen 2000). When sulfur was applied in soils, total bacteria population increased, population of fungi and actinomycetes decreased and population of nitrogen fixing organisms were unaffected (Lopez-Aguirre et al. 1999).
Concentration of active constituent	High. Increasing the sulphur application rate from 50 to 100 kg/ha significantly improved in foliar sulphur concentration and content (Brockley and Sheran 1994).
Sunlight	Low. There is no volatile component in sulphur (Crop Care Australia Pty Ltd 1995).

	This indicates sulfur may not be degraded by sunlight.
Temperature	Positive relationship. Oxidation of elemental sulphur increases with higher temperatures (Jaggi, Aulakh and Sharma 1996).

General Information:

Sulphur is pale, yellow solid (lumps or powder) with a slight hydrogen sulphide odour.

Toxicity to humans:

Swallowing large amounts of sulphur may result in nausea, vomiting, diarrhoea, and may lead to hydrogen sulphide poisoning. Levels of 6-8 ppm will irritate human eyes. Exposure may result in conjunctivitis, corneal damage, cataracts, watering of the eyes, and light sensitivity. Contact with skin may result in irritation and repeated or prolonged skin contact may lead to irritant or allergic contact dermatitis, however sulphur is not absorbed through the skin. Inhalation of dust may result in respiratory irritation. Chronic exposure can cause bronchitis, which may be complicated by emphysema, bronchiectosis, or asthma.

Toxicity to other mammals:

Sulfur was reported to have a rat oral LD_{50} of greater than 5,000 mg/kg - than 8,437 mg/kg (Meister 1994; U.S. National Library of Medicine 2002q). The acute inhalation LC_{50} for 98% sulfur in rats is greater than 2.56 mg/L; and greater than 5.74 mg/L for 80 % sulfur (U.S. National Library of Medicine 2002q). Oral lowest lethal dose in rabbit is 175 mg/kg (Crop Care Australia Pty Ltd 1995b).

Toxicity to non-mammalian species:

Aquatic organisms: Very low. The 96-hour LC_{50} values for two fish species, bluegill sunfish and rainbow trout, are greater than 180 ppm in a study using a 99.5% sulfur dust formulation. The 48-hour LC_{50} for daphnia and the 96-hour LC_{50} for mysid shrimp is reported to be greater than 5,000 and 736 ppm, respectively, in a study using 90% sulfur (U.S. National Library of Medicine 2002q). In studies on ecological effects involving two fish species, daphnia, and mysid shrimp, sulfur has been shown to be practically nontoxic to the species tested (Kidd and James 1991; Meister 1994; U.S. EPA 1991).

Birds: None. Sulfur is considered nontoxic to birds (U.S. National Library of Medicine 2002q). The 8-day dietary LC_{50} for bobwhite quail is reported to be greater than 5,620 ppm in a study using a 95% sulfur wettable powder formulation (U.S. National Library of Medicine 2002q). In studies on ecological effects involving bobwhite quail, sulfur has been shown to be practically nontoxic to the species tested (U.S. EPA 1991).

Other species: Beneficial insect studies demonstrated that sulfur (98% dust and 92% wettable powder) is of low toxicity to the honeybee through contact and ingestion (U.S. National Library of Medicine 2002q; Kidd and James 1991; Meister 1994). Although there is potential for non-target organisms to be exposed to sulfur, little hazard to these species is expected to result (U.S. EPA 1991).

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22. Active constituent: **tebufenozide** (controls lightbrown apple moth and grapevine moth)

Some registered products: Mimic 700 WP

Mode of Metabolism: Photolysis (Sundaram 1997a), oxidative metabolism in insect larvae (Smagghe et al. 2001).

Common metabolites: No specific information available.

Time taken for half of the initial amount of a pesticide to break down (half-life):

	The half-life of tebufenozide in soil, sprayed at different concentration, varied between 52 - 115 days (Sundaram 1997a).
Water solubility:	None. Dispersable in water (Bayer Australia Limited 1998b).
Soil adsorption/mobility:	High / Low. Downward movement of tebufenozide in soil occurred only in trace amounts, suggesting strong soil adsorption (Sundaram 1997a).
Volatility:	Low. Volatilisation of tebufenozide depends upon the ambient temperature and the duration of air passing through the substrates (Sundaram 1997a). However the loss of tebufenozide by volatilisation was much lower compared with the loss by photolysis and rainfall (Sundaram 1997a).

Influence of environmental factors on degradation rates:

Water	Low. Persistence of tebufenozide in aquatic ecosystems was studied under laboratory and field conditions (Sundaram 1997b). The results showed that the chemical moved from treated water into sediment due to adsorption. This indicates that the water may not degrade tebufenozide.
Vegetation	No specific information available.
Increasing Soil pH	No specific information available.
Soil microorganisms	High. Safety testing of tebufenozide was carried out (Addison 1996) for effects on non-target forest soil invertebrates (earthworm and species of Collembola). Survival, growth and reproduction in soil invertebrates were unaffected by exposure at concentrations up to and including 100 times the expected environmental concentration over 10-weeks.
Concentration of active constituent	None. Sundaram (1997a) applied tebufenozide at three different rates however, there was no clear correlation between half-life and the concentration of active constituents. This indicates that concentration of active constituents may not influence the degradation of tebufenozide.
Sunlight	High. The photolysis study indicated that disappearance of tebufenozide was directly related to the duration of exposure to radiation and radiation intensity (Sundaram 1997a).
Temperature	Positive relationship. Volatilisation of tebufenozide depends upon the ambient temperature and the duration of air passing through the substrates (Sundaram 1997a). Volatilisation increases with high temperature

General Information:

Tebufenozide is a non-steroidal insect growth regulator.

Toxicity to humans:

Tebufenozide is possibly harmful if swallowed (Bayer Australia Limited 1998b) and direct contact with the eyes can cause moderate irritation. Prolonged or repeated skin contact can cause slight skin irritation and may cause slight skin sensitisation. Inhalation of dust can cause irritation of the nose, throat and lungs. Repeated over exposure to the active ingredient in this material may adversely affect reproductive function and cause blood changes.

Toxicity to other mammals:

Animal studies with technical tebufenozide show no evidence of oncogenic effect or carcinogenic effects and no teratogenic potential (Bayer Australia Limited 1998b).

LD_{50} oral (ingestion) - rat: > 5000 mg/kg ie. practically nontoxic

LD_{50} dermal (skin contact) - rat: > 2000 mg/kg ie. practically nontoxic

LC_{50} inhalation - rat: 1.8 mg/L (4hr) ie. harmful

Toxicity to non-mammalian species:

Aquatic organisms: Medium. Kreutzweiser et al. (1994) tested toxicity of tebufenozide to aquatic macroinvertebrates and the results showed that there was no feeding inhibition or lethal effect on either test species resulting from consumption of the contaminated foliage . Toxicity to fish: (active ingredient): LC_{50}: 5.7 mg/L (96 h): rainbow trout (Salmo gairdneri) LC_{50}: 3.0 mg/L (96 h): bluegill (Lepomis macrochirus) (Bayer Australia Limited 1998b).

Birds: No specific information is available.

Other species: Low hazard to bees. May be applied to plants at any time (Bayer Australia Limited 1998b). For nontarget forest soil invertebrates (earthworm and species of Collembola), survival, growth and reproduction in soil invertebrates were unaffected by exposure at concentrations up to and including 100 times the expected environmental concentration over 10-weeks (Addison 1996).

23.	**Active constituent:**	**triadimenol** (controls powdery mildew)
	Some registered products:	Bayfidan 250 EC, Triadimenol 250 EC, Tridim 250 EC
	Mode of Metabolism:	Triadimenol photodegraded readily when irradiated in methanol under ultra-violet light from a medium pressure mercury lamp to a number of photoproducts (Nag and Dureja 1999).
	Common metabolites:	Nag and Dureja (1999) concluded that triadimenol will be broken down to less toxic products in the environment.
	Time taken for half of the initial amount of a pesticide to break down (half-life):	
		Triadimenol was very persistent in clay loam and sandy loam soils with half-life >400 days (Bromilow, Evans and Nicholls, 1999b)
	Water solubility:	Very low. Emulsifiable and up to 0.15% soluble in water (Bayer Australia Limited 1998a).
	Soil adsorption/mobility:	Medium / Medium. Triadimenol residues were detectable in the leachates after 10 months of fungicide application (Petrovic et al. 1994). The concentration of triadimenol was much higher in the leachates of the sand than other soils (Petrovic et al. 1993). Triadimefon and its residues are moderately mobile and may have potential to leach to groundwater (U.S. National Library of Medicine 1995). Various fungi have been found to metabolise triadimefon to triadimenol (Deas et al. 1984). Therefore, triadimenol as a metabolite of triadimefon is expected to be moderately mobile in soil.
	Volatility:	Very low. The vapour pressure of triadimenol is very low, 0.00002 mbar at 20°C (Bayer Australia Limited 1998a), suggesting that the volatility of triadimenol is very low.

Influence of environmental factors on degradation rates:

Water	Low. Triadimefon is very stable in water and does not readily undergo hydrolysis (Kidd and James 1991). Triadimenol the common metabolite of triadimefon may also be stable in water.
Vegetation	Very low. In grapes, triadimefon does not breakdown into simpler compounds, but rather forms bigger conjugates (Bromilow, Evans and Nicholls, 1999a).
Increasing Soil pH	No specific information available.
Soil microorganisms	Very low. Toxic to bacteria (Oros and Gasztonyi 1987). This may indicate that biodegradation of triadimenol may be very slow in soil.
Concentration of active constituent	No specific information available.
Sunlight	High. Triadimenol photodegraded readily when irradiated in methanol under ultra-violet light from a medium pressure mercury lamp to a number of photoproducts (Nag and Dureja 1999).
Temperature	Positive relationship. Degradation rates of triadimenol increased about 3-fold as the temperature was increased from 5 to 18ºC (Bromilow, Evans and Nicholls, 1999a).

General Information:

Triadimenol is a systemic fungicide.

Toxicity to humans:

No adverse health effects are expected if this product is used in accordance with the label (Bayer Australia Limited 1998a). It may irritate the eyes and may produce respiratory irritation if inhaled.

Toxicity to other mammals:

Toxicity data by Bayer Australia Limited (1998a) are presented below:

The oral LD_{50} for male rats is 3700 mg/kg (ie. practically nontoxic), and for female rats is 1720 mg/kg (ie. harmful). The dermal (skin contact) LD_{50} for rats is >5000 mg/kg (ie. practically nontoxic).

Toxicity to non-mammalian species:

Aquatic organisms: High. Harmful to fish. LC_{50}: 42 mg/L (96 h): Rainbow trout (*Salmo gairdneri*). LC_{50}: 79 mg/L (96 h): Golden orfe (*Leuciscus idus*). LC_{50}: 253 mg/L (96 h): Water flea (*Daphnia magna*).

Other species: Low toxicity to bees (Bayer Australia Limited 1998a).

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24. Active constituent: **ziram** (controls black spot)

Some registered products: Fulasin DF, Ziragranz, Ziram Granuflo

Mode of Metabolism: Acid-catalysed hydrolysis (Weissmahr and Sedlak 2000). Ziram is decomposed by acids and UV radiation, but is otherwise stable (Hartley 1984). Under acidic conditions, dimethyldithiocarbamates readily decompose to form carbon disulfide and dimethylamine (Rajagopal et al. 1984).

Common metabolites:	Carbon disulfide (CS2), Dimethyldithiocarbamate, sulphate, formaldehyde, dimethylthiocarbamate, dimethylthiocarbamic acid, glucuromide (World Health Organisation 2001)
Time taken for half of the initial amount of a pesticide to break down (half-life):	30 days is estimated in the field, indicating a low to moderate persistence (Augustijn-Beckers, Hornsby and Wauchope 1994).
Water solubility:	Medium. 65 mg/L (Kidd and James 1991)
Soil adsorption/mobility:	Medium / Low. If released on land, ziram would adsorb moderately to the soil. Whilst it reportedly ionises and biodegrades in soil (Rajagopal et al. 1984), no data could be found concerning its persistence. Ziram has not been detected in groundwater (Howard 1989). In soils with medium to high content of soil organic matter, ziram will be bound moderately .
Volatility:	Low. Volatility of ziram is low (World Health Organisation 2001).

Influence of environmental factors on degradation rates:

Water	Low. Ziram is the most stable of the metallic dithiocarbamate fungicides. If it gets to the bottom bodies?? Lower levels?? of water, it may persist for months (Oregon State University 2001b).
Vegetation	High. Persistent breakdown of ziram to carbon disulphide is evident on vegetation (Oregon State University 2001b). Ethylene thiourea is the major metabolite in plants. Ethylene thiuram monosulfide and presumably ethylene thiuram disulfide and sulfur are also formed (Hartley and Kidd 1987).
Increasing Soil pH	Low. Ziram is unstable in acidic conditions (Weissmahr and Sedlak, 2000). Under acidic conditions, dimethyldithiocarbamates readily decompose to form carbon disulfide and dimethylamine (Rajagopal et al. 1984).
Soil microorganisms	Low. Ziram is toxic to bacteria. Biodegradation is slow (U.S. National Library of Medicine 2002s).
Concentration of active constituent	Low. Degradation of ziram only occurs at very low concentration (Oregon State University 2001b). Since it is fairly toxic to bacteria (Hansen 1972), biodegradation may only occur at very low concentrations.
Sunlight	Low. Ziram is decomposed by acids and UV radiation, but is otherwise stable (Hartley 1984).
Temperature	None. Ziram is stable under normal conditions and its vapour pressure is negligible at room temperature (World Health Organisation 2001). This may indicate that temperature has negligible effects on degradation of ziram.

General Information:

Ziram is a dithiocarbamate fungicide with some insect repellent properties. It is a metabolic poison of low acute toxicity to mammals: it may cause skin irritation. It is listed in World Health Organisation Hazard Class III. Ziram is toxic to zinc sensitive plants. Ziram is stable under normal conditions but decomposes in acid media. It does not accumulate in soil. Ziram is slowly absorbed from the gastrointestinal tract; through the intact skin; and by inhalation of spray mist and dusts (World Health Organisation 2001).

Toxicity to humans:

Ziram is poorly absorbed in the absence of oils. However, it may be readily absorbed into the body in the presence of oil, including through the skin. Acute exposure among industrial farm workers in former U.S.S.R. caused irritation of the skin, nose, eyes and throat. Ziram is corrosive to eyes and may cause irreversible eye damage (Oregon State University 2001b).

Toxicity to other mammals:

The oral LD_{50} for ziram is 1400 mg/kg in rats and 480 and 400 mg/kg in mice and rabbits, respectively. Ziram has an LD_{50} of 100 to 150 mg/kg in guinea pigs. The acute dermal LD_{50} in rats is greater than 6000 mg/kg.

Toxicity to non-mammalian species:

Aquatic organisms: Medium. Based on data from only one species, the goldfish, ziram appears to be moderately toxic to fish. The 5-hour LC_{50} for ziram in goldfish was between 5 and 10 mg/L (Oregon State University 2001b).

Birds: Low – medium. LD_{50} Wild Bird 100 mg/kg body weight. Ziram has been shown to have an adverse effect on body weight, to retard testicular development, and to induce degeneration in seminiferous epithelium of mature fowl (World Health Organisation 2001).

Toxicity of ziram to birds varies from essentially nontoxic to moderately toxic. Its LD_{50} is 100 mg/kg in European starlings and red-wing blackbirds. In a 2-year study, the dietary LC_{50} in quail was 3346 ppm (Smith 1992). In chickens, doses of 56 mg/kg were toxic (National Research Council 1977). Ziram has an antifertility action in laying hens. When given to chickens under unspecified conditions, there were adverse effects on body weight and retarded testicular development (U.S. National Library of Medicine 1995).

Other species: No information available.

Appendix B: Minutes of the project review workshop held at Sunraysia Horticultural Centre on 27 August 2002

Appendix B includes:

- Sample invitation to the review workshop
- Agenda for the review workshop
- Additional attachments to the invitation letter (list of invited participants and project summary)
- Minutes of the review workshop
- Printed versions of the PowerPoint presentations given by speakers

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2 August 2002

Mr David Hall
GWRDC
PO Box 2592
KENT TOWN SA 5071

Our Ref: 07792

Review of CRCV project 2.5.2: 'Retaining the *Clean and Green* image of Australian viticulture: minimising the effects of agrichemicals on the environment'

Dear David

I would like to invite you, or your nominee, to a workshop to review project 2.5.2 of the Cooperative Research Centre for Viticulture.

27th August 2002
10:30 am – 1:30 pm
Sunraysia Horticultural Centre
Cnr Eleventh St and Koorlong Ave, Irymple, Vic

The aim of the workshop is to generate interaction between industry and project staff on issues that influence the risks of environmental impacts from agrichemicals used in viticulture.

At the workshop we will present (and summarise the findings of) a comprehensive review of existing information on off-target impacts of agrichemicals. The review describes information sources and decision tools related to environmental risk assessment and eco-toxicology, monitoring techniques, critical information deficiencies and recommendations for ongoing research directions.

Your participation will clarify directions for our research, ensuring that they are aligned with industry priorities and will provide outcomes valued by industry.

Please RSVP by August 24th on 03 5051 4500.

Yours sincerely

Alison MacGregor

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Victoria
The Place To Be

Retaining the "Clean and Green" image of Australian viticulture: minimising the effects of agrochemicals on the environment. CRCV program 2.5.2

Project review workshop

August 27th, 2002
Sunraysia Horticultural Centre Conference Room
10:30 am – 1:30 pm

Agenda

10:00 *Morning tea on arrival*

10 30 **Welcome and introduction** *Keith Leamon, Institute Director Sunraysia Horticultural Centre (SHC)*

10:35 **Meeting the challenge to take increasing responsibility for our environment**
Tony Martin, Chairman CRCV, Mallee Catchment Management Authority board

10:45 **Assessing the impacts of agrochemicals in viticulture – A review**
Alison MacGregor, SHC

11:20 **Key issues that need to be addressed**
Greg Buchanan, SHC

11:30 *brief tea break*

11:40 **Research methodology to address the key issues**
Outline of three trials for 2002/03 season - *Mahabubur Mollah, SHC*

11:50 Details of trial 1: Relative risks of drift or soil contamination - *Nicholas Woods, Centre for Pesticide Safety and Application, UQ.*

12:05 Details of trial 2: Leaching of soluble agrochemicals. - *Mahabubur Mollah*

12:15 Details of trial 3: Accumulation of agrochemicals in vineyard soils. - *Mahabubur Mollah*

12:25 **Project deliverables and outcomes, and opportunities to expand the program** - *Alison MacGregor, SHC*

12:35 **Facilitated discussion about the implications and benefits of the project** - *Facilitated by Stephen Kelly*

1:20 **Summary of the discussion - directions and priorities**

1:30 *Close and lunch*

List of invited workshop participants

Mr	Ian Ballantyne	Project Manager, Mallee Catchment Management Authority
Dr	Anne-Maree Boland	Environmental Management Systems, NRE Knoxfield
Dr	Greg Buchanan	Group Leader, Crop Production, NRE Mildura
Ms	Joan Burns	Chairman, Mallee Catchment Management Authority
Mr	Cecil Camilleri	Yalumba Wine Company
Mr	Merv Cupper	Chairman, Mallee Irrigation Environment Committee
Mr	Michael de Palma	Chairman, Vic. & Murray Valley Wine Grape Growers' Council Inc.
Ms	Kerry Degaris	Research Viticulturist, McWilliams Wines
Mr	Brian Englefield	Victorian & Murray Valley Wine Grape Growers' Council Inc.
Mr.	Colin Free	Mid Murray Winegrape Growers Association
Dr	DeAnn Glenn	Program Manager, GWRDC
Mr	David Hall	Executive Director, GWRDC
Dr.	Jim Hardie	CEO, CRC for Viticulture
Mr	Rob Hayes	Viticulturist, Milburn Park Winery
Mr	Dick Hilder	Viticulturist, Rosemount Estate
Prof	Ary Hoffmann	Director, Centre for Environmental Stress and Adaptation Research, La Trobe University
Mr	Russell Johnstone	Viticulturist, Orlando Wyndham
Mr	Peter Jones	Chairman, Australian Dried Fruits Association
Mr	Keith Leamon	Director, Sunraysia Horticultural Centre
Ms	Inca Lee	Viticulturist, Orlando Wyndham
Ms	Alison MacGregor	Research Scientist, Sunraysia Horticultural Centre
Mr	Barrie MacMillan	Mallee CMA
Mr	Tony Martin	Chairman, Cooperative Research Centre for Viticulture
Ms.	Di McArthur	Executive Officer, Vineyard Association of Tasmania Inc
Ms	Sue McConnell	Group Leader, Crop Quality, Sunraysia Horticultural Ce
Mr.	David McCulloch	Chief Executive, Wine Industry Association of WA Inc
Dr	Sean Merideth	Manager, Lower Basin Laboratory, Murray Darling Freshwater Research Centre
Dr	Mahabubur Mollah	Agricultural Engineer, Sunraysia Horticultural Centre
Mr	Alan Roberts	Chemical Standards Officer, NRE Regional Office - North West
Mr.	Graham Robertson	Chairman, ADFA
Mr	Alex Sas	Viticulturist, BRL Hardy Limited
Mr	Ross Skinner	Executive Officer, Horticulture Australia
Dr	Mark Smith	Viticulturist, Southcorp Wines Pty Ltd
Mr	David Thompson	Group Production Manager, Simeon Wines
Mr.	Benjamin Vagnarelli	Vineyard Manager, Banrock Station Wine & Wetland Centre
Dr	Rob Walker	Program Leader, CSIRO Plant Industry
Mr	Graham Wellman	Viticulturist, Dorian Estate Winery, Beringer Blass
Mr	Damien Wells	Mallee CMA
Mr	Richard Wells	Viticulturist, LWRRDC Grower Representative
Mr.	Bill Wilden	Viticulturist, BRL Hardy Wines - Berri Estates
Mr	Nicholas Woods	Director, Centre for Pesticide Application and Safety, School of Agriculture and Horticulture, University of Queensland, Gatton.
Mr.	Kevin Pfeiffer, OAM	General Manager Operations, Simeon Wines – Austvin

Retaining the "Clean and Green" image of Australian viticulture: minimising the effects of agrochemicals on the environment. CRCV program 2.5.2

Project review workshop

August 27th, 2002
Sunraysia Horticultural Centre Conference Room
10:30 am – 1:30 pm

Minutes

Present:

Ian Ballantyne, Chris Biesaga, Anne-Maree Boland, Greg Buchanan, Simone Crothers, Louise Deed, Geoff Furness, DeAnn Glenn, Peter Jones, Keith Leamon, Alison MacGregor, Tony Martin, Sue McConnell, Shaun Merideth, Mahabubur Mollah, Mark Smith, Rob Walker, Greg Walsh, Richard Wells, Nicholas Woods.

Apologies:

Ross Skinner, Joan Burns, Susan Byrne, Cecil Camilleri Michael de Palma, Kerry Degaris, Jim Grant, David Hall, Rob Hayes, Jim Hardie, Ary Hoffmann, Inca Lee, Barrie MacMillan, David McCulloch, Mark McKenzie, Richard Mintern, Kevin Pfeiffer, Alan Roberts, Alex Sas, David Thompson, Ben Vagnarelli, Graeme Wellman, Damien Wells, Bill Wilden.

Welcome and introduction - *Keith Leamon (Institute Director Sunraysia Horticultural Centre).*

Today we are presenting the findings of a review conducted during the last year by Alison MacGregor and Mahabubur Mollah. Three copies are available today for key stakeholders. We will now incorporate the discussion and outcomes of today as an appendix into the report and copies will be posted to participants in the next fortnight.

Meeting the challenge to take increasing responsibility for our environment. - *Tony Martin (CRCV Chairman and member of the Mallee CMA).*

Governments and the CRCV have agreed to the development of an EMS code of conduct. Meanwhile growers need education to direct their usage. We have MRL/residue type information but we don't know about appropriate chemical choices for environmental protection. The legacy of some now outdated practices (OC and arsenic use) may still come back to haunt us (Adelaide Hills example).

The 'clean and green' flag is one we should be nervous to wave too vigorously. One wrong move and we could blow the image. It is very hard to support a claim of being 'clean and green'. Yet the market wants reassurance that we are clean and green.

Marketers are donating more and more money to environmental causes to show customers that they understand EMS, but growers need to embrace EMS. Growers will want to know what is in it for them. A Federal grant from AFFA was recently announced, that will assist some growers to develop an EMS, but income has to be less than $35K.

Under the *Living Murray* program, which aims to return water to the Murray and increase environmental flows, it may become very prudent for an irrigator to have an EMS. If there is a

mandatory 'claw back' of water, an EMS may indeed become a pre-requisite for a grower to maintain their water allocation. To develop an EMS means knowing what impacts irrigation has, for which growers will need the sort of tools proposed in CRCV Project 2.5.2. Growers will also need simple ways to measure off target movement.

Presentations

The PowerPoint slides presented by the presenters below are provided at the end of Appendix B. The key issues raised in the review presentation are outlined in the Executive Summary (page 3). The hypotheses and methods proposed in the presentations on research methodology are described in detail in section 10.

Assessing the impacts of agrochemicals in viticulture – A review. - *Alison MacGregor, SHC*

Key issues that need to be addressed - *Greg Buchanan, SHC*

Research methodology to address the key issues

Outline of three trials for 2002/03 season - *Mahabubur Mollah, SHC*

Details of trial 1: Relative risks of drift or soil contamination - *Nicholas Woods, Centre for Pesticide Safety and Application, UQ*.

Details of trial 2: Leaching of soluble agrochemicals. - *Mahabubur Mollah*

Details of trial 3: Accumulation of agrochemicals in vineyard soils. - *Mahabubur Mollah*

Project deliverables and outcomes, and opportunities to expand the program - *Alison MacGregor, SHC*

The project deliverables promised in the original proposal to GWRDC were:

a) Review report and industry workshop

b) Recommend models suited to predicting drift or leaching

c) Checklist of potential environmental impacts

d) Modifications to best Practices for chemical use based on research data.

e) Grower friendly kit for monitoring drift and soil-water contamination

f) Training of extension personnel

g) Policy recommendations

Question to the audience: *Is it still appropriate to maintain all these objectives for the project, or do they need modifying in the light of the discussions today?*

Discussion

A) The review (content, process and implications)

- The average grower needs readily accessible information in order to chose between management options and to make decisions. There will need to be a process for people to get involved in this topic, like the assistance provided for growers using IPM (RW).
- When the EPA make decisions they default to worst case modelled scenarios unless there is data to suggest that a situation is not as severe as worst case (DG).

- Growers will need specific recommendations about what to use or what to do, or else they rely on their own (sometimes less informed) judgement. This means that industry and government need to get past their fear of making specific recommendations (PJ).
- Chemical retailers need good information, as they are an important source of information for growers making chemical choices.
- To get more information out to industry, we need direct access to data and other information on environmental impacts of specific agrochemical products, for example the type of information available in Public Release Summaries from the NRA. We need a mechanism for this information to feed straight into industry, so that growers have confidence that they are getting the right information for making decisions (MS).

B) Mass balance experiments to ascertain relative importance of spray drift versus soil contamination

- Isn't it easier to measure what lands than what goes elsewhere, and then determine the off target component by extracting what lands from what was delivered? (*TM*).
- Easier, yes, but not as informative because we wouldn't learn the relative importance of drift compared to run-off (*AM*).
- How will we relate the 'good' sprayer and 'bad' sprayer drift and run-off data, from our narrow range of sprayers, to the breadth of machinery used across the industry? (?).
- The range of sprayers we use will reflect some best and worst cases, ie show extremes of drift and run-off. This initial season pilot study aims to identify what those extremes are (*NW*).
- The drift trials need to address the variation that will exist if sprays are directed at bare canes or small canopy early season, compared to full canopy, because lots of drift is inevitable when spraying sparse canopy early season. Also, the reality is that when you have to spray, you have to spray, yet conditions (wind) from start to end of tank will vary (*RW*).
- Using the drift models you can, to some extent, manipulate the variables. We can do this later, once we have the basic data from the wind tunnel and pilot field trial. (*NW*).
- How do you scale up from drift trials at the vine row level to a catchment level? (*IB*).
- The cotton industry has modelled endosulfan flux at the catchment level in a cotton valley, by scaling up from drift trials. There is a good paper on this that we should see (*NW*).

C) Leaching and soil accumulation experiments

- Will we test drainage water in the perched water table? (*IB*)
- Copper issue is a big one (*MS*).
- It is important that we get a correct history of copper usage on sampled vineyards.
- Cultivations may make a big difference.
- It is very important that we use controlled experiments, otherwise we won't be able to interpret the results. Be very careful using groundwater access tubes as these are a classic place for contamination to enter the groundwater, and give biased results (*RW*)
- There are a lot of assumptions about Red Cliffs Catchment 8 that need to be cleared up before we interpret too much from this site (*AB*).
- Ceramic samplers need to be calibrated. In nitrate work (in catchment 8) there was a lot of variability. Also, the samplers don't tell you how much is going into drains. (*AB*)

- Talk to Rob Brambley about the precision viticulture project, in particular for ideas about sampling positions, as they have data on many vineyards. (*DG*)

D) Project deliverables and outcomes, and opportunities to expand the program

- Alter the word 'impacts' in point c) to 'risks', to sound less condemning (*TM*).
- Question: What form would policy recommendations take? (*MS*).
- Grape industry can put pressure onto EA and NRA to be include more relevant data requirements into chemical review process, as they pressured NRA to consider overseas MRLs and trade when setting MRLs and withholding periods– a decision now reflected in NRA policy and very much to industries advantage (*AM*).
- NAP may fund a project to look at buffer zones, through the Mallee CMA. This could be a good linkage (*IB*).
- A 'grower friendly kit' should be for sampling rather than monitoring (analysis or interpretation). Leave monitoring to the experts.
- Chemical recommendations (to protect the environment) must take into account the need for best management, ie not compromise disease or pest control.
- Question: will results be chemical specific, or will the results be transferable to other similar chemicals or similar use situations?
- Questions : What will be the implication of mixing chemicals together in tank mixes?
- Growers will need to be able to make decisions based on soil types, ground water levels etc.
- The project may not change practices but it may give us a give us a focus for further research work.
- Do an evaluation plan for extension, adoption etc.
- We need to determine what level of information the grower wants to know. Growers probably want to know 'what is the potential risk to the environment?'
- It is premature to focus on extension activities at the cost of collecting good raw data. Leave the extension for the next project round and focus on getting data in this project. Drop the last three points from the list above of promises to GWRDC (*General*).

Facilitated discussion about the implications and benefits of the project - Facilitated by Stephen Kelly

Highlights about the project, the information presented or the discussions

- The way the team have come together (*MS*)
- The link between the grape industry NRE and Gatton is good (*GB*)
- It is good that we are on the front foot. The cotton industry had to do all this work but they still fight for credibility because they started behind (*RW*)
- The review seems comprehensive (*SM*)
- There seems to be good balance in the proposed research (*GF*)
- There is obviously a shared concern among all sectors (participants) regarding the importance of the issues (*KL*)
- The process of developing an EMS for viticulture, and the VERA tool, identified gaps. Project 2.5.2 fills one of those gaps (*AB*).

- The interrelationships are good – This process takes focus away from production and into environmental impacts (*IB*).

Concerns about the project or process or about related issues:

- Government agencies are making policy on models that aren't tested. Our challenge is to test things (*PJ*).
- It is amazing that the Europeans cannot reach consensus on risk models (*LD*).
- Europeans won't harmonise any of their pesticide legislation, which makes our position look simple and easy to manage (*GF*).
- Having sound aims in the project is one thing, but more importantly we **must** convince growers that we are not proposing anything that will increase the risk of crop damage or undermine their security (*RW*).
- We have a lot of data now to help growers set up machinery, so they won't be left without support to, for example, reduce drift (*GF*).
- Telling growers to set machinery up well is not sufficient unless they can also judge whether one set up causes more or less drift than another, and how their drift compares to benchmarks (*AM*).
- Warning. If we set up any demonstration trials for grower groups then we have to use sites and practices that are typical. For example, don't use metalaxyl. Use a chemical that more people use. We must use majority equip, canopies, varieties, irrigation, etc. If it's not a good commercial site, growers won't respect the whole project. It's important to retain credibility with growers (*MS, RW, KL*)
- Lots of the decisions about what chemical to use, what site to use, can be resolved at the hypothesis stage. Be clear about the hypothesis, and then be clear about how to defend it (*SM*).
- Its still hard to visualise what a grower will be able to do with the results, what the project will do for viticulture. Adoption or interest among the industry will depend on perceptions about the project (*DG*).
- Lead growers adopt if they can see a reason to go with a new practice or idea (*LD*)
- The project may show that the industry is not putting the environment at risk, ie it might show that things aren't too bad (*GF*).
- We're already saying that we're 'clean and green'. What if we now suddenly find that the trigger value concentrations are so low that no one can spray? (*PJ*)
- The NRA gives great credence to real data. Usually there isn't any data to allay fears about potential risks but once data exists it can be very useful to halt a panic, or a panic policy response (*NW*).
- We need to allay community fear about drift, which causes disputes between neighbours (*RW*).
- Spraying causes drift. What the industry needs is a means to minimise drift. To achieve that we need to understand the mechanisms/dynamics of drift (*NW*).
- We are muddling the issues. The real issue is 'what are the potential risks to the environment?' The project needs to look at worst cases (*IB, GB*)
- Water is so expensive, no one should have drains running (*RW*).
- In that case the results may make farmers look good (*SM*).

- It sounds as though the outcome should focus on acquisition of knowledge, not worry about adoption (*SK*).
- Don't put too much emphasis on extension at the cost of research, ie don't get distracted (*MS*)
- Be careful about ground water sampling. Contact Greg Hoxley, hyrogeologist, as he knows lots about the soil profile/water relationships and also the groundwater (*IB*).
- West Australian leaching trials (P Mathieson) may be valuable to the project (*MS*).
- Should we ignore canopy applications and just focus on soil applications? (*DG*)
- Set things up to have least variability (*?*).
- We must apply treatments that growers apply, in ways they use them, or we will lose credibility! Using herbicide it is easier to apply a standard application than from a high volume canopy spray. This is a good argument for using herbicides for leaching experiment (*General*)
- Please include some risk assessment as growers would like information from this project in defence of spraying, ie information to allay concerns of neighbours. The project could produce/promote some good news stories to calm concerns re drift (*RW*).
- Risk assessment may go beyond the responsibility/scope of this project (*DG*).

Directions and priorities

- Planned research is appropriate.
- Credibility of the project will depend on the relevance of practices in our trials.
- Don't put too much emphasis on extension at the cost of research. Focus on the top three deliverables. Look at number 4. The last three deliverables may be appropriate, but must not come at the expense of the first three deliverables.
- Trials must reflect current grower practices.

2:30 pm - Close and lunch