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Retaining the clean and green image of Australian viticulture: minimising the effects of agrochemicals on the environment



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RETAINING THE 'CLEAN AND GREEN' IMAGE OF AUSTRALIAN VITICULTURE: MINIMISING THE EFFECTS OF AGROCHEMICALS ON THE ENVIRONMENT

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ABSTRACT

This research has provided data on the movement of key agrochemicals through air, soil and water within and beyond vineyards, which can be used to improve Best Management Practices that minimise the potential environmental impacts of vineyard spraying.

An initial scoping study identified spray drift, leaching of agrochemicals through vineyard soils and the accumulation of copper in vineyard soils as being key issues to investigate further. Twenty-four agrochemicals were ranked according to their leaching potential, persistence in soil and toxicity.

Spray drift field trials showed that sprays leaving the vineyard as drift, or wasted as ground deposits, accounted for 7 - 31% of the sprayer output. This was influenced primarily by how well the air and spray plume were directed at that canopy rather than nozzle type. Fine droplets did not have high associated drift if they were applied using a well set-up, directed sprayer**.**

Accumulation of copper was assessed in a national survey of nearly 100 vineyard soils. Copper concentrations ranged from 5 – 223 mg/kg (average 60 mg/kg). These values are lower than are reported in European vineyards (130 - 1280 mg/kg), but exceeded the ANZECC soil quality guideline value in 38% of the soils sampled. The potential impact of these concentrations on soil health, if any, is yet to be determined.

Leaching trials confirmed that time-integrated, solvent-filled, passive samplers are a cost-effective tool for monitoring agrochemicals in drainage water, while ceramic and rhizon suction cups for extracting soil water were not suitable for this task.

Field validation of a Pesticide Impact Risk Index (PIRI) model showed that PIRI could predict the leaching risk of several, but not all, agrochemicals from irrigated horticultural properties. With further validation, combined with the use of tools such as passive samplers, the PIRI model could potentially be used to generate vineyard-specific information about leaching risk.

EXECUTIVE SUMMARY

This report describes work conducted between 2001 and 2005 that aimed to understand and measure the movement of key agrochemicals through air, soil and water, within and beyond vineyards.

A scoping study, conducted prior to doing any experimental work, addressed A) current knowledge on known or predicted environmental impacts of key agrochemicals used in Australian viticulture, and B) techniques to predict and measure movement of agrochemicals and to assess impacts. The scoping study, provided to Grape and Wine Research and Development Corporation, concluded that off-target movement and non-target impacts of agrochemicals used in vineyards are primarily caused by:

- Spray drift, potentially impacting on nearby crops, housing, and terrestrial or aquatic species;
- Leaching, potentially resulting in contamination of water courses and affecting aquatic species;
- Accumulation of agrochemicals in soil, potentially impacting on soil health and ultimately vineyard sustainability.

Field trials were conducted to quantify off-target movement of agrochemicals in commercial vineyards that represented a range of soil types, irrigation management and agrochemical use.

Spray drift trials showed that the sprayer-nozzle combination influences the distribution of aerial and ground deposits, rather than these being influenced just by the sprayer or the nozzle choice. Contrary to an international trend towards regulating for use of 'medium' or 'coarse' nozzles to minimise the risk of drift, this study indicated that 'fine' nozzles could be used responsibly in a well-directed sprayer. Sedimenting drift recovered from the ground within 10 metres of the sprayed row represented the greatest (measured) proportion of off-target loss (7 - 24% of the sprayer output). Aerial drift represented between 0.06 and 7% of sprayer output. The worst losses were associated with spraying a 'fine' droplet from a sprayer that had a poorly directed spray plume. However spraying fine droplets using a well set-up, directed sprayer caused less airborne drift than most other sprayer-nozzle combinations trialed.

Accumulation of copper was assessed in a national survey of nearly 100 vineyards. Almost all the vineyards surveyed (96%) had elevated soil copper concentrations compared to the background soil concentration in their region (average increase 49 mg/kg). While copper concentrations were generally much lower (range 5 – 222 mg/kg) than those reported as found in European vineyard soils (130 - 1280 mg/kg), the data suggested that use of copper-based fungicides has resulted in some copper accumulation in Australian viticultural soils. The extent of copper accumulation appears to be related to management and soil factors, including total amount of copper applied, soil pH, salinity and exchangeable sodium and calcium. Thirty eight percent of the vineyards surveyed, in eight out of ten grape-growing regions, had soil copper concentrations that exceeded the ANZECC Soil Quality guidelines.

Leaching trials found that traces of agrochemical were leaching into irrigation drainage from vineyards and other horticultural properties. Because of their high risk of leaching, and their detection in drainage water, use of some agrochemicals on sandy, irrigated soils should be avoided. This issue warrants review by the industry.

The incidence of detection of agrochemicals tended to reflect the predicted risks of leaching. Two compounds that were deemed low risk, according to a leaching model, were detected in more than half the drainage water samples. Another two, deemed as 'no risk' because they were not used at the sites, appeared in 20-30% of samples. These results have highlighted the need to include agrochemicals used in other enterprises within a landscape in risk assessments and monitoring programs in the vineyard.

Modelling to predict the behaviour of agrochemicals applied in the vineyards: Results of the field trials were compared with predicted behaviours from models. The vineyard drift data concurred with predictions of drift and data from other studies except with regard to the effect

of droplet size. Sprayer configuration affected spray drift behaviour and this is difficult to address in a model. Pesticide Impact Risk Index (PIRI) predictions of the risk of leaching were based on detailed site information regarding soil type, irrigation and chemical use for 7 drainage sites. The PIRI model predicted a high risk of simazine leaching and a low risk of chlorothalonil or methidathion leaching and this was supported by field data. However, the PIRI model underestimated the risk of dicofol or chlorpyrifos leaching. With inclusion of site-specific information and further validation against field data, the PIRI model has potential to be a very useful tool for predicting leaching risk from vineyards.

Tools for monitoring agrochemical movement: Throughout this project we aimed to use and evaluate methods that vineyard managers might also be able to use to monitor off-target movement or impacts of agrochemicals as part of their Environmental Management Systems.

The solvent-filled 'passive' water sampler, used to monitor chemicals in drainage water, was found to be inexpensive to make, simple to use, absorb a relevant range of different agrochemicals, reliable in water that had fluctuating concentrations of agrochemical, and well suited to being used in irrigation drains. Being recent technology, at this stage not all agrochemicals are captured by the passive samplers. Also, calibrations and methods for analysis are still being refined, and only a few commercial laboratories can currently recover and measure agrochemicals from the solvents. Analysis of these passive samplers requires a commercial laboratory. However extracting and measuring agrochemical from the solvent involves a simpler sample clean-up than standard analysis of agrochemicals in soil or plant material, making the samplers relatively fast and cheap to analyse.

Standardised methods for collecting drift, under development in Europe, are not suitable for vineyard managers as environmental self-auditing tools. However pigments, water sensitive papers and other tracers can provide qualitative data about off-target losses from vineyards.

The scoping study and the field research reported here have provided data that industry can use to develop and improve best management practices that minimise the potential environmental impacts of vineyard spraying.

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ABBREVIATIONS AND DEFINITIONS USED IN THIS REPORT

ADFA	Australian Dried Fruits Association
APVMA	Agricultural Pesticides & Veterinary Medicines Authority
AWBC	Australian Wine and Brandy Corporation
BMP	Best Management Practice
CESAR	The Centre for Environmental Stress and Adaptation Research
CMA	Catchment Management Authority
CPAS	Centre for Pesticide Application and Safety, University of Qld, Gatton
CRCV	Cooperative Research Centre for Viticulture, Adelaide
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DE&C	Department of Environment & Conservation (NSW)
DPIW&E	Department of Primary Industries, Water & Environment (TAS)
EA	Environment Australia
ELISA	Enzyme Linked Immuno-Sorbent Assays
EPA	Environment Protection Authority
GC	Gas Chromatography
GWRDC	Grape and Wine Research and Development Corporation
LAI	Leaf Area Index
LOR	Limit Of Reporting
PIRI	Pesticide Impact Risk Index
RMIT	Royal Melbourne Institute of Technology
SARDI	South Australian Research and Development Institute
SDTF	Spray Drift Task Force
VERA	Viticare Environmental Risk Assessment
VMD	Volume Median Diameter
VD_{10}	Volume diameter 10%
VD_{90}	Volume diameter 90%
WINEC	Wine Industry National Environment Committee
WSP	Water sensitive paper

Agrochemical definition: For the purpose of this report, the term agrochemical is used to mean insecticide, fungicide or herbicide.

SECTION 1

INTRODUCTION AND PROJECT OBJECTIVES

The assessment of environmental impacts due to agrochemical use is emerging as a key area of policy development and research investment within agricultural industries in Australia. Industries are seeking to: a) increase on-farm sustainability, b) reduce the environmental damage caused by farm practices, and c) secure their position in a competitive marketplace by reassuring customers that their product is eco-friendly. However, since the early 1990s consumers in our key markets have questioned the "Clean and Green" image of Australian viticultural practices.

Based on a conservative spray program to protect against powdery and downy mildew, Botrytis, phomopsis (or black spot) and lightbrown apple moth, 150,561 hectares of Australian vineyards (ABS 2005) will have 4 million litres (before dilution) of agrochemicals sprayed on them each year. However, there is very little information in the public domain about the actual or potential off-target movement or environmental impacts of viticultural chemical usage at the regional level.

Concerns about agrochemicals can be catalysts to inflame community concerns. Fears about off-target impacts of viticulture among consumers and communities in North America and Europe have been exacerbated by, for example, the detection of agrochemicals in waterways and altered soil biology in Europe due to prolonged use of copper. Europe is increasingly restricting agrochemical use in vineyards. Copper use for example, is restricted to reduce its impact on soil, and the height of sprayer outlets (nozzles) is also restricted. Growers are encouraged to use tunnel sprayers for controlled and localised treatments in vineyards to minimise agrochemical drift and run-off onto soil. Drift classifications for vines and other crops (Ganzelmeier & Rautmann 2000; Walklate & Miller 2000) and drift modelling (Ganzelmeier et al. 1995; Hewitt 2000) have led to the EU, UK and USA prescribing 'no-spray' buffer zones around spray areas.

In 2000, prior to this project (CRV01/04) commencing, the grape industries in South Africa, New Zealand and Europe were progressing with defining Best Management Practices (BMPs) to minimise environmental impacts. These included strategic selection of chemicals and reducing the total amounts of agrochemical applied in vineyards (Borgo 2000; Coulon & Senetac 2000; Jordan 1997; Tromp & Marais 2000). New Zealand and South Africa had already implemented auditable Integrated Winegrape Production programs, with a goal of "eco-" brand recognition (David Jordan, Sustainable Viticulture Scheme, NZ, personal communication 2000; Tromp & Marais 2000). The BMPs varied between, and even within countries, to address perceived risks.

In 2001, when this project had just begun, the Australian wine industry had been exploring management systems to reduce environmental impacts, but with respect to chemical use the recommendations produced were very general. They lacked regional relevance and growers had no means to assess actual impacts of their practices. The CRCV 'Environmental Management Systems' and DPI 'Naturally Victorian' programs underway at that time aimed, by promoting BMPs, to increase adoption of management options that minimise impacts. Those programs also aimed to identify gaps in knowledge, and it became clear that one gap was lack of local and site specific data on which to base BMPs for chemical use.

Potential impacts of agrochemicals on the environment are considered by Environment Australia (EA) during the registration process of agrochemicals. EA's review is based on: a) drift modelling, b) predicted concentration in a 15-cm depth of water assuming spray lands on water, and c) lethal concentrations to a range of test species (Sinclair 2000). EA lack the data or models to predict leaching or drainage of chemicals into waterways (Sinclair 2000). The Agricultural Pesticides & Veterinary Medicines Authority (APVMA) and EA do not require

chemical companies to provide data generated in Australia. The data used is not in the public domain, and not easy for a lay-person to interpret or context in their own vineyard situation.

Prioritising and recommending viticultural chemicals according to their risks to the environment would be valid and defensible once a comprehensive review and interpretation of existing relevant information was coupled with field validation of predicted behaviours of chemicals.

1.1 Project objectives

The project objectives were to:

1) Provide industry with a comprehensive review of: a) current knowledge on known or predicted environmental impacts of key agrochemicals used in Australian viticulture, and b) techniques to predict and measure movement of agrochemicals and to assess impacts.
2) Evaluate simulation models and risk quotients for predicting agrochemical behaviour in areas around vineyards, and basic tools for measuring movement or impacts of agrochemicals.
3) Measure movement of key agrochemicals in commercial vineyards representing a range of soil types, soil water behaviours, climates and agrochemical application practices, in order to ground-truth predicted behaviours.

SECTION 2

2001-2002 SCOPING STUDY TO REVIEW EXISTING INFORMATION AND DECISION SUPPORT TOOLS RELATED TO THE OFF-TARGET MOVEMENT OR IMPACTS OF AGROCHEMICALS USED IN VITICULTURE

The first year (2001-2002) of this project was a scoping study to review published and unpublished information on actual or likely impacts of vineyard sprays on the environment, and decision support tools. A range of existing sampling and analysis techniques were reviewed for their suitability as ready-to-use tools for growers to monitor soil, water, air or biota within or around a vineyard. Travel to viticultural, spray application and ecotoxicology research centres provided additional opportunity to enhance networks, review and discuss techniques.

The scoping study considered published literature and concurrent research relating to:

- legislation intended 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 agrochemicals in air/soil/water
- biological significance of the level of chemical present in the environment.

The report, 'Review of the potential for agrochemicals used in viticulture to impact on the environment' (Mollah & MacGregor 2002) was provided to GWRDC and results were presented to an Industry Reference Group in August 2002. The report included proposed research for years 2-4 of the project.

2.1 SUMMARY OF INFORMATION INCLUDED IN THE SCOPING STUDY REPORT

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 environmental impact. However Most 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. Futhermore, 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 grape growers 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.

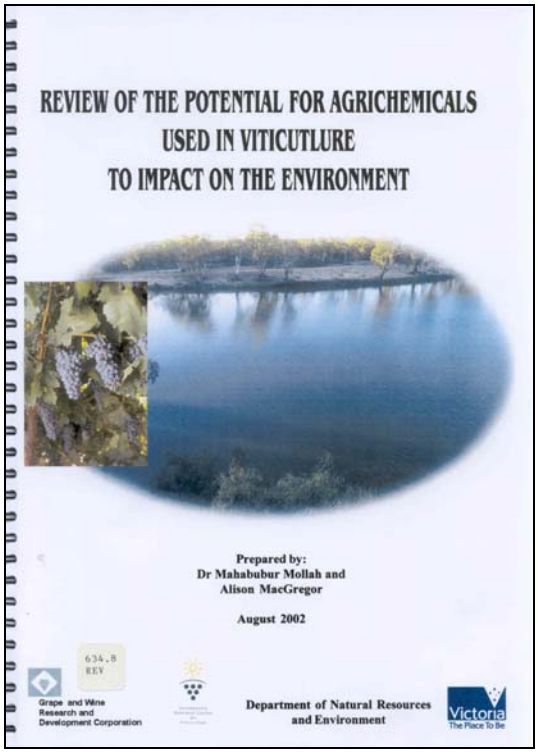


Figure 2.1: Review document provided to GWRDC and CRCV in August 2002

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. Once agrochemicals break down in the environment, they form products usually less toxic than the parent compound. The original agrochemical and the breakdown products may both redistribute within the application site or move off site.

Solubility in water and adsorption to soil are both 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 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 profile at a moderate rate. The degree of accumulation or persistence of a particular agrochemical in soil depends on the percentage of organic matter and clay present in the soil. Accumulation will be higher in soils with higher 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 them to comply with such protocols, for example with respect to selection and use of low risk chemicals.

The environmental data reviewed by APVMA and EA when chemicals are registered is not in the 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 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) and Soil Plant Atmosphere System Model (SPASMO) are useful tools to compare risks of particular practices, and Viticare Environmental Risk Assessment (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.

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

Various models have been developed internationally to predict movement of agrochemicals and to estimate environmental concentrations in air, soil and water. The models are being continuously validated and improved, but all have limitations and are no substitute for field data collected by monitoring.

Current drift models describing vineyard spraying contain limited data, but are being improved as field data becomes available.

The available leaching models present a trade-off between simplicity and accuracy and few leaching models make predictions relevant to Australian soils. 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.

Field data collected during this project should be compared with the estimates from models 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. Analytical methods preferred in standard protocols are laboratory-based and expensive.

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 techniques.

It is recommended that the suitability and accuracy of cheap and simple-to-use tools such as Enzyme Linked Immuno-Sorbent Assays (ELISA) kits for measuring agrochemicals, and the photometer for measuring metals in soil and water from vineyards, be tested for their merit as tools for industry to use.

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 under way 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 the SA Environment Protection Authority (EPA) and 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 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.

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?

2.2 CONCLUSIONS AND RECOMMENDATIONS

Off-target movement and non-target impacts of agrochemicals used in vineyards are primarily caused by:

a) spray drift, which may impact on nearby crops, housing, and terrestrial or aquatic species

b) leaching, which may contaminate water courses, affecting aquatic species

c) accumulation of agrochemicals in soil, which may impact on soil health and ultimately vineyard sustainability.

Recommendations from the scoping study, presented to an industry reference group in August 2002, were that the project staff:

- Predict spray behaviour from nozzles in wind tunnel experiments and model the spray plume using the Gaussian diffusion model.
- Measure distribution of spray drift in vineyards by collecting drift samples from collectors on towers and on the ground. Investigate the combination of four nozzle types and two nozzle pressures using 'worst', 'average' and 'best' spray applicators. Determine relative risks of drift versus soil contamination from spraying.
- Monitor the movement of agrochemicals with high leaching potential (for example simazine or metalaxyl) through soil profiles 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 concentrations are linked to history of use of agrochemicals containing copper and whether bioavailable copper is approaching concentrations known to impact on soil organisms[1].

[1] Accumulation of copper in European vineyard soils has led to its use being restricted in various countries. For this reason copper was identified as being a priority agrochemical to consider in studies to determine its accumulation in soil.

SECTION 3

VINEYARD TRIALS TO ASSESS THE PROPORTION OF AGROCHEMICAL LEAVING THE VINEYARD AS DRIFT

3.1 INTRODUCTION AND AIMS

The high priority that Australian grape growers place on improving the efficiency of their spray applications is indicated by the high proportion that participated, between 1998 and 2004, in the 3-day *Viticulture Research to Practice*® training workshop on vineyard spray application (Agriculture Victoria Services, 2002).

The training workshop focused on sprayer configuration and calibration, but also addressed social and environmental responsibilities such as awareness zones around vineyards, neighbour notification and buffers. Discussion about drift was necessarily limited to general principles as outlined in the Australian Guidelines on Minimising Drift Risk (PISC, 2002). This was because a) growers cannot always tell if they are causing drift; b) drift risk changes as the canopy develops; and c) canopy types and spray equipment vary widely between vineyards. Growers were merely encouraged to adhere to the Guidelines (PISC 2002), i.e. to direct the spray plume into the crop canopy; to define an 'awareness zone' downwind; to use existing rows as unsprayed buffers; and to spray rows near the edge of the crop from the downwind side only.

Industry documents that recommend processes for environmental management, such as VERA (Tee, undated) and the Code of Environmental Best Practice for Viticulture: Sunraysia Region (McConnell et al. 2003), similarly draw on general principles for application efficiency rather than being able to relate the principles to specific vineyard situations.

With respect to their adherence to the guidelines, most Australian grape growers do re-configure their equipment as the canopy develops, to direct spray into the canopy. They also vary their spray volumes according to canopy size, for example using Unit Canopy Row (Furness & Magarey 2000). However many would consider that leaving unsprayed buffers or spraying only one side of a vine row, is likely to increase the risk of disease outbreaks. The buffer width of 100 metres that is recommended around small acreages such as vineyards (PISC 2002) has not been adopted in small vineyards because of the high cost associated with having a high proportion of unproductive land.

Managing spray drift from vineyards or orchards is equally a challenge in other regions of the world, resulting in the development of various drift mitigation strategies based on principles of drift behaviour and backed with varying amounts of data and modelling. The contributions of modelling and application technology (regulation of, developments in) are discussed briefly below:

Of the four key models of relevance to viticulture, below, only the last has been designed to suit applicators wishing to predict the off-target movement of agrochemicals as drift from vineyards.

- The *Basic Drift Values* (Ganzelemeier & Rautmann, 2000) (Table 3.1) are based on 77 German vineyard trials and represent the greatest body of vineyard drift data. They are used by the APVMA and EA during the agrochemical registration process, to predict the concentration of agrochemical that may reach a water body and so pose an ecotoxicological risk to the environment (APVMA 2005). They do not directly indicate the total amount of spray that will be lost from the vineyard as drift.
- The Spray Drift Task Force (SDTF) in the USA developed the *AgDrift* model (Teske et al. 1997) for predicting drift predominantly from aerial and broadacre spraying. Lower order modelling does include limited vineyard trial data (8 trials: Andrew Hewitt, SDTF, pers.

comm., SDTF 1997). The SDTF describes droplet size as having the major influence on drift, followed by spray release height, then wind speed (SDTF 1997). Access to *AgDrift* is restricted.

- The *Gaussian diffusion model* (Bache and Sayer 1975, cited in Woods et al. 2001), and Australian data from aerial and broadacre spraying, have been used to develop the Australian Government's recommendations for managing drift, including buffer distances around sprayed areas (PISC 2002). Predictions of drift behaviour from the *Gaussian diffusion model* have matched well against drift measured in field studies (Woods et al. 2001), and against predictions from the *AgDrift* model (Teske et al. 1997, Woods et al. 2001).
- The *SprayCan* model (Maber et al. 2002), developed in New Zealand, predicts drift onto neighbouring properties and rates the hazard associated with each prediction scenario based on the sensitivity of neighbouring enterprises to particular chemicals. The *SprayCan* model is based on the *AgDrift* model with further New Zealand spray trial data and modelling.

The Australian Government is increasingly using the *Gaussian diffusion* and *AgDrift* models and *Basic Drift Values* during the agrochemical registration process. However, none of these are readily available to an individual vineyard manager for applying to the conditions in their vineyard. The APVMA (2005) is developing '*standard model output datasheets*' for applicators to assess risks of drift in various situations, but the current on-line template only relates to drift from 100 m to 2.5 km downwind of the sprayed crop. Models are clearly not yet designed for use by spray applicators in vineyards.

Table 3.1: Basic Drift Values derived by Ganzelmeier and Rautmann (2000) computed from the 95th percentiles of 77 vineyard trials and adjusted to account for a sparse canopy or full canopy.

Distance from sprayer (m)	**Computed drift values (% of sprayer output landing at distance from the vineyard)** extracted from Ganzelmeier & Rautmann, 2000	
	Early season vine growth (sparse canopy, no air assistance)	Late season vine growth (full canopy, air assisted sprayer)
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	0.10	0.31
40	0.06	0.21
50	0.05	0.16

The German solution to managing drift from vineyards is to be prescriptive about nozzle selection and maximum release heights for spray plumes (coarser nozzles and lower release heights will reduce the risk of drift). The German Government provides certification for vineyard sprayers, and compares sprayers against standards outlined in a "Register of drift-

mitigating machinery" (Ganzelmeier 2002). According to the standards, a 'tunnel' sprayer in a vineyard may reduce drift by 90% compared to conventional sprayers (Ganzelemeier & Rautmann 2000). Detectors that shut nozzles off when there is no foliage to be sprayed are deemed to reduce drift by a further 25-50% (Ganzelemeier & Rautmann 2000).

The USA provide standards for classifying nozzles as 'very fine', 'fine', 'medium', 'coarse', 'very coarse' or 'extremely coarse' based on the droplet spectra and compared against reference nozzles (ASAE Standards 2000). The ASAE (American Society of Agricultural Engineers) standards are similar to the British Crop Protection Council (BCPC) classification for nozzles, which includes all the same categories except 'extremely coarse' (Doble et al. 1985). Many agrochemical labels in the USA recommend particular nozzles for use with particular agrochemicals, to minimise drift risk (under the premise that coarser nozzles reduce drift risk).

In the UK, the *Local Environmental Risk Assessment of Pesticides* (LERAP) scheme allows growers to reduce the width required of the 'no-spray zone' around their sprayed crop if they use nozzles classified as 'low drift' (DEFRA 2002). They can also progressively reduce the width of their 'no-spray zones' further, by adopting other practices that reduce drift potential (e.g. reducing rates by adjusting spray volumes to match canopy size, or planting vegetative buffers to intercept drift) (Walklate & Cross undated; DEFRA 2002).

Large droplets are less efficient than fine droplets at covering a plant surface (Mathews 2000). Promoting or regulating for the use of coarse droplets to reduce drift risk may therefore compromise efficacy, and would directly contradict the current message that finer droplets improve deposition on grapevines, being taught in spray application workshops (Agriculture Victoria Services 2002). Air inclusion nozzles allow small volumes of liquid to be delivered in droplets made large by containing bubbles of air (Mathews 2000) and may satisfy both needs, i.e. for fine droplets to spread on a surface and large droplets to resist drifting.

Australian agriculture prefers an approach of industry self-regulation and codes of best practice rather than legislating practices. We would need to be certain about the relative effects of coarse or fine droplets on spray drift, and the drift potential from typical Australian equipment, before arguing for clear prescriptions for spray equipment. APVMA (2005) released a discussion paper '*Operating principles and proposed registration requirements in relation to spray drift risk*' with proposed changes to the registration process to minimise drift risk. With regard to viticulture there may not be many changes required from current best practice. Aspects of the discussion paper relevant to viticulture are summarised in Table 10.1 (Appendix 1).

The chemical industry has responded to concerns about drift by exploring the potential for additives in tank mixtures to reduce drift. Such additives alter the physical properties of the liquid so that it atomises into larger droplets than the agrochemical formulation would otherwise form. Bozdogan and Bozdogan (2004), reviewing the effects of adjuvants on spray drift, concluded that any drift reduction achieved using additives to spray mixtures could be overridden by the influences of equipment and application method. Also, many drift-reducing adjuvants degrade rapidly under a pump's shear stress, and if the spray solution is agitated through the pump more than two to three times, the adjuvant degrades and loses most of its effectiveness (Wolf 1997, cited by Bozdogan & Bozdogan 2004). The APVMA makes no recommendations regarding the use of drift retardants in their *Operating principles and proposed registration requirements in relation to spray drift risk* (APVMA 2005), as they have no conclusive data.

Manufacturers of nozzles have also responded to concerns about drift, and developed air induction nozzles. Air induction nozzles create droplets that contain bubbles of air. The number of droplets and liquid volume held by each droplet are maintained, but average droplet size increases due to the bubbles. The spray plume has the efficacy of a plume with a smaller droplet, but lower drift risk. Various air induction nozzles are available and have been tested on boom sprayers. There is no published data describing their effectiveness in vine canopies, but

New Zealand vineyard trials in 2004-05 showed that disease control in vineyards was improved using air induction nozzles, and drift from orchards was reduced, particularly during dormancy (David Manktelow pers. comm.).

Aim of field trials to assess the risk of off target movement of agrochemical as drift from Australian vineyards

Before adopting a regulatory approach and recommending coarse droplets at the expense of efficiency of deposition, investing in modelling or encouraging growers to upgrade machinery to minimise the risk of drift, it was important to provide clearer context to the discussion by gathering data from Australian vineyards.

For this purpose, field trials were conducted to measure spray drift within and beyond vineyards and are reported below. The objective of these trials was to examine the off-target losses, as drift or ground deposition, associated with nozzles and sprayers used in Australian viticulture and under typical Australian conditions.

Table 3.2: Treatments (sprayers, nozzles and settings) used in spray drift field trials.

Treatment code	A1	A2	B1	B2	C1	C2	D1	D2
Sprayer type	Airshear mister (converging air)		Conventional airblast (diverging air)				Ducted airblast (converging air)	
Model selected as typifying the sprayer type	Silvan 'P55 Turbomiser'		Agrimaster 'Charlie'				Silvan 'SLV'	
Nozzle type	Airshear flute 10		1.8 mm ceramic cone		Albuz ATR 80 cone		Albuz ATR 80 cone	
Nozzle description	(well directed)	(poorly directed)	Closed swirl	1.5 mm swirl plate	Green	Yellow	Yellow	Green
Nozzle code	1	1	2	3	4	5	5	4
Droplet size (VMD)[2]	86	86	190	300	210	77	77	210
Classification[3]	mist	mist	fine-medium	medium-coarse	medium	mist	mist	medium
Number of nozzles	16	20	12	12	12	14	13	13
Nozzle output (L/min)	22.9	22.9	37	60	25.5	18	16.3	28.6
Pressure (bar)	1	1	15	15	9	18	15	8
Airspeed (ms^{-1}) at the nozzle	79	79	40	40	40	40	42	42
Travel speed (kph)	7.8	7.8	7.8	7.8	7.8	5.3	5.3	7.8
L/ha applied	550	550	889	1442	613	640	578	688

[2] Data based on wind tunnel measurements. Volume Median Diameter (VMD) describes the spray plume. Spray plumes are classified according to the diameters (microns) of the droplets in the plume. No nozzle produces a uniform droplet size, so sprays are described by the Volume Median Diameter (VMD) of the droplets in the plume. Half the volume in the spray plume will be delivered in droplets smaller than the VMD and half the volume in the spray plume will be delivered in droplets larger than the VMD. Note that in the spray plume there are many more droplets smaller than the VMD in comparison with droplets larger than the VMD, because it takes many small droplets to make the equivalent volume of a larger droplet.

[3] Classifications of spray quality according to International (British Crop Protection Council) standards (Mathews 2000).

3.2 MATERIALS AND METHODS

The field trials were conducted in November 2002 at a commercial vineyard in Merbein, Victoria, South Eastern Australia (34° 21′ south; 142° 04′ east). The vineyard was of minimally pruned Chardonnay grapevines irrigated with micro-sprinklers.

There were no standardised methods for testing drift from vineyard sprayers when these trials were conducted. Therefore we sought collaboration from the Centre for Pesticide Application and Safety (CPAS) at the University of Queensland, Gatton, so that our methods would be compatible with methods used in SDTF trials.

3.2.1 Treatments

Eight treatments were applied. The treatments represented differing drift potential, achieved by using a range of sprayers and sprayer configuration, including varying nozzle type or direction (Table 3.2). Application of each treatment was replicated across four separate days. The order of applying the treatments on each day (replicate) was rotated to ensure that each was applied at each stage in the day.

Sprayer selection

Three types of air-assisted sprayer were included in the treatments:

- Airshear mister
- Conventional airblast
- Ducted airblast

These represent the three major types of sprayers used in Australian viticulture, and are used on 34%, 46% and 26% of vineyards respectively (CRCV 2001)[4]. The example model selected as typifying each type of sprayer, and the nozzles and settings used as each treatment in the field trials, are presented in Table 3.2. The spray plume from an airshear mister is very fine, with high assoociated drift risk. The conventional airblast is not a directed sprayer (increasing risk) but tends to be used to deliver a larger droplet (lowering risk).

Nozzle selection

Prior to the field experiment, sixteen nozzles from the range used typically in viticulture were evaluated. Nozzles were placed in a wind tunnel at CPAS, and their droplet sizes measured using a Malvern laser diffraction particle sizer under a range of wind speeds (10 – 79 ms^{-1}) and spray pressures (1 – 25 bar) (see Table 10.2, Appendix 2).

The following five nozzles were subsequently selected as representing common sizes for use in treatments in the field trials:

- Airshear flute (fluid fed by a low-pressure line into a fast airstream for atomisation)
- 1.8 mm orifice ceramic hydraulic nozzle with a closed spinner plate
- 1.8 mm orifice ceramic hydraulic nozzle and a 1.5 mm orifice steel spinner plate
- ATR 80 (Albuz® yellow)
- ATR 80 (Albuz® green)

Nozzles providing finer or coarser sprays than the five selected are also used within the industry, but are less common.

[4] Figures from a questionaire completed by 450 participants in the sprayer training course run by the Cooperative Research Centre for Viticulture (CRCV 2001). Note that many vineyards have more than one type of sprayer.

3.2.2 **Plot layout**

The trial was laid out across 64 rows of minimally pruned grapevines grown at a row spacing of approximately 3.2 metres. The vine rows were 224 metres long and ran almost north-south (170-350°). Each treatment was applied to the full length of the row, and applied from both sides of the row. Treatments were allocated to every second row in the chronological order in which they would be applied. An unsprayed buffer row separated each sprayed row.

At the time of the trial the vines were at E-L growth stage 27 (Coombe 1995). The canopy was approaching the point of being at its maximum dimensions, although not yet maximum leaf area, for the season.



Figure 3.1: Three sprayers used in spray drift trials. Conventional airblast (top); airshear mister (bottom left) and ducted airblast (bottom right).

3.2.3 **Tracer**

To trace spray deposits, a green fluorescein dye (pyranine: 1, 3, 6, 8-pyrenetetrasulphuric acid) was mixed into each spray tank at a concentration of 0.1 g/L. No wetting agents or agrochemicals were added. The sprayer output (litres per 100 metres) and therefore dye output (grams per 100 metres) varied according to the nozzle size and travel speed, and this variation was accounted for in subsequent calculations.

3.2.4 Weather data

Air temperature, wind direction, wind speed and humidity were recorded at 30-second intervals for the duration of the trial using a weather station placed two metres above the canopy in the vineyard (see Appendix 3).

3.2.5 Collection of airborne drift

During spraying, a 12.75-metre tall tower was positioned halfway along the vine row, four midrows (10.5 metres) downwind from the treatment row (Figure 3.2).

Two 12-metre vertical lengths (duplicates) of embroidery thread were suspended, one metre apart, from a horizontal bar at the top of the tower and secured to a one-metre horizontal bar positioned 0.75 metre above the ground.

After spraying, the duplicate embroidery threads were lowered and each cut into six 2-metre sections, to provide two sub-sample threads from each of six different heights. When in position on the tower, the midpoints of the six sample threads were 1.75 m, 3.75 m, 5.75 m, 7.75 m, 9.75 m and 11.75 m above the ground. These heights were constant throughout the trial. Duplicate threads were collected on each (replicate) application date.

The tower was designed and built by Paul Burrow and Mahabubur Mollah, It has four telescoping stages made of aluminium pipe, raised using compressed air, and was based on design concepts from Silsoe Research Institute in the UK (Paul Miller pers. comm.).

The thread was Coats Mercer™ crochet cotton #20, comprised of six cords of mercerised cotton, and has good capturing properties and provides good recovery of fluorescein dye (Gary Dorr, CPAS, pers. comm.).

3.2.6 Collection of ground deposits

Ground deposits of sprays were collected on horizontal filter paper collectors stapled to plastic-covered wooden blocks. The plastic was replaced after each sampling to prevent cross-contamination of dye between treatments. Seven collectors were placed along each of three transects running perpendicular to the sprayed row. In each transect, a 900 × 30 mm collector was placed under the sprayed row and smaller collectors (70 × 30 mm) were placed at distances of 1.6, 3.2, 4.8, 6.4, 8.0 and 9.6 metres from the sprayed row. The 900 × 30 mm collector under the sprayed row was subsequently cut into three sections of 300 × 30 mm to reflect the edges and centre of the undervine bank, because the outer sections (edges) were expected to have higher deposits due to dripping of spray from saturated outer canopy. The three transects were laid out in parallel at 20-m intervals along the sprayed row (Figure 3.2).

3.2.7 Collection of canopy deposits

Deposits landing at three heights (below the lower cordon, centre of the canopy, in high foliage) in the mid-line of the sprayed row were collected on filter papers (70 × 30 mm) clipped to three spray monitoring poles (Anon 2000) positioned in line with the three ground collector transects. A pair of collectors, one vertical and one horizontal, was clipped at each height. A further pair of vertical and horizontal papers was clipped to each of three poles placed two rows downwind, at a height that represented the top of the canopy.

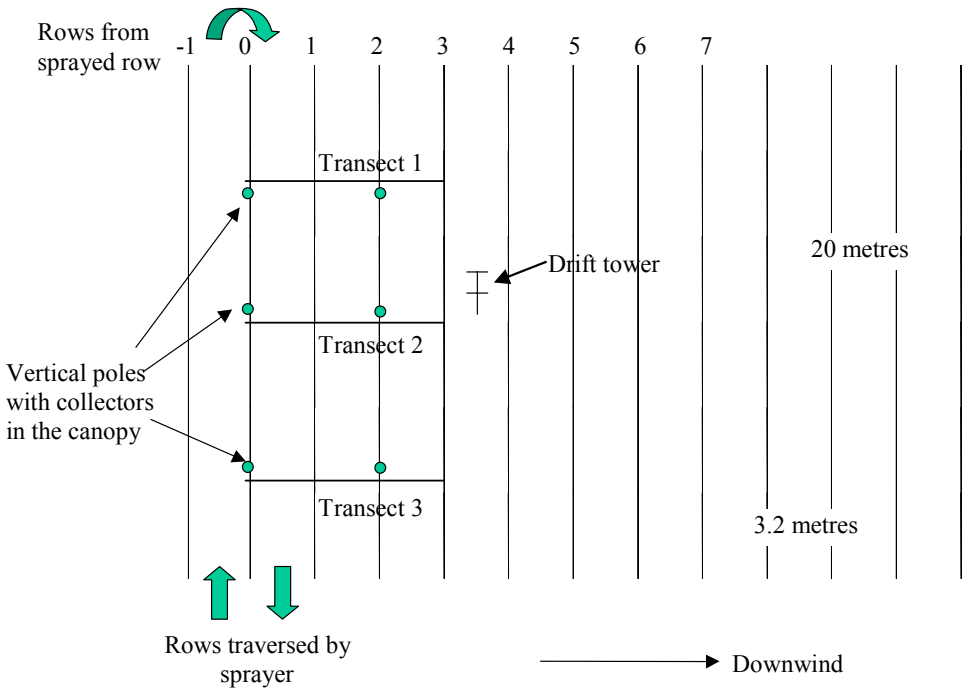


Figure 3.2: Aerial view showing locations of the three horizontal transects and six vertical canopy poles per treatment, and the tower (with two suspended threads). While the relative positions of samplers were maintained in each treatment, the whole set was moved across two rows for each new treatment.

3.2.8 **Tracer recovery**

To minimise ultraviolet degradation of the fluorescein, collectors were retrieved, placed in McCartney vials and stored in a black plastic bag in a cooler within ten minutes of each spray treatment being applied. Within two hours of spraying the dye was rinsed from the collectors into 10 ml of distilled water and analysed using a fluorometer. Samples were also collected from each tank mix for fluorometric analysis of actual concentration of the dye in the spray.

3.2.9 **Data analysis**

To estimate the mass balance of deposition (proportions of sprayer output collected from air, ground or canopy), the amounts captured were extrapolated from the deposits captured on the samplers.

To remove the effect of spray volume on amount of dye recovered, deposits were expressed as a percentage of each sprayer's output, based on their measured tank concentration, flow rates and travel speeds (Table 3.2).

The percent of sprayer output landing in the zone was calculated as:

$$\% \text{ in Zone } = \frac{Dc \times Vr}{Dm \times Dr \times Ac \times 1000} \times \frac{Az}{Va \times 1{,}000{,}000} \times 100$$

where:

- Dc = dye concentration (μg/L) rinsed from collectors (corrected for background)
- Vr = volume of rinsate (mL) used to wash fluor dye from a collector
- Dm = concentration (g/L) of fluor dye mixed in the tank
- Dr =a constant representing dye recovery (a pre-determined constant for each collector)
- Ac = the surface area (cm^2) of collector (filter paper or string)
- Az = the area (cm^2) of the zone (Figure 3.3)
- Va = volume applied per metre of row (L/m).

Deposits in the canopy were also expressed as hypothetical agrochemical deposits. First the volume of water deposited on each sampler ($\mu L/cm^2$) in the six canopy positions was calculated using the dye recovered from each sampler, plus fluorometry measurements of each tank mix. The deposits were then converted to reflect the tank mix concentration of an agrochemical (sulphur was used as an example). Once converted to equivalent agrochemical doses, the deposits were compared against data from Warren et al (1997) that showed that sulphur provides effective control of powdery mildew spores if deposited at a dose of 2.3 $\mu g/cm^2$.

Data were analysed using GenStat Release 6.1 (6^{th} Edition, 2002, Lawes Agricultural Trust, Rothamsted Experimental Station) and compared using Analysis of Variance. The 'percentage in zone' deposit data was log-transformed log(% in zone + 0.01) to stabilize the variance of the residuals. The analysis explored the extent to which the factors sampling positon, sprayer type, nozzle type, day and time of day were sources of variation, and also interactions between those factors.

Orthogonal polynomials, using the height midpoints of the collector threads, were fitted to the drift data from the tower, and cubic and quadratic functions were compared by regression analysis to investigate any trends with height above the ground. Trends associated with the distances of the ground collectors along the transects were also modelled using orthogonal polynomials.

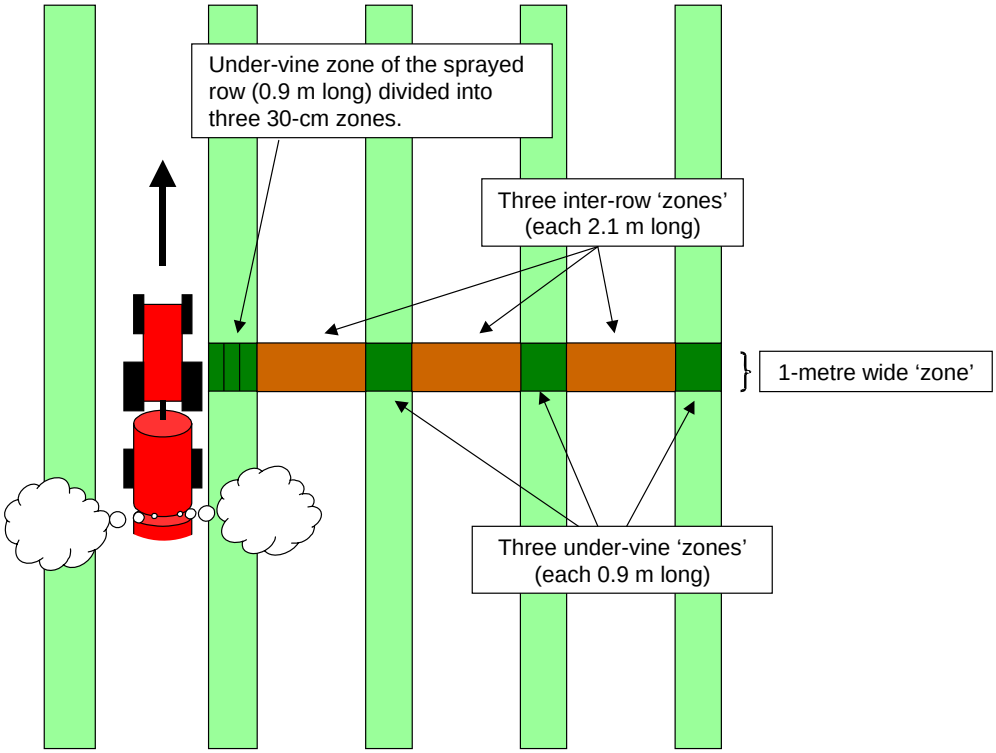


Figure 3.3: Aerial view showing the 1-metre wide band of ground area, extending under vines and through the inter-rows, illustrating the relative position and sizes of the ground ‘zones’ described in the analysis.

3.3 RESULTS

3.3.1 Mass balance

The distribution of sprayer output from all sprayer-nozzle combinations and across all sampling zones is shown in Figure 3.4. A high proportion of the sprayer output was unaccounted for. The magnitude of the 'missing' spray deposits varied between sprayers, and tended to be higher when the sprayer produced fine droplets.

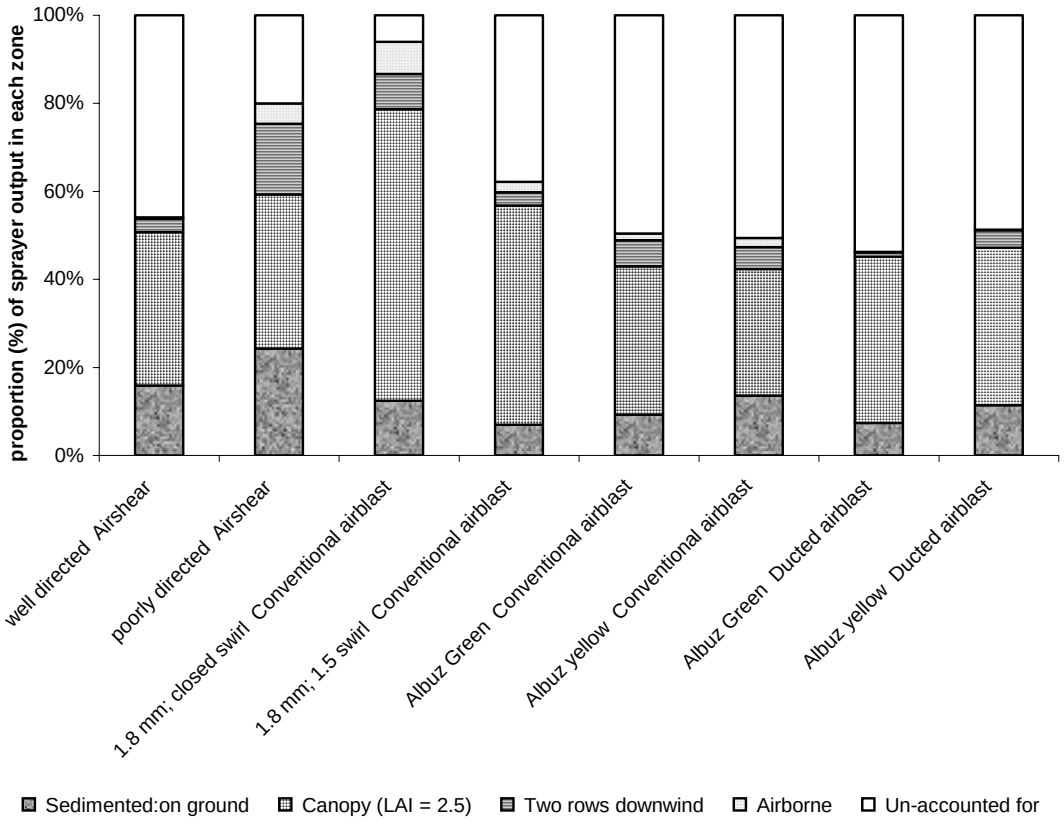


Figure 3.4: Mass balance of deposits (expressed as % sprayer output) using an estimated Leaf Area Index of 2.5.

[#] Airborne drift values measured on one side of the sprayer only.

[ϕ] Ground deposits measured on one side of the sprayer but doubled to account for spray to both sides.

3.3.2 Spray quality of nozzles used in viticulture

The ranges of droplet sizes produced by the five nozzles included in the field trials are shown in Figure 3.5. The VMD, VD_{10} and VD_{90}[5] for all 16 nozzles that were tested in the wind tunnel are shown in Appendix 2.

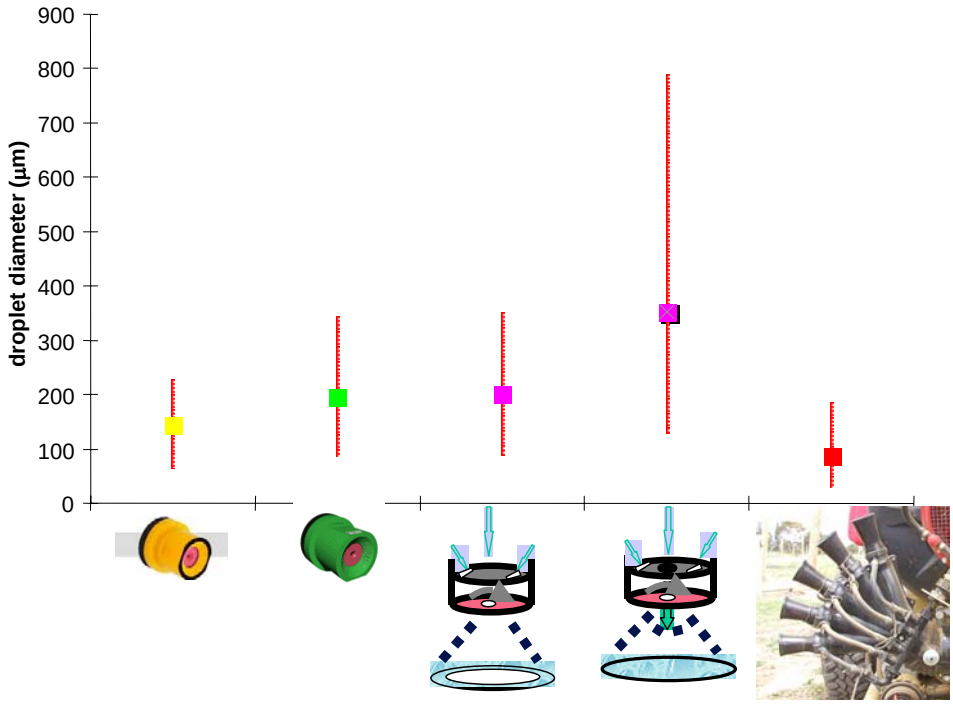


Figure 3.5: Droplet diameter (µm) for nozzles used in the vineyard drift trials (VD_{50} indicated by the box. The bars extend between VD_{10} and VD_{90}).

[5] The descriptions VD_{10} and VD_{90} indicate droplet diameters (microns) below which 10% and 90% of the volume is delivered.

3.3.3 Effectiveness of spray deposition in the sprayed vine canopies

Samplers placed within the canopy confirmed that there was no bias in setting up the sprayers, that would increase off-target movement, and that each sprayer was set up adequately to provide disease control. The equivalent doses of sulphur that would have been applied in the measured deposits would have been adequate in all but the mid canopy (Table 3.5).

Deposits varied significantly between the different canopy positions when the data were averaged across all the sprayers (F pr =<0.001, Table 3.3). Deposits were not, however, significantly influenced by position when compared within each individual sprayer or sprayer-nozzle combination (P>0.05), showing that no sprayer was set up to purposefully miss canopy and cause drift.

Table 3.3: Deposits at each height in the inner canopy (log (PiZ + 0.01) averaged across all sprayers, nozzles and orientation of samplers.

Low canopy	mid canopy	High canopy
-0.680 b	-1.462 a	-0.056 c
F-prob=<0.001; LSD = 0.1717		

Table 3.4: Deposits on vertical and horizontal samplers in the inner canopy (log (PiZ + 0.01), averaged across all heights.

Sprayer	Horizontal samplers	Vertical samplers
Airshear	-0.937	-0.883 a
Conventional airblast with 1.8 cc and 1.5 (or closed) swirl	-0.482	0.038 b
Conventional airblast with Albuz nozzles	-1.093	-0.979 a
Ducted airblast with Albuz nozzles	- 1.016	-0.511 ab
Mean *	**-0.882**	**-0.584**
F-prob = 0.028; LSD = 0.8656 when comparing between different sprayers, or 0.2804 when comparing within same sprayer		
*F-prob = <0.001; LSD = 0.1402 when comparing between the means of each orientation		

There were more deposits on vertical than horizontal samplers (Table 3.4), consistent with the majority of droplets still travelling horizontally in the sprayer airstream when they reached the sampler, and relatively few having begun to fall.

Table 3.5: Mean water volumes (μL/cm^2) deposited and equivalent (hypothetical) sulphur dose (μg/cm^2) on samplers (back and front surfaces) at six positions in the centre of the vine canopy of the sprayed row.

Sprayer	Nozzle or setting	Water volume applied L/100 m	Volume of water deposited in each zone (μL/cm^2)					
			high canopy horizontal	high canopy vertical	low canopy horizontal	low canopy vertical	mid canopy horizontal	mid canopy vertical
Airshear	Well directed	550	1.71	1.32	0.35	0.83	0.21	0.17
Airshear	Poorly directed	550	1.26	1.44	0.43	0.51	0.50	0.45
Conventional airblast	1.8 mm core; closed swirl	889	3.31	3.16	1.30	4.53	0.64	1.19
Conventional airblast	1.8 mm core; 1.5 mm disc	1442	3.28	4.65	3.09	3.19	0.72	2.27
Conventional airblast	Albuz Green	613	1.35	1.45	0.62	1.00	0.30	0.25
Conventional airblast	Albuz Yellow	640	1.21	1.03	0.62	0.89	0.29	0.36
Ducted airblast	Albuz Yellow	578	0.78	1.95	0.35	1.06	0.37	0.40
Ducted airblast	Albuz Green	688	1.29	1.65	0.72	1.21	0.35	1.10
			Equivalent sulphur dose (μg/cm^2) that would have been deposited in each zone[1]					
Airshear	Well directed	550	10.25	7.91	2.07	4.96	1.27	1.03
Airshear	Poorly directed	550	7.54	8.61	2.57	3.08	3.01	2.68
Conventional airblast	1.8 mm core; closed swirl	889	19.86	18.98	7.79	27.17	3.81	7.12
Conventional airblast	1.8 mm core; 1.5 mm disc	1442	19.69	27.90	18.57	19.13	4.34	13.64
Conventional airblast	Albuz Green	613	8.07	8.70	3.70	5.98	1.77	1.48
Conventional airblast	Albuz Yellow	640	7.25	6.16	3.71	5.37	1.71	2.15
Ducted airblast	Albuz Yellow	578	4.68	11.72	2.12	6.33	2.23	2.42
Ducted airblast	Albuz Green	688	7.76	9.89	4.34	7.27	2.10	6.63

[1] Assuming a tank mix of 600 g/100L as per label*. 2.3 μg/cm^2 is required for disease control (Warren et al. 1997).

Note that values in this table have not been normalised to account for being applied in different water volumes, which is of particular relevance in the low volume applications, as then the tank concentration would typically increase proportionally to the reduction in water volume.

The greatest overall amount of spray deposited on the canopy was associated with spraying using the conventional airblast with either of the 1.8 mm cone nozzles treatments (Table 3.5). However, as Table 3.5 shows, these two treatments had also received the highest spray volumes. Notably they also had the greatest disparity between vertical and horizontal deposits (F pr <0.05, Table 3.4). Using finer Albuz nozzles in the same sprayer evened out the difference but reduced the net volume applied. This was at the expense of deposits on both vertical and horizontal surfaces. When the Albuz nozzles were used in the ducted airblast, there was also less deposition on horizontal than vertical surfaces, which was not expected. Looking at separate heights in Table 3.5, deposits on the high canopy horizontal sampler were improved using the well-directed airshear sprayer.

An accurate measure of canopy deposits needs a precise measure of leaf area index (LAI), which was only approximated in this trial using number of leaf layers as 2.5. An accurate measure of canopy deposits also requires that deposits be sampled from positions that reflect the entire canopy profile. Samplers in this trial were positioned towards the centre of the canopy so the estimates provided are likely to be conservative. Given these limitations, Figure 3.4 shows the approximated proportions of each sprayer output that were accounted for in the canopy.

3.3.4 Deposits drifting to canopy in other rows

Deposits were compared between samplers in upper foliage of the sprayed row and two rows away. Comparison of the back-transformed values shows that averaged across all sprayer-nozzle combinations, drift to the top of canopy two rows away was approximately 5% of the amount deposited in the top of the sprayed canopy (Table 3.6).

Table 3.6: Deposits on vertical or horizontal samplers set at two distances (0 and 6.4 metres) from the sprayed row, in high canopy (transformed log(PiZ) + 0.01).

	Distance from the sprayed row	
	0m	6.4m
Horizontal samplers	-0.166 a	-2.859 c
Vertical samplers	0.054 b	-2.917 c
Mean	-0.056	-2.888
(back transformed mean)	**(0.936)**	**(0.046)**
F-prob=0.048; LSD = 0.1948 for comparing orientations at the same distance F-prob = <0.001		

The proportion that drifted across the canopies was significantly affected by the sprayer-nozzle combination (F pr = 0.002) (Table 3.7). In the sprayed row, deposits on the vertical sampler were significantly higher than on the horizontal surface (F pr = 0.048) (Table 3.6), which is consistent with the canopy having been sprayed from the side. In contrast, deposits settling in the high canopy two rows away were not affected by orientation of the samplers. The proportion of drift precipitating from spray directed above the canopy was similar to the proportion directly projected from the sprayer two rows away.

Table 3.7: Effects of nozzle type, distance and sampler orientation on the proportion of spray (Log percent in zone) deposited by each sprayer high in the canopy of the sprayed row and two rows away.

	Nozzle setting		Distance from sprayed row		Sampler orientation	
Sprayer and nozzle type	1	2	0 m	6.4 m	horizontal	Vertical
Airshear	-1.682 b	-0.885 a	-0.074 x	-2.494 y	-1.328	-1.239
Conventional airblast with ceramic disc and core nozzles	-0.95 a	-1.504 b	0.343 x	-2.796 y	-1.221	-1.232
Conventional airblast with Albuz nozzles	-1.326 a	-1.759 a	-0.330 x	-2.755 y	-1.513	-1.572
Ducted airblast with Albuz nozzles	-2.079 b	-1.591 a	-0.163 x	-3.506 y	-1.989	-1.681

Values followed by the same letter are not significantly different.
F-prob = 0.002 and LSD = 0.4472 for comparing effect of nozzles on drift within the same sprayer type.
F-prob = 0.04 and LSD = 0.3043 for comparing effect of distance on drift within the same sprayer type.
The effect of orientation on deposits by the individual sprayers was not significant.

3.3.5 **Airborne drift landing on the tower**

Neither time-of-day nor day-of-treatment affected airborne drift collected on the tower (P<0.05).

Drift captured by threads that extended up to 12.75 metres above the ground, and were set to one side of the sprayed row, ranged from 0.06% to 7.25 % of the sprayer output. The average deposits at each height from each sprayer, to only one side of the sprayer, are shown in Figure 3.6 and Table 3.8. When expressed relative to the applied volumes, these proportions are equivalent to a range from 0.7 to 65 L/ha. The transformed data are provided in Table 3.8 to show the treatment and height effects interactions.

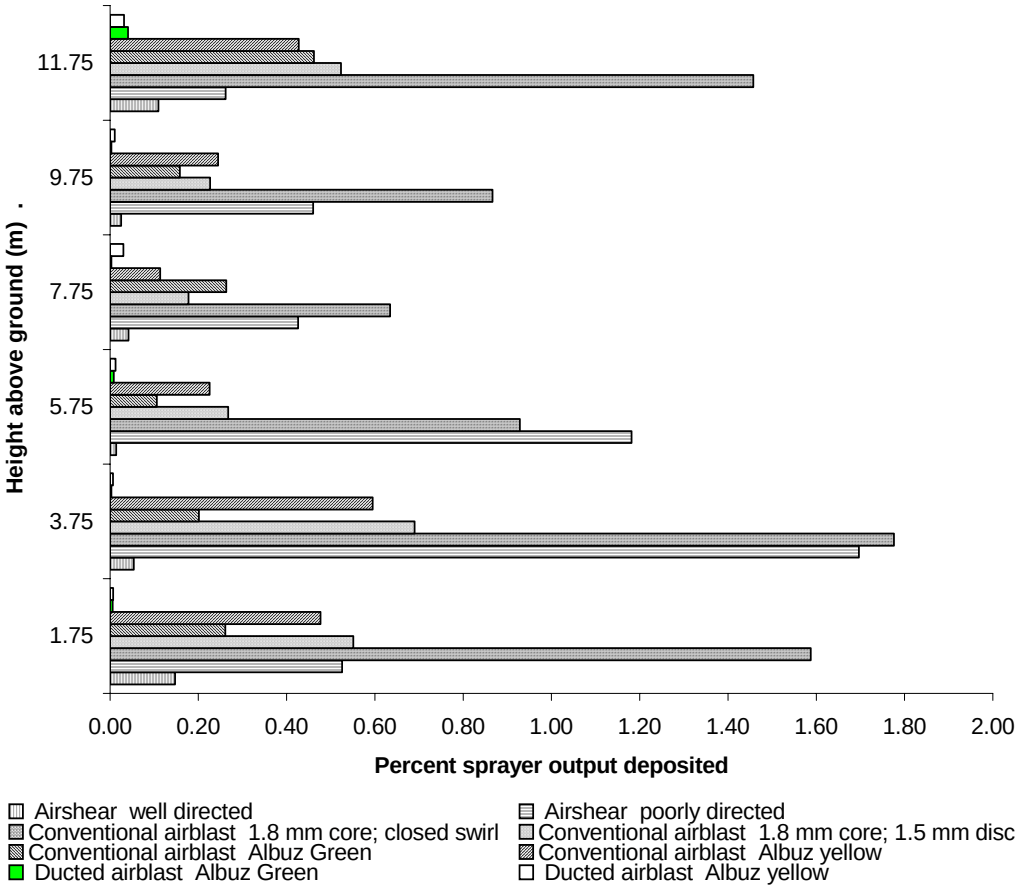


Figure 3.6: Proportion of sprayer output collected 4 midrows away, in one direction, from a sprayed row, on 2-metre sections of string suspended 12 metres vertically from a tower. Values are back-transformed from means of the Log(PiZ+0.01)[6]

[6] Log(percent in zone +0.01). The zone in this case is a 1-metre wide, 2-metre high 'window' of air at each height.

Table 3.8: Proportion of sprayer output landed at each height on vertical threads suspended from a 12-metre tower. Backtransformed data are shown, with log (PiZ + 0.01) values in parentheses.

	Proportion of output anding at each height (m) on the 12-metre tower						Cumulative total (%) back-transformed	Mean Log (PiZ + 0.01) across all heights *
Section of thread (m)	0-2 m	2-4 m	4-6 m	6-8 m	8-10 m	10-12 m		
Height above ground of the section midpoint	1.75 m	3.75 m	5.75 m	7.75 m	9.75 m	11.75 m		
Sprayer and nozzle setting								
Airshear (Silvan Turbomiser)								
well directed	0.15 (-1.849)	0.05 (-2.755)	0.01 (-3.729)	0.04 (-2.961)	0.03 (-3.351)	0.11 (-2.125)	**0.39**	**(-2.795 wx)**
poorly directed	0.53 (-0.625)	1.70 (0.535)	1.18 (0.175)	0.43 (-0.830)	0.46 (-0.754)	0.26 (-1.302)	**4.55**	**(-0.467 yz)**
Airblast (Agrimaster 'charlie')								
1.8 cc closed spinner	1.59 (0.468)	1.78 (0.580)	0.93 (-0.063)	0.63 (-0.439)	0.87 (-0.132)	1.46 (0.383)	**7.25**	**(0.133 z)**
1.8 cc 1.5 spinner	0.55 (-0.577)	0.69 (-0.357)	0.27 (-1.282)	0.18 (-1.672)	0.23 (-1.442)	0.52 (-0.629)	**2.44**	**(-0.993 yz)**
Albuz green	0.26 (-1.305)	0.20 (-1.555)	0.11 (-2.155)	0.26 (-1.296)	0.16 (-1.782)	0.46 (-0.751)	**1.45**	**(-1.474 xy)**
Albuz yellow	0.48 (-0.719)	0.60 (-0.502)	0.23 (-1.447)	0.11 (-2.090)	0.24 (-1.368)	0.43 (-0.826)	**2.08**	**(-1.159 yz)**
Airblast (Silvan ducted)								
Albuz yellow	0.01 (-4.074)	0.01 (-4.109)	0.01 (-3.796)	0.03 (-3.217)	0.01 (-3.881)	0.03 (-3.182)	**0.10**	**(-3.710 w)**
Albuz green	0.01 (-4.133)	0.00 (-4.342)	0.01 (-3.999)	0.00 (-4.342)	0.00 (-4.342)	0.04 (-2.982)	**0.06**	**(-4.023 w)**
Mean across all sprayers *	**0.19 (-1.602 b)**	**0.2 (-1.563 b)**	**0.12 (-2.037 a)**	**0.11 (-2.106 a)**	**0.11 (-2.131 a)**	**0.23 (-1.427 b)**		
Signficanance (F probability) of the effects and interactions for the transformed data								
Height	<.001 (LSD = 0.4137)							
Sprayers	<0.001 (LSD = 1.11, data shown in Table 3.9)							
Height × sprayers	0.244							
sprayer × nozzle interaction	0.028 (LSD = 1.434)							
Height × sprayer × nozzle	0.022							

*Mean log (PiZ + 0.01) values followed by the same letter are not significantly different

A total amount of airborne drift moving in a 180° arc above each sprayer could be estimated by extrapolation from deposits on the tower, but only by making assumptions about the pattern of the spray plume at each height. Variability shown here in the drift patterns within and between sprayers suggests that such extrapolation might be misleading. However it is appropriate to assume that the measured values are conservative.

The optimum directions for a crosswind during spraying were 260° or 80° from north, but it was difficult to maintain these optimum directions, particularly later on the second and fourth days (Figure 3.7). Spray plumes carried by wind at other than these optimum directions necessarily travelled much further than 10.5 metres before being intercepted by the tower, and the spray plume would have dissipated with distance. The average wind directions during each application were therefore expressed in terms of their deviation from a true cross wind and these deviations compared with the deposits landing on the tower (Figure 3.8). There was very poor correlation between the deviations in wind direction and deposits on the tower ($R^2 = 0.12$), indicating that shifting wind direction was not responsible for the variation in deposits on the tower (Figure 3.8).

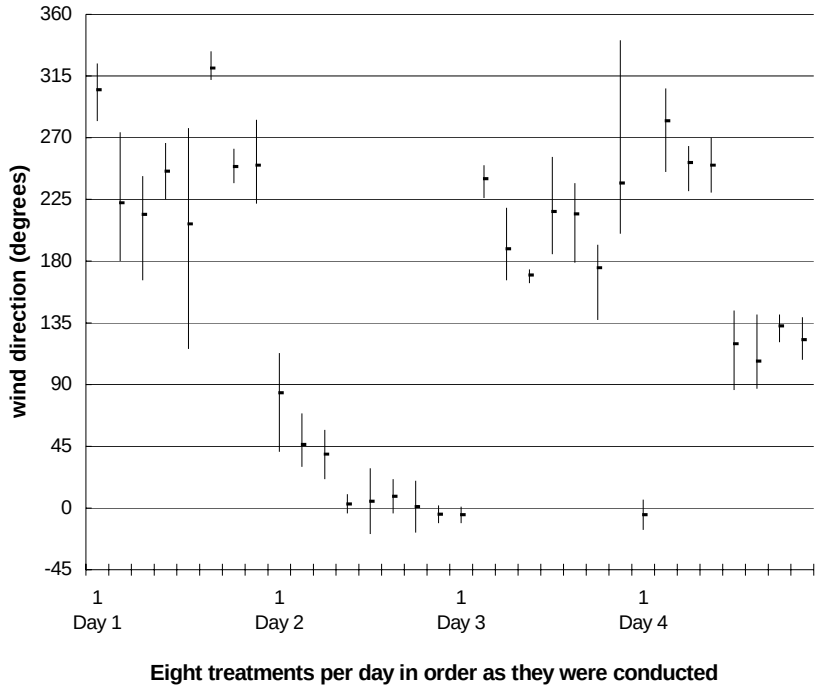


Figure 3.7: Wind direction relative to north (range and average) recorded at 30-second intervals in the vineyard while spraying each treatment. Average wind speed was 2 m/s.

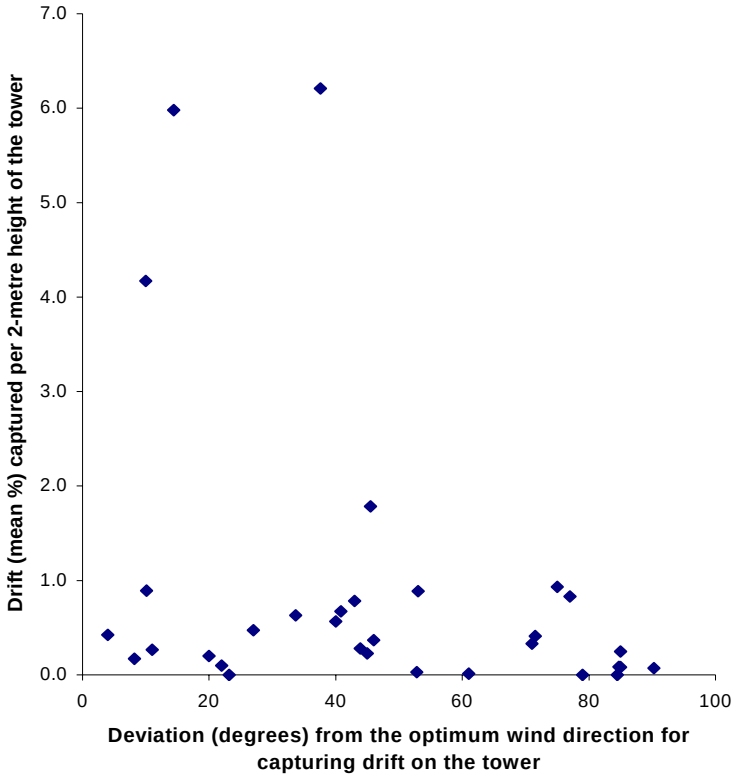


Figure 3.8: Capture of drift (% of applied) when the wind shifts away from the optimum direction for deposition on the tower.

The main influence on airborne drift was the type and set-up of the sprayer (F pr = 0.001) (Table 3.9).

- The ducted airblast caused the least drift while the conventional airblast with a 1.8 mm (medium-coarse) nozzle produced the most drift (Figure 3.6 and Table 3.8).
- The ducted airblast produced significantly less "percentage in zone over all heights" than all other sprayers (Figure 3.6 and Table 3.9).
- Depending on its set up, the airshear sprayer was as capable of minimising drift (up to 12.75 metres) as the ducted airblast (P>0.05). With small but inappropriate adjustments, however, (opening the top air flute to target higher shoots, and inappropriately angling air outlets so they produced a wide plume) the same sprayer was capable of causing almost as much drift as the worst set-up (the conventional airblast with 1.8 mm ceramic cone, closed swirl) (Figure 3.6 and Table 3.8).

Table 3.9: Average drift collected (% of sprayer output) on each 2-metre section of vertical collector thread, averaged across all heights and expressed as log of the percent output collected in the 2-metre zone.

Sprayer *	log(PiZ + 0.01)	% in zone (back-transformed)
Airshear (Silvan Turbomiser)	-1.631 b	0.186
Conventional airblast with 1.8 mm disc and core nozzles	-0.430 c	0.641
Conventional airblast with Albuz green or yellow nozzles	-1.316 bc	0.258
Ducted airblast with Albuz green or yellow nozzles	-3.866 a	0.011
F-prob = 0.001 and LSD = 1.112		

(NB the Agrimaster airblast, using two very different nozzle technologies, is considered here as two separate sprayers).

The Spray Drift Task Force nominated droplet size (determined by nozzle size) as the primary determinant of drift risk (SDTF 1997, 2001). Figure 3.6 and Table 3.8 provide the more complex picture, with airborne drift clearly affected by the sprayer-nozzle combination (F pr = 0.028) rather than just droplet size from that particular nozzle. When the sprayer could be directed into the canopy, fine droplets did not increase drift.

- Fine droplets produced by the airshear sprayer caused little drift on the tower four midrows downwind when they were directed into the canopy, but considerable drift when the top outlets were directed to the top of the canopy.
- Despite their misting droplets and therefore high drift potential, when the yellow ('fine') Albuz cone nozzles were used in the ducted airblast they caused very little drift on the tower, four midrows downwind. However, droplets from the same nozzles used in an undirected conventional airblast sprayer had a significantly higher (P=0.05) proportion drifting to the tower.
- When the green (medium) Albuz cone nozzles were compared across two different sprayers, drift was very low from the ducted airblast but significantly higher (P=0.05) from the conventional airblast.
- Coarse droplets from disc and core nozzles on the conventional airblast caused greater drift to the tower than fine droplets from the well-directed airshear sprayer or fine droplets from yellow Albuz nozzles on the ducted airblast.

In addition to the influences of sprayer type and sprayer-nozzle combination, the way droplets were atomised also appeared to influence drift risk. The green Albuz nozzle and the 1.8 mm ceramic cone with closed swirl produced similar droplet spectra (VMD 181-195 μm, VD10 79-88 μm, VD90 310-348 μm) and may therefore be expected to have similar drift risk (Figure 3.5 and Appendix 2, Table 10.2). However, they deposited significantly different amounts (log(PiZ + 0.01) = -1.474 and 0.133 respectively) on the tower when they were both used in the same conventional airblast (Table 3.8: Column showing means across all heights).

The height above the canopy at which drift was sampled had a significant effect overall on the proportion of spray that was measured on the collectors (F prob=0.001) (Row showing 'mean across all sprayers' in Table 3.8). When drift landing on the vertical threads was averaged across all sprayers, significantly more drift (P<0.05) landed below 5.75 metres and above 9.75 metres than landed between these two heights (Table 3.8, Figure 3.6). The interactions between height and sprayer, or between height, sprayer and nozzle, were not significant (P>0.05).

3.3.6 Drift landing on the ground

Drift landing on samplers on the ground, in a zone extending from the sprayed row to 9.6 metres (five rows) away, varied according to the sprayer and nozzle used. Ground deposits are not affected greatly by cross winds, so it was appropriate to extrapolate the measurements taken on one side of the sprayer to derive a total for both sides. This showed that the ducted and conventional airblasts caused the least ground deposition, ranging between 7 and 13.7% of sprayer output. The set up poorly (not adequately directed into the canopy), the airshear sprayer caused the most ground deposits (24.2% of sprayer output) (Figure 3.9).

Ground deposits were not caused by run-off from over spraying. Run-off from foliage would have been evident as an increase in the deposits in the 30 cm 'zones' under the edges of the sprayed canopy, but deposits in these zones were lower than in the next row (Figure 3.10 and Table 3.10).

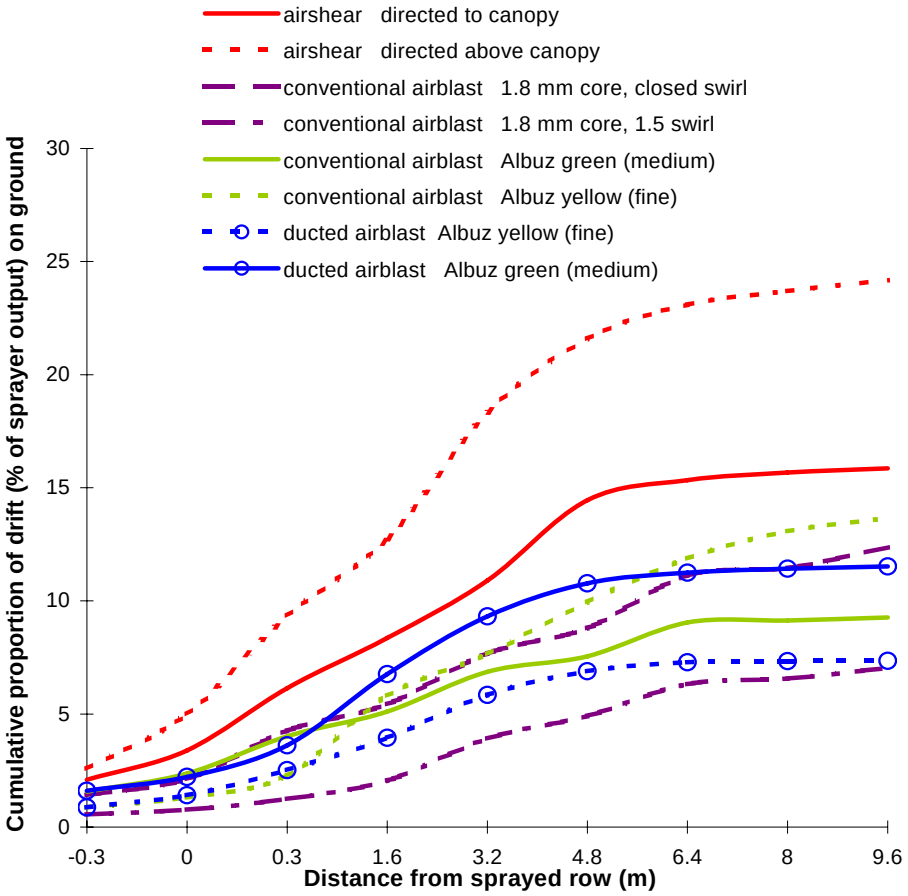


Figure 3.9: Cumulative deposition (as a percent of sprayer output, back transformed) with distance from the sprayed row. The values account for spray to the ground on both sides of the sprayer.

The main factor determining how much drift was collected on a ground sampler was its location (F pr = <0.001). Overall, across all sprayers the greatest amount of drift was collected from under the row adjacent to the one being sprayed (Figure 3.10 and Table 3.10).

The type of sprayer influenced ground deposits. The airshear sprayer deposited more spray directly under the sprayed vines than the conventional or ducted airblasts (Table 3.11). The ducted airblast deposited less under the further vine rows compared to the conventional airblast or airshear sprayer (Table 3.11).

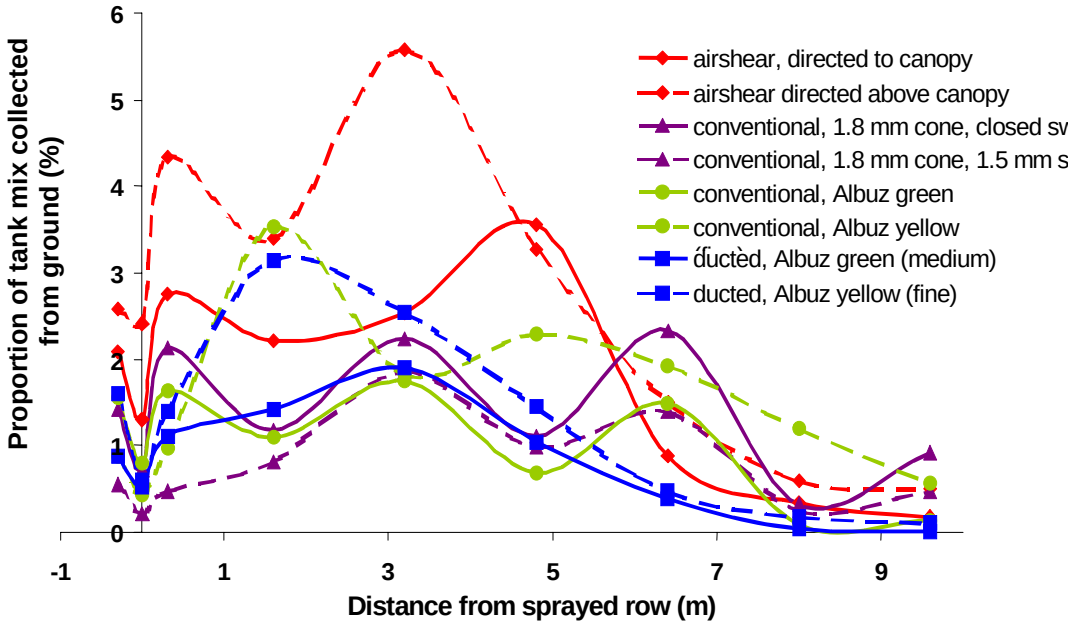


Figure 3.10: Distribution of deposits (as a percent of sprayer output, back transformed) with distance from the sprayed row. The values account for spray to the ground on both sides of the sprayer.

The sprayer-nozzle combination had a significant effect on the proportion of sprayer output (log PiZ + 0.01) that landed on the ground in each sampling position (F prob = 0.013).

- The conventional airblast with 'medium-coarse' nozzles (1.8 mm cone and 1.5 mm swirl) caused significantly more ground deposits than the 'fine-medium' version (hollow cone, closed swirl) of the same 1.8 mm nozzle (Table 3.10).
- The ducted airblast set up with the Albuz yellow 'mist' nozzles caused more ground deposition than the same sprayer set up with Albuz green 'medium' nozzles. The droplets tended to fall out in the inter-row area immediately adjacent to the sprayed row rather than moving across several rows (Table 3.10).

▪

Table 3.10: Proportion of sprayer output (% Log PiZ+0.01) landing on the ground at each distance (m) from the sprayed row. Backtransformed values are shown in Figure 3.10.

	Proportion of output (log transformed) landing at each distance (m) from the centre of the sprayed row $^{\phi}$									
Distance from spayed row	- 0.3 m	0 m	0.3 m	1.6 m	3.2 m	4.8 m	6.4 m	8.0 m	9.6 m	**Mean***
Area of the sampling zone (m^2)	0.3 m^2	0.3 m^2	0.3 m^2	2.1 m^2	0.9 m^2	2.1 m^2	0.9 m^2	2.1 m^2	0.9 m^2	
Sprayer and nozzle setting										
Airshear (Silvan Turbomiser)										
well directed	0.053	-0.417	0.327	0.112	0.246	0.580	-0.790	-1.707	-2.292	**-0.432 yz**
poorly directed	0.262	0.198	0.780	0.536	1.030	0.499	-0.271	-1.186	-1.355	**0.055 z**
Airblast (Agrimaster 'charlie')										
1.8 cc closed spinner	-0.328	-1.004	0.071	-0.513	0.120	-0.565	0.161	-1.744	-0.748	***-0.505 xy***
1.8 cc 1.5 spinner	-1.247	-2.142	-1.403	-0.876	-0.061	-0.677	-0.343	-1.997	-1.392	***-1.126 yz***
Albuz green	-0.231	-0.890	-0.182	-0.585	-0.123	-1.029	-0.281	-2.903	-2.524	**-0.972 xy**
Albuz yellow	-0.802	-1.488	-0.702	0.574	-0.076	0.148	-0.028	-0.483	-1.218	**-0.453 yz**
Airblast (Silvan ducted)										
Albuz yellow	-0.801	-1.288	-0.572	-0.325	-0.040	-0.629	-1.575	-3.390	-3.991	***-1.401 x***
Albuz green	-0.208	-1.153	-0.341	0.461	0.252	-0.307	-1.402	-2.342	-2.770	***-0.868 xy***
Mean[#]	**-0.413 bc**	**-1.023 d**	**-0.253 abc**	**-0.077 ab**	**0.169 a**	**-0.247 abc**	**-0.566 cd**	**-1.969 e**	**-2.036 e**	

[#] F-prob=<0.001; LSD=0.4669 to compare means between distances (values followed by same letters a,b or c are not significantly different)
* F-prob = 0.013; LSD = 0.7691 to compare between all sprayer nozzle combinations (values followed by same letters x,y or z are not significantly different)
* F-prob = 0.013; LSD = 0.5295 to compare nozzles within the same sprayer (*italicised pairs are significantly different*).

$^{\phi}$ LSD = 1.4247 when comparing across all sprayers, nozzles and distances.
LSD=1.3343 when comparing between nozzles, from the same sprayer at a given distance
LSD=1.3205 when comparing between distances from a particular sprayer and nozzle

Table 3.11: Percent of sprayer output (log PiZ + 0.01) deposited in each zone by each sprayer type.

Zone	Description of sampling zone	Percent of deposited by each sprayer in each zone(log(PiZ +0.01)) *			
		Airshear (Turbomiser)	Axial fan airblast with medium or coarse 1.8 - mm disc and core nozzles	Axial fan airblast with fine or medium Albuz nozzles	Ducted airblast sprayed with fine or medium Albuz nozzles
1-1		0.158	-0.787	-0.516	-0.505
1-2	Under sprayed row	-0.110 b	-1.573 a	-1.189 a	-1.221 a
1-3		0.553	-0.666	-0.442	-0.457
2	1st interrow	0.324	-0.694	-0.005	0.068
3	2nd undervine	0.638	0.029	-0.099	0.106
4	2nd interrow	0.539 b	-0.621 a	-0.440 ab	-0.468 ab
5	3rd undervine	-0.530 ab	-0.091 b	-0.154 b	-1.489 a
6	3rd interrow	-1.447 b	-1.871 ab	-1.693 b	-2.866 a
7	4th undervine	-1.824 b	-1.070 b	-1.871 b	-3.380 a
F-prob = 0.006; LSD = 1.0778					

* Values followed by the same letter are not significantly different

3.4 DISCUSSION

The mass balance study suggests that:

- 29-66% of sprayer output was captured within the sprayed canopy. Up to 16% was captured by vine canopy 6.4 metres further downwind.
- 0.1-7.25% of sprayer output was present up to 12.75 m in the air, downwind of the sprayed row.
- 7-24% of sprayer output was deposited onto the ground (including both sides of the sprayed row).

The discrepancy between sprayer output and spray deposits recorded, could be attributed to airborne drift being measured to one side of the sprayer only, and only up to 12.75 metres above ground. The discrepancy may also lie in the canopy deposits, because deposits measured in the canopy were taken from positions aligned with the cordon, which under-represent deposition on the outer canopy. Deposits on outer vine foliage are typically two or three times greater than deposits around the cordon (Murphy 1998; Manktelow & Praat 2000; Manktelow et al. 2004; MacGregor 2005).

Samples had to be collected immediately after spraying each test row, to minimise UV degradation of the fluorescent dye, and we were not able to explore any accumulation of drift deposits over time. However, other studies have shown that volatile agrochemicals continue to deposit on samplers above the canopy for over an hour after spraying (Holland et al. 1997) or even for several days (Glotfelty et al. 1990; Woodrow et al. 1977, 1997, all described in Holland et al. 1997).

The drift trials in Australian vineyards provide a picture of off-target losses as being less than or comparable to those measured in European and USA vineyards (SDTF 1997). The range of 7-31% of sprayer output leaving the vineyard as airborne and precipitating drift, at a growth stage when the canopy is at maximum dimensions (mid November) is less than predicted in the Basic Drift Values from Germany. Cumulative data interpolated from Ganzelmeier and Rautmann (2000) (Figure 3.11) suggest that up to 45% of output from an air-assisted sprayer might move beyond a vineyard at full canopy.

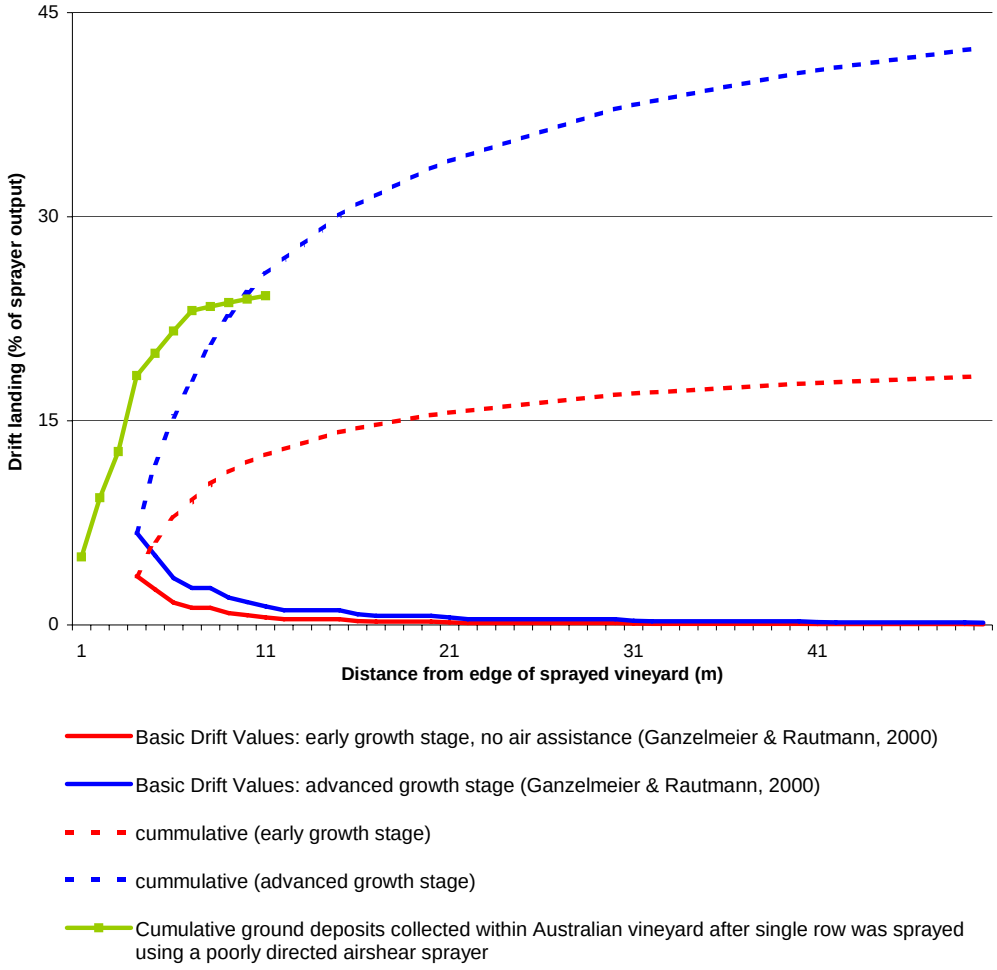


Figure 3.11: Basic drift values from German vineyard trials derived from Ganzelmeier and Rautmann (2000), with interpolated cumulative drift, and overlayed with one data set from the Australian vineyard trials.

The overall significant effect of height on deposits up to 12 metres is interesting to compare with vineyard trial data used to support the *AgDrift* model (SDTF 1997). Like our data, the SDTF data show that drift collected on vertical samplers in vineyards declined at increments up to a sampling height of six metres above the ground. Sampling in the SDTF vineyard trials did not extend above six metres.

Drift risk must be managed, particularly during the early part of the growing season, and this can be achieved using buffers

The amount of foliage available to intercept sprays, either as crop or as a vegetative buffer, has an impact on the proportion of spray that leaves an orchard or field crop (Ganzelmeier 1993; Praat et al. 2000; Dorr et al. 1998), and the same can be presumed for a vineyard. In accordance with German definitions of good professional practice, the Basic Drift Values for grapevines sprayed early in the season assume spraying without air assistance (Ganzelemeier 1993), with resultant low values early in the season. By contrast, the Basic Drift Values within 30 metres of orchards, where spraying with air-assistance is presumed at the early growth stages, are at least double the values for later in the season (Ganzelemeier 1993). In NZ apple trials, 1.95% of sprayer output landed 7.6 metres beyond the edge of an orchard in full foliage, but this amount increased to 17.8% landing at the same distance when the orchard was dormant (Praat et al. 2000). Cross et al. (2001b) also describe increasing drift with decreasing canopy density in orchards. Planting a vegetative buffer on the boundary of a sprayed area reduces the risk of drift. The Centre for Pesticide Application and Safety at the University of Queensland has conducted a variety of studies on drift reduction using buffers, and describe the ideal buffer as having a porosity of 40-50% and being at least 1.5 times the release height of the spray (Dorr et al. 1998).

Conventional airblast sprayers can be adjusted to minimise drift

While the proportion of grape growers using directed sprayers is increasing, many still use conventional airblasts. The latter growers tend to make few adjustments, and may not feel that their sprayer can be manipulated to reduce drift. Studies in apple orchards in the UK, where drift represented 16-30% of sprayer output, confirmed that drift from a conventional airblast could be managed. Three key adjustments were tested: droplet size, airflow and water volume. Reducing airflow (volume and speed) from the conventional airblast from 11.3 to 4.1 m^3/s (by adjusting the fan gear) reduced drift by 55-93% without compromising deposition in tree canopies (Cross et al. 2003). Increasing droplet size from 'very fine' to 'fine' to 'medium' was associated with a significant reduction in drift in one trial, although a barely significant reduction in another, which Cross et al. (2001b) attribute to wind conditions overriding the droplet size effect. Increasing application volume but maintaining droplet size, and so maintaining the quality of the spray plume, caused some reduction in drift, perhaps because having more droplets in a higher flow reduced the driftable fraction of the spray plume (Cross et al. 2001a). An optimum setting for an airblast sprayer to minimise drift might therefore be on low fan, delivering medium sized droplets in a medium to high water volume.

Using coarser nozzles does not guarantee a reduction in drift risk

The International (British Crop Protection Council) nozzle classification system, developed to describe the quality of a spray plume based on droplet size, now incorporates a drift potential factor (Southcombe et al. 1997). Although drift reductions have been reported when medium nozzles were used instead of fine nozzles (Cross et al. 2001b), a wide range of droplet spectra (and resultant drift) is also reported from a comparison of different nozzles classified as 'medium' (ASAE Standards 2000; Hoffmann & Kirk 2002).

Data from this study (Table 3.8) show that two nozzles with similar droplet spectra produced different amounts of drift, a reminder that vineyard managers cannot change nozzle type and then presume to have minimised drift.

Coarse droplets have a high initial momentum but once they slow down, fall to the ground within a few seconds. The relatively higher proportion of ground deposition when the 'coarse' 1.8 mm nozzle had a 1.5 mm steel disc (swirl plate) behind it (Table 3.10) was consistent with this predicted behaviour of 'coarse' droplets.

By contrast 'fine' or 'mist' droplets may stay airborne, in still air, for up to a minute or longer (Mathews 2000), where they are vulnerable to air movement that may further slow their settling time. Sprayer set-up was clearly as critical a factor as droplet size, because contrary to the generally predicted behaviour, a higher proportion of fine droplets than medium droplets were collected on the ground after spraying with the ducted airblast.

Using a directed sprayer can achieve (but does not guarantee) a reduction in drift risk

Drift risk can be reduced if a sprayer has nozzles and air outlets that can be directed into the canopy. Moreover, by directing sprayer outlets into the canopy, finer nozzles can be used to improve coverage without increasing drift, and the minimal airborne drift from the 'well-directed airshear' treatment (Figure 3.4) exemplified this. However Figure 3.4 also shows that a 'directed sprayer' can be poorly directed, increasing drift. Vineyard managers have varied perceptions about what 'well-directed' looks like, particularly regarding how much they can restrict heights and directions of nozzles, yet protect high or low shoot tips. Directing the sprayer towards the top and bottom foliage was shown to be wasteful, increases losses to air and ground, and is environmentally irresponsible.

Recirculating 'tunnel' sprayers capture spray that is not intercepted by canopy. Ganzlemeier (1993) recommends that about one third of the annually applied spray can be saved by using recirculating sprayers instead of conventional sprayers.

Several strategies can be combined to reduce the risk of spray drift

Management approaches such as the UK system *Local Environmental Risk Assessment of Pesticides* (LERAP), or the German standards for sprayers assume a progressive reduction in drift potential as the spray operator makes each of a series of adjustments to the sprayer or crop (Ganzelmeier & Rautmannm 2000; DEFRA 2002). Selecting particular nozzles, lowering the nozzle height, introducing drift buffers, using recirculating spray machinery and reducing airflow would all reduce drift risk. Where one stops in this process however, and decides that drift is minimal, becomes arbitrary unless drift is measured.

Quantitative methods for monitoring drift are useful for research. Vineyard managers are still confined to using simple qualitative methods.

Just as grape growers need simple ways to measure deposits in the vine canopy if they are to optimise deposition (MacGregor 2005; Manktelow et al. 2004; Riches et al. 2002), they also need simple ways to assess off-target deposits if they are to be confident that they are reducing losses to the air or vineyard floor.

In 2001, IUPAC (International Union of Pure and Applied Chemistry) launched a project to harmonise the conduct of trials for drift risk assessment and drift mitigation (IUPAC 2002), and in 2003 Germany and Spain commenced the joint project '*Test procedures for atomisers in fruit growing and viticulture*' (BBA 2005). Recommendations that emerge from those projects will be of interest to the Australian grape industry, but it is unlikely that the tracers, collectors, quantification methods and need for replication recommended for collecting aerial deposits could be used by vineyard managers. Compounds used for tracing drift include food dyes (red erythrosine, water blue), fluorescent dyes, chelated metal salts (manganese, zinc, copper and cobalt) or residues of the applied agrochemical (Fox et al. 1993; Mathews 2000). The use of some tracers after berry set raises quality assurance issues because of potential for residues at harvest. Moreover, recovery and quantification of tracers requires use of an appropriately equipped laboratory.

Some of the larger Australian winegrape producers have attempted to measure the drift produced from their vineyards. Whether their motive is to guide and justify adjustments in company expenditure on environmental management programs, or to assess whether current management has low enviromental

impact, having evidence that drift is minimal is a very positive measurable output for an environmental audit. An ideal method would be simple, visual, give a yes/no answer, and come with an easy system for documenting the assessments.

Vineyard managers are familiar with using yellow fluorescent pigment (Furness 2000) up until berry set, or water sensitive papers (WSP) (Ciba Giegy undated) to assess deposits in the canopy. Medium and coarse droplets that land on the ground in a sprayed vineyard can be visually noted using WSP as collectors, or using the fluorescent pigment. WSP do not register the impacts of the fine or very fine droplets in a spray plume and are useless as collectors of aerial drift. It is not surprising that one company using WSP to monitor drift beyond their vineyard's boundaries were pleased to find no deposits on the papers. Fluorescent pigment also has limitations. Ground deposits can be collected and cursorily assessed in the way that WSPs can be assessed, but deposits moving as drift outside the vineyard are likely to be at concentrations too low for the pigment to be easily seen on collectors. Kaolin powder is available for use in horticulture in Australia (Agnova 2005) and can be used as a tracer, providing a visual guide to deposition in the canopy or on air or ground collectors.

Drift experiments were limited to the one season in this project, and we have not yet had opportunity to measure drift at heights greater than 12 metres or directly above the sprayer. The pattern up to 12 metres does illustrate clearly how a spray plume that rises above the canopy becomes subject to the influences of atmospheric conditions (cross-winds, temperature, convection), more than to the controllable influences of droplet size or formulation. Appropriate placement of vertical samplers is therefore critical to being able to collect a representative measure of drift.

There is a large body of ecotoxicological data relevant to aquatic species, but very little data at this stage relevant to non-target terrestrial species. For this reason we have not attempted to make the link between measured drift and toxicity to non-target species. The data from these trials may, however, be valuable to researchers interested in terrestrial impacts and soil health, and to the APVMA staff assessing environmental risks during agrochemical registration.

3.5 CONCLUSIONS

Spray drift trials showed that the vine canopy intercepted between 29% and 66% of sprayer output, and therefore the sprayers were set up adequately to provide disease control. The trials were conducted in a vineyard with a well-developed canopy, and interception would have been substantially less early in the growing season, when the canopy was smaller and sparse.

Vines that were 6.4 metres downwind of the sprayed row collected between 1% and 16% of the sprayer output. The sprayer-nozzle combination determined how much drifted to downwind rows. The proportion of deposits that precipitated from air above the downwind canopy was similar to the proportion projected horizontally from the sprayer two rows away.

Aerial drift collected on a 12-metre tower represented between 0.06 and 7% of sprayer output. The main influence on airborne drift was the type of sprayer, but choice of nozzles on the sprayer also influenced airborne drift. The worst losses were associated with spraying a fine droplet from a 'directed sprayer' that was poorly set up, but fine droplets did not increase airborne drift when the same sprayer was well set up.

Sedimenting drift collected on the ground within 9.6 metres of the sprayed row represented the greatest (measured) proportion of off-target loss (7 - 24% of the sprayer output) (not including run-off from over-

sprayed foliage). This represents a high degree of wastage, and repeated dosing of the vineyard soil may affect soil health and/or lead to off-target contamination by erosion of, or leaching through, sprayed soils. It was the sprayer-nozzle combination that most influenced the distribution of ground deposits, rather than the sprayer itself. All sprayers caused losses to the ground, and the conventional airblast seemed as able to keep these to a minimum as the ducted sprayer.

Standardised methods for collecting drift and conducting trials are under development but are unlikely to be suitable for implementation by Australian vineyard managers as part of environmental self-auditing. Despite not providing quantitative data, there is a place for pigments, water sensitive papers and other tracers for monitoring (and then minimising) off-target losses in a commercial vineyard. Any spray moving above or below the canopy may be lost to the canopy. Comparing deposits on samplers above and below the canopy with deposits in the inner canopy provides a rough balance of where the sprayer output is going. If vineyard managers were to use simple monitoring tools (e.g. water sensitive papers or pigments) they could at least confirm that they have set up their sprayers to minimise losses to the air or ground.

Several models are available to predict drift, based on the observed behaviours of spray plumes under varying conditions, however like all models they are limited by inherent assumptions. The trials highlighted the role of sprayer set-up in determining drift behaviour, with airborne drift for each of the eight sprayer-nozzle combinations being best described by a separate quadratic model. Overall, drift to the ground at the different distances was best described with a linear model, despite the patterns of deposits for the individual sprayers being highly non-linear. Other than regarding droplet size, the results of our trials concur with data from other drift studies.

SECTION 4

TRIALS TO EXPLORE GROWER-FRIENDLY METHODS OF MEASURING MOVEMENT OF AGROCHEMICALS THROUGH VINEYARD SOILS

4.1 INTRODUCTION AND AIMS

Agrochemicals can be transported from agricultural land as a result of movement (leaching) through the soil profile with infiltrating water (Oregon State University 1993; Kookana et al. 1998). Leaching of agrochemicals can lead to contamination of groundwater or surface waters (e.g. rivers and lakes), which in turn may impact on aquatic ecosystems and drinking water quality (Kookana et al. 1998). Concerns about these impacts have prompted research in many regions of the world to both understand and prevent the leaching of agrochemicals through agricultural soils (Kookana et al. 1998).

The scoping study conducted as the initial phase of this project identified that leaching was likely to be a significant pathway for off-site movement of agrochemical from Australian vineyards (Mollah and MacGregor 2002). That study ranked 24 agrochemicals commonly used in Australian viticulture according to their likelihood of leaching (Table 4.1) and the risk they pose to water quality. The rankings were based on the persistence, mobility/adsorption, and water solubility for each agrochemical in soil. Five of the 24 agrochemicals were identified as having a moderate to high leaching potential.

At a project workshop held on 27 August 2002 (see Section 8.8), the project reference committee supported the recommendation by Mollah and MacGregor (2002) that before developing best practice recommendations to minimise the risk of agrochemical leaching, the grape industry needed a better understanding of the movement of agrochemicals through Australian vineyard soils.

Wine industry, research and government participants at the workshop also agreed that field trials were needed to validate the rankings of leaching likelihood and to determine whether the leaching of agrochemicals from Australian vineyards is therefore likely to impact on water quality.

As the leaching potential of agrochemicals is influenced by soil type and irrigation volume, it was considered necessary to investigate leaching scenarios that represent a range of soil and irrigation types.

Simazine was chosen as a suitable tracer for use in leaching trials. Simazine was rated as having moderate leaching potential (Table 4.1) and has been detected in groundwater and waterways within agricultural catchments (Bubb 2001; Domagalski & Dubrovsky 1992; Spurlock et al. 2000; Vidacek et al. 1996; Walls et al. 1996).

Table 4.1: Twenty-four agrochemicals used in Australian vineyards ranked according to their relative leaching potential (extracted from Mollah & MacGregor 2002)

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

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

In parallel with the aim of assessing leaching, the project aimed also to explore sampling and analytical methods that the industry could use for ongoing monitoring as part of best practice environmental management. Therefore, in selecting sampling tools/techniques we considered methods that would be suitable to use on commercial vineyards. 'Suction cup' samplers were identified as a potential sampling tool for extracting soil-water that could then be analysed for agrochemicals. A preliminary trial using suction cup samplers is detailed as Appendix 6.

4.1.1 Aims of agrochemical leaching studies

The aims of the work described in this section were to compare the rates of leaching through the soil profile, using simazine as an agrochemical tracer, under varying soil types and irrigation systems.

4.2 MATERIALS AND METHODS

A field study was designed to investigate three scenarios of agrochemical leaching. Overhead irrigation on sandy soil represented a high leaching potential, drip irrigation on sandy soil represented a medium leaching potential, and drip irrigation on clay soil represented a low leaching potential. Nine vineyards across Karadoc, Red Cliffs, Merbein and Irymple, all in north west Victoria, were selected to represent and replicate each scenario. Simazine was used as the leaching tracer at each site.

Four plots were selected at each vineyard site. Each plot was five metres in length along the under-vine bank, and 2.25 metres wide, extending across the undervine bank and into the interrow. Three plots were sprayed with simazine (treatment) and one was unsprayed (control) (Figure 4.1). The plots were close enough to be on similar soils, but distant enough from each other to avoid interference from simazine spraying or lateral or capillary movement of soil water.

Simazine was applied from both sides of the vine-row, at label rate (2.3 L/ha) using a 1.125 metre wide boom spray attached to a four-wheeled motor bike (Figure 4.2). The spray unit was turned on ten metres before reaching the start of each plot to allow the sprayer output to stabilise. The sprayer was turned off two metres past the end of the plot. The simazine application was timed to be immediately prior to a scheduled irrigation.

At each site, irrigation commenced within two hours of applying the simazine, to minimise any breakdown of the chemical before it could be leached into the soil profile. The irrigation was according to standard practice at that property.

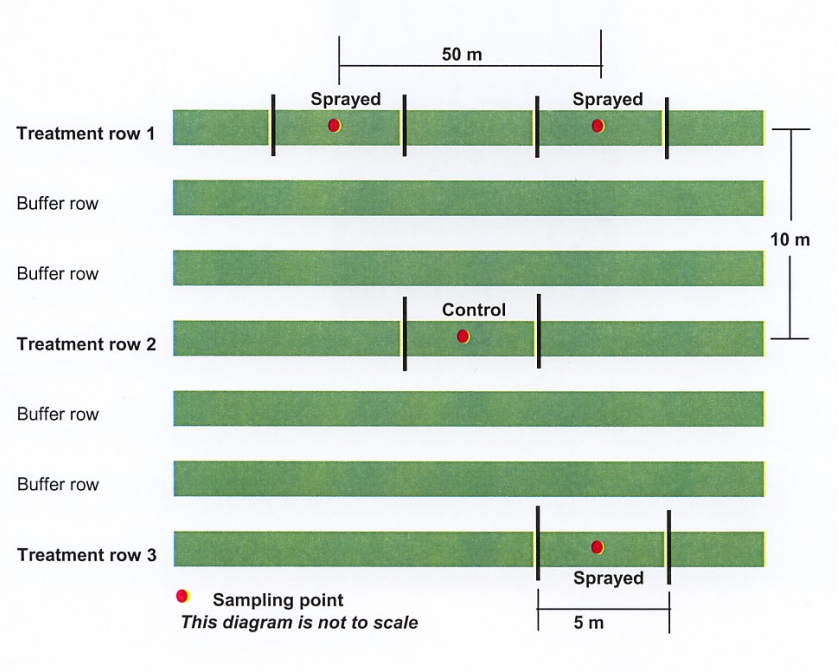


Figure 4.1 Location of treatment plots and soil sampling points at each site.

A Diviner2000™ probe was used to monitor movement of irrigation water through the soil profile. One access tube for the Diviner2000™ was installed at each site, in a central position relative to the treatment and control plots. Soil moisture was recorded at 10-cm intervals to a depth of 1 metre, prior to, during and following the irrigation, to track the infiltration of water.

As suction cups were found to be unsuitable for extracting soil-water for simazine analysis (Appendix 6), soil cores were collected and agrochemical concentrations measured in the soil.

Soil cores were collected after the treatment was applied. Sampling commenced either when the irrigation water reached a depth of one metre, or once water movement ceased at a depth of less than one metre. The length (hours) of irrigation and the time since the irrigation commenced were recorded.

Soil cores were drawn from up to 1-metre depths from the centre of each plot (Figure 4.1, Figure 4.2). In drip irrigated plots, the core was within the zone of influence of the dripper. Depth of the wetting front in each core was measured and recorded. Soil beyond the wetting front was discarded and the core then divided into three sub-samples:

- Subsample A – From the soil surface to a depth of 10 cm (this is the soil depth in which simazine is expected to remain to be active in controlling weeds).
- Subsample C – From 30 cm above the wetting front to the bottom of the wetting front (to determine the concentration of simazine that had leached with the wetting front).
- Subsample B - The remaining section of soil core between Subsample A and Subsample C.

Each sample was sealed in a plastic bag and placed into a cooler in the field. The samples were transferred to a minus 20^{o}C freezer within two hours of collection, prior to being sent to Australian Laboratory Services, Melbourne for analysis. Simazine was extracted from the soil samples using standard ALS methods (method reference: EP-068C-SS), with care being taken to minimise losses of soil

water (ie through evaporation). Sample extracts were analysed by Capillary GC/MS (method reference:USEPA SW 846 - 8270A).



Figure 4.2: Left: Applying simazine to the under-vine bank with a sprayer mounted on a four-wheel motor bike. Centre: Testing water movement through the soil profile using a Diviner2000. Right: A soil core removed for residue analysis.

4.2.1 Data analysis

Data were analysed by Analysis of Variance using GenStat Release 6.1 (6th Edition, 2002, Lawes Agricultural Trust, Rothamsted Experimental Station).

4.3 RESULTS AND DISCUSSION

Irrigations at the trial sites wetted soils to depths of 30 - 87 cm (Table 4.2). Rates of water infiltration were highest in vineyards with overhead irrigation and sandy soils, and lowest in vineyards with drip irrigation regardless of soil type. The exceptions were site 8 which had a carbonate layer under the sandy top-soil, and site 3 (Table 4.2).

Simazine was detected in the top 10 cm of soil in 23 of the 27 core samples. There was more simazine in the top 10 cm of soil in the overhead irrigated, sandy soil (0.407 mg/kg) than in the drip irrigated clay or sand (0.160 mg/kg) ($P=0.001$). However, there was no significant difference ($P>0.05$) between simazine concentrations in clay or sandy soil under drip irrigation (Table 4.3). A possible explanation for there being more simazine in the surface soil under overhead than under drip irrigation is that the overhead irrigation was more successful than drip irrigation at washing the herbicide treatment into the soil profile. This would protect the simazine from degrading effects of UV and temperature (Walker and Blacklow 1994) on the soil surface.

Simazine was detected beyond a 10-cm depth in only five of the 27 soil cores, and was at very low concentrations (0.05 – 0.08 mg/kg). Four of these soil cores were taken from drip irrigated vineyards and one from an overhead irrigated vineyard. If the saturated zone had an uneven shape, with ‘fingers’ of preferential water movement, this would influence the depth and shape of the wetting front and probably

also simazine movement. Additional cores within each sampling plot may have revealed 'fingering' and a hence a different result, but were beyond the budget of the project.

No simazine was reported beyond a soil depth of 45 cm. Concentrations of simazine less than the Limit of reporting (0.05 mg/kg) may have leached beyond 45 cm but were undetected.

Simazine may also leach further following subsequent irrigation or rainfall events. Low concentrations were detected in drainage water under one of the trial sites in the subsequent season, but its source was not determined.

Table 4.2: Infiltration of irrigation water through the soil profile at each site

Site	Scenario	Hours of irrigation	Hours samples were collected after commencement of irrigation[1]	Depth of wetting front in soil (cm)	Irrigation water infiltration rate cm/hour
1	Low leaching potential (drip irrigation on clay soil)	8	22	65	2.96
2		8	12	30	2.50
3		8	10	75	7.50
4	Moderate leaching potential (drip irrigation on sand)	32	52	55 - 70	1.06 - 1.35
5		12	15.5	70 - 87	4.52 - 5.61
6		12	15	65 - 75	4.33 - 5.00
7	High leaching potential (overhead irrigation on sand)	2	2.5	87	34.80
8		8	8.5	55	6.47
9		2	2.5	50 - 70	20.00 - 28.00

[1] Samples were collected when the irrigation water reached a depth of one metre, or ceased moving through the soil.

Table 4.3: Mean simazine concentration (mg/kg) measured in the top 10 cm of soil.

	Clay soil		Sandy soil	
	Treated	control	Treated	control
Drip irrigated	0.202 b	<0.05	0.118 b	<0.05
Overhead irrigated			0.407 a	<0.05
LSD = 0.114				

4.4 CONCLUSION

More simazine was measured in the top 10 cm of overhead-irrigated, sandy soil than in drip-irrigated clay or sand.

There was no significant difference between simazine concentrations in clay or sandy soil under drip irrigation, in the top 10 cm.

Simazine was detected beyond a 10-cm depth in 22% of the soil cores from drip-irrigated soils and 11% of cores from overhead-irrigated soils.

No simazine was reported beyond a soil depth of 45 cm.

As a method, using soil cores to monitor leaching had drawbacks:

- The limit of reporting for soil samples (ppm) is too high relative to the limit of reporting for water (ppb).
- Soils are expensive to analyse which precluded repeated sampling after subsequent irrigations.

SECTION 5

COMPARISON BETWEEN MODELLED PREDICTIONS OF LEACHING RISK AND RESULTS OF FIELD MONITORING

5.1 INTRODUCTION AND AIMS

There are various computer-based models to predict the off-target movement of agrochemicals, or associated risks, and several were described in a review for the wine industry (Mollah & MacGregor 2002). One is the Pesticide Impact Risk Index (PIRI) (Kookana et al. 2005), developed to estimate the contamination of waterways attributable to agrochemicals. PIRI considers leaching, surface water run-off, movement of agrochemical in soil erosion and spray drift, and includes such conditions as soil type, infiltration rate, irrigation and rainfall. PIRI assesses the risk of leaching (high, medium or low) and the potential impact on aquatic species. Based on its successful use in other industries to predict leaching of agrochemicals, PIRI was considered likely to be useful for predicting leaching from vineyards, and so assist in the development/refinement of best practice recommendations for Australian grape growers, to reduce the risk of agrochemical leaching.

Predictions from PIRI were not supported by field data specifically from vineyards (Kookana, pers. comm.). Some validation was therefore required, prior to its broad scale adoption for predicting agrochemical leaching in vineyard soils. A field trial was conducted in irrigation Catchment 8 at Red Cliffs near Mildura, Victoria, as a first step towards validating PIRI for Australian vineyard scenarios.

Catchment 8 consists of 169 hectares of land, of which 122 hectares are irrigated for horticultural production (Dudley 2001). The irrigated properties within this catchment all contain sub-surface tile drainage that can be accessed at a number of locations throughout the catchment, making it possible to monitor drainage water from various irrigated properties. We believed therefore, that Catchment 8 was well suited to conducting the PIRI validation trial. Previous studies conducted within Catchment 8 investigated the leaching of salt and nutrients into sub-surface drainage water, and a considerable amount of information (e.g. soils data, drainage volumes, contaminant leaching) already existed for this catchment.

Sampling of drainage water to measure agrochemicals presents some challenges. Sampling to assess water quality has conventionally involved collecting and analysing ‘grab samples’ of water. Grab samples provide accurate measures of water quality, but only at the specific time of collection (ANZECC and ARMCANZ 2000).

Water quality in drains or waterways is likely to vary over time, for example agrochemical is likely to enter a waterway as a single pulse or a series of short pulses. Sampling needs to take account of this to avoid over- or under-estimates of agrochemical concentrations (ANZECC and ARMCANZ 2000, Hyne et al. 2004a). To be effective, grab samples therefore need to be very strategically timed and/or taken frequently, the latter being costly to analyse. Sampling and analytical methods also need to account for the fact that agrochemicals can be present in drainage water at very low concentrations (parts per billion - ppb).

To overcome the issue of pulses in agrochemical contamination, some effort has been directed to developing time-integrated “passive samplers” (ANZECC and ARMCANZ 2000; Hyne et al. 2004b; Koci et al. 2004; Lu and Wang 2003; Wennrich et al. 2003). Passive samplers gradually accumulate agrochemicals from surrounding water, typically over two to three weeks. Their capacity to accumulate agrochemicals depends on properties of the agrochemicals and the solvent used in the sampler

(Appendices 4 and 5). By calibrating the samplers the concentration of agrochemical can be expressed as a daily average.

Time-integrated 'passive' samplers consist of solvent in a low-density polyethylene membrane bag. The solvent attracts and accumulates agrochemical from surrounding water. A summary of passive samplers and their construction is provided in Appendix 4 and described in more detail by Hyne et al. (2004b).

Not all agrochemicals can be monitored using passive samplers. The rate of chemical uptake through the membrane bag and into the solvent depends on its octanol-water partition coefficient (K_{ow}) and exposure time (Leonard et al. 2002). The K_{ow} of a chemical or compound is a measure of the solubility of the compound in octanol compared with water.

Different solvents are required to attract chemicals with different K_{ow} values. A passive sampler filled with 2,2,4-trimethylpentane solvent can efficiently gather chemicals with log K_{ow} > 3.5. Mixing three parts of 1-dodecanol with two parts of 2,2,4-trimethylpentane allows for efficient gathering of chemicals with log K_{ow} > 2.9. i.e. combining two solvents increases the capability of the passive sampler to gather a wider range of chemicals.

Passive samplers had been used in 2003/04 to monitor agrochemicals in irrigation drainage water in the Mallee, in a complimentary project being conducted with the Mallee CMA, funded by the National Action Plan for Salinity and Water Quality. Results of that work indicated that the passive samplers would be a cost-effective way to monitoring agrochemicals in drainage water for the PIRI validation study.

5.1.1 Aims of agrochemical monitoring and comparison of model predicted values

The aims of the work reported in this section were to:

- Predict the leaching of agrochemical from horticultural properties within a pilot catchment, using the Pesticide Impact Risk Index (PIRI).
- Monitor agrochemicals leaching from horticultural properties in the pilot catchment.
- Compare predicted results with monitored data to evaluate the suitability of PIRI as a tool to predict leaching from vineyards.

5.2 MATERIALS AND METHODS

5.2.1 Predicting the relative risks of agrochemical leaching using the PIRI model

Seven horticultural properties from Catchment 8 in Red Cliffs in northwest Victoria were selected to generate seven scenarios in PIRI. These scenarios represent a variety of management approaches, crops, soil characteristics, chemical use patterns and irrigation systems.

The drainage sampling point for scenario 1 was at the head of the catchment and had no interference from other drains, while scenarios 6 and 7, at the foot of the catchment, had the greatest accumulation of water from other scenarios or other properties (Figure 5.1). It was not always clear which properties might contribute to drainage at each sampling point, but every effort was made to identify the properties that affected each scenario.

Input data was collected from the properties in each scenario (Table 5.1) and provided to CSIRO Land and Water in Adelaide, where they were incorporated into the PIRI model to predict the risk (low, medium or high) of agrochemical leaching in each of the seven scenarios. Only limited site details are reported (Table 5.3), to protect the anonymity of the growers who participated in the trial.

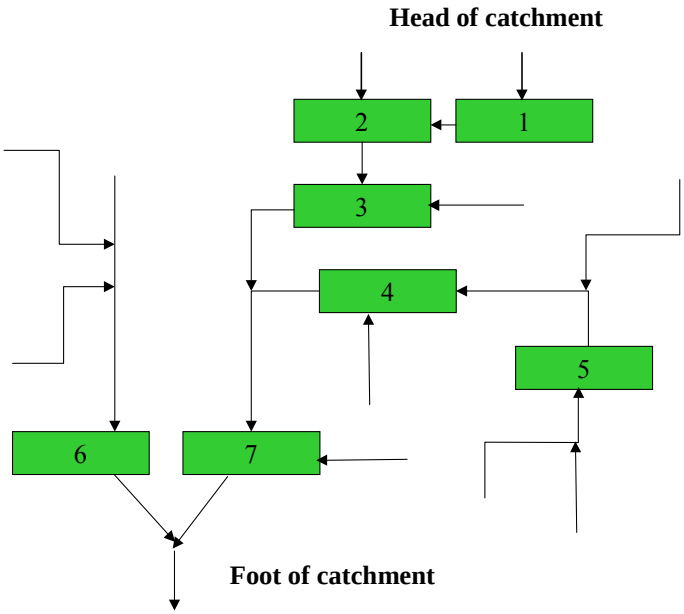


Figure 5.1: Location of drainage sampling points in Catchment 8. The arrows indicate drainage flows in relation to the seven sampling points.

Table 5.1: Input data describing the seven horticultural property scenarios, required for the PIRI prediction model.

Data Type	General crop data	Agrochemical data	Description of soil type	Irrigation and drainage data
Components of data type	Crop type Property size Crop season Temperature range	Chemical trade name Active ingredients and their concentration Frequency and rate of application (provided by property managers)	Depth of top soil Carbonate type below the top soil Depth in profile Type of soil in the profile Percent $CaCo_3$ in top 10 cm soil Carbonate reaction R.A.W. in top soil and plant root zone Soil bulk density	Irrigation method Depth of ground water or tile drains Drainage flow rate Irrigation per hectare per week in the growing season Annual rainfall

The PIRI model was used to predict leaching risk only for the agrochemicals stated as having been used on properties in each scenario. This risk was predicted by PIRI assuming two different situations regarding water movement through the soil profile:

a) typical situation, where 20% of applied water reached the tile drains
b) worst-case situation, where 40% of applied water reached the tile drains.

5.2.2 Monitoring of agrochemicals in drainage water

Drainage water from each of the seven Catchment 8 sites was monitored for agrochemical contamination between January and May 2005 using integrated 'passive' samplers (ANZECC & ARMCANZ 2000, Hyne et al. 2004b) (Figure 5.2).

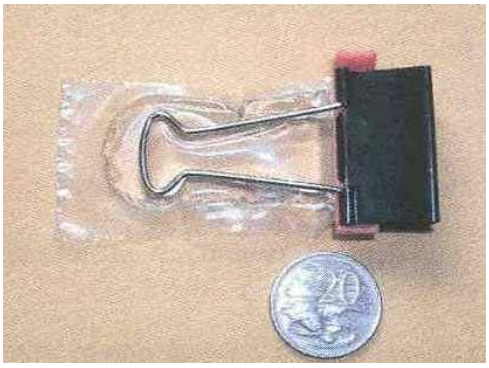


Figure 5.2: Integrated passive sampler. A low-density polyethylene (LDPE) membrane bag containing a solvent which absorbs agrochemicals.

Only a select number of the agrochemicals used on Catchment 8 sites could be monitored using passive samplers as only a limited number have log K_{ow} > 2.9 and even fewer have K_{ow} > 3.5. To maximise the screening potential of samplers deployed in Catchment 8, they were made using three parts of 1-dodecanol and two parts 2,2,4-trimethylpentane (referred to below as 'DIPS' samplers). However, it became apparent that combining the solvents reduced the precision of analysis by the laboratory. For this reason the passive samplers used during the final three sampling periods (April-May 2005) contained only 2,2,4-trimethylpentane (referred to below as 'TRIMPS' samplers).

The first set of seven passive samplers was deployed in Catchment 8 drains in January 2005. Prior to deployment, the samplers were stored and transported to the field in a container of deionised water. After being left for 21 days in a drain, each sampler was collected and a subsequent set of samplers was deployed for a further 21 days. After being collected, the solvent from each sampler was decanted into a separate glass vial and kept in a portable ice-cooled insulated box in the field before being transferred to a minus 70°C refrigerator for storage prior to analysis.

At each sample time, two additional 'control samplers' were handled, stored and processed in the same way as those deployed in drains, but were not actually left in situ at any site. After each set of seven 'drainage samplers' had been positioned in drains, the solvent from each of the two control samplers was

decanted, cooled then frozen as described above. These control samplers were used as unexposed controls when the drainage samplers were analysed.

Monitoring ceased at the end of May 2005. By that time, a total of 28 DIPS samplers (four sample times in Jan-Mar 2005) and 21 TRIMPS samplers (three sample times in April and May 2005) had been exposed to drainage water. The samples were then sent to the Centre for Ecotoxicology, NSW Department of Environment and Conservation, Sydney for analysis. Concentrations of different agrochemicals in each sample were measured using GC with an electron capture and verified with a nitrogen/phosphorus detector on a DB1 column (Agilent Technologies, Australia Pty Ltd).

Details of analytical methods provided by the Centre for Ecotoxicology, Sydney

The 2,2,4- trimethylpentane solvent from the TRIMPS and the (3:2) 1- dodecanol: 2,2,4- trimethylpentane mixed solvent from the DIPS deployed were analysed for agrochemicals by direct injection into the GC. Agochemical concentrations were measured with an electron-capture detector (ECD) on an AT-1 (Alltech) column (30m x 0.25mm x 0.25μm) using a temperature program of 4°C/minute increments from 100 to 275°C, nitrogen was used as the carrier gas at 30ml/min in a Agilent 6890N GC system. Agrochemicals were confirmed on a nitrogen-phosphrous detector (NPD) using the above same GC conditions and column. Using ChemStation software, chromatographs were manually integrated to look for compounds of interest and any large re-occurrring unknown peaks. Two-point regression (a blank and a previously confirmed standard solution from a concentration series) was used to convert these peak areas within the calibration standards to agrochemical concentrations. For this purpose a series of duplicate standard solutions were prepared from high-purity pesticides obtained from Chem Service (Alltech, Sydney, Australia) or Riedel de Hahn (Sigma Aldrich).

Table 5.2: Analyses of passive samplers in a standard screening provided by the Centre for Ecotoxicology, NSW.

Sampler type	Number of samplers	Sampling periods	Chemicals included in the screening
DIPS	28	Four sampling periods, January to March 2005	dicofol simazine chlorpyrifos captan malathion methidathion oxyfluorfen chlorothalonil
TRIMPS	21	Three sampling periods, April and May 2005	dicofol chlorpyrifos methidathion oxyfluorfen

The Centre for Ecotoxicology laboratory conducted a standard screening across all the DIPS samples for eight chemicals, and a standard screening across all the TRIMPS samples for four chemicals (Table 5.2). Those chemicals were selected for screening as the laboratory already had the necessary methods and

calibrations. The chemicals were considered relevant as they had previously been detected in drainage water in the Mallee through monitoring conducted under a complimentary Mallee CMA project. Each of the chemicals listed in Table 5.2 was used by at least one grower in Catchment 8 during the current project. The narrow range analysed was associated with the laboratories' preparedness to procure standards and lack of resources to develop the calibrations for quantitative reporting across the whole range of agrochemicals.

Table 5.3: A selection of details collected from sites selected for the leaching scenarios in the PIRI validation trial, provided to CSIRO Land and Water for inclusion in the PIRI model.*

Scenario	Lists of chemicals used (provided by property managers)	Soil type	Irrigation applied during growing season (ML/ha/week)
1	*Bacillus Thuringiensis,* canola oil, chlorothalonil, chlorpyrifos, dithianon, glyphosate, mancozeb, sulphur, triadimenol	Mixture of fine carbonate in clay and fine carbonate in sandy loam to clay loam under 20 - 80 cm top soil	0.44
2	Captan, carbaryl, dicofol, iprodione, mancozeb, methidathion, paraquat/diquat, parathion-methyl, penconazole, prothiofos, pyrimethanil, spiroxamine, sulphur, tau-fluvalinate, ziram	Mixture of fine carbonate in clay and fine carbonate in sandy loam to clay loam under 20 - 80 cm top soil	0.37
3	Carbendazim, chlorpyrifos, cuprous hydroxide, dicofol, glyphosate, gluphosinate ammonium, mancozeb, paraquat/diquat, penconazole, pendimethalin, prothiofos, pyrimethanil, simazine, sulphur, tau-fluvalinate, ziram	Mixture of calcrete rubble up to 10 cm in diameter, fine carbonate in clay and fine carbonate in sandy loam to clay loam under 35 – 120 cm top soil	0.40
4	Captan, glyphosate, mancozeb, paraquat/diquat, sulphur	Fine carbonate in sandy loam to clay loam under 30 - 70 cm top soil	0.58
5	glyphosate	Mixture of fine carbonate in clay and sandy loam to clay loam under 30 - 70 cm top soil.	0.39
6	carbendazim, chlorpyrifos, fenarimol, glyphosate, mancozeb, paraquat/diquat, penconazole, prothiofos, simazine, sulphur, triadimenol	Mixture of calcrete rubble up to 30 cm in diameter and fine carbonate in sandy loam to sandy clay under 35 – 110 cm top soil	0.37
7	glyphosate, mancozeb, sulphur	Mixture of calcrete rubble up to 30 cm in diameter and fine carbonate in sandy loam to sandy clay under 20 – 50 cm top soil	0.29

* Additional detail has been withheld to protect privacy of participating growers

The analytes in Table 5.2 do not encompass the wider range of agrochemicals applied to each scenario in the trial (Table 5.3) nor do they reflect the full range of chemicals that can be absorbed by DIPS or TRIMPS samplers. Interpretation of the results focused on the few agrochemicals that were applied and also included in the laboratory screening.

The concentrations of agrochemical detected in drainage water were compared against the relative risks of leaching (low, medium, and high) predicted by PIRI, according to the input data from each site/scenario.

5.3 RESULTS

5.3.1 Comparison between the results of field monitoring and the leaching risk as predicted by PIRI

There was evidence of agrochemical leaching from vineyards and other horticulture in Catchment 8. Table 5.4 shows the proportions of samplers, sites and sampling periods in which seven agrochemicals were detected in passive samplers from drains in the study area.

Simazine had the highest ratio of detection, with a positive finding in 61% of the samplers screened for the chemical. Chlorpyrifos and simazine were detected at the greatest number of sites and over the longest periods. According to PIRI, there was a high risk of simazine leaching, and a low risk of chlorpyrifos leaching (Table 5.6).

Table 5.4: Incidence of agrochemical leaching into irrigation drainage from vineyards and other horticulture in Catchment 8.

Agrochemical	Total number of samplers	Incidence of detections			
		Number of detections	Proportion of detections %	Number of sites *	Proportion of sampling periods
simazine	28	17	61	6	4 out of 4
chlorpyrifos	49	29	59	7	6 out of 7
malathion	28	9	32	5	3 out of 4
dicofol	49	15	31	5	3 out of 7
methidathion	49	13	27	5	5 out of 7
oxyfluorfen	49	5	18	3	4 out of 7
chlorothalonil	28	3	11	3	1 out of 4
captan	28	0	0	0	0 out of 4

* There were seven sites in total

Of the chemicals applied under the seven scenarios, five were considered by PIRI to have a high leaching risk (Table 5.5). Of the two of these that could be absorbed by the passive samplers, the laboratory only analysed for simazine.

Table 5.5: Active ingredients of products used on properties in Catchment 8, the relative risk of their leaching as predicted by PIRI (Kookana 2005) and the potential to monitor for them using DIPS or TRIMPS passive samplers.

active ingredient	Risk of leaching in Catchment 8 under average and worst-case irrigation* or rainfall		Absorbed by DIPS (K_{ow} > 2.9)	Absorbed by TRIMPS (K_{ow} > 3.5)
	Average	Worst-case		
carbendazim	high	high	N	N
sulphur	high	high	N	N
copper hydroxide	medium	high	N	N
triadimenol	medium	high	Y	Y
simazine	low	high	Y	Y
fenarimol	low	Medium	nd	nd
mancozeb	low	Medium	nd	nd
penconazole	low	Medium	Y	Y
ziram	low	Medium	N	N
captan	low	low	Y	N
carbaryl	low	low	Y	N
chlorothalonil	low	low	Y	Y
chlorpyrifos	low	low	Y	Y
dicofol	low	low	Y	Y
dithianon	low	low	Y	Y
glyphosate	low	low	N	N
iprodione	low	low	Y	Y
methidathion	low	low	Y	Y
paraquat/diquat	low	low	N	N
parathion-methyl	low	low	Y	Y
pendimethalin	low	low	Y	Y
tau-fluvalinate	low	low	Y	Y
prothiofos	N.A.	N.A.	Y	Y
spiroxamine	N.A.	N.A.	nd	nd
pyrimethanil	N.A.	N.A.	Y	N
bacillus thuringiensis	N.A.	N.A.	N	N
canola oil	N.A.	N.A.	N	N

* The degree of risk predicted by PIRI was influenced by frequency of application, information provided by the growers.

nd = not determined.

The risk of leaching associated with each agrochemical varies according to the frequency of chemical application, and irrigation management and soil properties at a specific site. The overall relative risks shown in Table 5.5 are presented in Table 5.6 as they relate to each scenario in Catchment 8.

Table 5.6: Agrochemicals recommended for monitoring in drainage from properties in Catchment 8, based on their leaching potential as predicted by PIRI (Kookana 2005).

Scenario	**Predicted leaching potential** (assuming at worst that 40% of total water applied leaches through the soil profile)		
	High leaching potential	Medium leaching potential	Low leaching potential (monitor to validate its absence)
1	sulphur	mancozeb	chlorpyrifos
2	sulphur	ziram, and penconazole	iprodione
3	sulphur, copper, simazine and carbendazim	ziram and penconazole	chlorpyrifos and pendimethalin
4	mancozeb and sulphur	captan	glyphosate
5	-	-	glyphosate
6	sulphur, simazine and carbendazim	fenarimol	chlorpyrifos
7	sulphur	-	mancozeb

The relative risks predicted by PIRI (Table 5.5) differ in some cases from the relative risks in Table 4.1. The latter was based solely on physical and chemical properties while Table 5.5 also takes into account the rate and frequency of chemical and irrigation applications and site characteristics. The differences between the risk predictions for some chemicals in the two tables (Table 5.7) highlights the importance of including specific site information.

Table 5.7: Comparison between leaching potential, predicted based on chemical properties alone (from Table 4.1) or from PIRI (Table 5.5).

Active constituent	Leaching potential	
	Based on solely on chemical properties (from Table 4.1)	Based on site information and chemical properties (from Table 5.5)
Sulphur- elemental	Low	high
Copper hydroxide	Low	Medium – high
Triadimenol	medium	Medium – high
Simazine	medium	Low – high
Captan	medium	low
Carbaryl	medium	low
Fenarimol	Very low	Low – medium
Mancozeb	Low	Low – medium
Penconazole	Low	Low – medium
Ziram	Low	Low – medium
Chlorothalonil	Low	low
Paraquat/diquat	Very low	low
Iprodione	Low	low
Chlorpyrifos	Very low	low
Glyphosate	Low	low

The risks associated with each individual scenario, as predicted by PIRI, are compared against results of monitoring from drains under each scenario, in the following pages.

Scenario 1

PIRI predicted a low risk that chlorothalonil would leach under scenario 1. The drainage monitoring supported this prediction.

PIRI also predicted a low risk that chlorpyrifos would leach under scenario 1, which may have been an underestimate as chlorpyrifos was detected during the first sampling period at a moderate concentration and a low concentration in the second sampling period, although not detected after that.

Agrochemicals that apparently were not used on these properties appeared in the irrigation drainage water. Methidathion, malathion and oxyfluorfen were all detected in samplers from scenario 1, despite not being listed as used on these properties. PIRI had not been used to assess leaching risk of these chemicals.

Scenario 1	Predicted risk ϕ	Concentration (μg/L) in passive sampler solvent						
		25-Jan 2005	15-Feb 2005	8-Mar 2005	28-Mar 2005	19-Apr 2005	11-May 2005	31-May 2005
Chemicals applied								
sulphur	High	Not absorbed by DIPS or TRIMPS						
mancozeb	Medium							
triadimenol	Low	Absorbed, but not included in the analysis						
dithianon	Low							
chlorpyrifos	Low	2.68	0.184	ND	ND			
chlorothalonil	Low	ND	ND	ND	ND			
glyphosate	Low	Not absorbed by DIPS or TRIMPS				Drain ran dry, preventing further sampling		
Bacillus thuringiensis	NA [1]							
canola oil	NA [1]							
Chemicals not reported as applied, but detected								
methidathion	Risk not predicted	ND	3.17	ND	ND			
malathion		2.24	ND	ND	30.4			
oxyfluorfen		ND	ND	0.074	ND			

ϕ In worst case of high irrigation or rainfall (40% of applied water leaching to the tile drain).

[1] Not supported by sufficient environmental fate data to make any leaching risk assessment

NA = not applicable, ND = not detected

In this table, chemicals are ranked by predicted risk and grouped (by shading) according to the outcome of the analysis.

Scenario 2

PIRI predicted a low risk that dicofol, captan or methidation would leach under scenario 2. The drainage monitoring supported this prediction. Methidathion was detected during the first sampling period, but not thereafter. Neither dicofol nor captan was detected throughout the trial at this site.

Chlorpyrifos and simazine were detected in samplers from scenario 2, although not listed as being used on those properties. The chlorpyrifos concentrations were similar to concentrations found in scenario 1, which is adjacent land. The detection may be due to sub-surface lateral movement of irrigation from other properties, or due to chlorpyrifos having been used although not reported. Simazine appeared in late March, coinciding perhaps with post-harvest irrigations applied elsewhere in the catchment, and lateral movement of soil water to this site. Simazine was not detected in the adjacent properties (in scenario 1).

Scenario 2	Predicted risk ϕ	Concentration (μg/L) in passive sampler solvent						
		25-Jan 2005	15-Feb 2005	8-Mar 2005	28-Mar 2005 [2]	19-Apr 2005	11-May 2005	31-May 2005
chemicals applied								
sulphur	High	Not absorbed by DIPS or TRIMPS						
ziram	Medium							
penconazole	Medium	Absorbed but not included in the analysis						
captan	Low	ND	ND	Drain ran dry and sampler dried out	ND	Drain ran dry, preventing further sampling		
dicofol	Low	ND	ND		ND			
methidathion	Low	4.48	ND		ND			
iprodione	Low							
parathion-methyl	Low	Absorbed but not included in the analysis						
tau-fluvalinate	Low							
carbaryl	Low	Absorbed by DIPS, but not included in the analysis						
prothiofos	NA [1]							
pyrimethanil	NA [1]							
spiroxamine	NA [1]							
mancozeb	Low	Not absorbed by DIPS or TRIMPS						
paraquat/diquat	Low							
Chemicals not reported as applied, but detected								
simazine	Risk not predicted	ND	ND	Drain ran dry and sampler dried out	29.8			
chlorpyrifos		2.52	0.858		ND			

ϕ In worst case of high irrigation or rainfall (40% of applied water leaching to the tile drain).

[1] Not supported by sufficient environmental fate data to make any leaching risk assessment

[2] The blank sampler on this date was contaminated with simazine, however the contamination did not affect samplers from all the sampling sites.

NA = not applicable, ND = not detected

In this table, chemicals are ranked by predicted risk and grouped (by shading) according to the outcome of the analysis.

Scenario 3

The PIRI prediction that there was a high risk of simazine leaching under this scenario was supported by the drainage monitoring.

PIRI may have underestimated the risk of chlorpyrifos and dicofol leaching. Chlorpyrifos and dicofol were predicted by PIRI to have low leaching potential under this scenario, but both were detected intermittently in drainage throughout the trial period.

Malathion appeared in the irrigation drainage at relatively high concentrations during the post-harvest sampling periods. PIRI had not made an assessment of leaching risk as malathion was not listed as used on these properties.

Scenario 3	Predicted risk ϕ	Concentration (μg/L) in passive sampler solvent						
		25-Jan 2005	15-Feb 2005	8-Mar 2005	28-Mar 2005 [1]	19-Apr 2005	11-May 2005 [2]	31-May 2005 [2]
chemicals applied								
simazine	High	13.8	ND	37.1	27.3			
carbendazim	High	Not absorbed by DIPS or TRIMPS						
sulphur	High							
copper hydroxide	High							
cuprous hydroxide	High							
ziram	Medium							
penconazole	Medium	Absorbed but not included in the analysis						
tau-fluvaliinate	Low							
pendimethalin	Low							
prothiofos	NA							
pyrimethanil	NA							
chlorpyrifos	Low	1.15	ND	2.37	ND	ND	0.336	0.071
dicofol	Low	ND	ND	ND	ND	1.132	0.310	0.221
glyphosate	Low	Not absorbed by DIPS or TRIMPS						
gluphosinate ammonium	Low							
paraquat/diquat	Low							
mancozeb	Low							
Chemicals not reported as applied, but detected								
malathion	Risk not predicted	ND	ND	45.6	18.2			

ϕ In worst case of high irrigation or rainfall (40% of applied water leaching to the tile drain).

[1] The blank sampler on this date was contaminated with simazine.

[2] The blank sampler on this date was contaminated with chlorpyrifos.

These contaminations did not affect samplers from all the sampling sites.

NA = not applicable, ND = not detected

In this table, chemicals are ranked by predicted risk and grouped (by shading) according to the outcome of the analysis.

Scenario 4

PIRI predicted a medium risk that captan would leach under scenario 4, but none was detected in the samplers, which may suggest that PIRI overestimated the risk.

None of the other chemicals listed as being used under this scenario could be measured using DIPS or TRIMPS samplers, precluding any comparison between field monitoring and the model predictions.

Simazine, chlorpyrifos, chlorothalonil, dicofol, methidathion and malathion were detected in scenario 4 drains during one or more sampling periods. This result suggests that the extent of land draining into the sampling point 4 was not accurately identified on the maps from the water authority, i.e. there is a lateral movement in the sub surface water between sections of the catchment.

The results of this scenario also highlight that the value of using the passive samplers in irrigation drains is limited by the range of products they can measure, which may not be aligned with chemicals being used. In contrast, the results also highlight that it may be important to screen for a broader range of chemicals than are being currently used on a property.

Scenario 4	Predicted risk ϕ	Concentration (μg/L) in passive sampler solvent						
		25-Jan 2005	15-Feb 2005	8-Mar 2005	28-Mar 2005 [1]	19-Apr 2005	11-May 2005 [2]	31-May 2005 [2]
chemicals applied								
sulphur	High	Not absorbed by DIPS or TRIMPS						
mancozeb	High							
captan	Medium	ND	ND	ND	ND			
glyphosate	Low	Not absorbed by DIPS or TRIMPS						
paraquat / diquat	Low							
chemicals not reported as applied, but detected								
simazine	Risk not predicted	68.2	13.8	ND	ND			
chlorpyrifos		2.17	ND	0.70	ND	0.328	0.255	0.062
chlorothalonil		1.64	ND	ND	ND			
dicofol		ND	ND	ND	ND	0.519	0.507	0.353
methidathion		ND	4.56	ND	ND	2.37	ND	3.02
malathion		ND	ND	7.93	30.4			

ϕ In worst case of high irrigation or rainfall (40% of applied water leaching to the tile drain).

[1] The blank sampler on this date was contaminated with simazine.

[2] The blank sampler on this date was contaminated with chlorpyrifos.

These contaminations did not affect samplers from all the sampling sites.

ND = not detected

In this table, chemicals are ranked by predicted risk and grouped (by shading) according to the outcome of the analysis.

Scenario 5

Glyphosate was the only agrochemical listed as used on the horticultural property under scenario 5. Scenario 5 was a commercial horticultural enterprise growing two different crops, neither being vines. The glyphosate was deemed to have low risk of leaching, but this could not be confirmed using the passive samplers.

All seven of the agrochemicals screened for in the passive samplers (simazine, chlorpyrifos, chlorothalonil, dicofol, methidathion, malathion and oxyfluorfen) were detected in drains from scenario 5 at some stage during the seven sampling periods.

The unexpected occurrence of several agrochemicals is presumed to be due either to the grower providing an inaccurate list of products used, or the drain intercepting irrigation from properties further away, or a combination of both.

Scenario 5	Predicted riskϕ	Concentration (μg/L) in passive sampler solvent						
		25-Jan 2005	15-Feb 2005	8-Mar 2005	28-Mar 2005 [1]	19-Apr 2005	11-May 2005 [2,3]	31-May 2005 [2]
chemicals applied								
glyphosate	Low	Not absorbed by DIPS or TRIMPS						
Chemicals not reported as applied, but detected								
simazine	Risk not predicted	34.8	41.3	26.8	30.5			
chlorpyrifos		2.66	0.382	ND	ND	0.372	0.198	0.629
chlorothalonil		16.6	ND	ND	ND			
dicofol		ND	ND	ND	ND	0.539	0.715	1.056
methidathion		ND	ND	ND	ND	2.67	7.47	8.07
malathion		ND	ND	67.3	ND			
oxyfluorfen		ND	ND	ND	0.417	0.769	-	2.79

ϕ In worst case of high irrigation or rainfall (40% of applied water leaching to the tile drain).

[1] The blank sampler on this date was contaminated with simazine.

[2] The blank sampler on this date was contaminated with chlorpyrifos.

[3] The blank sampler on this date was contaminated with oxyfluorfen.

These contaminations did not affect samplers from all the sampling sites.

NA = not applicable, ND = not detected

In this table, chemicals are ranked by predicted risk and grouped (by shading) according to the outcome of the analysis.

Scenario 6

PIRI predicted a high risk that simazine would leach under scenario 6. Results of the drainage monitoring supported this prediction.

PIRI may have underestimated the risk of chlorpyrifos leaching. Chlorpyrifos was detected at this site during most of the sampling periods, although at low concentrations.

In addition to chlorpyrifos and simazine, all the other five agrochemicals included in the screening of passive samplers (chlorothalonil, dicofol, methidathion, malathion and oxyfluorfen) were detected in drains from scenario 6 at some stage during the seven sampling periods.

Scenario 6	Predicted risk ϕ	Concentration (μg/L) in passive sampler solvent						
		25-Jan 2005	15-Feb 2005	8-Mar 2005	28-Mar 2005 [1]	19-Apr 2005	11-May 2005 [2,3]	31-May 2005 [2]
chemicals applied								
simazine	High	18.2	10.1	34.9	50.3			
sulphur	High							
carbendazim	High			Not absorbed by DIPS or TRIMPS				
fenarimol	Medium							
chlorpyrifos	Low	2.48	0.389	ND	ND	0.210	0.475	0.142
mancozeb	Low							
paraquat / diquat	Low			Not absorbed by DIPS or TRIMPS				
glyphosate	Low							
penconazole	Low							
triadimenol	Low			Absorbed but not included in the analysis				
prothiofos	NA							
chemicals not reported as applied, but detected								
chlorothalonil	Risk not predicted	22.7	ND	ND	ND			
dicofol		ND	ND	ND	ND	8.13	3.59	0.929
methidathion		ND	1.26	ND	2.98	6.63	5.41	3.49
malathion		ND	ND	4.29	14.8			
oxyfluorfen		ND	ND	ND	ND	0.494	-	ND

ϕ In worst case of high irrigation or rainfall (40% of applied water leaching to the tile drain).

[1] The blank sampler on this date was contaminated with simazine.

[2] The blank sampler on this date was contaminated with chlorpyrifos.

[3] The blank sampler on this date was contaminated with oxyfluorfen.

These contaminations did not affect samplers from all the sampling sites.

ND = not detected

In this table, chemicals are ranked by predicted risk and grouped (by shading) according to the outcome of the analysis.

Scenario 7

PIRI predictions could not be confirmed with field data under this scenario because there was no overlap between the products nominated by growers as having been used, and so included in the PIRI predictions, and the products able to be captured using passive samplers.

However, simazine, chlorpyrifos and dicofol had been identified as having high, low and low risk, respectively, under other scenarios, and had been detected in drains further up the catchment. The concentrations detected in drains under scenario 7 may have come from the merging of waters from other drains. If this was the case, malathion, methidathion, oxyfluorfen and chlorothalonil should also have been detected. The latter may have been sufficiently diluted by the merging of drainage to fall below detection.

Scenario 7	Predicted risk ϕ	Concentration (μg/L) in passive sampler solvent						
		25-Jan 2005	15-Feb 2005	8-Mar 2005	28-Mar 2005 [1]	19-Apr 2005	11-May 2005 [2]	31-May 2005 [2]
chemicals applied								
sulphur	High							
glyphosate	Low	Not absorbed by DIPS or TRIMPS						
mancozeb	Low							
chemicals not reported as applied, but detected								
simazine	Risk not predicted	47.4	ND	35.9	31.5			
chlorpyrifos		2.24	0.386	1.26	ND	1.41	0.352	0.246
dicofol		ND	ND	ND	ND	0.526	0.240	0.649

ϕ In worst case of high irrigation or rainfall (40% of applied water leaching to the tile drain).

[1] The blank sampler on this date was contaminated with simazine.

[2] The blank sampler on this date was contaminated with chlorpyrifos.

These contaminations did not affect samplers from all the sampling sites.

ND = not detected

In this table, chemicals are ranked by predicted risk and grouped (by shading) according to the outcome of the analysis.

5.4 DISCUSSION

5.4.1 Selecting chemicals to include in monitoring programs

Kookana (2005) used the PIRI predictions to recommend agrochemicals to include in future monitoring from sampling points 1-7 in Catchment 8 (Table 5.6) The recommendations took into account the chemicals used in each scenario.

Chemicals that had not been listed as used on particular properties were frequently detected in drainage from those individual or grouped properties. This highlights how difficult it can be to accurately define the boundaries of properties that feed a particular line of drainage. All effort was made to determine those boundaries from drainage maps, but the data suggests that there was a high degree of lateral movement of sub surface water between sections of the catchment.

Ease, accuracy and cost of analysing different chemicals influences what can be included in a monitoring program. Of the chemicals applied under the seven scenarios, five were considered by PIRI to have a high leaching risk (Table 5.5). Of the two of these that were absorbed using the passive samplers, the laboratory only analysed for simazine as it already had the necessary methods and calibrations on hand. Table 5.5 combines an overall assessment of leaching risk in Catchment 8 (from Kookana 2005) with an indication of how readily each chemical might be absorbed using passive samplers, plus an indication of whether the chemical was detected in drainage from Catchment 8.

5.4.2 PIRI predictions versus leaching measured in the field

Field monitoring supported PIRI's predictions of a high leaching risk for simazine. When PIRI predicted a low risk of leaching of agrochemicals, field monitoring showed that 'low risk' must not be interpreted as 'no risk', as these agrochemicals were still detected in a proportion of the drains. In particular:

- Simazine was used on properties in scenarios 3 and 6 and was predicted to have a high risk of leaching in both. Simazine was consistently found in drainage water from these sites, which supports the prediction of high risk by PIRI.

- Dicofol was used on properties in scenarios 2 and 3 and was predicted to have a low risk of leaching in both. Dicofol was detected in drainage water from scenario 3 but not from scenario 2. This result suggests that PIRI may have underestimated the risk of dicofol leaching.

- Chlorothalonil was used on properties in scenario 1, and was predicted to have a low risk of leaching. Chlorothalonil was not detected in drainage water from these sites, which supports PIRI's prediction of low risk.

- Chlorpyrifos was used on properties in scenarios 1, 3 and 6 and was predicted to have a low risk of leaching in each scenario. Chlorpyrifos was detected in the majority of samples from these sites, which suggests that PIRI may have underestimated the risk of chlorpyrifos leaching.

- Methidathion was used on properties in scenario 2 and was predicted to have a low risk of leaching. Methidathion was detected in only one sample from this site, which supports the low-risk prediction by PIRI.

- Captan was used on properties in scenarios 2 and 4, and was predicted to have low to medium risk of leaching. Captan was not detected in drainage water from these sites, which supports or perhaps suggests an overestimate of the risk by PIRI.

By using time-integrated 'passive' samplers in this study we ensured that fluctuations in water quality did not interfere with the PIRI validation. At the same time, the PIRI validation was limited by the range of agrochemicals that the laboratory tested for, which was not exactly aligned with the range that was used, nor did it reflect the whole range that can be absorbed by the samplers. Until a wider range of agrochemicals can be measured using the samplers, the range of agrochemical predictions that can be validated is limited.

5.4.3 Leaching models are limited by the site details they contain

Models make many assumptions. To increase the accuracy of PIRI some of its assumptions regarding soil type, irrigation and chemical use were supported by detailed site information. However, refining the assumptions in a model is not always an option. Models should therefore continue to be validated by comparison against monitoring data. PIRI will become more accurate as it incorporates more site-specific detail into the layers of data.

5.4.4 Leaching risk is different from environmental risk

The risk of leaching predicted by PIRI was not also a measure of the risk of environmental impact. The latter can be derived from PIRI, but the two measures are distinctly different. Many of the agrochemical concentrations that were detected in samplers in this study were very low, but they have not been discussed in the context of their potential for environmental impacts. Impacts of water quality from Catchment 8 drains and other sites in Sunraysia are being reported under CRCV project 2.5.1 as part of David Sharley's doctoral thesis (University of Melbourne).

Environmental effect data is available but can be difficult to synthesise. The various sources of information are inconsistent in the type of data they include, which consequently affects the weighting of risks and therefore ranking of different products. According to Guerbet and Guyodo (2002), who compared 35 electronic databases for environmental risk assessment, the five most efficient to use and containing most information in an urgent search of environmental data were, in order, IUCLID, Extoxnet, HSDB, TOMES and CESARS. The ranking was based on the number of compounds included plus whether they provide certain information (11 physiochemical, 8 toxicological and 8 ecotoxicological criteria), not quality of information.

5.4.5 Limitations of field sampling

The following limitations of field sampling for agrochemical leaching should be taken into account before field implementation:

- If analysis is restricted to the agrochemicals used on the vineyard, yet sub-surface soil drainage is connected with that of other properties, samples may contain agrochemicals that remain undetected.
- The fluctuations in chemical concentration in successive samples from drains in Catchment 8 demonstrated that contaminants in drainage should be monitored over a period of time, rather than a single occasion.
- While time-integrated 'passive' samplers appear well suited to being used in irrigation drains, calibrations and methods for analysis are still being refined. The list of chemicals that can be included in a screening is increasing, but still not all-inclusive.

5.4.6 Risk

While quantitative measurement or prediction may indicate '*low risk'* of agrochemical movement, 'low' is relative. 'Low risk' should not be interpreted as 'no risk'. The risk of leaching predicted by PIRI was not a measure of the risk of environmental impact. The latter can also be derived from PIRI, but the two measures are distinctly different. Many of the concentrations that were detected in samplers in this study were very low, but they have not been discussed in the context of their potential for environmental impacts. Impacts of water quality from Catchment 8 drains, and other sites in Sunraysia, are being reported under CRCV project 2.5.1 as part of David Sharley's doctoral thesis.

5.5 CONCLUSIONS

The 2004-05 monitoring program at Catchment 8 indicated that there was a high incidence of leaching into irrigation drainage from vineyards and other horticulture. The range of agrochemicals detected in drainage water was greater than the range that growers had listed as being used. Of the agrochemicals screened in the samplers, dicofol was the most consistently found in samplers (71%), followed by simazine (61%), chlorpyrifos (59%), malathion (32%), methidathion (27%), oxyfluorfen (18%) and chlorothalonil (11%).

The incidence of detections of agrochemical did not always reflect the predicted risk of it leaching. Although dicofol and chlorpyrifos were deemed low risk according to PIRI, they occurred in more than half the samplers. Malathion and oxyfluorfen were deemed as 'no risk' as they were not used in the sites, yet they appeared in approximately 20-30% of samplers. This highlights is that if analysis is restricted to the agrochemicals used on the vineyard, yet sub-surface soil drainage is connected with that of other properties, samples may contain agrochemicals that remain undetected.

As it can be difficult to define the boundaries of properties that feed a particular line of drainage, managing leaching of agrochemicals is a responsibility that must be shared among managers across a catchment, not simply a single vineyard.

Chemicals do not leach at a consistent rate, but fluctuate during the season, highlighting that sampling to monitor for contaminants in drainage water should extend over a period of time.

Solvent-filled, time-integrated 'passive' water samplers were used to monitor chemicals in drainage water. They were found to be cheap to make, simple to use, able to capture a range of different agrochemicals, and reliable in water that has fluctuating concentrations of agrochemical. These samplers are well suited to being used in irrigation drains, but calibrations and methods for analysis are still being refined. The list of chemicals that can be included in a screening is increasing, but still not all-inclusive. Moreover, only a limited number of commercial laboratories can currently recover and measure agrochemicals from the solvents, which limits adoption of the samplers.

PIRI predictions that there was a high risk of simazine leaching and a low risk of chlorothalonil or methidathion leaching were supported by the field data, but PIRI appears to have underestimated the risk of dicofol or chlorpyrifos leaching.

Models make many assumptions. Leaching models are limited by the site details they contain. To increase the accuracy of PIRI some of the assumptions regarding soil type, irrigation and chemical use were supported by detailed site information. But refining the assumptions in a model is not always an option. Models should therefore continue to be validated by comparison against monitoring data. PIRI will become more accurate as it incorporates more site-specific detail into the layers of data.

SECTION 6

SURVEY OF COPPER IN AUSTRALIAN VINEYARD SOIL

6.1 INTRODUCTION AND AIMS

Copper-based fungicides have been sprayed in vineyards throughout the world, including Australia, for many decades to control downy mildew and are still frequently used in vineyard spray programs.

It is known that the use of copper-based fungicides results in an accumulation of copper in surface soils (Delusia et al. 1996; Tiller & Merry 1981). For example, copper concentrations ranging from 130 to 1280 mg/kg have been detected in the surface soil of European vineyards that have a history of copper-based fungicide use (Besnard et al. 2001; Delusia et al. 1996; Flores-Velez et al.1996; Magalhaes et al. 1985; Tiller & Merry 1981). This is an increase from natural background copper concentrations in soils, which worldwide are typically no higher than ~20 mg/kg but can be as high as 100 mg/kg depending on the parent soil material (NEPC 1999; Sauve 2002). Copper accumulation has also occurred in orchard soils where copper-based fungicides have been used (e.g. Tiller & Merry 1981; Merrington et al. 2002).

In many regions of the world there are concerns about the risks that accumulation of copper in agricultural soils may pose to human health, ecological health, and the long-term sustainability of agricultural land (Gardner 2003). In an agricultural setting, food-safety concerns can arise if copper enters agricultural produce as a result of the uptake of copper from the soil by plants. However, evidence suggests that this presents a low risk in vine and tree crops (Biswas et al. 2002), due to the size of the plant and the depth of the roots. Concerns can also arise if residential areas are developed on previously contaminated agricultural land (Chaignon et al. 2003; McLaughlin et al. 2000; NEPC 1999).

Copper can also be toxic to plants (Brun et al. 2001, 2003; McLaughlin et al. 2000; Song et al. 2004). Evidence suggests this is unlikely in mature grapevines, although young vines may be affected in re-planted vineyards (Conradie 2000; Delas 1981). As copper accumulates and persists in surface soils (Tiller & Merry 1981; Flores-Velez et al.1996; Chaignon et al. 2003), beneficial soil organisms such as earthworms, springtails, bacteria, protozoa, mites, nematodes and fungi which inhabit this soil layer are at risk (Stirling 2001). This has significance for soil health as these organisms regulate many key soil processes such as the maintenance of soil structure, nutrient cycling, the suppression of plant pathogens, and the inactivation of toxic compounds (Stirling 2001).

Given that copper is unlikely to cause phytotoxicity in grapevines, the greatest risk posed by the accumulation of copper in vineyard soils is likely to be to the long-term sustainability of vineyards as a result of impacts on soil health. This is supported by studies showing that copper has impacted on the health of vineyard soils (Van Rhee 1976; Paoletti et al. 1998).

A number of ecotoxicological studies have been undertaken to understand the effect of copper on different earthworm species (Table 6.1), because earthworms have been suggested as useful biological indicators of soil health (Paoletti et al.1998; Sheppard et al. 1998). Results from these studies show that a wide range of copper concentrations (53 - 1000 mg/kg) can be toxic to earthworm species. Wide variations in both lethal (218 - 927 mg/kg copper) and sub-lethal (53 - 1000 mg/kg copper) 'effect' concentrations have been reported, due to the use of different test conditions (i.e. endpoint, duration of exposure, soil types) and species. Field investigations have also shown a relationship between reduced earthworm abundance and elevated concentrations of copper (80 - 338 mg/kg copper) in vineyard and orchard soils (Van Rhee 1976; Paoletti et al.1998; Van Zwieten et al. 2004).

Table 6.1: Selected species-specific ecotoxicological studies that investigated the effects of soil copper concentration on earthworms.

Species	Soil pH	Soil Organic matter content (%)	Endpoint	Exposure duration	Effect concentration (mg/kg total copper)	Reference
Aporrectodea caliginosa	6.2	5.2	Growth	14 day	99 - 125 (EC50)	O'Halloran and Booth (2000)
	-	-	Weight gain	6 week	82 (EC50)	Khalil et al. (1996)
Aporrectodea tuberculate	5.6 - 6.2	6.2 – 7.9	Mortality	14 days	333 – 361 (LC50)	Lukkari et al. (2005)
	5.8 – 6.0	6.5 – 7.5	Avoidance	48 hour	79 (EC80)	Lukkari et al. (2005)
Eisenia andrei	6.0	7.0	Survival	14 day	927 (LC50)	Markich et al. (2002)
Eisenia fetida	6.3	-	Mortality	14 day	683 (LC50)	Spurgeon et al. (1994)
	6.3	-	Mortality	56 day	555 (LC50)	Spurgeon et al. (1994)
	6.5 - 7	-	Weight	21day	1000 (LOEC)	Scott-Fordsman et al. (2000)
	6.5 - 7	-	Reproduction	21day	517 (EC50)	Scott-Fordsman et al. (2000)
	6.3	-	Cocoon production	56 day	53 (EC50)	Spurgeon et al. (1994)
	6.0 - 7.0	-	Avoidance	48 hours	553 (EC90)	Van Zwieten (2004)
Enchytraeus albidus	7.3	1.5	Mortality	14 day	700 (LC50)	Lock and Janssen (2003)
	4.3	4.8	Mortality	14 day	250 (LC50)	Lock and Janssen (2003)

Note: EC = effect concentration, LC = lethal concentration, LOEC = lowest observable effect concentration

To gain an understanding of the effect of copper on long-term soil health, studies have also investigated the effect of copper concentrations on soil processes such as microbial activity and the breakdown of litter (Bogomolov et al. 1996; Ma 1984; Merrington et al. 2002). An Australian study of avocado orchards showed that the microbial activity of orchard soils containing elevated copper concentrations (176 – 345 mg/kg) was significantly lower than in control sites (no artificial inputs of copper) located near the orchards under study (Merrington et al. 2002). Field investigations in the same orchards have also shown reduced earthworm populations and a reduction in rate of litter decomposition. A laboratory study by Ma (1984) also found that the breakdown of litter was significantly reduced when copper concentrations in soil were above 130 mg/kg. Taking a soil microcosm approach, Bogomolov et al. (1996) showed that elevated concentrations of copper affected microbial biomass, earthworm survival, nitrogen transformations and litter breakdown over a 40-day period.

In response to concerns over the accumulation of copper in vineyard soils, regulators in some European countries have imposed restrictions on the use of copper-based fungicides. For example, copper use has been banned in the Netherlands, while Switzerland has restricted the amount of copper that can be applied per hectare (Gardner 2003). In Australia, there are currently no restrictions on copper use in conventional viticulture, however organic standards limit annual copper use to a maximum of 8 kg/ha (Organic Industry Export Consultative Committee 2005).

Concerns over the long-term use of copper-based fungicides have been recognised by viticultural industries, and internationally research has been funded to develop safer alternatives. Alternatives that show promise for downy mildew control include phosphorus acid, plant extracts, biological control with micro-organisms and the use of substances that trigger the vines' natural immune system (Kast 2002; LVWO 2002; Riches et al. 2005; Van Zwieten, NSW DPI pers. comm. 2005). However further work is needed to demonstrate that these products can provide economically effective control of downy mildew, and to progress them to registration as plant protection products with the APVMA. Until suitable safer alternatives become commercially available, Australian viticultural industries consider copper-based fungicides to be important for disease control.

Currently in Australia there are no guideline values available that specifically address the contamination of land with regard to the health of agricultural soils. Therefore, it is difficult to determine the concentration of copper in vineyard soils that is likely to impact on soil health without undertaking site-specific investigations. This is made even more difficult by the variability in reported 'effect' concentrations (to soil organisms). We also recognise that of the studies reported, relatively few have investigated the effects of copper on Australian earthworm species and under typical Australian vineyard soil conditions.

The Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites (ANZECC & NHMRC 1992) and the National Environmental Protection Measure (NEPM) for the Assessment of Site Contamination (NEPC 1999) both provide environmental/ecological investigation levels for copper in soils (Table 6.2). However, these guidelines are designed for assessing phytotoxicity to smaller plants (e.g. cropping) and human health concerns in urban settings. Similar guidelines also exist in other parts of the world (Table 6.2), however like the Australian guidelines, none relate specifically to the protection of the health of agricultural soils. Another limitation to the soil quality guidelines listed in Table 6.2 is that they provide values for total copper only, whereas it is recognised that bioavailability needs to be considered when assessing risk (McLaughlin et al. 2000; NEPC 1999). The guideline values stated in Table 6.2 should only be used as a reference to provide an indication of likely toxicity/risk.

It is difficult to assess the risks that the use of copper-based fungicides pose to long-term soil health in Australia as there is little published data reporting concentrations of copper in Australian vineyard soils (Biswas et al. 2002; Pietrzak & McPhail 2004; Wightwick et al, undated (attached as Appendix 9)). Studies undertaken on a small number of vineyards in the Murrumbidgee Irrigation Area (MIA) of New South Wales (Biswas et al. 2002) and in the Sunraysia region of Victoria (see Appendix 9), found that copper concentrations in vineyard soils were below the ANZECC soil contamination guideline value of 60 mg/kg. It should be noted that vineyard age in the MIA study was not reported. In contrast, a study of 14 Victorian vineyards by Pietrzak and McPhail (2004) found eight to contain copper concentrations greater than the ANZECC soil guideline value of 60 mg/kg. Whilst the Pietrzak and McPhail study suggests that the accumulation of copper poses some risk to the long-term health of Australian vineyard soils, it is acknowledged that further information is required to enable a more comprehensive assessment of these risks.

Table 6.2: A selection of currently available guideline values for assessing copper contamination in soils.*

Guideline	Guideline value – Copper (mg/kg)	Comments	Reference
Australian and New Zealand Environmental Soil Quality Guidelines	60	Environmental investigation level - based on threshold levels for phytotoxicity and uptake by plants which may impair growth or produce unacceptable residue levels.	ANZECC and NHMRC (1992)
Australian, National Environment Protection Council (NEPC) Guideline on the investigation levels for soil and groundwater	100	Ecological investigation level - interim guideline level for urban land use settings.	NEPC (1999)
Dutch Intervention Value for Contaminants in Soil	190	Intervention value – maximum tolerable concentration above which remediation is required	VROM International (2000)
Canadian Soil Quality Guideline	63	Agriculture guideline value - based on the greatest sensitivity across both environmental and human receptors.	CCME (2003)
Swedish Guideline for Polluted Soils	100	Guideline value for polluted soils - developed to assess risks to human health and the environment, this value is based on the most sensitive type of land use.	Swedish EPA (2002)
Danish Guidelines for Classification of Polluted Soil	<500	Class II slightly polluted value - interim guideline, soil is considered slightly polluted and can be used under roads etc where access is prevented.	Johnson (2005)
French Guideline Values for Contaminated Land Management	190	Fix Impact Value (FIV) sensitive use - based on toxicity to human health and used to assess public health risks associated with land use.	Darmendrail (2003)

*It should be noted that none of these guidelines relate specifically to copper contamination in agricultural soils and should be used as a reference point only.

This section describes an Australia-wide survey undertaken to determine copper concentrations in vineyard soils and to assess the risks to the long-term agricultural sustainability of these soils. The design of the survey was based on findings from an earlier study to determine a sampling protocol for surveying copper in Australian vineyard soils (attached as Appendix 9). The National Environmental Protection Council suggests that it is preferable to overestimate rather than underestimate risk when conducting risk assessments (NEPC 1999). Therefore in this study we have collected soil samples from vineyards where copper accumulation is most likely to have occurred (i.e. older vineyards, heavy soil), to provide an indication of the greatest risk that copper is likely to pose to the long-term agricultural sustainability of viticultural soils.

In this report we have limited the risk assessment to considering implications of copper accumulation on the long-term sustainability of Australian viticultural soils. In doing so, we have assumed that sites will

continue to be operated as vineyards and have focussed on risks to soil health. We acknowledge that copper accumulation in vineyard soils can present other risks to human and ecological health (e.g. as a result of changed land use), however an assessment of these risks was outside the scope of the study.

A detailed assessment of the impact of copper on soil health in Australian vineyards was outside the scope of this project; however we were able to gain assistance from the NSW Department of Primary Industries, Wollongbar Agricultural Institute; to conduct an initial earthworm avoidance trial. That trial is reported in Appendix 8.

6.1.1 Aims

Aims of the Australia-wide copper survey were to:

- assess the extent and magnitude of copper accumulation in Australian vineyard soils
- provide an indication of the likely risks that copper accumulation poses to the long-term sustainability of vineyards in Australia.

6.2 MATERIALS AND METHODS

The design of the survey was based on recommendations from the first stage of this study to determine sampling considerations for surveying copper in Australian vineyard soils. This work is presented in Appendix 9. The initial study found that the variation in copper concentrations in soils was greater between vineyards than within a vineyard. Using data on the variation between and within vineyards the precision of various possible sampling schemes was determined, as shown in Table 6.3. It was found that for a given number of samples, the most precise estimate of copper would be obtained by taking a single composite sample from as many vineyards as possible, rather than many samples from fewer vineyards.

Table 6.3 The estimated standard error (se) of the overall mean for potential sampling schemes to determine copper concentrations in Australian vineyard soils.

Scenario	Number of vineyards	Samples per vineyard	Total samples	Estimated se of mean
1	6	6	36	0.36
2	60	6	360	0.11
3	60	1	60	0.12
4	100	1	100	0.10
5	360	1	360	0.05

Balancing an acceptable level of precision with the resources required to collect and analyse samples, we decided to collect one composite soil sample from each of approximately 100 vineyards across Australia. To ensure adequate representation of Australian grape growing regions, we aimed to survey approximately 10 vineyards in each of 10 regions. The regions included in the Australia-wide survey (Table 6.4) were selected to represent a range of growing conditions (e.g. climate, soils) and histories of copper use across five key grape producing states of Australia (Victoria, New South Wales, South Australia, Western Australia and Tasmania).

Table 6.4: Grape growing regions included in the Australia-wide copper survey.

State	Region	Number of vineyards
Victoria	Sunraysia	10
	Yarra Valley	9
South Australia	Riverland	10
	Barossa	10
	Coonawarra	10
New South Wales	Riverina	10
	Mudgee	9
Western Australia	Swan Valley	10
	Margaret River	13
Tasmania*		7
All states		98

* Tasmania is classified as one region and vineyards from the south, east, and north of the state were included in the survey.

In each region the objective was to survey vineyards with the greatest potential for having high accumulated copper concentrations. This was achieved by selecting vineyards that had:

- been operated as a vineyard for at least 30 years but preferably more than 60 years
- heavy soil (e.g. clay) for that region
- an established history of copper-based fungicide use.

Additional information obtained for each vineyard, to assist with the interpretation of the results, included:

- the number of years the property has been operated as a vineyard
- the history of the property prior to the establishment of the vineyard (e.g. other farming systems)
- the history of copper-based fungicide use (years of copper use, number and rate of applications per year).

6.2.1 **Sampling**

Soils were collected from the vineyards between April and December 2004. In each vineyard, samples from the surface soil (10-cm depth) were collected from ten locations across the vineyard using a 10-cm diameter soil auger, providing 4 kg soil per vineyard. The sampling locations were determined according to a standardised sampling layout (Figure 6.1), to account for variation within the vineyard and to ensure consistency in sampling across vineyards. At each of the sampling locations, soil was collected from an area within 30 cm of the vine line.

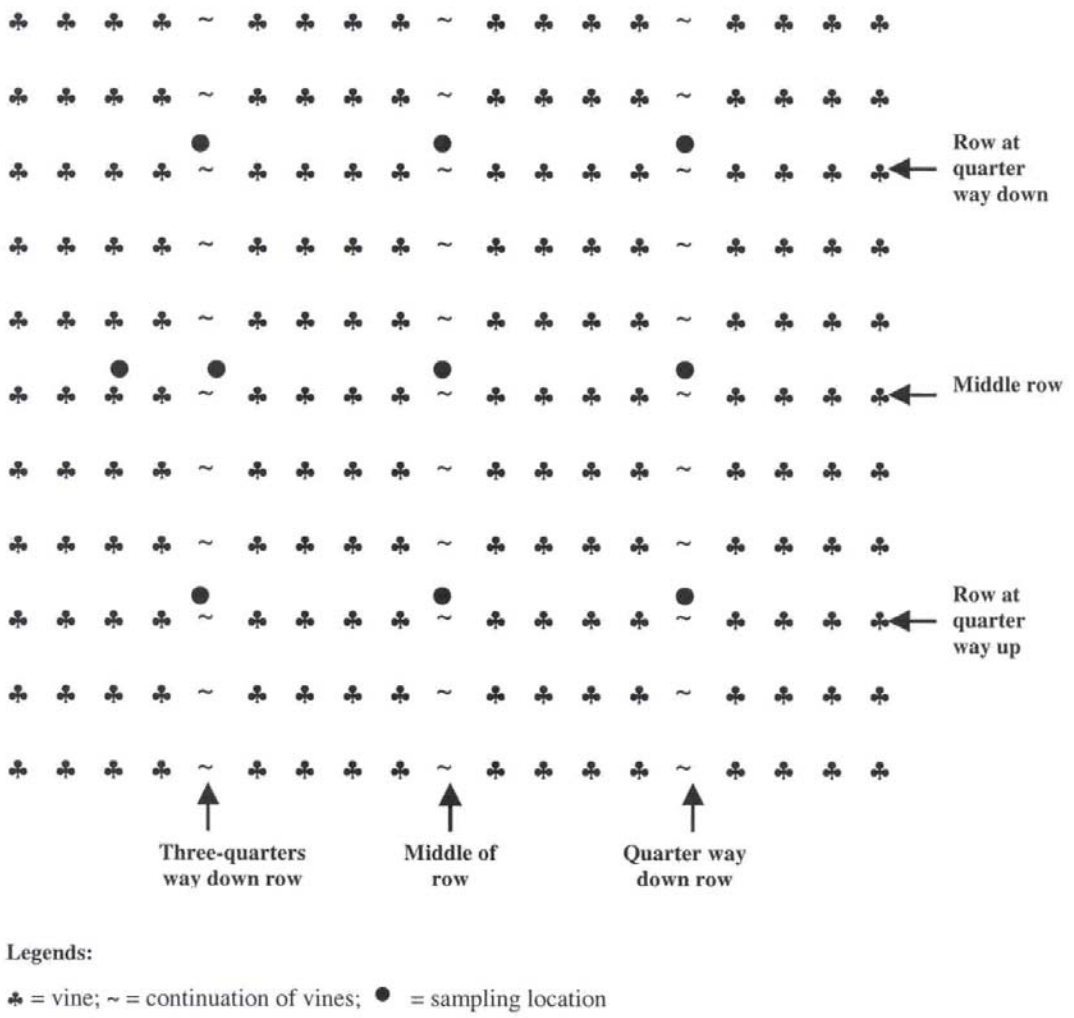


Figure 6.1: Layout of soil sampling locations in vineyards

The ten sub-samples were combined to obtain a composite sample for each vineyard, which was homogenised and then re-divided into sub-samples using a soil sample divider, to obtain representative 200g (approx) duplicates for each vineyard/site.

The duplicate soil samples were dried at approximately 30^{o}C for at least seven days, passed through a 2-mm stainless steel sieve, then homogenised to provide a uniform sample of <2 mm particles for chemical analysis.

A composite soil sample comprising ten sub-samples was also obtained from two or three different 'control' locations in each region. The 'control' locations were areas of remnant vegetation that had not

received any artificial inputs of copper, located within 10 kms of surveyed vineyards. The control samples were collected to provide an indication of the background copper concentrations in soil for each region.

6.2.2 Soil analysis

Samples were analysed by CSIRO Land and Water Soils Laboratory, Adelaide.

Copper was extracted from soil samples using the acid dissolution method described in Zarcinas et al. (1996). This method involves digesting 0.5 g of soil in 5 ml of aqua regia (HNO_3:HCl, 1:3). The soil extracts were then analysed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), with a limit of reporting (LOR) of 0.84 mg/kg.

Total copper content was measured in the surveyed soils, to provide an indication of worst possible risk, the intention being to measure bioavailable copper only if copper exceeded toxicity limits. While bioavailable metal is a more relevant measure than total metal, methods for measuring bioavailable metals can underestimate labile metal content and there are few benchmarks against which to compare measured amounts of bioavailable copper.

In addition to copper, concentrations of other metals including arsenic, cadmium, chromium, lead and zinc were also determined. For quality control purposes 5% of the soil samples were analysed in duplicate and two different internal standards were analysed in quadruplicate.

Physical properties of vineyard soils, including total organic carbon, calcium carbonate, pH, cation exchange capacity and particle size analysis were predicted using Mid Infrared (MIR) with Partial Least Square (PLS) analysis by CSIRO Land and Water in Adelaide. Analysis was undertaken according to the methods described in Forrester et al. (2004). For these analyses, soil sub-samples (10 g) from each vineyard were ground to <100 μm by processing in a steel vibrating puck mill for 60 seconds. Soil MIR spectra were scanned directly by diffuse reflectance on the neat powdered soil samples. Spectra were recorded in the 7800-400 cm^{-1} spectral range using a Perkin-Elmer Spectrum-One Fourier Transform Infra-Red (FITR) instrument with an auto-focussing Perkin-Elmer Diffuse Reflectance accessory, using a one-minute scan (Forrester et al. 2004).

Partial Least Square calibration training, where different calibrations were tested by cross-validation performance, was used to generate the optimum regression model that was then used for prediction from the unkown sample spectrum. Software used was either PLSplus-IQ® (GRAMS, Galatic NH), or Unscrambler® (Camo AS, Norway) (Forrester et al. 2004).

6.2.3 Risk characterisation

The general approach outlined in the *National Environment Protection (Assessment of Site Contamination) Measure* (NEPC 1999) was used to gain an indication of the likely risks that accumulated copper poses to the long-term health of Australian vineyard soils. In the NEPC guidelines, risk is characterised by evaluating both exposure (i.e. measured concentrations) and toxicity information to determine the probable impact on organisms.

The lack of appropriate soil quality guideline values specifically addressing soil health, and a lack of appropriate ecotoxicological studies undertaken in an Australian context, make it difficult to characterise the risk that copper currently poses to the health of Australian vineyard soils. For the purpose of this study we have estimated the risks posed to long-term soil health by comparing the copper concentrations measured in vineyard soils against the ANZECC soil quality guideline value (60 mg/kg total copper). We selected the lower ANZECC guideline value over other published guidelines (Table 6.2), because it is preferable to overestimate rather than underestimate risk (NEPC 1999). To describe the potential risks

posed by copper in Australian vineyard soils we compared measured copper concentrations against 'effect' concentrations reported for soil organisms (Table 6.1).

6.2.4 Data analysis

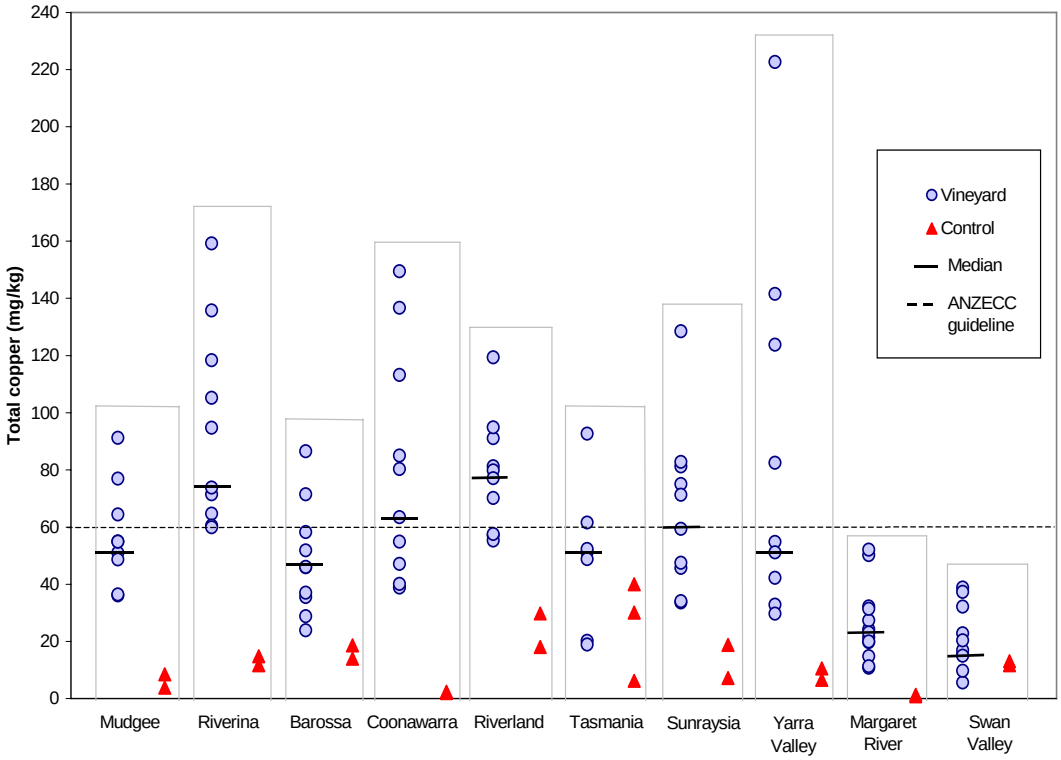
Data were analysed using GenStat Release 6.1 (6th Edition, 2002, Lawes Agricultural Trust, Rothamsted Experimental Station). Regression analysis was used to determine relationships between vineyard copper concentrations and factors which may have influenced the accumulation of copper, such as the estimated total amount of copper applied (i.e. years of copper use × annual copper use) or the properties of the soil. Lines of best fit were established to correlate variations in vineyard copper concentrations with other parameters within each of the regions. Outliers were removed from the regression analysis in some instances to improve the fit.

6.3 RESULTS

In each region surveyed, the total copper concentrations in vineyard soils were greater than in control locations, with the exception of some vineyards in Tasmania and the Swan Valley (Figure 6.2). Copper concentrations in the vineyard soils varied both between regions and within regions. In eight out of the ten regions surveyed, vineyard soils had copper concentrations that exceeded the soil quality guideline value for copper of 60 mg/kg (ANZECC and NHMRC 1992).

The results from copper analysis of the duplicate samples used for quality control, varied by 0.9% to 5.8% of the mean of each set of duplicates. Results from analysis of the two different internal standards varied from the standards by ± 0 to 9.6%.

Annual copper use was estimated as being highest (> 9 kg/ha/yr) in the Riverina, Coonawarra, and Yarra Valley regions, and lowest (< 7 kg/ha/yr) in the Sunraysia, Margaret River, Tasmania, and Barossa regions (Table 6.5). Annual copper use was found to vary widely between vineyards in each region, with the exception of the Barossa region. The Riverina, Barossa, Coonawarra, Riverland, and Sunraysia regions have the longest histories of copper-based fungicide use (> 49 years of use, on average).



Notes: - The dotted line represents the ANZECC soil quality guideline value of 60 mg/kg;
- The horizontal lines are the median values in each region.

Figure 6.2: Range of total copper concentrations (mg/kg) detected in vineyards and control locations for each region

Table 6.5: Estimated use of copper-based fungicides, by region*

State	Region	Annual copper use (kg/ha/yr)		Years of copper use	
		Range	Average	Range	Average
New South Wales	Mudgee	3 - 14	8.7	4 - 50	30
	Riverina	5 - 20	12.9	38 - 84	53
South Australia	Barossa	5 - 8	6.1	30 - 100	66
	Coonawarra	7.5 - 20	10.7	30 - 100	51
	Riverland	3 - 15	8.6	25 - 80	49
Tasmania		1 - 10	5.7	30 - 50	35
Victoria	Sunraysia	2 - 14	5.2	30 - 100	62
	Yarra Valley	2 - 24	9.35	20 - 38	31
Western Australia	Margaret River	2 - 20	5.3	1 - 28	10
	Swan Valley	2 - 15	7.1	0 - 30	13

* Copper usage information was calculated from survey responses. This information should be viewed with some caution, as it is relies on the accuracy of information provided by survey respondents.

Table 6.6: Selected physical properties of vineyard soils surveyed in each region[1]

State	Region	Range of different physical soil properties						
		TOC (%)[2]	$CaCO_3$ (%)[3]	pH	CEC[4]	Sand (>20μm)	Silt (2-20μm)	Clay (<2μm)
				(H_2O)	($cmol_c/kg$)	(%)	(%)	(%)
New South Wales	Mudgee	0.75 - 3.68	< LOR[5] - 0.81	5.58 - 6.4 0	1.46 - 22.47	36.98 - 75.73	8.18 - 34.12	14.19 - 28.90
	Riverina	0.52 - 3.05	< LOR - 0.75	5.91 - 7.17	15.87 - 25.35	49.20 - 71.98	2.56 - 12.97	23.53 - 38.17
South Australia	Barossa	0.45 - 6.97	0.05 - 0.96	6.08 - 7.80	0.03 - 36.95	64.35 - 87.56	0.56 - 16.75	7.66 - 34.27
	Coonawarra	1.05 - 3.52	0.14 - 2.51	7.18 - 8.56	11.08 - 35.90	44.35 - 74.46	7.18 - 19.53	18.36 - 34.70
	Riverland	0.66 - 1.40	0.15 - 1.25	7.08 - 9.18	11.49 - 31.16	56.09 - 74.17	1.73 - 15.74	19.66 - 41.12
Tasmania		2.75 - 8.96	< LOR - 1.41	5.70 - 7.74	3.59 - 52.22	26.65 - 96.06	0 - 31.31	4.94 - 43.07
Victoria	Sunraysia	<LOR - 2.64	0.09 - 5.03	6.78 - 9.86	6.01 - 26.82	53.56 - 81.03	3.12 - 17.76	7.75 - 33.48
	Yarra Valley	2.11 - 4.82	< LOR - 1.17	5.05 - 6.25	5.10 - 20.92	51.29 - 81.78	7.78 - 39.38	10.44 - 20.09
Western Australia	Margaret River	3.47 - 6.41	< LOR - 1.38	5.27 - 7.17	3.60 - 17.26	72.96 - 94.50	0 - 16.82	4.70 - 16.11
	Swan Valley	0.71 - 2.37	< LOR - 0.64	5.05 - 6.96	<LOR - 6.30	83.79 - 95.39	0 - 6.04	4.61 - 11.97

1. Soil properties reported are predicted values determined from the MIR analysis of vineyard soils.
2. TOC - Total organic carbon
3. $CaCO_3$ - Calcium carbonate
4. CEC - Cation exchange capacity
5. LOR – Limit of reporting

Physical properties of the vineyard soils varied both between and within the regions surveyed (Table 6.6). On average CEC and clay content was highest in vineyard soils from the Coonawarra, Riverland, and Riverina regions and lowest in the Margaret River and Swan Valley regions. Soils from vineyards in the Mudgee, Riverina, Tasmania, Yarra Valley, Margaret River and Swan Valley regions were typically acidic (pH < 7).

When all vineyards were considered together, the copper concentration in vineyard soils was found to be poorly correlated with the estimated total copper applied (i.e. years of copper use × annual copper use) (adjusted R^2 0.278) (Figure 6.3).

However when the regions were considered separately, the concentrations of copper in two of the regions (Riverland and Yarra Valley) did increase with increasing 'estimated' amounts of total copper applied (years of copper use × annual copper use) (adjusted R^2 0.846) (Figure 6.4). Within this relationship, a difference in both the intercept and slope was found between regions. The difference in intercept can be explained by different background concentrations of soil copper in the two regions, as indicated by copper levels in soil under remnant vegetation (10.64 and 6.56 mg/kg copper in the Yarra Valley and 29.80 and 18.08 mg/kg copper in the Riverland). The variance in slope between regions in Figure 6.4 indicates that the rate at which copper has accumulated is greater in the Yarra Valley compared to the Riverland.

In each other region, parameters other than application history accounted for the majority of variation in soil copper concentrations (Table 6.7).

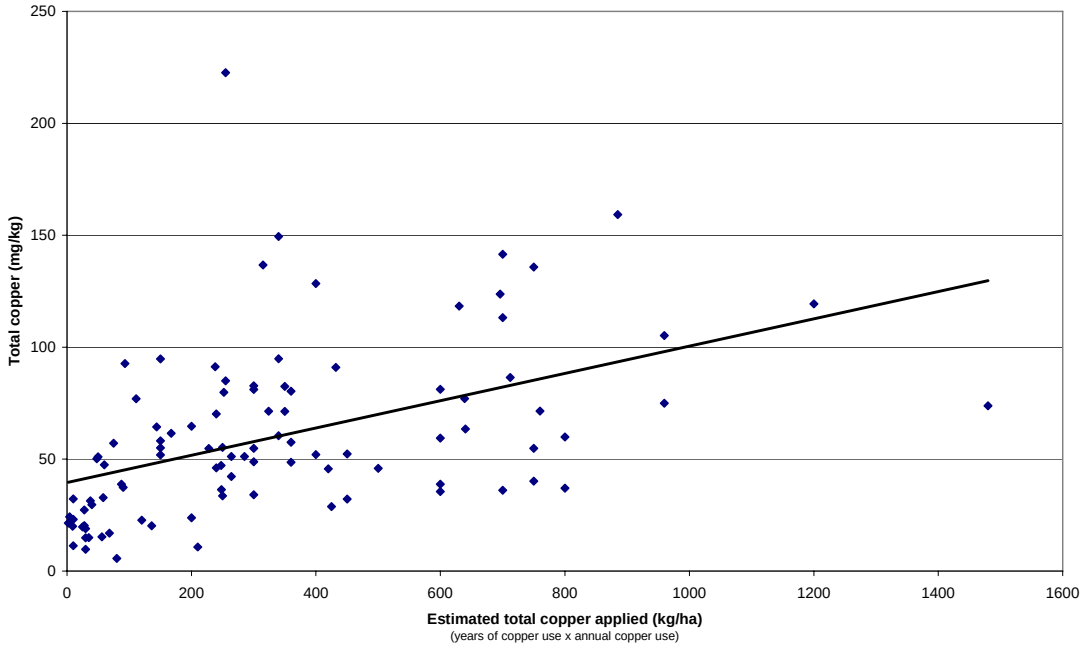


Figure 6.3: Relationship between copper concentration in soil and the estimated total copper applied (i.e. years of copper use × annual application (kg/year)) across all 98 vineyards.

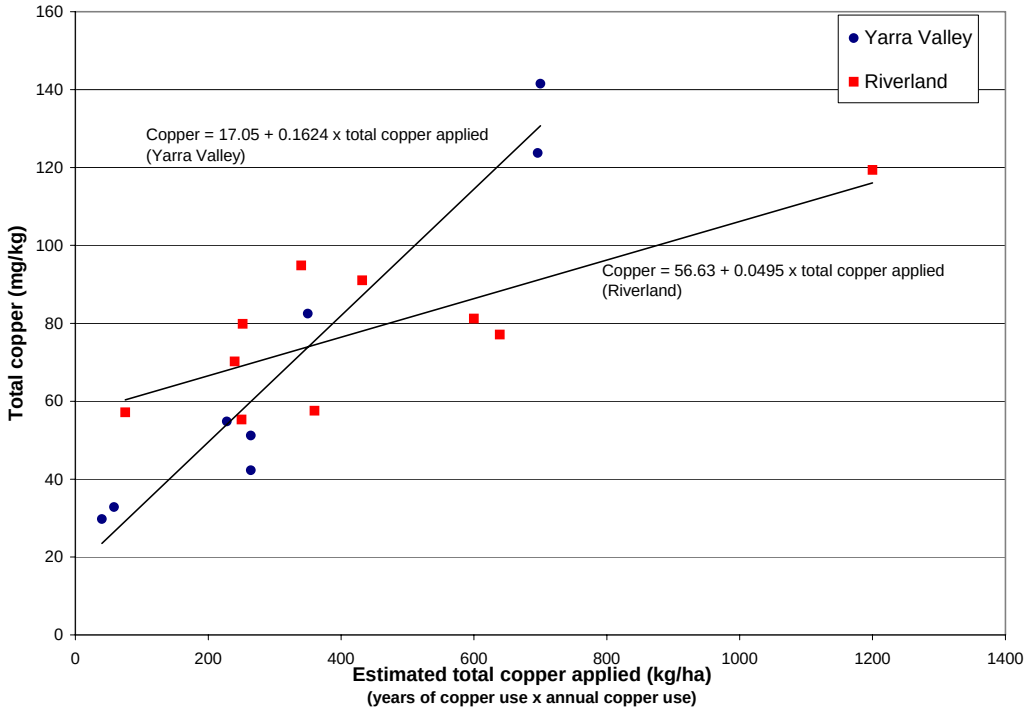


Figure 6.4: Relationship between copper concentration in the soil and estimated total copper applied (i.e. years of copper use by annual copper use) for the Yarra Valley and Riverland regions.

Table 6.7: physical and chemical parameters and fitted relationships accounting for the majority of variation in soil copper concentrations in each region

Region/s	Physical-chemical soil parameter	Correlation for fitted relationship (adjusted R^2)	Equation
Barossa			36.62 + 53.4 x EC
Margaret River	Soil salinity (EC)	0.697	36.62 - 18.34 + (63.4-10.7)EC
Tasmania			30.09 + 100.8 x EC
Coonawarra	Exchangeable sodium (Na)	0.695	46.55 + 80.5 x Exchangeable Na
Swan Valley	pH	0.685	14.2 x (pH) - 62.7
Sunraysia	Exchangeable calcium (Ca)	0.577	15.9 + 5.02 x Exchangeable Ca
Riverina			43.0 + 5.02 x Echangeable Ca
Mudgee	Regression did not reveal any significant relationships		

In Barossa, Margaret River, and Tasmanian vineyard soils, total copper was found to increase with increasing soil salinity (EC) (adjusted R^2 0.697) (Table 6.7). The intercept for the relationship was found to vary between regions due to the different background soil copper concentrations (Margaret River - 0.84 and 1.4 mg/kg, Barossa - 18.56 and 14.00 mg/kg, Tasmania - 40.00, 30.12, and 6.24 mg/kg). The slopes of the fitted relationships were found to be similar for both the Margaret River and Barossa regions, suggesting a similar rate of copper accumulation in these regions. It appears that copper has accumlated at a faster rate in Tasmania, as indicated by the steeper slope for the fitted relationship.

In Coonawarra vineyard soils, total copper measured was found to increase with increasing exchangeable sodium (adjusted R^2 0.695) (Table 6.7).

In Swan Valley vineyard soils, total copper measured was found to increase with increasing soil pH (adjusted R^2 0.685) (Table 6.7).

In Sunraysia and Riverina vineyard soils, exchangeable calcium accounted for the majority of variation in soil copper concentrations (adjusted R^2 0.577) (Table 6.7).

The regression analysis on vineyard soils from Mudgee did not reveal any significant relationships for this region.

6.3.1 Risk assessment

Overall, soils from 38% of the vineyards contained copper at concentrations exceeding the ANZECC soil quality guideline value for copper (60 mg/kg) (ANZECC & NHMRC 1992) (Table 6.8). In four out of the ten regions (Riverina, Coonawarra, Riverland, Sunraysia), half or more of the vineyards surveyed were found to have copper concentrations exceeding the ANZECC soil quality guideline. In two regions (Margaret River, Swan Valley) none of the vineyards surveyed contained copper concentrations in soil that exceeded the ANZECC soil quality guideline.

Table 6.8: Percentage of vineyards with soil copper concentrations exceeding the ANZECC soil quality guideline value for copper (60 mg/kg).

State	Region	Percentage of vineyards with soil copper concentrations exceeding ANZECC soil quality guideline value (60 mg/kg)
New South Wales	Mudgee	33
	Riverina	100
South Australia	Barossa	20
	Coonawarra	50
	Riverland	70
Tasmania		28
Victoria	Sunraysia	50
	Yarra Valley	40
Western Australia	Margaret River	0
	Swan Valley	0
Across all regions		**38**

6.4 DISCUSSION

The use of copper-based fungicides has been associated with an accumulation of copper in vineyard soils, with an average increase of 49 mg/kg in vineyard soils compared to the nearby control sites. Exceptions were two vineyards in Tasmania and two vineyards in the Swan Valley (Figure 6.2). This trend towards copper accumulation supports the findings from studies in European vineyards (Besnard et al. 2001; Delusia et al. 1996; Flores-Velez et al.1996; Magalhaes et al. 1985; Tiller & Merry 1981). Such a trend was expected, as copper is known to bind strongly to clay, organic matter and minerals in soil (McLaughlin et al. 2000; Sauve 2002).

Median copper concentrations were highest in the Riverina, Coonawarra, Riverland, and Sunraysia regions (Figure 6.2), which had long histories (averaging ≥ 49 years) of copper-based fungicide use. Median copper concentrations were lowest in the two Western Australian regions (Margaret River and the Swan Valley) (Figure 6.2), which reflects the fact that the wide use of copper-based fungicides in these regions has only occurred in the last 10-15 years due to the low incidence of downy mildew. The exception to this trend is the Barossa region where vineyards had long-histories of copper-based fungicide use (30 - 100 years, average 66 years). The median copper concentration was found to be comparable to the Mudgee, Tasmania, and Yarra Valley, regions with relatively short histories of copper-based fungicide use (average years of copper use 30 - 35). This result suggests that factors other than copper use have also influenced the accumulation of copper in the Barossa. Further investigations to explain the unexpected result in the Barossa were outside the scope of this project.

Variation in total copper concentrations

Concentrations of total copper in vineyard soils varied both between and within regions. The wide variation between regions was expected because the vineyards surveyed in the different regions had different histories of copper use (e.g. years of use, frequency of use) (Table 6.5). The variation in copper concentrations within regions is presumably related to differences (eg. copper use history, soil properties and topography) between the vineyards within regions. Every effort was made to survey vineyards with similar copper use histories and soil types within each region; however this was difficult to achieve due to challenges involved in identifying suitable vineyards and gaining agreement from property owners.

The survey undertaken was not designed to assess the influence of soil properties on copper accumulation (i.e. we only targeted soils with high adsorption capacity). However, the regression analysis has provided an indication of the interactions between copper and various soil properties within the vineyards surveyed. There are many factors which can influence the sorption of copper in soil and further investigations would be needed to gain a clearer understanding of the factors influencing the accumulation of copper in Australian vineyard soils (e.g. the influence of different clay minerals and the formation of inorganic/organic complexes).

Our results have shown a relationship between copper in vineyard soils and exchangeable cations: exchangeable sodium in the Coonawarra region and exchangeable calcium in the Sunraysia and Riverina regions (Table 6.7). It is known that the sorption of copper (a positively charged ion) in soil is influenced by the presence of clay and other negatively charged soil fractions (Sauve 2002). A correlation between exchangeable cations (an indication of the number of negatively charged binding sites) and copper in vineyard soils was therefore expected. Whilst there was only a general trend between vineyard copper concentrations and CEC, the fact that specific relationships with exchangeable cations (i.e. sodium, calcium) have been found indicates the influence of more specific copper sorption processes in vineyard soils.

It has been reported that copper can be adsorbed onto calcium carbonate ($CaCO_3$) present in soil (McBride 1981; McClean & Bledsoe 1992; Rodriguez-Rubio et al. 2003). It is possible that this sorption

process has influenced the accumulation of copper in the Sunraysia and Riverina regions, where a relationship between copper and exchangeable calcium (a measure of calcium ions displaced from negatively charged binding sites in soil) has been found (Table 6.7). The reasons for the relationship with exchangeable sodium, found in the Coonawarra region (Table 6.7), are less clear, however it has been suggested that the specific adsorption of copper in soil can occur in the presence of excess quantities of non-specifically bonded cations (McBride 1981).

The relationship between copper in vineyard soils and soil pH found in the Swan Valley region (Table 6.7) was expected as it is known that copper sorption increases with increasing pH (Sauve 2002). It is likely that pH had the greatest influence on copper sorption in the Swan Valley region as vineyard soils in this region had very low CEC (≤ 6.30 cmol/kg).

The reasons for the relationship between vineyard copper concentration and soil salinity, found in the Barossa, Margaret River and Tasmania regions (Table 6.7) are less clear. It is generally considered that the mobility of metals will increase in saline soil due to the formation of chloride complexes (Oliver & Naidu 2003). Whilst little is known about the effect of salinity on the sorption of copper in soil, there is some evidence suggesting that increased sodium chloride concentrations can increase the sorption of copper (Gunton et al. 2005).

Comparisons with other regions

In general, the accumulation of copper in Australian vineyard soils has not occurred to the same extent as in European vineyards. Our results have shown that the concentrations of copper (24 - 159 mg/kg) measured in regions with long-histories of copper use (averaging 49 - 66 years) were lower than those typically reported in European vineyards (130 - 1280 mg/kg) (Besnard et al. 2001; Delusia et al. 1996; Florez-Velez et al. 1996; Magalhaes et al. 1985; Tiller & Merry 1981). The most likely reason for this is that the typical annual usage of copper-based fungicide in European vineyards (10 – 50 kg/ha) is higher than in Australian vineyards (average found in this study: 5.2 – 12.9 kg/ha/yr).

6.4.1 Risk assessment

In this study we assessed the risks of copper to soil organisms/soil health by targeting vineyards in each region where the accumulation of copper was likely to be high (i.e. older vineyards on heavy soil). Taking this approach, it is likely that we have overstated the typical copper concentrations in Australian vineyard soils representing different scenarios (e.g. younger vineyards on lighter soil). However, we believed it was preferable to overestimate risk in this initial investigation as it would enable us to assess whether copper accumulation was likely to impact on vineyard soil health under worst-case scenarios.

Comparison with the soil quality guideline value

A moderate proportion (38%) of the vineyard soils surveyed exceeded the ANZECC soil quality guideline (60 mg/kg). As expected, exceedence of the ANZECC soil quality guideline was highest in the regions with longer histories of copper use (Riverina, Riverland, Coonawarra, Sunraysia). The Barossa region is an exception to this. Results from this study are comparable to those from an earlier survey of 14 Victorian vineyards (Pietrzak & McPhail 2004) where copper concentrations in surface soils exceeded the ANZECC soil quality guideline in 57% of the vineyards.

In this study the wide variation in the exceedence of the ANZECC guideline between regions (0 - 100%) can largely be explained by differences in the number of years copper has been used. As discussed earlier it is also clear that soil properties (e.g. exchangeable cations, pH, salinity) influence the rate of copper accumulation in Australian vineyard soils. By default these influences have affected the number of vineyards exceeding the ANZECC guideline in different regions. The fact that the majority of the

vineyards (≥ 50%) in four of the regions (Riverina, Coonawarra, Riverland, Sunraysia) surveyed exceeded the ANZECC guideline suggests that further investigations to understand current and future implications for soil health are warranted.

Concentrations of other metals including arsenic, cadmium, chromium, lead and zinc in the vineyard soils were also obtained from the soil analysis. A comparison of these metals against the ANZECC soil quality guidelines revealed that in most vineyards concentrations were below the guideline value, therefore copper is considered the most significant metal present. The exceptions were the Coonawarra where seven vineyards contained concentrations of arsenic (29.68 - 72.08 mg/kg) above the guideline of 20 mg/kg, and Tasmania where three vineyards contained concentrations of chromium (71.96 - 133.12 mg/kg) above the guideline of 50 mg/kg.

Toxicity to soil organisms

Given the wide variation in 'effect' concentrations reported in the literature (Table 6.1) it is difficult to predict the likely toxicity of copper concentrations in Australian vineyards, to soil organisms. However, it appears that at the concentrations detected during this study, copper is unlikely to cause lethal effects to macro-organisms such as earthworms. The copper concentrations present may however cause sub-lethal effects to soil organisms (i.e. inhibit growth, effect reproduction, cause avoidance behaviour); result in reduced earthworm abundance; and disrupt key soil processes such as the breakdown of litter and the cycling of nutrients.

It is known that the bioavailability and hence toxicity of copper in soil is influenced by the pH and CEC of the soil, where bioavailability increases with decreasing pH and CEC (Sauve 2002; Sauve et al. 1997). Therefore, at a given concentration of total copper in soil, toxicity can vary according to soil type. Sauve et al. (1998) has suggested that the bioavailability of copper is reduced above a soil pH of 7. Considering this, the bioavailability of copper detected in vineyard soils in this study is likely to be greatest in the regions with soil pH < 7 (Mudgee, Riverina, Tasmania, Yarra Valley, Margaret River, and Swan Valley). It should be noted that the bioavailability of copper present in the Riverina region is likely to be reduced by the relatively high CEC of these soils. Whilst copper concentrations detected in the Coonawarra, Riverland, and Sunraysia regions were relatively high, due to the alkaline nature (pH > 7) of these soils it is expected that the bioavailability and hence toxicity of the copper present is likely to be low in comparison to other regions surveyed.

To enable more accurate assessments of the impact of copper to soil organisms and the health of Australian vineyard soils, it is clear that further studies need to be conducted under Australian field conditions. Single-species ecotoxicological studies need to be undertaken to investigate the effects of copper on soil organisms which are representative of sensitive beneficial organisms in Australian vineyard soils. Conducting field surveys and microcosm-based studies would enable the effects of copper on the functionality and overall health of Australian vineyard soils to be determined. The influence of other persistent contaminants, in particular agrochemicals, also needs to be considered.

Future work will also need to consider the bioavailability of the copper present in vineyard soils. In Australia, the bioavailability and hence the toxicity of copper present in vineyard soils is likely to vary between vineyards (i.e. due to differences in soil pH, clay content, and CEC), particularly where regional variation exists. The bioavailability of copper in soil can also decrease over time due to an 'ageing' effect. The 'ageing' of copper is described as the irreversible binding of copper to clay, organic and mineral components in the soil, which depletes the bioavailable proportion of copper in the soil (Lock and Janssen 2003; McLaughlin 2001). Copper ‘ageing’ will be an important factor to consider in future studies investigating the effect of copper on the health of Australian vineyard soils.

Depending on the outcomes from impact assessment studies, it may also be necessary to investigate suitable vineyard management options to:

- remediate current effects of copper (e.g. through the use of organic/inorganic soil amendments)
- prevent future effects on soil health caused by high copper concentrations (e.g. through development and adoption of suitable safer alternatives).

A detailed assessment of the impact of copper on the health of Australian vineyard soils was outside the scope of the project, however results of an initial earthworm avoidance trial are described in Appendix 8.

Risk characterisation

The absence of appropriate soil quality guideline values and lack of appropriate ecotoxicological studies make it difficult to characterise the risks posed by copper. However, using the conservative approach taken in this study, our results suggest that the accumulation of copper may pose a risk to the long-term health of Australian vineyard soils. It is recognised that further studies are needed to fully characterise these risks.

It should also be recognised that the accumulation of copper in vineyard soils can pose a risk to water quality if copper is transported off-site as a result of run-off or leaching.

6.5 Conclusions

Almost all the vineyards surveyed (96%) had elevated soil copper concentrations compared to the background soil concentration in their region. While the copper concentrations were generally much lower than those found in European vineyard soils, the use of copper-based fungicides is associated with some copper accumulation in Australian viticultural soils.

The extent of copper accumulation in Australian viticultural soils appears to be related to different management and soil factors in different regions, including total amount of copper applied, soil pH, salinity and exchangeable sodium and calcium.

Thirty eight percent of Australian vineyards surveyed, representing eight out of ten grape growing regions, had soil copper concentrations that exceeded the ANZECC Soil Quality guidelines. Copper in vineyard soils surveyed also exceeded concentrations that have been shown to have sub-lethal effects on soil organisms.

SECTION 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 SCOPING STUDY

One objective of this project was to undertake a scoping study to "*provide industry with a comprehensive review of a) current knowledge on known or predicted environmental impacts of key agrochemicals used in Australian viticulture, b) techniques to predict and measure movement of agrochemicals and to assess impacts*."

The comprehensive report 'Review of the potential for agrochemicals used in viticulture to impact on the environment' (Mollah & MacGregor 2002), was provided to GWRDC in August 2002. The report concluded that off-target movement and non-target impacts of agrochemicals used in vineyards are primarily caused by:

- Spray drift, potentially impacting on nearby crops, housing, and terrestrial or aquatic species;
- Leaching, potentially causing contamination of water courses, affecting aquatic species;
- Accumulation of agrochemicals in soil, potentially impacting on soil health and ultimately vineyard sustainability.

7.2 AGROCHEMICALS APPLIED IN VINEYARDS WERE DETECTED MOVING BEYOND THEIR TARGET OR ACCUMULATING IN VINEYARD SOILS

Another objective of this project was to "*measure movement of key agrochemicals in commercial vineyards representing a range of soil types, soil water behaviours, climates and agrochemical application practices, in order to ground-truth predicted behaviours*". A series of field trials provided data to quantify off-target movement of agrochemicals.

7.2.1 Spray drift

Spray drift trials showed that the vine canopy intercepted between 29% and 66% of sprayer output, and therefore the sprayers were set up adequately to provide disease control. The trials were conducted in a vineyard with a well-developed canopy, and interception would have been substantially less early in the growing season, when the canopy was smaller and sparse.

- Recommendation: Vineyard managers should be encouraged to optimise sprayer set up so that the canopy captures the majority of spray, reducing the proportion of spray that can drift off site or sediment to the vineyard floor.

Vines that were 6.4 metres downwind of the sprayed row collected between 1% and 16% of the sprayer output. The sprayer-nozzle combination determined how much drifted to downwind rows. The proportion of deposits that precipitated from air above the downwind canopy was similar to the proportion projected horizontally from the sprayer two rows away.

- Recommendation: Vineyard managers must be discouraged from a view that fall-out of drift in downwind rows can assist with disease control, as the proportion that settles from above the canopy is relatively small and might, under different conditions, not settle but drift higher and beyond the vineyard.

Aerial drift collected on a 12-metre tower represented between 0.06 and 7% of sprayer output. The main influence on airborne drift was the type of sprayer, but choice of nozzles on the sprayer also influenced airborne drift. The worst losses were associated with spraying a fine droplet from a 'directed sprayer' that was poorly set up, but fine droplets did not increase airborne drift when the same sprayer was well set up.

Sedimenting drift collected on the ground within 10 metres of the sprayed row represented the greatest (measured) proportion of off-target loss (7 - 24% of the sprayer output) (not including run-off from over-sprayed foliage). This represents a high degree of wastage, and repeated dosing of the vineyard soil may affect soil health and/or lead to off-target contamination by erosion of, or leaching through, sprayed soils. It was the sprayer-nozzle combination that most influenced the distribution of ground deposits, rather than the sprayer itself. All sprayers caused losses to the ground, and the conventional airblast seemed as able to keep these to a minimum as the ducted sprayer.

- Recommendation: Sprayer set up should be recognised as having a significant effect on drift potential. Greater benefits in drift reduction may come from directing the splay plume into the canopy than from increasing nozzle size.

7.2.2 Leaching

The 2004-05 monitoring program at Catchment 8 indicated that there was a high incidence of leaching into irrigation drainage from vineyards and other horticulture. The range of agrochemicals detected in drainage water was greater than the range that growers had listed as being used. Of the agrochemicals screened in the samplers, dicofol was the most consistently found in samplers (71%), followed by simazine (61%), chlorpyrifos (59%), malathion (32%), methidathion (27%), oxyfluorfen (18%) and chlorothalonil (11%).

The incidence of detections of each agrochemical did not reflect the predicted risk of it leaching. Although dicofol and chlorpyrifos were deemed low risk according to PIRI, they occurred in more than half the samplers. Malathion and oxyfluorfen were deemed as 'no risk' as they were not used in the sites, yet they appeared in approximately 20-30% of samplers. If analysis of samplers from a vineyard is restricted to agrochemicals used on that vineyard, the samplers are likely to contain additional contaminants that are overlooked.

- Recommendation: Monitoring should focus on those agrochemicals having a medium to high risk of leaching, to test for their presence, but also include some agrochemicals with predicted low risk, to confirm their absence.

The field monitoring shows that managing leaching of agrochemicals is a responsibility that must be shared among managers across a catchment, not simply a single vineyard. It is difficult to define the boundaries of properties that feed a particular line of drainage, which means that chemicals that are not used on a property may occur in drainage from that property.

- Recommendation: When designing a program to monitor leaching, it must be acknowledged that drainage or sub-surface water can move across a catchment.
- Recommendation: Testing should be for as broad a suite of agrochemicals as possible, particularly those with high solubility and low sorption.

7.2.3 Accumulation of copper in vineyard soils

Almost all the vineyards surveyed (96%) had elevated soil copper concentrations compared to the background soil concentration in their region. While the copper concentrations were generally much lower than those found in European vineyard soils, the use of copper-based fungicides is associated with some copper accumulation in Australian viticultural soils.

- Recommendation: The pattern of copper-based fungicide use in Australian viticulture, and possible alternative controls for downy mildew, should be investigated further.

The extent of copper accumulation in Australian viticultural soils appears to be related to different management and soil factors in different regions, including total amount of copper applied, soil pH, salinity and exchangeable sodium and calcium.

- Recommendation: Factors affecting the rate of copper accumulation in soil should be investigated in more detail, to allow the development of guidelines for use of copper-based fungicides, that have relevance to specific regions, soils and vineyard management.

7.2.4 Linking off-target movement of agrochemicals with environmental impacts

Thirty eight percent of Australian vineyards surveyed, representing eight out of ten grape growing regions, had soil copper concentrations that exceeded the ANZECC Soil Quality guidelines. Copper in vineyard soils surveyed also exceeded concentrations that have been shown to have sub-lethal effects on soil organisms. Earthworm avoidance behaviour was recorded for soil containing 42.6 mg/kg or more of copper (Appendix 8). This suggests that copper may be having a negative effect on the biological health of Australian vineyard soils.

- Recommendation: Further studies should investigate whether the copper concentrations in Australian vineyards are impacting on soil health. The bioavailability of copper in Australian vineyard soils should be determined and related to effects on key soil organisms (e.g. earthworms and microbes) and the functionality of vineyard soil systems (e.g. microbial respiration and nutrient cycling).

7.3 'GROWER-FRIENDLY' TOOLS FOR MONITORING OFF-TARGET MOVEMENT OF AGROCHEMICALS

The final project objective was to *"evaluate simulation models and risk quotients for predicting agrochemical behaviour in areas around vineyards, and basic tools for measuring movement or impacts of agrochemicals"*. Throughout this project we were therefore mindful of exploring tools that vineyard managers might be able to use to monitor off-target movement or impacts of agrochemicals, as part of their Environmental Management Systems. The methods we used were considered in terms of the ease and cost of sampling and analysis, and interpretation of results.

7.3.1 Simple alternatives to conventional chemical analysis

ELISA test kits (Appendix 7), in the plate format that we trialed, require a precision in their use that probably precludes them from being 'grower friendly' for quantitative assessment of agrochemicals in soil-water. However wine industry members have argued that ELISA test kits still have merit as a qualitative measure (presence/absence) of agrochemicals.

Analysis of the solvent-filled passive samplers that we trialed requires a commercial laboratory, but extracting and measuring agrochemical from the solvent involves a simpler sample clean-up than standard analysis of agrochemicals in soil or plant material. The passive samplers therefore have potential to be faster and cheaper than conventional analysis. At this stage there are few laboratories able to analyse the passive samplers.

7.3.2 Methods for sampling soil-water

Ceramic or plastic polymer 'suction cups', and soil cores, were two methods used in preliminary trials for extracting soil-water. Both types of suction cup adsorbed and re-released agrochemical, and were also

considered too slow to collect the large volumes (> 1L) of soil-water required for conventional chemical analysis. The level of reporting on concentrations in the soil cores exceeded the concentrations of concern regarding water quality.

Solvent-filled, time-integrated 'passive' water samplers were used to monitor chemicals in drainage water. They were found to be cheap to make, simple to use, able to detect a range of different agrochemicals, and reliable in water that has fluctuating concentrations of agrochemical.

The time integrated 'passive' samplers are well suited to being used in irrigation drains, but calibrations and methods for analysis are still being refined. The list of chemicals that can be included in a screening is increasing, but still not all-inclusive.

- Recommendation: Because of their low cost, ease of use and reliability, the passive samplers used in this study should be considered for use by the Australian grape industries.

7.3.3 Monitoring drift

Standardised methods for collecting drift and conducting trials are under development but are unlikely to be suitable for implementation by Australian vineyard managers as part of environmental self-auditing. Despite not providing quantitative data, there is a place for pigments, water sensitive papers and other tracers for monitoring (and then minimising) off-target losses in a commercial vineyard. Any spray moving above or below the canopy may be lost to the canopy. Comparing deposits on samplers above and below the canopy with deposits in the inner canopy provides a rough balance of where the sprayer output is going.

7.4 MODELS THAT PREDICT THE FATE OF AGROCHEMICALS IN VINEYARDS

Towards achieving the project objective: "*Evaluate simulation models and risk quotients for predicting agrochemical behaviour in areas around vineyards, and basic tools for measuring movement or impacts of agrochemicals*", we considered the relevance and application of these tools to drift and leaching.

7.4.1 Drift models

Several models are available to predict drift, based on the observed behaviours of spray plumes under varying conditions, however like all models they are limited by inherent assumptions. The trials highlighted the role of sprayer set-up in determining drift behaviour, with airborne drift for each of the eight sprayer-nozzle combinations being best described by a separate quadratic model. Overall, drift to the ground at the different distances was best described with a linear model, despite the patterns of deposits for the individual sprayers being highly non-linear. Other than regarding droplet size, the results of our trials concur with data from other drift studies.

- Recommendation: The industry should consider strategies for drift minimisation recommended for vineyards and orchards in the UK, USA and Germany, as they are probably also appropriate for Australia. They include using buffers, low air flow/volume in sparse canopies, directed or recirculating sprayers and sensors to detect foliage.

7.4.2 PIRI

PIRI predictions that there was a high risk of simazine leaching and a low risk of chlorothalonil or methidathion leaching were supported by the field data, but PIRI appears to have underestimated the risk of dicofol or chlorpyrifos leaching.

Models make many assumptions. Leaching models are limited by the site details they contain. To increase the accuracy of PIRI some of the assumptions regarding soil type, irrigation and chemical use were supported by detailed site information. But refining the assumptions in a model is not always an option. Models should therefore continue to be validated by comparison against monitoring data. PIRI will become more accurate as it incorporates more site-specific detail into the layers of data.

7.5 RECOMMENDATIONS FOR FURTHER RESEARCH

The following recommendations were provided to CRCV in July 2005, for inclusion in the CRCV Exit Strategy.

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

Dr Mahabubur Mollah, Alison MacGregor and Adam Wightwick, PIRVic, DPI - Mildura

Aims
Project 2.5.2 aimed to understand and measure the movement (through air, soil and water) of key agrochemicals within and beyond vineyards. This project intended to provide scientific data that could be used for the development and improvement of best management practices to minimise the potential environmental impacts resulting from vineyard spraying.

Objectives
- Review environmental risks of key agrochemicals;
- Quantify the distribution of spray application (i.e. % of spray on canopy, in the air as drift and landing on the ground);
- Measure agrochemicals in leachate from vineyards;
- Determine the extent of copper accumulation in Australian vineyard soils; and
- Evaluate tools/models for measuring/predicting agrochemical movement.

Milestones
- All milestones were achieved

Implications for industry
1. ***The review*** identified spray drift, leaching of agrochemicals through vineyard soils and the accumulation of copper in vineyard soils as being key issues to investigate further. Twenty-four agrochemicals were ranked according to their leaching potential. ***Conclusion***: *The review document provides the industry with a resource for developing extension materials regarding relative risks of different agrochemicals.*

2. ***Spray drift field trials*** quantified the distribution of drift from typical vineyard sprayers. Drift was primarily influenced by sprayer and nozzle selection and sprayer set-up. The data collected has been provided to other groups modelling vineyard and orchard drift. ***Conclusion***: *Vineyard spraying can cause significant drift through inappropriate management but can be negligible if well managed. However growers need ways to assess drift so they can make appropriate sprayer adjustments.*

3. ***Leaching trials*** confirmed that passive water samplers are a cost effective tool for monitoring agrochemicals in drainage water, while two suction tools for extracting drainage water were found to

be unsuitable. Monitoring conducted in a complimentary project[7] confirmed that even chemicals with 'low leaching potential' are leaching through the soil profile. Vineyard details from 2.5.2 trial sites have been included in the Pesticide Impact Risk Index (PIRI) model, and leachates in 2004/05 drainage water samples from those sites are being correlated against PIRI to confirm that it provides valid predictions of leaching from vineyards. ***Conclusion***: *Leaching from vineyards contributes to the contamination of drainage water and potentially of aquatic environments (e.g. rivers, lakes, wetlands). Monitoring using passive samplers would assist managers to develop strategies to reduce those risks. PIRI now includes vineyard data to improve its accuracy in ranking the risks of leaching of several vineyard chemicals. The coordinated use of passive samplers by industry and provision of results for further validation of PIRI would allow PIRI to be used as a research tool to generate grower-friendly information for chemical selection.*

4. ***Accumulation of copper*** was assessed in a national survey of 100 vineyard soils. Copper concentrations (6-223 mg/kg) were lower than are reported in European vineyards (130-1280 mg/kg). Copper in 38% of the surveyed soils exceeded the ANZECC soil quality guideline value but whether these concentrations impact on soil health is yet to be determined. ***Conclusion***: *Copper has accumulated in Australian vineyard soils, however further work is needed to assess the long-term impacts of copper on soil health before the grape industry changes recommendations for the use of copper-base fungicides.*

Project 2.5.2 was linked with CRCV project 2.5.1 (Prof. Ary Hoffman, Linda Thomson and David Sharley) which identified terrestrial and aquatic species with potential to be used as bioindicators for assessing impacts of agrochemicals. The industry has an opportunity to further refine techniques for using bioindicators, particularly to assess impacts on soil health.

Future Directions

CRCV project 2.5.2 arose when managers and researchers, trying to comply with and refine codes of practice for agrochemical use, found that information relevant to selecting or using chemicals in ways that would minimise risk to the environment was not available in an accessible format. The project collated much existing information into a more useable form, and generated new data to quantify and prioritise risk. The original project objectives included extension but this was removed after the first year by the project reference committee, reasoning that project 2.5.2 should focus on research and leave extension to be a subsequent project. To ensure that the Australian wine industry can use the information generated from project 2.5.2 to meet its commitment to environmental stewardship and public environmental reporting, to support the "Clean and Green" image, the following program of new research is recommended.

For measuring improvements in environmental performance:

Cost-effective, easy to use and reliable methods are required for assessing spray drift and soil contamination, similar to the passive sampler for testing water quality now available to the industry. The output of new research should be:

- Guidelines for using bioindicators to assess vineyard health (e.g. soil health) and aquatic health
- A simple method for drift collection and assessment.

For improving policy on use of copper in Australian vineyards:

Further work is needed to assess the impacts of copper on long-term soil health. The output of new research would be recommendations for copper use in Australian vineyards.

For better informed decision-making regarding chemical choice:

[7] Mallee Catchment Management Authority project funded by the National Action Plan for Salinity and Water Quality.

Recommendations for chemical selection reported in project 2.5.2 relate to relative risk based on predicted chemical behaviour, but should be refined based on an increased body of real data and more accurate predictions. The output of new research should be:

- The CSIRO model PIRI more accurately able to compare risks associated with use of agrochemicals in vineyards, through inclusion of new data from water monitoring by the industry, plus emerging data from tests with drift collectors and use of bioindicators
- Publication of simple risk-rating lists, derived from the refined PIRI model and from monitoring data, to assist managers to choose between chemicals according to the risks in specific regions/scenarios.

Action (if recommended by industry reference group): Mahabubur Mollah, Alison MacGregor and Adam Wightwick

- Develop proposals to deliver the proposed outputs
- Link to research on biodiversity (Prof. Ary Hoffmann, Linda Thompson) and modelling with PIRI (Rai Kookana) and movement of nutrients from vineyards (Ron Hutton).

SECTION 8

PROJECT OUTPUTS

In addition to this final report, the following reports, papers and presentations were delivered during the project:

8.1 REVIEW OF PUBLISHED LITERATURE AND CURRENT RESEARCH

Mollah M, MacGregor A (2002) Review of the potential for agrochemicals used in viticulture to impact on the environment. A Review Report. Grape and Wine Research and Development Corporation. August 2002. 120 pages.

This review, provided to GWRDC in August 2002, covered the following topics:

- Legislation intended 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 agrochemicals in air/soil/water
- Biological significance of chemical levels

8.2 PRELIMINARY REPORT ON THE SOIL COPPER SURVEY

Wightwick A, Mollah M, MacGregor A (2005) Survey of copper in Australian vineyard soils: assessing risks to soil health - prelimary report presented to the National Wine Industry Environment Committe (WINEC). Department of Primary Industries, Victoria.

8.3 PROGRESS REPORTS TO CRCV AND GWRDC

Progress reports were provided to CRCV and GWRDC as per requirements.

8.4 DRAFT JOURNAL ARTICLE

Wightwick A, Mollah M, Smith J, MacGregor A (submitted) Sampling considerations for surveying copper concentrations in Australian vineyard soils. Submitted to the *Australian Journal of Soil Research*.

This article is attached as Appendix 9, page 143.

8.5 MISCELLENEOUS PAPERS AND/OR ADDRESSES

MacGregor A (2002) Agrochemicals and the environment. Presentation to 30 viticulture staff at Yalumba Agrochemical Information Day, Angaston, S.A, 30th August.

MacGregor A (2003) Spray drift – economically wasteful, but you can influence it. Presentation to 60 growers at a spray night organised by Silvan Australia Ltd and GBC Motors. DPI Mildura, November 2003.

MacGregor A (2003) Spray drift – economically wasteful, but you can influence it. Presentation to 15 students as part of the Horticulture Diploma at Sunraysia TAFE. October 2003.

MacGregor A, Mollah M (2002) Agrochemicals move within and beyond the vineyard - A review of their potential environmental impacts. In proceedings of *Second National Wine Industry Environment Conference & Exhibition*. Adelaide, SA. 25th – 26th November. (unpaged)

MacGregor A, Mollah M (2002) Chemical use and spray drift. Presentation at Riverlink GAP forum, Mildura, 18th November.

MacGregor A, Mollah M, Dorr G, Reynolds J, Woods N, Wightwick A (2004) Quantifying off-target movement of pesticides from vineyards. Abstract in proceedings – *New Directions in Agroecology: Productivity and Sustainability* conference, Mildura 29 Aug - 3 Sept 2004.

MacGregor A, Mollah M, Wightwick A, Dorr G, Woods N, Reynolds J (2004) Spray drift - a case study from Sunraysia. *12th Australian Wine Industry Technical Conference*, Workshop 70 - Movement of agrochemicals within and beyond vineyards. Melbourne, 24 - 29 July, 2004.

MacGregor A, Mollah M, Dorr G, Reynolds J, Woods N, Wightwick A (2004) Spray drift: The proportion that drifts out of the vineyard is small compared to the proportion that gets wasted onto the ground. Abstract in proceedings – *Interact 2004* Australasian Society for Ecotoxicology conference, Gold Coast, July 2004.

MacGregor A (2005) Improving spray coverage and minimising drift through sprayer set up. Seminar and field demonstration to 100 growers at 2005 Vineyard Association of Tasmania annual field day Spray Application, 10th November 2005, Richmond, Tasmania.

Mollah M, Wightwick A, MacGregor A, Gordon J (2004) Very little simazine leached beyond 10 cm soil depth in Sunraysia vineyards following an irrigation application. Abstract in proceedings - *New Directions in Agroecology: Productivity and Sustainability* conference, Mildura 29 Aug - 3 Sept 2004.

Wightwick A, MacGregor A, Mollah M (2004) Movement of contaminants in leachates - a case study from Sunraysia. *12th Australian Wine Industry Technical Conference*, Workshop 70 - Movement of agrochemicals within and beyond vineyards. Melbourne, 24 - 29 July, 2004.

Wightwick A, MacGregor A, Mollah M (2004) Copper use in Australian vineyards: is it sustainable? Abstract in proceedings - *New Directions in Agroecology: Productivity and Sustainability* conference, Mildura 29 Aug - 3 Sept 2004.

Wightwick A, MacGregor A, Mollah M (2004) Accumulation of copper in Australian vineyard soils. *12th Australian Wine Industry Technical Conference*, Workshop 70 - Movement of agrochemicals within and beyond vineyards. Melbourne, 24 - 29 July, 2004.

Wightwick A, MacGregor A, Mollah M (2004) Breakdown and movement - the influencing factors. *12th Australian Wine Industry Technical Conference*, Workshop 70 - Movement of agrochemicals within and beyond vineyards. Melbourne, 24 - 29 July, 2004.

Wightwick A, MacGregor A, Mollah M (2004) Copper levels in Australian vineyard soils: are they a biological concern. *Interact 2004*, Australasian Society for Ecotoxicology conference, Gold Coast, 4 - 8 July 2004.

Wightwick A, Mollah M, MacGregor A, Smith T, Sharley D, Hoxley G, Ballantyne I (2003) River contaminants – sources, transformation and movement within the mallee catchment. Research review workshop conducted for project stakeholders. DPI Mildura December 2003.

8.6 POSTERS

MacGregor A, Mollah M, Dorr G, Reynolds J, Woods N, Wightwick A (2004) Spray drift: an environmental issue? Poster abstract in proceedings - *12th Australian Wine Industry Technical Conference*, Melbourne, July 2004.

MacGregor A, Mollah M (2002) Agrochemicals move within and beyond the vineyard - A review of their potential environmental impacts. *Interact 2002* conference of the Australasian Society for Ecotoxicology and Royal Australian Chemical Institute. University of Technology. Sydney, 21-25 July 2002.

Wightwick A, MacGregor A, Mollah M, Gordon J (2004) Are copper levels in Australian vineyard soils biologically significant? Poster abstract in proceedings - *12th Australian Wine Industry Technical Conference*, Melbourne, July 2004.

Wightwick A, MacGregor A, Mollah M, Gordon J (2004) Are copper levels in Australian vineyard soils biologically significant? Development of a sampling protocol. Poster abstract in proceedings – *International Workshop on Chemical Bioavailability*, Adelaide, Sept 2004.

MacGregor A, Mollah M (2002) Minimising the environmental impact of agrochemical use in Australian vineyards. *Interact 2002* conference of the Australasian Ecotoxicology Society and Royal Australian Chemical Institute. University of Technology Sydney, July 2002.

Mollah M, MacGregor A (2002b) Minimising the environmental impact of agrochemical use in Australian vineyards. 10th IUPAC International Congress on the Chemistry of Crop Protection, Basel, Switzerland, August 2002.

8.7 TECHNICAL REPORTS AND INDUSTRY JOURNAL ARTICLES (NON-REFEREED)

Mollah M, MacGregor A, Wightwick A, Gordon J, Sharley D (2004) Contaminants from irrigated horticulture. A review of the movement, transformation and fate of agrochemicals, nutrients and heavy metals from irrigated horticultural properties in the Mallee. PIRVic, DPI - Mildura.

Wightwick A, Mollah M, MacGregor A, Gordon J, Sharley D (2004) Is copper reaching biologically significant levels in Australian vineyards? *The Australian and New Zealand Grapegrower & Winemaker*. No. 481, 33 - 34.

MacGregor A, Mollah M, Wightwick A, Dorr G, Woods N, Reynolds J (2004) Spray drift: The proportion that drifts out of the vineyard is small compared with the proportion that gets wasted on the ground. *The Australian and New Zealand Grapegrower & Winemaker*. No. 481, 35 - 37.

Mollah M (2003) Keeping a close eye on water quality. *The Irrigator*, Nov/Dec, 24.

MacGregor A, Mollah M (2002) Agrochemicals move within and beyond the vineyard: a review of their potential environmental impacts. *Australian Viticulture*. Vol. 7(2), 42 –47. [Reprinted from proceedings of Second National Wine Industry Environment Conference & Exhibition. Adelaide, SA. 25th –26th November].

Mollah M, MacGregor A (2002c) How do agrochemicals move in the environment, where do they end up, and do we need to know? *The Australian and New Zealand Grapegrower & Winemaker*. No. 456, 13 – 15.

Mollah M, MacGregor A (2002d) New environmental project for the CRCV. *Cooperative Research Centre for Viticulture Newsletter*. Vol. 8(2).

8.8 OTHER COMMUNICATIONS

Three workshops were held during the project to provide industry stakeholders with feedback on the results and seek input into trial planning. Project progress was also reported to the CRCV at the annual program review days and copper results were presented to the Wine Industry National Environment Committee.

19th June 2002. CSIRO Merbein

CRCV Program 2 Review.

Approx 50 researchers, managers and stakeholders involved in CRCV Program 2

27th August 2002. DPI Mildura.

CRCV program 2.5.2 Project Review Workshop. (1st project workshop to review/refine directions).

20 participants from DPI, GWRDC, Mallee Catchment Management Authority (CMA), Orlando, Southcorp, Australian Dried Fruits Association (ADFA), CRCV, CRC for Freshwater Ecology, South Australian Research and Development Institute, Simeon, Land and Water R&D Corporation, University of Qld.

5th September 2003. CRCV Adelaide

CRCV Review of Program 2.

Approximately 50 participants from the CRCV research program and panel of reviewers.

10th December 2003. Mildura.

2nd project workshop to review/refine directions.

29 participants from ADFA, La Trobe University, NSW Agriculture, NSW Department of Environment and Conservation, DPI, growers, Lower Murray Water, Mallee CMA, Sinclair Knight Mertz, Sunraysia TAFE, Sunraysia Rural Water Authority.

29th July 2004. Melbourne.

12th Australian Wine Industry Technical Conference. Workshop 70 Movement of agrochemicals within or beyond the vineyard.

22 participants from Vic DPI, CSIRO Land and Water, La Trobe University, Orica, NSW Agriculture, Orlando Wyndham, Yalumba, Curtin University, Beringer Blass, Hardy, Lincoln Ventures NZ, Taylors Wines, Brookland Valley Wines, Food & Beverage Australia Limited.

30th August 2004. Mildura

3rd project workshop to review/refine directions.

20 participants from DPI, GWRDC, Mallee CMA, CRCV, Orlando, Southcorp, ADFA, SARDI, Simeon, Australian Wine and Brandy Corporation (AWBC), Beringer, Hardy, La Trobe University.

30th August 2005, WFA boardroom, National Wine Centre, Adelaide

30 minute presentation to the Wine Industry National Environment Committee (WINEC) regarding results from the Australia-wide copper survey and to seek feedback on how to communicate those results. WINEC members received the preliminary report on the copper survey prior to the meeting.

Approximately 12 participants representing the project staff and members of WINEC (Winemakers Federation of Australia, Winegrape Growers Council of Australia, GWRDC, CRCV, Australian Wine Research Institute, AWBC).

SECTION 9

REFERENCES

ABS (2005) Australian Wine and Grape Industry, Catalogue No. 1329.0, 2003-04. Australian Bureau of Statistics.

Agnova (2005) Engelhard WP Surround Crop Protectant. Label – AU-04-1. © 2004 Engelhard Corporation. www.agnova.com.au/resources/Surround-crop-protectant-label.pdf

Agriculture Victoria Services (2002) Viticulture Research to Practice®: Spray application manual. Licensed to the Cooperative Research Centre for Viticulture.

Anon (2000) Tips on using a spray pole. *The Australian Grapegrower and Winemaker*.**442**:52-53.

ANZECC and ARMCANZ (2000) Chapter 4 - Field Sampling. Australian Guidelines for Water Quality Monitoring and Reporting. *National Water Quality Management Strategy No. 7.* Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand.

ANZECC and NHMRC (1992) 'Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites'. Australian and New Zealand Environment and Conservation Council, National Health and Medical Research Council.

APVMA (2005) Operating principles and proposed registration requirements in relation to spray drift risk. Discussion paper. Agricultural Pesticides and Veterinary Medicines Authority, August 2005.

ASAE Standards (2000) ASAE Standards 47th Ed. S572 AUG99. Spray nozzle classification by droplet spectra. St Josephs, MI: ASAE.

Australian Wine Industry Technical Conference Inc. (2004) Workshop 70: Movement of agrochemicals beyond the vineyard. 12th Australian Wine Industry Technical Conference, Melbourne, 24-29 July.

Bache DH, Sayer WJD (1975) Transport of aerial spray. 1. A model of aerial dispersion. *Agricultural Meteorology*. **15**:257-271

BBA (2005) Application Techniques Division Brunswick. Pages 69-72. http://www.bba.de/english/pub_eng/document/ar2003/21-AP_web.pdf

Beier C, Hansen K (1992) Evaluation of porous cup soil-water samplers under controlled field conditions: comparison of ceramic and PTFE cups. *Journal of Soil Science*. **43** : 262 - 271.

Besnard E, Chenu C, Robert M (2001) Influence of organic amendments on copper distribution among particle size and density fractions in Champagne vineyard soils. *Environmental Pollution.* **112**, 329 – 337.

Biswas T, Christen E, Quayle W, Beijert M (2002) Copper toxicity associated with viticulture in southeastern New South Wales, Australia. In 'Future soils'. Conference proceedings Australian Society of Soil Science national conference, Perth, Western Australia, 2 - 6 December 2002'. (Eds D Williamson, C Tang, A Rate) pp 32 - 33. (Australian Society of Soil Science)

Bogomolov DM, Chen SK, Parmelee RW, Subler S, Edwards CA (1996) An ecosystem approach to soil toxicity testing: a study of copper contamination in laboratory soil microcosms. *Applied Soil Ecology.* **4**, 95 - 105.

Borgo M (2000) Anciennes et nouvelles adversites de la vigne en Italie: importance de la protection integree. *in* Proceedings of the *25th World Congress of Vine and Wine*. Paris, 19-23rd June 2000.

Bozdogan AM, Bozdogan NY (2004) A Review of the Effects of Adjuvants on Spray Drift in Pesticide Applications. pp 92 – 98 *in* Proceedings of the *7th International Symposium on Adjuvants for Agrochemicals (ISAA2004),* Cape Town, South Africa, 8 – 12 November 2004.

Brun LA, Le Corff J, Maillet J (2003) Effects of elevated soil copper on phenology, growth and reproduction of five ruderal plant species. *Environmental Pollution*. **122** : 361 - 368.

Brun LA, Maillet J, Hinsinger P, Pepin M (2001) Evaluation of copper availability to plants in copper-contaminated vineyard soils. *Environmental Pollution*. **111** : 293 - 302.

Bubb K A (2001) Simazine concentrations in soil, groundwater and stream water following application to Pinus plantations in the coastal lowlands of south-east Queensland. *Australian Forestry*, **64**(1), 8 – 13.

CCME (2003) 'Canadian Environmental Quality Guidelines'. Canadian Council of Ministers of the Environment, Canada. Available at: http://www.ccme.ca/publications/can_guidelines.html

Chaignon V, Sanchez-Neira I, Herrmann P, Jaillard B, Hinsinger P (2003) Copper bioavailability and extractability as related to chemical properties of contaminated soils from a vine-growing area. *Environmental Pollution*. **123**, 229 - 238

Ciba Geigy (undated) Water sensitive paper for monitoring spray distribution. (Bul 332-W) AG7.3 11510e[691], Ciba Geigy Limited.

Conradie K (2000) Copper levels in South African nursery soils: possible effects on the propagation of grapevines. In 'Wynboer - a technical guide for wine producers'. (WineLand, South Africa). Available at: http://www.wynboer.co.za/recentarticles/0406copper.php3

Cooinda Ceramics Pty Ltd (2003) 126 Canterbury Road, Bayswater, Victoria 3153, Australia.

Coombe BG (1995) Adoption of a system for identifying grapevine growth stages. *Australian Journal of Grape Wine Research*. **1:**100-110.

Coulon T, Sentenac G (2000) Un referentiel national "production integree des raisins' pour les vignobles francais. *Proc. of the 25th World Congress of Vine and Wine*. Paris, 19-23rd June 2000.

CRCV (2001) survey data from 450 grapegrowers participating in training workshops (Viticulture Research to Practice® - Spray Application) presented between 1999 and 2001.

Cross JV, Walklate PJ, Murray RA, Richardson GM (2001a) Spray deposits and losses in different sized apple trees from an conventional airblast orchard sprayer: 1. Effects of spray liquid flow rate. *Crop Protection* **20**:13-30.

Cross JV, Walklate PJ, Murray RA, Richardson GM (2001b) Spray deposits and losses in different sized apple trees from an conventional airblast orchard sprayer: 2. Effects of spray quality. *Crop Protection.* **20**:333-343.

Cross JV, Walklate PJ, Murray RA, Richardson GM (2003) Spray deposits and losses in different sized apple trees from an conventional airblast orchard sprayer: 3. Effects of air volumetric flow rate. *Crop Protection.* **22**:381-394.

Darmendrail D (2003) 'The French approach to contaminated land management - Revision 1: BRGM/RP-51098-FR'. BRGM, France.

DEFRA (2002) Local Environment Risk Assessment for Pesticides (LERAP): Broadcast Air-assisted Sprayers. A step-by-step guide to reducing aquatic buffer zones (New scheme from 2002).

Department for Environment, Food and Rural Affairs and the Pesticides Safety Directorate. UK. Available at www.pesticides.gov.uk/uploadedfiles/Web_Assets/PSD/LERAP_Orchard(1).pdf. Last accessed Novmeber 2005.

Delas J (1981) Copper toxicity in viticultural soils. In 'Copper in animal waste and sewage sludge' (Eds PL Hermite, J Dehandtshutter) pp 136 - 142 (D. Reidel, Dordrecht, the Netherlands).

Delusia A, Giandon P, Aichner M, Bortolami P, Bruna L, Lupetti A, Nardelli F, Stringari G (1996) Copper pollution in Italian vineyard soils. *Communications in Soil Science and Plant Analysis*. **27**, 1537 – 1548.

Doble SJ, Mathews GA, Rutherford I, Southcombe ESE (1985) A system for classifying hydraulic and other atomisers into categories of spray quality, *in* Proceedings of the *British Crop Protection Conference – Weeds*. **3**:1125-1133.

Domagalski JL, Dubrovsky NM (1992) Pesticide residues in ground water of the San Joaquin Valley, California. *Journal of Hydrology*, **130**(1-4):299–338.

Dorr G, Woods N, Craig I (1998) Buffer zones for reducing drift from the application of pesticides. *Paper No. SEAAg 98/008*. International Conference on Engineering in Agriculture, 1998.

Dudley RE (2001) Sunraysia drainage strategy 2000 – Stage 1, Current situation report, April 2001. Mildura Rural City Council, Victoria.

Envirologix (2003) 500 Riverside Indl Pkwy, Portland, 04103, USA.

Flores-Velez LM, Ducarior J, Jaunet AM, Robert M (1996) Study of the distribution of copper in an acid sandy vineyard soil by three different methods. *European Journal of Soil Science*. **47**, 523 – 532.

Forrester ST, Janik LJ, Beech TA, McLaughlin MJ (2004) Recent developments in routine soil analysis by mid-infrared; rapid and cost effective laboratory analysis", Occasional Report No.17, ASPAC NZ (2004)

Fox RD, Hall DL, Reichard DL, Brazee RD, Krueger HR (1993) Pesticide tracers for measuring orchard spray drift. *Applied Engineering in Agriculture* **9**(6): 501-505.

Furness GO (2000) Droplet rating chart: a simple way to measure spray coverage and dose of pesticides on grapevines. *The Australian Grapegrower and Winemaker* No. 439, August 2000.

Furness GO, Magarey PA (2000) Unit canopy row calibration and a new pesticide label format to improve dose consistency on different canopy sizes with spray application to fruit trees and vines in Australia. *Aspects of Applied Biology*. **57**:309-312.

Ganzelmeier H (1993) Drift of plant protection products in field crops, vineyards, orchards and hops. pages 125-130 *in* Proceedings of the A.N.P.P. – B.C.P.C Second International Symposium on Pesticide Application Techniques, Strasbourg, 22-24 September 1993.

Ganzelmeier H (2002) The prospect of European harmonisation: plant protection equipment under test. *Journal of Central European Agriculture***. 3**(4): 302-311.

Ganzelmeier H, Rautmann D (2000) Drift, drift reducing sprayers and sprayer testing. *Aspects of Applied Biology*. **57**: 1-10.

Ganzelmeier H, Rautmann D, Spangenberg R, Streloke M, Herrman M, Wenzelberger HJ, Walter HF (1995) Studies on the spray drift of plant protection products. Results of a test program carried out throughout the Federal Republic of Germany. *Mitteilungen aus der Biologischen Bundesanstalt fur land und forstwirtschaft*, Berlin Dahlam. Blackwell Wissenschafts-Verlag.

Gardner J (2003) Copper usage controversy heats up in Europe [online]. Ministry of Agriculture and Food, Ontario, Canada. Available at:

http://www.gov.on.ca/OMAFRA/english/crops/hort/news/hortmatt/2003/03hrt03a3.htm [accessed 2004].

Genstat (2002) GenStat Release 6.1. 6th Edition, 2002, Lawes Agricultural Trust, Rothamsted Experimental Station, UK.

Glotfelty DE, Schomburg CJ, McChesney MM, Sagebiel JC, Seiber JN (1990) Studies on distribution drift and volatolisation of diazinon resulting from spray application to a dormant orchard. *Chemosphere*. **21**:1303-1324. (Cited in Holland et al. 1997).

Guerbet M, Guyodo G (2002) Comparison of 35 electronic databases for environmental risk assessment. *Environmental Toxicology*. **17**:7-13.

Gunton CG, Christy AG, McPhail DC (2005) The effect of NaCl on Cu(II) sorption on goethite. In Abstracts book, 15th Annual Goldschmidt conference: a voyage of discovery, 20 – 25 May 2005, Moscow, Idaho, USA.

Hewitt AJ (2000) Spray drift modelling, labelling and management in the US. *Aspects of Applied Biology*. **57**:11-19.

Hoffmann WC, Kirk IW (2002) Spray deposition and drift from two 'medium' nozzles. ASAE Meeting Paper No. 02-AA04. St Joseph, Michigan, ASAE.

Holland PT, Maber JF, May WA, Malcolm CP (1997) Drift from orchard spraying. pp 112-118 *in* Proceedings of the *50th N.Z. Plant Protection Conference, 1997*.

Hughes S, Reynolds B (1988) Cation exchange properties of porous ceramic cups: Implications for field use. *Plant and Soil*. **109**:141 - 144.

Hyne RV, Pablo F, Aistrope MA (2004a) Passive sampling for rice pesticides. *Irrigation Research and Extension Committee (IREC) Farmers' Newsletter, Rice R&D Summer Edition*, No. 165, pp 29-30.

Hyne RV, Pablo F, Aistrope M, Leonard A, Ahmad N (2004b) Comparison of time-integrated pesticide concentrations determined from field deployed passive samplers with daily river water extractions. *Environmental Toxicology and Chemistry*, **23**(9), 2090-2098.

IUPAC (2002) Agrochemical spray drift: Assessment and mitigation. Project number 2001-023-1-600. Available at http://www.iupac.org/projects/2001/2001-023-1-600.html (last accessed 24 Oct 2005).

Johnson S (2005) 'Danish (Zealand) guidelines: classification of polluted soil. Sanaterre Environmental'. Available at: http://www.sanaterre.com/guidelines/zealand.htm

Jordan (1997) *Sustainable viticulture scheme for the NZ wine industry. Project 6054*. Final report for Sustainable Management Fund Ministry for the Environment.

Kast WK (2002) 'Salicylic and phosphorous acid - possible alternatives to copper?' Staatliche Lehr- und Versuchsanstalt für Wein- und Obstbau. Available at: http://www.infodienst-mlr.bwl.de/la/lvwo/Veroeff/Alternativetocopper.htm

Khalil MA, Abdel-Lateif HM, Bayoumi BM, van Straalen NM (1996) Analysis of separate and combined effects of heavy metals on the growth of *Aporrectodea caliginosa* (Oligochaeta; Annelida), using the toxic unit approach. *Applied Soil Ecology*. **4**:213 - 219.

Koci V, Ocelka T, Mlejnek M, Grabic R (2004) Efficiency assessment of wastewater treatment plant based on SPMD sampling. *Central European Journal of Chemistry*. **2**(1):91-112.

Kookana (2005) Assessment of leaching potential of pesticides at a tile drained site under viticulture. CSIRO Land and Water. Report to Department of Primary Industries, August 2005.

Kookana RS, Baskaran S, Naidu R (1998) Pesticide fate and behaviour in Australian soils in relation to contamination and management of soil and water: a review. *Australian Journal of Soil Research*. **36**:715-64.

Kookana RS, Correll RL, Miller RB (2005) Pesticide Impact Rating Index – A pesticide risk indicator for water quality. *Water, Air, and Soil Pollution*. **5**, 45 – 65.

Leonard A, Hyne RV, Pablo F (2002) Trimethylpentane-containing passive samplers as a tool for predicting time-integrated concentrations of pesticides in water- a model based on laboratory and field studies. *Environmental Toxicology and Chemistry*. **21**: 2591-2599.

Lock K.,Janssen CR (2001) Test designs to assess the influence of soil characteristics on the toxicity of copper and lead to the oligochaete Enchytraeus albidus. *Ecotoxicology*. **10** : 137 - 144.

Lock K, Janssen CR (2003) Influence of aging on copper bioavailability in soils. *Environmental Toxicology and Chemistry*. **22**, 1162 - 1166.

Lord EI, Shepherd MA (1993) Developments in the use of porous ceramic cups for measuring nitrate leaching. *Journal of Soil Science*. **44** : 435 - 449.

Loureiro S, Soares AMVM, Nogueira AJA (2005) Terrestrial avoidance behaviour tests as screening tool to assess soil contamination. *Environmental Pollution*. **138:**121-131.

Lu Y, Wang Z (2003) Accumulation of organochlorinated pesticides by triolein containing semipermeable membrane device (triolein-SPMD) and rainbow trout. *Water Research* (Oxford), **37**(10), 2419-2425.

Lukkari R, Aatsinki M, Vaisanen A, Haimi J (2005) Toxicity of copper and zinc assessed with three different earthworm tests. *Applied Soil Ecology.* In press.

LVWO (2002) 'Proceedings Eco-fruit - 10th International Conference on Cultivation Technique and Phytopathological Problems in Organic Fruit-Growing and Viticulture, February 4th -7th, 2002 at Weinsberg, Germany'. LVWO, Germany. Available at: http://www.infodienst-mlr.bwl.de/la/lvwo/ecofruvit/contributions.htm

Ma W-C (1984) Sublethal toxic effects of copper on growth, reproduction and litter breakdown activity in the earthworm *Lumbricus rubellus*, with observations on the influence of temperature and soil pH. *Environmental Pollution (Series A).* **33:**207-219.

Maber J, Dewer P, Praat JP (2002) SprayCan - spray drift prediction model. Lincoln Ventures, Ltd, Hamilton, NZ.

MacGregor A (2005) How much is enough? A keystone issue to align dried fruit production with the policy and technology of spraying in the 21st century. Final Report for Project DAV90. Horticulture Australia Ltd.

Magalhaes MJ, Sequeria EM, Lucas MD (1985) Copper and zinc in vineyards of central Portugal. *Water, Air and Soil Pollution*. **26:**8-24.

Manktelow DW, MacGregor A, Gurnsey S (2004) Deposit variability and prediction in fruit crops - What use are label rates anyway? *International advances in pesticide application*, held at Royal Holloway, University of London, UK, 5-7 January 2004. *Aspects of Applied Biology*, **71:**

Manktelow DWL, Praat J-P (2000) Spray deposit variability in New Zealand winegrape canopies and implications for agrochemical application practices. *New Zealand Plant Protection* **53**:235-240.

Markich SJ, Warne MStJ, Westbury A-M, Roberts CJ (2002) A compilation of data on the toxicity of chemicals to species in Australasia. Part 3: Metals. *Australasian Journal of Ecotoxicology.* **8**:1-72.

Mathews GA (2000) Pesticide Application Methods. Third Edition. Blackwell Science.

McBride MB (1981) Forms and distribution of copper in solid and solution phases of soil. In 'Copper in soils and plants - Proceedings of the Golden Jubilee International Symposium, Murdoch University, Perth, Western Australia'. (Eds JF Loneragan, AD Robson, RD Graham) pp 25 - 45. (Academic Press, Sydney).

McConnell S, Wightwick A, Smith T, Porteous C (2003) Code of Environmental Best Practice for Viticulture Sunraysia Region - Volume 1. Department of Primary Industries, Victoria.

McLaughlin M (2001) 'Ageing of metals in soils changes bioavailability'. Fact sheet on Environmental Risk Assessment. International Council on Metals and the Environment (ICME), Ontario, Canada. Available at: http://www.icme.com.

McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers SL (2000) Review: A bioavialbility-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research.* **38:**1037-86.

McLean JE, Bledsoe BE (1992) Ground water issue – behaviour of metals in soils. United States Environmental Protection Agency.

Merrington G, Rogers SL, Van Zwieten L (2002) The potential impact of long-term copper fungicide usage on soil microbial biomass and microbial activity in an avocado orchard. *Australian Journal of Soil Research*. **40:**749-759.

Mollah M, MacGregor A (2002) Review of the potential for agrochemicals used in viticulture to impact on the environment. A Review Report. Grape and Wine Research and Development Corporation. August 2002.

Murphy K (1998) Machinery optimisation to maximise effectiveness of chemicals. *The Australian grapegrower and Winemaker* **417**:42-43.

NEPC (1999) 'National environment protection (assessment of site contamination) measure'. National Environmental Protection Council Service Corporation, Adelaide, Australia.

Nolan A, Lombi E, McLaughlin M (2003) Metal bioaccumulation and toxicity in soils - why bother with speciation? *Australian Journal of Chemistry*. **56** : 77 - 91.

OECD (1984) 'Earthworm acute toxicity tests. OECD Guidelines for testing of chemicals, Section 2, Effects on biotic systems'. Organisation for Economic Co-operation and Development, Paris, France.

O'Halloran K, Booth LH. (2000) 'New Zealand ecotoxicity data: Soil invertebrates and terrestrial plants'. In 'Ecological risk assessment at contaminated sites'. Manaaki Whenua Landcare Research, Lincoln, New Zealand. Available at: http://contamsites.landcare.cri.nz/nz_data.htm.

Oliver D, Naidu R (2003) Uptake of copper (Cu), lead (Pb), cadmium (Cd), arsenic (As) and dichlorodiphenyltrichloroethane (DDT) by vegetables grown in urban environments. *in* Proceedings of the *5th National Workshop on the Assessment of Site Contamination* (Eds A Langley, M Gilbey, B Kennedy). National Environment Protection Council, Adelaide.

Oregon State University (1993) Movement of pesticides in the environment. Extension Toxicology Network. http://ace.ace.orst.edu/info/extoxnet/tibs/movement.htm

Organic Industry Export Consultative Committee. (2005) 'National Standard for Organic and Bio-Dynamic Produce' (Draft). Australian Quarantine and Inspection Service. Available at: http://www.ofa.org.au/papers/2005%20Draft%20NATIONAL%20STANDARD.doc

Paoletti MG, Sommaggioa D, Favrettoa MR, Petruzzelli B, Pezzarossab B, Barbafieri M (1998) Earthworms as useful bioindicators of agroecosytem sustainability in orchards and vineyards with different inputs. *Applied Soil Ecology*. **10:**137–150.

Pietrzak U, McPhail DC (2004) Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. *Geoderma*. **122:**151-166.

PISC (2002) Spray Drift Management. Principles, strategies and supporting information. Primary Industries Standing Committee PISC (SCARM) Report 82. CSIRO Publishing.

Poss R, Noble AD, Dunin FX, Reyenga W (1995) Evaluation of ceramic cup samplers to measure nitrate leaching in the field. *European Journal of Soil Science*. 46 : 667 - 664

Praat J-P, Maber JF, Manktelow DWL (2000) The effect of canopy development and sprayer position on drift from a pipfruit orchard. *New Zealand Plant Protection* **53**:241-247.

Rhizosphere Research Products (2003) Dolderstraat 62, NL 6706 JG Wageningen, The Netherlands.

Riches D, Holmes R, Keane P, Joyce D (2005) Investigation of alternative controls for grapevine downy mildew, Paper presented at the *15th Australasian plant pathology society conference*, Sep 26-29th, 2005, Deakin University, Geelong. p86

Riches D, Warren M, Murphy K, Markovic V, Gayle K, Whyte L (2002) Rapid tests for quantifying spray application on vines. Final Report to Grape and Wine Research and Development Corporation for Project CRV 98/2 DAV. Department of Natural Resources and Environment 2002.

Rodriguez-Rubio P, Morillo E, Madrid L, Undabeytia T, Maqueda C (2003) Retention of copper by a calcareous soil and its textural fractions: influence of amendment with to agroindustrial residues. *European Journal of Soil Science.* **54:**401-409.

Sauve S (2002) Speciation of metals in soils. Bioavailability of metals in terrestrial ecosystems: importance of partitioning for bioavailability to invertebrates, microbes, and plants'. (Ed HE Allen). Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, Florida. pp 7 – 37.

Sauve S, Dumestre A, McBride M, Hendershot W (1998) Derivation of soil quality criteria using predicted chemical speciation of Pb^{2+} and Cu^{2+}. *Environmental Toxicology and Chemistry*. **17(8):**1481-1489.

Sauve S, McBride MB, Norvell WA, Hendershot WH (1997) Copper solubility and speciation of in situ contaminated soils: effects of copper level, pH and organic matter. *Water, air and soil pollution*. **100:**133-149.

Scott-Fordsman JJ, Weeks JM, Hopkin SP (2000) Importance of contamination history for understanding toxicity of copper to earthworm *Eisenia fetica* (Oligochaeta: Annelida), using neutral-red retention assay. *Environmental Toxicology and Chemistry.* **19**:1774-1780.

SDTF (1997) A summary of airblast application studies. Spray Drift Task Force. Available at http://www.agdrift.com/ Text%20pages/Pub_PDF.htm (last accessed 24/10/05).

SDTF (2001) A summary of tank mix and nozzle effects on droplet size. Spray Drift Task Force. Available at http://www.agdrift.com/Text%20pages/Pub_PDF.htm (last accessed 24/10/05).

Sharley D, Hoffmann A, Thomson L, MacGregor A, Pettigrove V (2004a) How does viticultural drainage water affect aquatic organisms? Developing biological indicators for river contamination. Abstract in proceedings, *Australian Society for Limnology 43rd Annual Congress*, Adelaide, Nov 30th - 3rd Dec 2004.

Sharley D, Thomson L, Hoffmann A, MacGregor A (2004b) What impact does viticultural management have on beneficial invertebrates? Developing bioindicators to assess vineyard health. Abstract in proceedings - *New Directions in Agroecology: Productivity and Sustainability* conference, Mildura 29 Aug - 3 Sept 2004.

Sheppard S, Bembridge J, Holmstrup M, Posthuma L (Eds) (1998). Advances in earthworm ecotoxicology. Society of Environmental Toxicology and Chemistry, USA.

Sinclair P (2000) Personal communication from Phil Sinclair, Senior Assessor, Risk Assesment and Policy Section, Chemicals and the Environment Branch, Environment Australia. November 2000.

Skerritt JH (1997) Enzyme-immunoassay: a simple test method for pesticide residues in grain, horticultural and environmental samples. Grain quality - from the inside out. *GASGA Executive Seminar Series*. No. 9: 58-65. Canberra, Australia. 16 September.

Song J, Zhao F-J, Luo Y-M, McGrath SP, Zhang H (2004) Copper uptake by *Elsholtzia splendens* and *Silene vulgaris* and assessment of copper phytoavailability in contaminated soil. *Environmental Pollution.* **128:**307-315.

Southcombe ESE, Miller PCH, Ganzelemeier H, Van de Zande JC, Mirales A, Hewitt A (1997) The International (BCPC) spray classification system including a drift potential factor. In *Proceedings of the 1997 Brighton Crop Protection Conference – Weeds.* **1**:371-380.

Spurgeon DJ, Hopkin SP, Jones DT (1994) Effects of cadmium, copper, lead and zinc on growth, reproduction and survival of the earthworm *Eisenia fetida* (savigny): assessing the environmental impact of point-source metal contamination in terrestrial ecosystems. *Environmental Pollution*. **84**:123-130.

Spurlock F, Burow K, Dubrovsky N (2000) Chlorofluorocarbon dating of herbicide-containing well waters in Fresno and Tulare counties, California. *Journal of Environmental Quality*, **29**(2), 474-483.

Sterling M (2001) Soil biology and its importance in soil health. In 'Soil health: the foundation of sustainable agriculture. Proceedings of a workshop on the importance of soil health in agriculture. Wollongbar Agricultural Institute. June 20-21 2001'. (Eds R Lines-Kelly. pp 8 - 13. NSW Agriculture, Wollongbar, NSW.

Swedish EPA (2002) 'Environmental Quality Criteria - Contaminated Sites'. Swedish Environmental Protection Agency, Sweden. Available at: http://www.internat.enviro.se/documents/legal/assess/assedoc/contdoc/pollevel.htm

Tee E (undated) VERA Product Sheet: National Good Environmental Management Project, Cooperative Research Centre for Viticulture and Department of Primary Industries, Primary Industries Research Victoria.

Teske EM, Bird S, Easterly D, Ray S, Perry S (1997) A users guide for AgDRIFT 1.0: A tiered approach for the assessment of spray drift of pesticides. CDI Tech Note no 95-10. Prepared on behalf of the Spray Drift Task Force, c/o Stewart Agricultural Research Services, Macon, MO.

Tiller KG, Merry RH (1981) Copper pollution of agricultural soils. In 'Copper in soils and plants - Proceedings of the Golden Jubilee International Symposium, Murdoch University, Perth, Western Australia'. (Eds JF Loneragan, AD Robson, RD Graham) pp 119 - 137. (Academic Press, Sydney).

Tromp A, Marais E (2000) Integrated production of wine (IPW) - the South African system as a consumer guarantee. In *Proceedings of the 25th World Congress of Vine and Wine*. Paris, 19-23rd June 2000.

Van Rhee JA (1976) Effects of soil pollution on earthworms. *Poedobiologia*. **17:**201–208.

Van Zwieten L, Rust J, Kingston T, Merrington G, Morris S (2004) Influence of copper fungicide residues on occurrence of earthworms in avocado orchard soils. *Science of the Total Environment*. **329:**29-41.

Vidacek Z, Bogunovic M, Husnjak S, Sraka M, Tadic L (1996) Nitrates, pesticides and heavy metals in drained soils and water in the Drava River Valley in Croatia. Proceedings of *6th Workshop on Drainage and the Environment*, April 21-29, Ljubljana, Slovenia, 255-264.

VROM International (2000) 'Circular on target values and intervention values for soil remediation: DBO/1999226863'. Netherlands Ministry of Housing, Spatial Planning and Environment, Netherlands. Available at: http://www2.minvrom.nl/Docs/internationaal/annexS_I2000.pdf

Walker SR, Blacklow WM (1994) Adsorption and degradation of triazine herbicides in soils used for lupin production in western australia laboratory studies and a simulation model. *Australian Journal of Soil Research* 32: 1189-1205. Quoted in U.S. National Library of Medicine. Hazardous substances data bank (Simazine). 2002p. http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~BAApYa4_E:1

Walklate P, Miller P (2000) Drift classification of boom sprayers based on single nozzle measurements in a wind tunnel. *Aspects of Applied Biology*. **57**:49-56.

Walklate PJ, Cross J (undated) Pesticide Dose Adjustment to the Crop Environment (PACE) for UK apple orchards. Leaflet published by Silsoe Research Institute, Department for Environment, Food and Rural Affairs, and Horticultural Research International.

Walls D, Smith PG, Mansell MG (1996) Pesticides in groundwater in Britain. *International Journal of Environmental Health Research.* **6**(1):55-62.

Warren M, Murphy K, Bianco V (1997) Relating bioefficacy to spray application. *The Australian Grapegrower and Winemaker* **405**:80-82.

Wennrich L, Vrana B, Popp P, Lorenz W (2003) Development of an integrative passive sampler for the monitoring of organic water pollutants. *Journal of Environmental Monitoring* **5**(5):813-822.

Wolf T (1997) Spray Drift - Causes and Solutions. Cited by Bozdogan, A.M. and Bozdogan, N.Y. (2004) A Review of the Effects of Adjuvants on Spray Drift in Pesticide Applications. pp 92 – 98 *in* Proceedings of the *7th International Symposium on Adjuvants for Agrochemicals (ISAA2004),* Cape Town, South Africa, 8 – 12 November 2004.

Woodrow JE, Seiber JN, Baker LW (1997) Correlation techniques for estimating pesticide volatolisation flux and downwind concentrations. *Environmental Science & Technology*. **31**:523-529. (Cited in Holland et al. 1997).

Woodrow JE, Seiber JN, Crosby DG, Moilanen KW, Soderquist CJ, Mourer C (1977) Airborne and surface residues of parathion and its conversion products in a treated plum orchard environment. *Archives of Environmental Contamination and Toxicology*. **6**:175-191. (Cited in Holland et al. 1997).

Woods N, Craig IP, Dorr G, Young B (2001) Spray drift of pesticides, arising from aerial application in cotton. *Journal of Environmental Quality* . **30**: 697-701.

Zarcinas BA, McLaughlin MJ, Smart MK (1996) The effect of acid digestion technique on the performance of nebulization systems used in inductively coupled plasma spectrometry. *Communications in Soil Science and Plant Analysis*. **27:**1331–1354.

SECTION 10

APPENDICES

Appendix 1:

Operating principles and proposed registration requirements in relation to spray drift risk – a summary of changes or requirements relevant to viticulture, proposed by APVMA (2005).

Table 10.1: *Operating principles and proposed registration requirements in relation to spray drift risk*. Extracted from the APVMA (2005) discussion paper of the same name, and limited to changes or requirements relevant to viticulture.

Nozzles	Applicators are encouraged to use the USA nozzle classifications *ASAE standard S572* (ASAE 2000) to select nozzles according to the spray quality (and drift risk) they produce. APVMA will only specify nozzle sizes on product labels when risks associated with drift are expected to be high. The expectation otherwise would be that applicators use industry best practice.
Spray machinery	Applicators are expected to comply with industry best practice, which will update with time. However APVMA may require shut-off controls on airblast sprayers, or specify a minimum application volume (per unit length of vine row). While maximum release heights for sprays might be specified for broad-acre and aerial spraying, none are yet proposed for vineyards. However APVMA may impose limits on how airblast applications are done, for example label wording may include more DO NOT restrictions, such as 'DO NOT direct spray above the canopy of grapevines'.
Weather conditions	Maximum (e.g. 15 kph) and minimum (e.g. 3 kph) wind speeds (and in some cases humidity and temperature limits) would be stipulated on some product labels, with detail about where wind speed is measured, e.g. xx metres upwind of the edge of a vineyard. APVMA recommends applicators avoid spraying in the evenings or at night when conditions can be associated with inversions, which increase drift risk.
Crop growth stage	There may be restrictions on how sprays can be applied during dormancy or when there is limited canopy to trap droplets.
High risk products	Some products may be restricted to being used by trained applicators.
Buffer zones	A 'no-spray zone' may be required downwind if drift is likely to A) cause harm to human health, B) reach an environmentally sensitive area, or C) contaminate a neighbouring crop.

Appendix 2:

Droplet sizes in spray plumes produced by a selection of nozzles used in viticulture.

Table 10.2: Droplet sizes of a selection of nozzles used in viticulture - data collected using a Malvern laser diffraction particle sizer in the wind tunnel at The Centre for Pesticide Application and Safety, University of Qld, Gatton College.

Nozzle type	Wind speed	Rep.	Nozzle Pressure	Droplet size (micrometer)			Vol < 102	Relative
	(m/s)		bar	VMD	D[v,0.1]	D[v,0.9]	%	Span
Spraying systems D range-hardened steel disc and brass core								
D2-33	40	1	10	198	82	428	16.6	1.75
		2	10	200	82	379	16.3	1.49
		1	15	164	63	338	25.8	1.68
		2	15	164	64	339	24.9	1.68
		1	20	139	53	301	33.4	1.78
		2	20	136	52	285	33.8	1.71
D1.5-33	40	1	10	198	81	375	17.4	1.48
		2	10	204	81	423	16.1	1.68
		1	15	168	65	348	24.6	1.68
		2	15	166	65	367	25.3	1.82
		1	20	137	53	314	33.9	1.91
		2	20	136	53	299	34.6	1.81
Spraying Systems Conejet nozzles								
TXVK-3 Yellow	10	1	5	101	51	181	50.9	1.29
		2	5	101	49	180	51.7	1.30
		1	10	89	42	169	65.1	1.43
		2	10	89	40	156	65.9	1.30
		1	15	83	39	132	73.1	1.12
		2	15	80	39	128	76.7	1.11
	40	1	5	105	52	188	47.6	1.30
		2	5	105	52	189	47.2	1.30
		1	10	86	39	145	68.1	1.23
		2	10	89	41	146	66.1	1.18
		1	15	79	37	139	73.4	1.29
		2	15	83	38	135	72.7	1.17
TXVK-4 Green	10	1	5	114	54	205	38	1.32
		2	5	113	54	195	39.4	1.25
		1	10	94	47	166	58.7	1.27
		2	10	95	48	169	57.2	1.27

		1	15	91	44	157	63.7	1.24
		2	15	90	46	158	63.5	1.24

Table 10.2 *continued*: Droplet sizes of a selection of nozzles used in viticulture - data collected using a Malvern laser diffraction particle sizer in the wind tunnel at The Centre for Pesticide Application and Safety, University of Qld, Gatton College.

Nozzle type	Wind speed	Rep.	Noz. Pres.	Droplet size (micrometer)			Vol < 102	Relative
	(m/s)		bar	VMD	D[v,0.1]	D[v,0.9]	%	Span
TXVK-4 Green	40	1	5	123	57	212	32.4	1.26
Continued		2	5	123	57	212	32.5	1.26
		1	10	105	49	194	47.7	1.38
		2	10	103	47	173	48.7	1.22
		1	15	94	45	166	58.1	1.29
		2	15	93	42	158	60.2	1.25
TXVK-6 Red	10	1	5	127	62	219	30.4	1.24
		2	5	127	62	215	29.6	1.20
		1	10	109	53	186	42.3	1.22
		2	10	106	55	196	46.6	1.33
		1	15	101	52	187	50.9	1.34
		2	15	101	52	184	51.3	1.31
	40	1	5	147	69	240	22.8	1.16
		2	5	147	70	239	21.9	1.15
		1	10	124	57	212	32.1	1.25
		2	10	122	56	208	33.5	1.25
		1	15	114	53	208	39	1.36
		2	15	114	49	194	39.2	1.27
TXVK-8 Grey	10	1	5	143	69	238	22.6	1.18
		2	5	147	75	243	20.6	1.14
		1	10	128	60	212	28.1	1.19
		2	10	131	65	229	27	1.25
		1	15	109	52	190	44	1.27
		2	15	113	56	200	40.2	1.27
	40	1	5	166	77	264	17.6	1.13
		2	5	165	80	250	18.7	1.03
		1	10	136	63	215	25.9	1.12
		2	10	134	60	236	27.5	1.31
		1	15	121	55	206	34.5	1.25
		2	15	120	53	202	35.2	1.24
Albuz ATR 80 cone nozzles								
Albuz- Yellow	10	1	5	143	70	241	24.2	1.20
		2	5	144	69	251	24.5	1.26
		1	10	131	65	225	29.4	1.22
		2	10	124	63	217	33.5	1.24
		1	15	116	59	203	38	1.24
		2	15	113	56	202	41.2	1.29

Table 10.2 *continued*: Droplet sizes of a selection of nozzles used in viticulture - data collected using a Malvern laser diffraction particle sizer in the wind tunnel at The Centre for Pesticide Application and Safety, University of Qld, Gatton College.

Nozzle type	Wind speed	Rep.	Noz. Pres.	Droplet size (micrometer)			Vol < 102	Relative
	(m/s)		bar	VMD	D[v,0.1]	D[v,0.9]	%	Span
Albuz ATR 80 cone nozzles								
Albuz- Yellow	40	1	5	159	76	257	20.5	1.14
continued		2	5	157	75	260	20	1.18
		1	10	144	67	225	23.4	1.10
		2	10	144	67	227	24.9	1.11
		1	15	131	59	214	28.4	1.18
		2	15	133	60	215	27.1	1.17
Albuz- Orange	10	1	5	159	78	268	19.8	1.19
		2	5	155	75	269	21.6	1.25
		1	10	138	67	250	27.2	1.33
		2	10	136	67	233	27.5	1.22
		1	15	121	61	215	36.1	1.27
		2	15	122	60	215	35.3	1.27
	40	1	5	184	85	293	15.3	1.13
		2	5	181	83	288	16.7	1.13
		1	10	159	74	252	21.4	1.12
		2	10	161	74	254	20.8	1.12
		1	15	143	64	231	23.3	1.17
		2	15	144	64	232	24	1.17
Albuz- Red	10	1	5	185	88	332	15.2	1.32
		2	5	184	88	328	15.2	1.30
		1	10	147	69	270	26.2	1.37
		2	10	153	71	274	23.6	1.33
		1	15	125	58	238	35.7	1.44
		2	15	131	61	239	32.1	1.36
	40	1	5	210	95	342	12	1.18
		2	5	210	96	350	11.7	1.21
		1	10	177	82	289	16.2	1.17
		2	10	175	80	278	17.1	1.13
		1	15	153	66	257	22.8	1.25
		2	15	153	66	265	21.5	1.30
Albuz- Green	10	1	5	204	91	359	13.5	1.31
		2	5	206	90	388	13.7	1.45
		1	10	163	69	317	23.5	1.52
		2	10	166	71	321	22.5	1.51
		1	15	142	60	271	29.9	1.49

		2	15	144	60	274	28.9	1.49

Table 10.2 *continued*: Droplet sizes of a selection of nozzles used in viticulture - data collected using a Malvern laser diffraction particle sizer in the wind tunnel at The Centre for Pesticide Application and Safety, University of Qld, Gatton College.

Nozzle type	Wind speed	Rep.	Noz. Pres.	Droplet size (micrometer)			Vol < 102	Relative
	(m/s)		bar	VMD	D[v,0.1]	D[v,0.9]	%	Span
Albuz- Green	40	1	5	229	104	377	9.6	1.19
continued		2	5	230	104	382	9.6	1.21
		1	10	195	88	348	14	1.33
		2	10	193	87	336	14.3	1.29
		1	15	171	73	285	19.9	1.24
		2	15	169	73	283	19.8	1.24
Ceramic disc and steel core								
P 1.2 closed	40	1	10	176	76	295	19	1.24
		2	10	175	75	301	18.1	1.29
		1	15	155	67	265	24.1	1.28
		2	15	158	66	294	23.7	1.44
		1	20	146	60	284	27.1	1.53
		2	20	140	58	247	27.9	1.35
		1	25	132	53	241	32.3	1.42
		2	25	134	55	247	30.8	1.43
P 1.2-1.0	40	1	10	227	92	437	13	1.52
		2	10	227	91	490	13.1	1.76
		1	15	187	73	426	20.3	1.89
		2	15	189	73	418	20.1	1.83
		1	20	164	63	393	26	2.01
		2	20	157	60	367	27.6	1.96
		1	25	144	55	353	32	2.07
		2	25	135	53	310	34	1.90
P 1.5-1.2	40	1	10	273	109	525	8.3	1.52
		2	10	279	110	554	8.4	1.59
		1	15	231	89	457	13.6	1.59
		2	15	234	89	475	13.6	1.65
		1	20	187	67	397	22.4	1.76
		2	20	197	73	424	19.4	1.78
P 1.8- closed	40	1	10	199	89	352	13.9	1.32
		2	10	204	91	346	13.1	1.25
		1	15	181	79	319	17.4	1.33
		2	15	185	84	310	15	1.22
		1	20	165	71	282	20	1.28

		2	20	170	74	288	19.5	1.26
P 1.8- 1.5	40	1	10	350	129	777	5.5	1.85
		2	10	355	131	800	5.3	1.88
		1	15	284	104	640	9.7	1.89
		2	15	295	118	627	6.3	1.73
		1	18	268	96	654	11.4	2.08
		2	18	252	94	534	12.1	1.75

Table 10.2 *continued*: Droplet sizes of a selection of nozzles used in viticulture - data collected using a Malvern laser diffraction particle sizer in the wind tunnel at The Centre for Pesticide Application and Safety, University of Qld, Gatton College.

Nozzle type	Wind speed	Rep.	Noz. Pres.	Droplet size (micrometer)			Vol < 102	Relative
	(m/s)		bar	VMD	D[v,0.1]	D[v,0.9]	%	Span
Silvan Turbomiser airshear								
	79	1	1 L/min	89	32	192	58.5	1.80
		2		85	31	181	61.6	1.76
		3		84	31	178	62.4	1.75
		1	3 L/min	92	32	214	56.7	1.98
		2		94	33	216	*	1.95
		1		95	34	224	55	2.00
		2		93	32	211	56	1.92

Appendix 3

Weather conditions during spray drift trials

Table 10.3: Weather conditions during spray drift trials

Day	Run		Date	Time	Wind speed (m/s)	Wind direction (degrees)	Temperature (°C)	Relative Humidity (%)
1	1	Start	11/19/2002	8:19:12	0.56	307	22.22	52.34
			11/19/2002	8:19:42	0.46	310	22.18	53.85
			11/19/2002	8:20:12	0.62	312	22.18	56.66
			11/19/2002	8:20:42	0.58	305	22.15	56.02
			11/19/2002	8:21:12	0.4	324	22.1	56.66
			11/19/2002	8:21:42	0.58	282	22.1	57.78
		Finish	11/19/2002	8:22:12	0.51	295	22.08	56.56
1	2	Start	11/19/2002	9:35:27	1.05	196	27.13	30.87
			11/19/2002	9:35:57	1.71	274	27.08	30.4
			11/19/2002	9:36:27	1.48	203	27.13	32.45
			11/19/2002	9:36:57	1.04	214	26.98	30.28
			11/19/2002	9:37:27	1.18	180	27.03	33.82
			11/19/2002	9:37:57	1.05	250	27.03	31.79
		Finish	11/19/2002	9:38:27	0.61	240	27.2	33.01
1	3	Start	11/19/2002	11:31:51	1.95	242	30.08	26.55
			11/19/2002	11:32:21	2.23	230	29.89	24.86
			11/19/2002	11:32:51	0.74	166	29.71	27.6
			11/19/2002	11:33:21	2.5	213	29.67	26.16
		Finish	11/19/2002	11:33:51	1.29	219	29.5	27.28
1	4	Start	11/19/2002	12:18:14	4.26	234	31.96	23.64
			11/19/2002	12:18:44	2.68	241	32.03	23.2
			11/19/2002	12:19:14	3.95	254	32.13	23.06
			11/19/2002	12:19:44	0.95	235	32.08	23.84
			11/19/2002	12:20:14	2.34	264	32.37	22.69
			11/19/2002	12:20:44	1.56	225	32.15	23.25
		Finish	11/19/2002	12:21:14	2.48	266	32.28	23.3
1	5	Start	11/19/2002	15:26:01	4.98	239	34.23	20.18
			11/19/2002	15:26:31	2.1	254	34.11	21.06
			11/19/2002	15:27:01	3.02	250	34.25	21.81
			11/19/2002	15:27:31	3.18	268	34.11	22.2
			11/19/2002	15:28:01	2.71	277	34.08	22.37
			11/19/2002	15:28:31	5.01	263	33.98	22.64
			11/19/2002	15:29:01	6.17	261	33.94	20.96
			11/19/2002	15:29:31	5.31	253	33.64	21.18
		Finish	11/19/2002	15:30:01	3.83	276	33.69	21.98
1	7	Start	11/19/2002	16:50:02	4.39	256	32.28	22.3
			11/19/2002	16:50:32	2.79	237	32.28	22.79
			11/19/2002	16:51:02	3.41	239	32.25	22.67
			11/19/2002	16:51:32	5.31	239	32.25	22.28
			11/19/2002	16:52:02	4.21	261	32.25	22.18
		Finish	11/19/2002	16:52:32	3.18	262	32.33	21.91
1	8	Start	11/19/2002	17:54:11	3.79	264	31.23	24.96
			11/19/2002	17:54:41	7.65	244	31.23	24.5

			11/19/2002	17:55:11	6.82	255	31.2	24.55
			11/19/2002	17:55:41	6.61	247	31.2	24.52
			11/19/2002	17:56:11	5.56	222	31.2	24.57
			11/19/2002	17:56:41	6.03	283	31.23	24.6
			11/19/2002	17:57:11	5.17	242	31.23	24.6
			11/19/2002	17:57:41	4.71	241	31.2	24.79
		Finish	11/19/2002	17:58:11	5.9	251	31.18	24.74
2	1	Start	11/23/2002	8:33:23	0.85	41	25.03	32.96
			11/23/2002	8:33:53	0.77	85	25.08	34.23
			11/23/2002	8:34:23	0.95	76	25.03	31.55
			11/23/2002	8:34:53	0.57	113	25.13	33.94
			11/23/2002	8:35:23	0.85	100	25.2	28.3
		Finish	11/23/2002	8:35:53	0.62	89	25.27	31.62
2	2	Start	11/23/2002	9:18:10	2.98	40	27.76	21.3
			11/23/2002	9:18:40	2.16	30	27.81	21.91
			11/23/2002	9:19:10	1.83	34	27.84	20.74
			11/23/2002	9:19:40	3.04	37	27.81	23.4
		Finish	11/23/2002	9:20:10	1.46	69	27.86	22.86
			11/23/2002	9:20:40	2.51	68	28.01	20.3
2	3	Start	11/23/2002	10:10:52	1.61	39	30.01	17.13
			11/23/2002	10:11:22	3.06	44	30.15	15.93
			11/23/2002	10:11:52	2.8	57	30.25	15.84
			11/23/2002	10:12:22	2.37	35	30.25	17.42
		Finish	11/23/2002	10:12:52	1.98	21	30.25	19.79
2	4	start	11/23/2002	10:57:52	1.38	356	31.42	15.45
			11/23/2002	10:58:22	0.68	300	31.42	15.93
			11/23/2002	10:58:52	0.62	10	31.5	17.69
			11/23/2002	10:59:22	1.16	88	31.67	18.71
			11/23/2002	10:59:52	3.07	84	31.91	14.32
		finish	11/23/2002	11:00:22	1.69	52	31.96	14.25
2	5	start	11/23/2002	11:51:11	1.65	339	32.94	17.59
			11/23/2002	11:51:41	1.89	37	32.79	17.52
			11/23/2002	11:52:11	1.26	29	32.79	18.08
		finish	11/23/2002	11:52:41	1.44	339	32.76	15.69
2	6	start	11/23/2002	12:56:22	1.5	344	34.47	21.23
			11/23/2002	12:56:52	1.73	38	34.57	18.28
			11/23/2002	12:57:22	1.74	54	34.57	18.45
			11/23/2002	12:57:52	1.4	28	34.57	18.54
			11/23/2002	12:58:22	2.43	21	34.5	19.69
			11/23/2002	12:58:52	1.38	345	34.18	18.1
		finish	11/23/2002	12:59:22	1.13	356	34.2	19.06
2	7	start	11/23/2002	13:00:52	1.74	341	33.79	18.23
			11/23/2002	13:01:22	2.15	313	33.64	15.86
			11/23/2002	13:01:52	2.07	316	33.59	19.57
			11/23/2002	13:02:22	2.15	342	33.79	19.86
			11/23/2002	13:02:52	1.34	20	33.67	16.3
			11/23/2002	13:03:22	1.71	308	33.79	16.2
			11/23/2002	13:03:52	0.89	21	33.72	16.64
		finish	11/23/2002	13:04:22	0.71	48	33.98	20.74
2	8	start	11/23/2002	16:00:54	0.99	2	36.13	18.35
			11/23/2002	16:01:24	1.56	331	36.03	16.74
			11/23/2002	16:01:54	0.46	274	35.89	16.88
			11/23/2002	16:02:24	1.19	349	35.89	18.62
		finish	11/23/2002	16:02:54	0.95	9	35.89	18.54

2	6	start	11/23/2002	16:43:46	2.32	333	35.11	18.71
			11/23/2002	16:44:16	1.15	312	34.86	18.52
		finish	11/23/2002	16:44:46	2.05	317	34.91	17.89
2	5	start	11/23/2002	17:49:11	0.93	145	35.94	18.52
			11/23/2002	17:49:41	0.35	147	35.94	19.59
			11/23/2002	17:50:11	1.24	120	36.06	16.67
			11/23/2002	17:50:41	1.28	127	36.11	17.28
			11/23/2002	17:51:11	0.46	116	36.16	17.74
			11/23/2002	17:51:41	-0.04	182	36.28	18.54
		finish	11/23/2002	17:52:11	0.45	137	36.28	16.54
3	1	start	11/24/2002	7:16:46	0.8	345	24.69	55
			11/24/2002	7:17:16	0.96	346	24.71	56.02
			11/24/2002	7:17:46	0.91	349	24.76	53.17
		finish	11/24/2002	7:18:16	1.22	1	24.79	55.29
3	2	start	11/24/2002	7:52:31	3.29	250	24.83	42.68
			11/24/2002	7:53:01	2.51	244	24.81	42.94
		finish	11/24/2002	7:53:31	2.76	226	24.83	42.65
3	3	start	11/24/2002	9:09:53	1.07	186	28.37	35.11
			11/24/2002	9:10:23	2.1	203	28.3	32.84
			11/24/2002	9:10:53	0.74	185	28.25	32.18
			11/24/2002	9:11:23	2.34	175	28.3	32.48
			11/24/2002	9:11:53	1.15	219	28.3	32.79
		finish	11/24/2002	9:12:23	0.62	166	28.3	32.5
3	4	start	11/24/2002	10:06:34	0.66	164	30.86	28.94
			11/24/2002	10:07:04	2.46	173	30.74	26.25
			11/24/2002	10:07:34	1.43	174	30.81	27.94
		finish	11/24/2002	10:08:04	2.95	168	30.79	27.11
3	5	start	11/24/2002	10:53:03	2.38	212	32.2	24.84
			11/24/2002	10:53:33	2.19	193	32.18	24.47
			11/24/2002	10:54:03	2.74	185	31.89	25.16
			11/24/2002	10:54:33	1.69	215	31.94	25.25
			11/24/2002	10:55:03	1.73	256	31.86	26.03
			11/24/2002	10:55:33	3.4	223	32.03	25.38
		finish	11/24/2002	10:56:03	2.3	229	32.15	25.45
3	6	start	11/24/2002	11:44:56	2.39	197	33.16	23.79
			11/24/2002	11:45:26	3.26	230	32.96	24.84
			11/24/2002	11:45:56	3.44	225	32.96	25.13
			11/24/2002	11:46:26	2.5	219	33.01	25.47
			11/24/2002	11:46:56	1.12	237	33.01	25.72
		finish	11/24/2002	11:47:26	0.78	179	33.18	26.28
3	7	start	11/24/2002	13:12:21	2.52	182	33.77	26.4
			11/24/2002	13:12:51	2.4	192	33.91	26.52
			11/24/2002	13:13:21	2.35	137	34.01	26.96
		finish	11/24/2002	13:13:51	4.12	190	33.84	26.23
3	8	start	11/24/2002	14:08:51	0.66	341	34.57	23.99
			11/24/2002	14:09:21	0.47	226	34.84	25.79
			11/24/2002	14:09:51	1.8	204	34.99	24.08
			11/24/2002	14:10:21	0.76	234	34.96	25.33
			11/24/2002	14:10:51	0.67	200	34.86	23.69
		finish	11/24/2002	14:11:21	0.44	216	35.01	24.6
4	1	start	11/25/2002	15:25:11	1.56	335	34.47	25.79
			11/25/2002	15:25:41	1.18	6	34.42	28.01
			11/25/2002	15:26:11	1.91	326	34.35	23.94
			11/25/2002	15:26:41	1.38	344	34.28	27.67

			11/25/2002	15:27:11	1.41	336	34.23	26.5
			11/25/2002	15:27:41	1.35	330	34.35	26.3
			11/25/2002	15:28:11	2.7	301	34.57	24.96
		finish	11/25/2002	15:28:41	1.63	291	34.69	23.77
4	2	start	11/25/2002	16:08:13	2.28	281	34.86	23.77
			11/25/2002	16:08:43	1.77	306	34.94	23.47
			11/25/2002	16:09:13	1.91	292	35.06	23.11
		finish	11/25/2002	16:09:43	1.67	287	35.16	23.72
			11/25/2002	16:47:41	3.28	245	35.47	21.72
4	3	start	11/25/2002	16:48:11	3.22	231	35.5	21.84
			11/25/2002	16:48:41	3.61	247	35.5	20.59
			11/25/2002	16:49:11	2.89	264	35.45	21.5
			11/25/2002	16:49:41	1.84	259	35.52	22.25
		finish	11/25/2002	16:50:11	2.18	258	35.57	22.16
4	4	start	11/25/2002	17:41:00	2	230	34.7	21
			11/25/2002	17:42:00	3	270	34.7	21
4	5	start	11/25/2002	8:53:44	0.28	124	23.44	64.73
			11/25/2002	8:54:14	1.15	124	23.47	65.17
			11/25/2002	8:54:44	1.06	112	23.47	64.73
			11/25/2002	8:55:14	1.4	144	23.47	64.98
			11/25/2002	8:55:44	0.95	122	23.49	64.59
			11/25/2002	8:56:14	0.36	86	23.57	66.49
			11/25/2002	8:56:44	0.65	117	23.64	64.81
		finish	11/25/2002	8:57:14	1.37	128	23.64	63.64
4	6	start	11/25/2002	9:43:35	1.04	94	25.25	56.22
			11/25/2002	9:44:05	1.91	87	25.27	55.14
			11/25/2002	9:44:35	1.44	141	25.27	55.17
			11/25/2002	9:45:05	1.63	99	25.27	55.9
			11/25/2002	9:45:35	1.44	119	25.32	55.51
		finish	11/25/2002	9:46:05	2.6	103	25.32	54.39
4	7	start	11/25/2002	10:38:18	2.48	130	25.66	53
			11/25/2002	10:38:48	0.88	139	25.64	53.95
			11/25/2002	10:39:18	1.19	141	25.66	53.7
			11/25/2002	10:39:48	1.55	141	25.66	54.44
			11/25/2002	10:40:18	1.22	124	25.66	54.19
		finish	11/25/2002	10:40:48	0.88	121	25.66	54.88
4	8	start	11/25/2002	11:41:48	1.78	123	26.35	52.05
			11/25/2002	11:42:18	2.19	108	26.35	51.53
			11/25/2002	11:42:48	2.77	117	26.35	51.65
			11/25/2002	11:43:18	2.3	139	26.35	50.83
			11/25/2002	11:43:48	1.87	115	26.35	51.8
			11/25/2002	11:44:18	1.65	138	26.35	53.31
		finish	11/25/2002	11:44:48	2.27	119	26.35	52.22

Appendix 4:

Passive samplers, the artificial fish – handout

Appendix 5: Agrochemicals registered for use in viticulture that can be monitored using dips or trimps passive samplers.

Active ingredient	DIPS	TRIMPS
2,2-DPA-sodium (dalapon sodium)		
amitrole + ammonium thiocyanate		
amitrole + glyphosate-ipa +		
azoxystrobin	N	N
benomyl	N	N
bifenthrin		
boscalid		
bromoxynil + diflufenican		
captan	Y	N
carbendazim	N	N
carfentrazone-ethyl		
chlorothalonil	Y	Y
chlorpyrifos	Y	Y
copper		
cyprodinil + fludioxonil		
diazinon		
dicofol	Y	Y
dimethoate	N	N
dimethomorph		N
diquat	N	Y
diquat + paraquat		
dithianon	Y	N
diuron	Y	Y
emamectin		
ethephon		
fenamiphos		
fenarimol		Y
fenhexamid		
fenitrothion		
fenthion		
fluazifop-P	Y	N
fluazinam		
flusilazole		
gibberellic acid		
glufosinate-ammonium	N	N
glyphosate- ipa + mas	N	Y
haloxyfop-R methyl ester		
H1exaconazole		
indoxacarb		
iprodione	Y	N
maldison	Y	
mancozeb		N
metalaxyl	N	
metaldehyde		Y
methidathion	Y	Y
methiocarb	Y	N
methomyl	N	
metiram		
myclobutanil		
napropamide		
norflurazon		Y
oryzalin	Y	Y
oxyfluorfen	Y	N
paraquat	N	N
parathion-methyl	Y	Y
penconazole	Y	Y
pendimethalin	Y	Y
phosphorous acid		N
prothiofos	Y	N
pyraclostrobin		
pyrimethanil	Y	N
quinoxyfen		
quizalofop-P-ethyl		
simazine	Y	Y
spinosad		
spiroxamine		
sulfur		
tebuconazole		
tebufenozide	Y	
thiram		
triadimefon		
triadimenol	Y	Y
trichlorfon		
trifloxystrobin	Y	Y
trifluralin	Y	N
zineb	N	N
ziram	N	N

DIPS : Passive samplers filled with three parts 1-dodecanol and two parts 2,2,4-trimethylpentane, able to absorb compounds with log K_{ow} > 2.9.

TRIMPS: Passive samplers filled with 2,2,4-trimethylpentane solvent able to absorb compounds with log Kow > 3.5

Appendix 6:

Laboratory trial to evaluate suction cup samplers for extracting agrochemicals in soil water

Introduction and aims

'Suction cups' have been used successfully to monitor the leaching of nutrients and salt (Beier & Hansen 1992; Lord & Shepherd 1993; Poss et al. 1995). They are relatively cheap to prepare and install (Figure 10.1). Soil water is extracted through the cup by creating a vacuum in a line of micro-tubing that leads from the buried suction cup to a hypodermic syringe at the soil surface.

The commonly used 'suction cup' is made of ceramic and often referred to as a 'ceramic tip' (Cooinda Ceramics Pty Ltd 2003) (Figure 10.2). While suited to extracting nutrients and salt in soil-water, there was a high possibility that ceramic tips would be unsuitable for extracting agrochemicals in soil-water because ceramics can adsorb agrochemicals (Hughes and Reynolds 1988).

Another suction cup, the 'Rhizon' (Rhizosphere Research Products 2003), made of an inert porous polymer instead of ceramic, was identified as a potential alternative to the ceramic suction cups (Figure 10.2). 'Rhizon' samplers are recommended for use in soil ecotoxicity tests when assessing the effects of metals in pore water (Nolan et al. 2003). At the time of this study, the 'Rhizon' sampler had not been used specifically to extract agrochemicals, but the manufacturer recommended that it would be suited to the purpose.

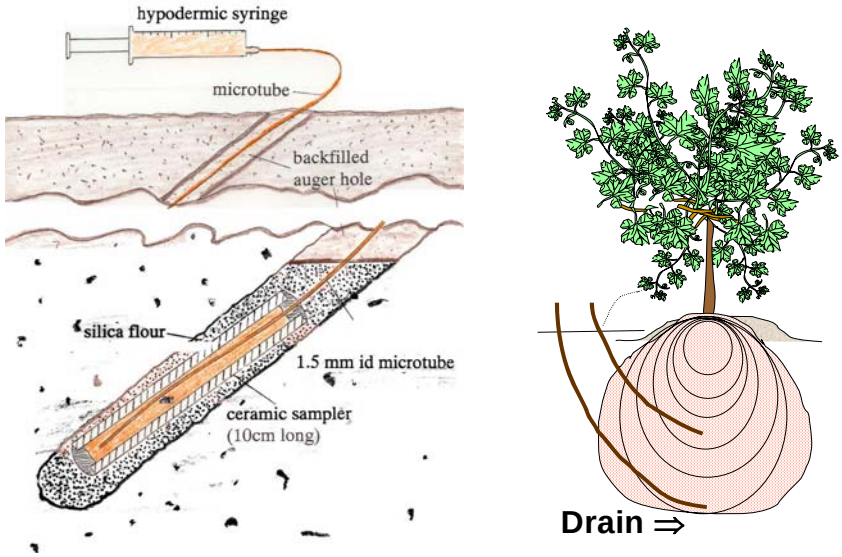


Figure 10.1: Installation of suction cup samplers for extracting soil-water to test for nutrients and salt.

The volume of soil-water that could be extracted by a 'suction cup' sampler was an important consideration, because analytical laboratories typically require large sample volumes (> 1 L) for the analysis of agrochemicals in water.

Aims

The aim of the work described in this section was to evaluate suction cups and ELISA analysis as possible cost-effective tools for sampling and measuring simazine leaching in vineyards.



Figure 10.2: Suction cups: Rhizon (left) and Ceramic tip (right).

Materials and methods

Ceramic suction cups (size 1A, high flow) were obtained from Cooinda Ceramics Pty Ltd. Plastic micro-tubing (1.5 mm internal diameter) was fixed into the ceramic cups using hot glue.

Porous plastic polymer macrorhizon "Rhizon" suction cups (9 cm length, 4.5 mm diameter), complete with 1.5 mm internal diameter micro-tubing, were obtained from Rhizosphere Research Products.

Before commencing the trial, ceramic tip and Rhizon samplers were pre-conditioned with either water or simazine. Four ceramic tip samplers and four Rhizon samplers were placed in conical glass flasks filled with simazine solution (1.1 ml/L i.e. 1,100,000 ppb, label rate). Two ceramic tip samplers and two Rhizon samplers were also placed in separate conical glass flasks filled with deionised water.

Over a 24-hour period simazine solution or deionised water was sucked through the samplers under a constant vacuum, by creating tension using the hypodermic syringe. A total of 600 ml of simazine solution was sucked through each of four ceramic tip samplers and four Rhizon samplers. The liquid collected in the syringe each time was recycled back into the respective conical flask.

Adsorption and re-release of simazine by each sampler type was tested by drawing test solutions through the suction cups that had been pre-conditioned as described above, in either water or simazine.

The test solutions were deionized water and simazine (4 ppm). The combinations of test solution and pre-conditioning (Table 10.4) were selected to show whether the concentration of sample drawn through the

suction cups was equivalent to the concentration in the test solution, or altered by release or adsorption of simazine by the suction cups.

The test solutions were made up in Winchester bottles. One suction cup was immersed in the test solution in each Winchester bottle according to the experimental design shown in Table 10.4.

A 60-ml syringe was attached to the end of the micro-tube of each sampler and its plunger pulled back and locked open to maintain suction. When full, the syringe was removed from the sampler tubing and the content of the syringe emptied into a glass screw top container. This procedure was repeated five times, with samples from extractions 1, 3 and 5 retained in separate glass containers.

Seven samples (Table 10.4) were sent to the DPI Victoria State Chemistry Laboratory (SCL) for analysis using gas chromatography (GC). The proportion of simazine adsorbed or re-released by each suction cup was then calculated. Three samples of the test solutions (two of deionised water and one of 4 ppm simazine) were also sent for analysis.

Table 10.4: Treatments and sampling regime to test for adsorption and re-release of agrochemical by the ceramic or plastic polymer (Rhizon) suction cups.

Winchester bottle	Sampler Type	Pre-conditioning	Test solution	Extraction 1, 3, or 5	Sample number
1 & 10	Ceramic tip	Simazine	Deionised water	1	1
6 & 12	Ceramic tip	Simazine	Simazine (4 ppm)	5	2
4 & 7	Ceramic tip	Deionised water	Simazine (4 ppm)	1 & 3	3, 4
3 & 8	Rhizon tip	Simazine	Deionised water	5	7
5 & 9	Rhizon tip	Simazine	Simazine (4 ppm)	Not analysed	
2 & 11	Rhizon tip	Deionised water	Simazine (4 ppm)	1 & 3	5 & 6

Data analysis

Data were analysed by Analysis of Variance using GenStat Release 6.1 (6th Edition, 2002, Lawes Agricultural Trust, Rothamsted Experimental Station).

Results

Results from the laboratory tests showed that both types of suction cup (ceramic and Rhizon) adsorbed unacceptable amounts of simazine during the pre-conditioning, as both released simazine when they were used to extract water (data available, but not presented here).

Conclusions and recommendations

Ceramic and plastic polymer 'suction cups' are a cheap and simple method for extracting soil-water, used successfully for monitoring leaching of salt and nutrients through the soil profile, but this trial found that both types of 'suction cups' adsorbed and re-released unacceptable amounts of agrochemical. The 'suction cups' were also unable to collect the large volumes (> 1 L) of soil-water required for conventional chemical analysis. Neither of these suction cups was deemed suitable for sampling soil-water to monitor agrochemical leaching.

Appendix 7:

Laboratory trial to evaluate ELISA (enzyme-linked immuno assay) kits to measure residues in the extracted soil water

Introduction and aims

ELISA (Enzyme-Linked Immunosorbant Assays) have been developed for analysis of residues in Australian grapes and wine (Skerritt 1997) and they offer a rapid and cost-effective alternative to conventional analysis. Kits are also commercially available for analysis of numerous agrochemicals in water and soil (Envirologix 2003). If ELISA kits could accurately report residues in soil water, they would be ideal to use in combination with suction cup samplers, as they need only small volumes of sample (< 1 ml).

The aim of the work described in this section was to evaluate ELISA analysis as possible cost-effective tools for measuring agrochemical leachates in soil water sampled from vineyards.

Materials and method

Elisa test kits for the analysis of metalaxyl and triazines (in particular simazine) were sourced from the USA (Envirologix 2003).

Accuracy of the ELISA test kits was assessed by comparing solutions of known concentration with standards supplied by the manufacturer. Samples were analysed using the micro-titre plate reader at the Dried Fruit Quality Centre, Mildura.

For these analyses, duplicate samples were pipetted into ELISA test wells in a row-column design. The design ensured that duplicates of a sample never appeared together in the same row or the same column of the plate. In this way, sample differences could be estimated free of any confounding effects of rows or columns.

The optical density (OD) of each cell in the plate was read at wavelengths of 450 nm and 630 nm. Chemical concentration was indicated by the depth of colour relative to negative controls and standard solutions and was expressed as %Bo, where:

$$\% \text{ Bo} = \frac{\text{average OD of standard solution or sample}}{\text{average OD of negative control}} \times 100$$

The accuracy of the ELISA test plate was determined by comparing the OD and %Bo results for duplicate samples.

Data were analysed by Analysis of Variance using GenStat Release 6.1 (6th Edition, 2002, Lawes Agricultural Trust, Rothamsted Experimental Station).

Results

The laboratory experiment to test the reliability of the simazine ELISA test was invalid due to technical errors in the preparation of the plates.

In the metalaxyl ELISA plate, there was an unacceptably high variation in optical density measured for duplicate samples, both for standards provided by the company (Envirologix) and for samples made up at DPI. The variation between duplicates was as high as 86% (Table 10.5). Moreover, concentrations measured using the ELISA kit were poorly correlated against results for duplicate samples from the State Chemistry Laboratory (data not shown).

Table 10.5: Variation between duplicate metalaxyl samples and standard solutions analysed for metalaxyl using a commercial ELISA kit.

Sample	%Bo measured in duplicates		Variation (%)
1	0.065	0.133	51
2	0.081	0.522	84
3	0.006	0.014	57
4	0.101	0.344	71
5	0.285	2.016	86
1.75 ppb standard	0.058	0.347	83

Conclusions and recommendations

To what extent the lack of consistency in results was due to the plates, and to what extent due to errors in the method used, the ELISA kits were considered to lack robustness as a method, making them unsuitable for use outside a laboratory, for example by vineyard managers. We therefore did not repeat the trial to explore reasons for the poor performance.

The lack of reliability of ELISA kits for agrochemical analysis was discussed by participants in a workshop at the 12th Australian Wine Industry Technical Conference (Australian Wine Industry Technical Conference Inc. 2004). Participants felt that despite being an inexact method for analysis, ELISA kits nonetheless provide a simple method for qualitative monitoring of agrochemical residues, and that their use as a grower-tool to screen for presence/absence of agrochemicals in drainage water should not be dismissed entirely.

Appendix 8:

Earthworm avoidance assay to assess toxicity of copper in vineyard soils

Introduction

Soil macro-organisms such as earthworms and springtails are able to detect and 'avoid' contaminated areas of soil, showing preference for cleaner environments (Sheppard et al. 1998; Van Zwieten et al. 2004). Whilst this can reduce the exposure of earthworms to copper, the health of the soil in the contaminated areas can suffer if the soil does not receive the beneficial services (e.g. nutrient cycling) that these organisms provide. Earthworm avoidance behaviour can therefore provide an indication that contaminants in soil may be impacting on soil health. As a result, earthworm avoidance assays have been developed and used to conduct rapid, cost-effective assessments of soil contamination in the laboratory (Sheppard et al. 1998; Van Zwieten et al. 2004).

An initial assessment of the effect of accumulated copper on the health of Australian vineyard soils was based on a preliminary earthworm avoidance assay. The NSW Department of Primary Industries at Wollongbar Agricultural Institute undertook the assay using the methods described in Van Zwieten et al. (2004). The assay provides a sensitive indication of soil contamination by exploiting the ability of earthworms to detect and 'avoid' contaminated areas of soil.

Materials and methods

A composite soil sample of approximately 10 kg was obtained from a vineyard in the Sunraysia region by combining samples collected from the soil surface (10 cm depth) at 10 different locations within the vineyard. A composite soil sample was also obtained from a nearby area of remnant vegetation (control site). The soils from both the vineyard and control site were similar in terms of pH, organic carbon content, nitrogen content and cation exchange capacity. A sub-sample of the soil from both the vineyard and the control site was then dried, sieved and analysed for total copper by NSW Department of Primary Industries, Wollongbar Agricultural Institute, Wollongbar, Australia. An acid extraction (method reference: USEPA 3050B) was used to extract metals from the soil. Acid extractable metals were then analysed by ICP (method reference: USEPA 6010).

Vineyard soil (140 mg/kg Cu) was progressively mixed with soil from the control site (9.4 mg/kg Cu) to create four treatment soils containing 140.0, 76.0, 42.6, and 22.3 mg/kg of total copper. The soils were then watered to approximately field capacity and stored at 4^0C prior to use in the laboratory experiment.

The earthworm *Eisenia fetida* was used in this study. This species is recommended as a test organism by the Organisation for Economic Co-operation and Development (OECD), as its sensitivity to contaminants resembles that of species that may be present in agricultural soils (OECD 1984).

Transparent plastic containers (170 × 120 × 70 mm) were divided in half by inserting a vertical plastic divider. A line was then drawn on the outside of the container along the mid-line (i.e. in line with the divider). The outside of each side of the container was labelled according to soil type (i.e. treatment or control). The container was then filled with 200g of treatment soil on one side of the plastic divider and 200 g of control soil on the other side of the plastic divider (Figure 10.3). The soils were at field capacity when placed into the container. The divider was then removed and the container lightly tapped to settle the soil. Ten mature worms were then placed on the soil surface in the centre of each container (Figure 10.3). This was repeated to create eight replicates for each of the four treatments. A treatment containing contaminated vineyard soil (140 mg/kg total copper) on both sides of the divider was also created to act as an extra quality control check. Once the worms were observed to enter the soil, the containers were

covered with a perforated lid and placed in a controlled environment chamber at 22^{o}C under constant illumination.

The containers were removed from the controlled environment chamber after 48 hours. The control and treatment soils were then separated along the mid-line with a spatula and the plastic divider inserted (Figure 10.3). Any worms found in contact with the mid-line were removed and recorded as 'mid-line'. The soils from each side of the container were transferred into separate containers and the number of worms present in each soil counted. Earthworm avoidance behaviour was indicated by comparing the number of worms in the control soil with the number of worms in the treatment soil.

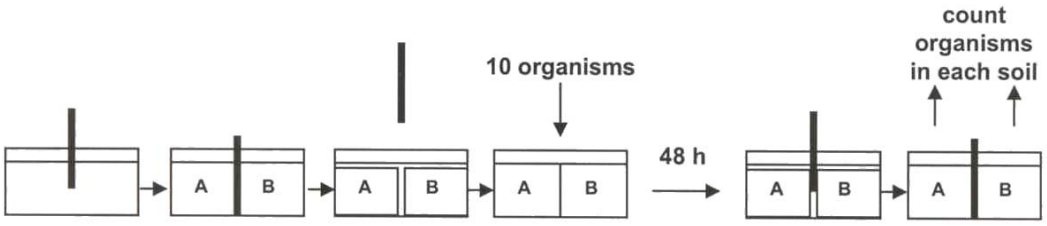


Figure 10.3 Design of the earthworm avoidance assay (from Loureiro et al. 2005). A = control soil, B= treatment soil

Results and Discussion

An earthworm avoidance effect was detected for each of the treatments, with the exception of the 22.01 mg/kg copper concentration and when the 140 mg/kg Cu treatment was used on both sides of the container (Figure 10.4).

Using soil from a vineyard in the Sunraysia region, results from the initial earthworm avoidance trial have shown a strong avoidance response at concentrations of 42-mg/kg total copper and above (Figure 10.4). A similar earthworm avoidance effect has been shown in trials undertaken using soils from Australian avocado orchards (Van Zwieten et al. 2004). Whilst a strong avoidance effect has been shown, the results should be viewed with some caution as further tests to relate the avoidance back to copper were not undertaken. It is therefore possible that the effect was due to some other soil factor (e.g. other metals or agrochemicals).

It is not possible to make general conclusions regarding the impact of copper on the health of Australian vineyard soils as the initial earthworm avoidance trial was undertaken using soil from only one vineyard. However the results support the need for more detailed investigations to understand the bioavailability/toxicity of copper present in Australian vineyard soils.

Pitfall trapping of terrestrial invertebrates (Sharley et al 2004b) and macrocosms to relate contaminants in drainage water to invertebrate diversity and abundance (Sharley et al 2004a) are other approaches being developed for use by viticultural industries.

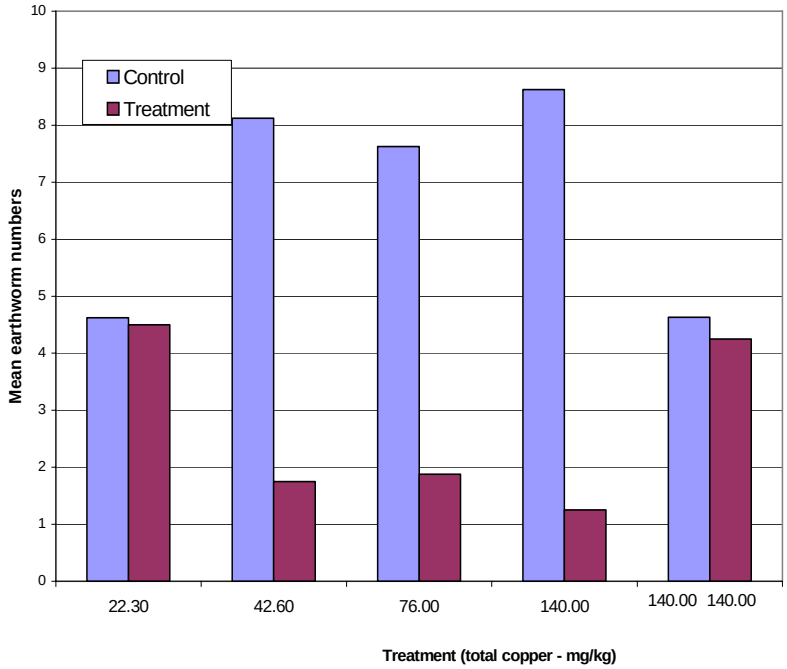


Figure 10.4: Earthworm avoidance response shown as the mean number of earthworms present in the contaminated and control soils for each of the treatments.

Conclusion

The earthworm avoidance assay has the potential to be used as a screening tool to determine whether copper and other soil contaminants may have a negative impact on soil-health, and should be further refined and assessed for its suitability in detecting biological impacts of copper and other key viticultural agrochemicals.

Australian viticultural industries should be encouraged to use a range of approaches such as earthworm avoidance assays and invertebrate surveys, to determine the extent to which vineyard soils are affected by agrochemicals.

Appendix 9:

Sampling considerations for surveying copper concentrations in Australian vineyard soils

Abstract

In order to develop a sampling protocol to determine the extent of the accumulated copper concentration in vineyard soils across different grape growing regions of Australia, a study was conducted in six vineyards near Mildura (34o S, 142o E), north-western Victoria, Australia. The study investigated the distribution of copper in the soils of vineyards with three different histories of use of copper-based fungicides: less than five years old; at least 30 years old during which time the vineyard had been ploughed and replanted; and at least 60 years old. At three locations in each vineyard, soil samples were collected from two depths (0-15 cm and 15-30 cm) at 30 cm intervals along two 150 cm long transects running at right angles in opposite directions from the vine trunk towards the inter-row areas. The results showed that copper concentrations were higher in the top 15 cm of soil ($P < 0.001$) and declined with distance from the vine ($P = 0.002$).

The variation in copper concentrations between vineyards was found to be much greater than the variation within vineyards. Balancing an acceptable level of error with the resources required to collect samples, we recommended obtaining one composite soil sample from each vineyard in the Australia-wide survey. To have the best chance at finding the highest concentration of copper at each vineyard the composite sample should consist of sub-samples collected from the shallow soil (0-15 cm) within 30 cm from the vine row.

Keywords: Copper concentration, soil, vineyards, sampling, copper fungicide

Introduction

Copper-based fungicides have been sprayed in vineyards throughout the world (including Australia) for many decades to control Downy Mildew. Although the use of these fungicides has declined in recent years, they are still frequently included in vineyard spray programs. It is known that the use of copper-based fungicides results in an accumulation of copper in surface soils (Tiller and Merry 1981; Magalhaes et al. 1985; Delusia et al. 1996; Flores-Velez et al.1996; Besnard et al. 2001; Chaignon et al. 2003). For example, copper concentrations ranging from 130 to 1280 mg/kg have been detected in the surface soil of European vineyards that have a history of copper-based fungicide use (Tiller and Merry 1981; Magalhaes et al. 1985; Delusia et al. 1996; Flores-Velez et al.1996; Besnard et al. 2001). This is an increase from natural background copper concentrations in soils, which worldwide are typically below about 20 mg/kg but can be as high as 100 mg/kg depending on the parent rock material (NEPC 1999; Sauve 2002).

In many viticultural regions of the world there are increasing concerns that copper may reach concentrations in vineyard soils that are toxic to soil organisms, or even phytotoxic to vines (Gardner 2003), potentially impacting on the long-term sustainability of these vineyards. Some European countries have imposed restrictions on the use of copper fungicides because of these concerns, and to satisfy eco-labelling scheme requirements. For example the Netherlands has banned copper use, while Switzerland has restricted the amount of copper that can be applied per hectare (Gardner 2003). These concerns are supported by studies showing that elevated concentrations of copper (52 - 236 mg/kg) are harmful to earthworm populations (Van Rhee 1976; Bogomolov et al. 1996; Khalil et al. 1996; Paoletti et al.1998;

O'Halloran and Booth 2000; Van Zwieten et al. 2004). Studies have also shown that copper has a detrimental effect on soil micro-organisms (Bogomolov et al. 1996; Dahlin et al. 1997, Merrington et al. 2002).

Currently in Australia there are no guideline values available specifically addressing the contamination of land in terms of the sustainability of agriculture, including vine and tree crops. Therefore, it is difficult to determine the concentration of copper in the soil that is significant in this regard without undertaking site-specific investigations and toxicology tests. The Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites (ANZECC and NHMRC 1992) and the National Environmental Protection Measure for the assessment of site contamination (NEPC 1999) both provide environmental/ecological investigation levels for copper in soils (Table 10.6). Similar guidelines exist in other parts of the world (Table 10.6) but once again none relate specifically to the protection of organisms in agricultural soils or phytotoxicity to vines. The guideline values given in Table 10.6 are total copper concentrations, however it is recognised that soil quality guidelines should be further refined to account for the biologically available fraction of copper in the soil (McLaughlin et al. 2000). As they are not directly relevant to the assessment of copper contamination in vineyard soils, the guideline values stated in Table 10.6 should only be used as a reference to provide an indication of likely toxicity.

Table 10.6 A selection of currently available guideline values for assessing copper contamination in soils.*

Guideline	Copper (mg/kg)	Comments	Reference
Australian and New Zealand Environmental Soil Quality Guidelines	60	Environmental investigation level - based on threshold levels for phytotoxicity and uptake by plants which may impair growth or produce unacceptable residue levels.	ANZECC and NHMRC (1992)
[Australian], National Environment Protection Council (NEPC) Guideline on the investigation levels for soil and groundwater	100	Ecological investigation level - interim guideline level for assessing human health concerns in urban land use settings.	NEPC (1999)
Dutch intervention value for contaminants in soil	190	Intervention value - maximum tolerable concentration above which remediation is required.	VROM International (2000)
Canadian Soil Quality Guideline	63	Agriculture guideline value - determined based on the greatest sensitivity across both environmental and human receptors.	CCME (2003)
Swedish guideline for polluted soils	100	Guideline value for polluted soils - developed to assess risks to human health and the environment, this value is based on the most sensitive type of land use.	Swedish EPA (2002)
Danish (Zealand) guidelines for classification of polluted soil	<500	Class II slightly polluted value - interim guideline, soil is considered slightly polluted and can be used under roads etc where access is prevented.	From Johnson (2005)
French guideline values for contaminated land management	190	Fix Impact Value (FIV) sensitive use - based on toxicity to human health and used to assess public health risks associated with land use.	Darmendrail (2003)

[*] It should be noted that none of these guidelines relate specifically to copper contamination in agricultural soils and should be used as a reference point only.

In Australia there is relatively little published information on the concentration of copper in vineyard soils. In a study of 14 Victorian vineyards, copper concentrations in surface soils ranged from 9 to 249 mg/kg (Pietrzak and McPhail 2004). Eight vineyards had copper concentrations greater than 60 mg/kg, and three vineyards had copper concentrations greater than 100 mg/kg. In a separate study on four vineyards in the Murrumbidgee Irrigation Area of New South Wales, the average copper concentrations in surface soil was found to be 22 mg/kg (Biswas et al. 2002). Due to the lack of information on copper concentrations in vineyards of different grape growing regions of Australia, the Australian wine industry has funded a study to determine if the continued use of copper-based fungicides is likely to be detrimental to the long-term agricultural sustainability of vineyard soils.

Before commencing an Australia-wide survey, it was necessary to develop a suitable soil sampling protocol for determining copper concentrations in vineyard soils within different grape growing regions.

As copper binds strongly to clay and organic matter it was expected that much of the copper applied would accumulate in the surface soil (i.e. 0-15 cm depth). Old vineyards are expected to have received higher total inputs of copper-based fungicides than younger vineyards as copper would have been applied for a greater number of years. However, the distribution of copper within a vineyard is difficult to predict, as many Australian vineyards have at some point been replanted.

This paper describes a study conducted in six vineyards near Mildura (34^{o} S, 142^{o} E) in northwestern Victoria, Australia, which investigated the distribution of copper in vineyard soils. This information was then used to develop a protocol for conducting a survey of copper concentrations in Australian vineyard soils. The aim of the Australia-wide survey was to assess the extent of copper contamination in vineyard soils in order to compare Australian concentrations with national and overseas guideline values and to help determine whether changes in viticultural practice are required.

Materials and Methods

Vineyards

Six vineyards near Mildura (34o S, 142o E, Sunraysia region) in north-western Victoria, Australia were selected for the purpose of this investigation. Two vineyards were less than five years old with no history of copper use prior to planting the vines; two had been in operation for at least 30 years with continual copper use during which time the land had been ploughed and replanted; and two had been in operation for at least 60 years with original vines and continual copper use. Each of the vineyards was located on sandy or sandy-loam topsoil.

Sample collection and processing

Soil samples were taken from each of the six vineyards during July 2003. At each vineyard samples were collected along transects on both sides of a vine row at three locations in the vineyard, representing a row one quarter of the way into the vineyard, the middle row and a row three quarters into the vineyard (Figure 10.5). Along each of these transects, soil samples were collected at two depths (0-15 cm and 15-30 cm) at five 30-cm intervals at right angles to the row of vines starting at a point midway between two vines in the row (0 cm) and progressing laterally towards the inter-row area (150 cm), as shown in Figure 10.5 and Figure 10.6. In total, 60 soil samples were collected from each vineyard.

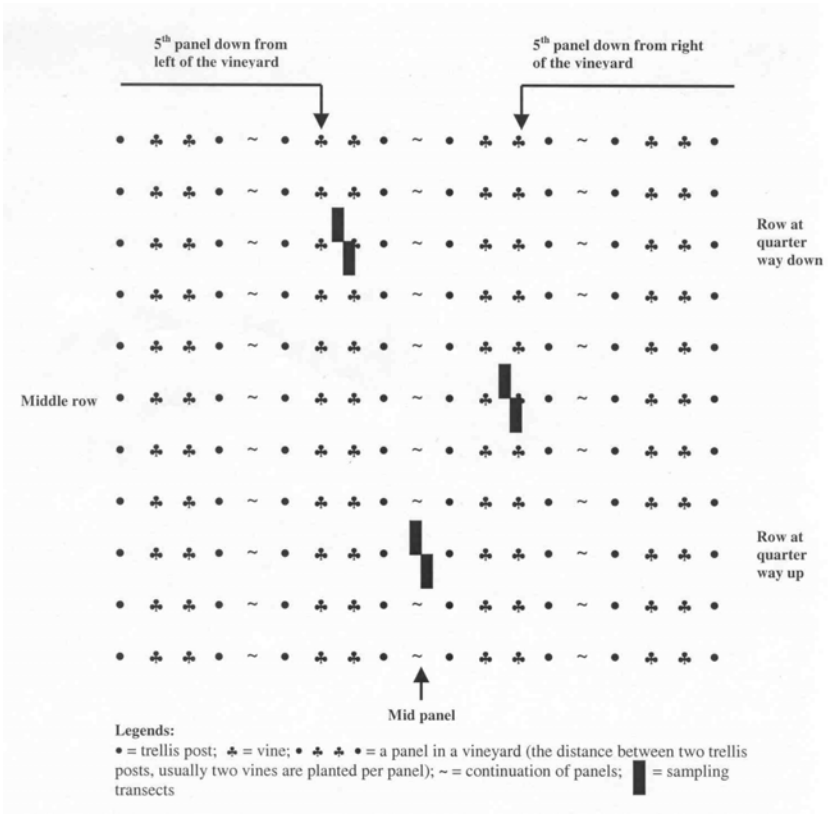


Figure 10.5: Map showing positions of the six transects. The same sampling layout was used in each vineyard

The soil samples were collected using a 10-cm diameter auger. Each of the soil samples was then dried at 40^{o}C (for at least 48 hours) and sieved (laboratory sieve, 2-mm aperture) prior to analysis to break down any aggregates and to improve the homogeneity of the samples.

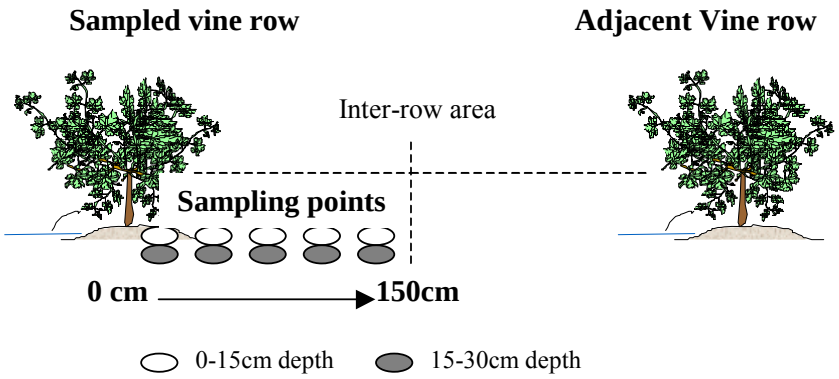


Figure 10.6: Diagram showing the location of the five sampling points along each of the six transects

Sample analysis

The soil samples were analysed at the CSIRO Land and Water Soils Laboratory in Adelaide, Australia. Copper was extracted from soil samples using the acid dissolution method described in Zarcinas et al. (1996) by digesting 0.5 g of soil in 5 ml of aqua regia (HNO_3:HCl 1:3). The soil extracts were analysed using inductively coupled plasma spectrometry (ICP). Samples that did not contain copper in concentrations above the limit of reporting for ICP were re-analysed using atomic absorption spectroscopy. The results were reported as milligrams of total copper per kilogram of soil (mg/kg).

Statistical analyses

Copper concentrations in soil were log transformed and analysed using analysis of variance (ANOVA) with Genstat for Windows release 6.1. The P-value for the variance ratio based on the F-distribution was used to test whether there was a trend in copper concentration with distance from the vines along the transects and whether there was any difference between the two sampling depths. The level of significance used for all analyses was $P \leq 0.05$. The means of the logs were back-transformed to provide geometric means of the copper concentrations. The ANOVA was also carried out separately for each type of vineyard history. To determine how many locations should be tested within each vineyard in the Australia-wide survey, another ANOVA was carried out to estimate the components of variance between and within vineyards, based on the samples at the shallower depth (0-15 cm) and shortest distance from the vines (0-30 cm). The standard error of the overall mean was estimated from the variance components in the ANOVA using the following modified equation from Snedecor and Cochran (1989):

$$S.E\ of\ mean = \sqrt{\frac{Variance\ component\ for\ vineyards}{Number\ of\ vineyards} + \frac{Variance\ component\ within\ vineyards}{Total\ number\ of\ samples}}$$

Results

Results indicated that the four older vineyards (at least 30 years old) had higher and more variable copper concentrations than the new vineyards (less than 5 years old) (Figure 10.7).

An examination of the sources of variation found that the "Type" of vineyard was by far the greatest contributor to the ANOVA total sum of squares and the second greatest was "Vineyard" (Table 10.7). The ANOVA of log-transformed copper concentrations (Table 10.7) shows that copper concentrations also decreased with distance from the vine ($P = 0.002$ for linear trend) and that shallower soil samples (0-15 cm) had significantly ($P < 0.001$) higher concentrations of copper than deeper samples (15-30 cm). There was no significant interaction between depth and distance ($P = 0.92$). Figure 10.8 shows the geometric means over the six vineyards of the copper concentrations at each distance along the transects and at each depth.

When each type of vineyard was analysed separately (120 samples in each ANOVA), the decline in copper concentration with distance from the vine row was pronounced for the 60+ year old vineyards ($P < 0.001$) but was not statistically significant for the new vineyards ($P = 0.52$) or the replanted 30+ year old vineyards ($P = 0.63$) (data not tabulated). Samples from the top 15 cm of soil had significantly higher concentrations than samples at 15-30 cm depth, regardless of the type of vineyard ($P < 0.001$ in each case) (data not tabulated).

Table 10.7: Analysis of variance of log (copper concentration) for all 360 samples from 6 vineyards.

Source of variation	Degrees of freedom	Sum of squares	Mean square	Variance ratio	F-prob
Type stratum	2	225.86	112.93	6.91	
Type.Vineyard stratum	3	49.02	16.34	26.64	
Type.Vineyard.Location stratum	12	7.36	0.61	2.70	
Type.Vineyard.Location.Transect stratum	18	4.09	0.23	2.61	
Type.Vineyard.Location.Transect.Sample stratum					
Depth	1	10.15	10.15	116.53	<.001
Distance	4	0.91	0.23	2.62	0.035
Linear	1	0.85	0.85	9.76	0.002
Deviations	3	0.06	0.02	0.24	0.866
Depth.Distance	4	0.08	0.02	0.23	0.923
Depth.Linear	1	0.01	0.01	0.07	0.796
Deviations	3	0.07	0.02	0.28	0.839
Residual	315	27.44	0.087		
Total	359	324.92			

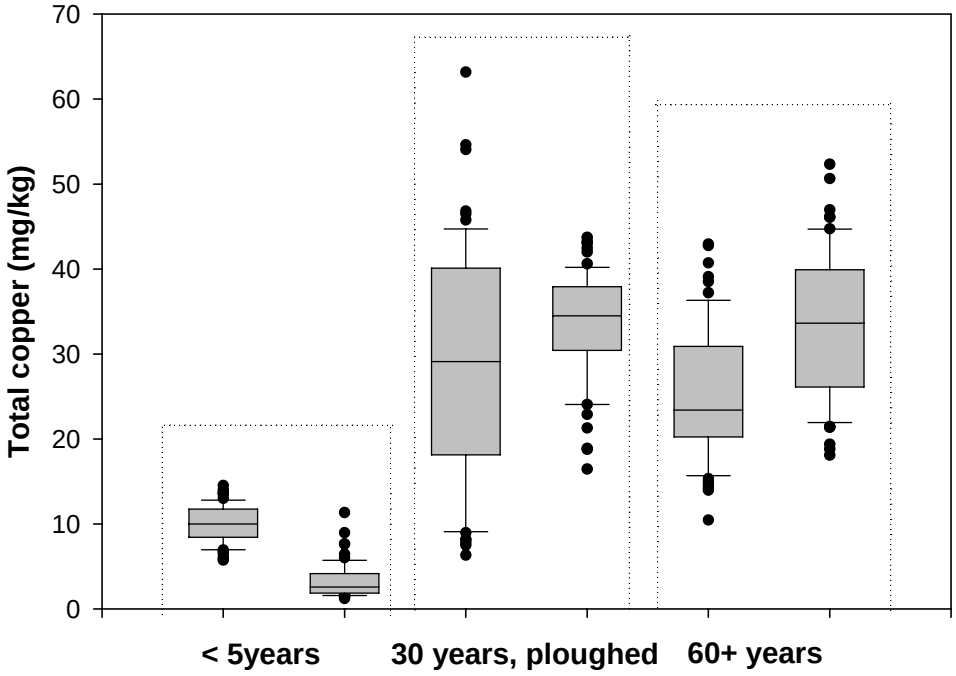


Figure 10.7: The range of copper concentrations detected in each vineyard. The central line in each box represents the median; the limits of the box represent the upper and lower quartiles; the horizontal bars outside the box represent the upper and lower deciles, and the dots represent the outlying values.

For the planned Australia-wide survey it was desired to obtain the most precise estimate of the overall mean of the estimated maximum soil copper concentrations at each vineyard, i.e. to minimise the standard error of the mean. When the ANOVA analysis was restricted to the samples at 0-15 cm depth and 0-30 cm distance from the vine row, the component of variance for vineyards was estimated to be 0.7746 and for positions within vineyards 0.0893 (combining locations and transects) (Table 10.8). Based on this variability, various sampling schemes comprising numbers of vineyards versus numbers of samples per vineyard were calculated (Table 10.9), together with the estimated standard error of the overall mean (se) for each scheme. It can be seen that, for the same number of samples, the lowest standard error (most precise estimate) would be obtained by taking one sample from as many vineyards as possible, rather than more samples from fewer vineyards.

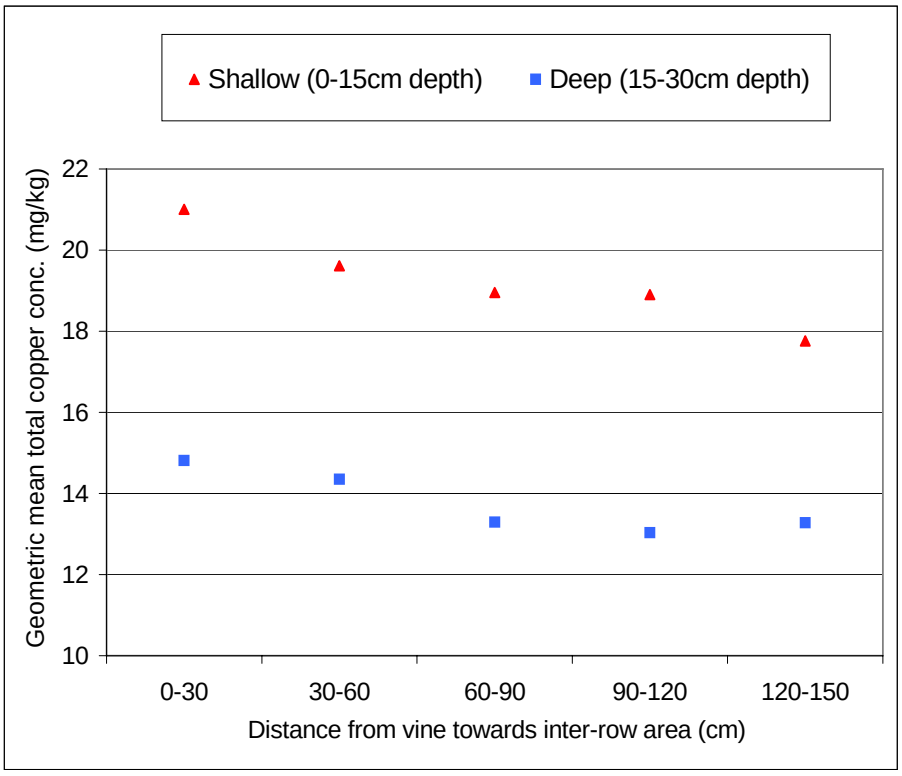


Figure 10.8: The geometric mean copper concentrations over six vineyards.

Table 10.8: Analysis of variance of log (copper concentration) for 36 samples from 6 vineyards at 0-15 cm depth and 0-30 cm from vine row.

Source of variation	Degrees of freedom	Sum of squares	Mean square	Variance ratio	Variance component
Vineyard stratum	5	23.68	4.74	67.10	0.778
Vineyard.Location stratum	12	0.85	0.07	0.69	-0.016
Vineyard.Location.Transect stratum	18	1.83	0.10		0.102
Total	35	26.36			

Table 10.9: The estimated standard error (se) of the overall mean for potential sampling schemes to determine copper concentrations in Australian vineyard soils.

Scenario	No. vineyards	Samples per vineyard	Total samples	Estimated se of mean
1	6	6	36	0.36
2	60	6	360	0.11
3	60	1	60	0.12
4	360	1	360	0.05

Discussion

In our study the highest concentrations of copper were found in the top 15 cm of soil. This was expected, as copper adsorbs strongly to clay and organic matter (McBride 1981; Stevenson and Fitch 1981; US National Library of Medicine 2003). Previous studies have also found that the highest copper concentrations in vineyards were present in surface soils (Delusia et al. 1996; Flores-Velez et al. 1996; Pietrzak and McPhail 2004). It is therefore expected that the highest concentrations of copper will also be found in the surface soil of vineyards to be included in the broader national survey, regardless of soil type.

The highest copper concentrations were found closest to the vine trunk (within 30 cm of the vine row). This was expected as the undervine area receives more run-off from the vine canopy sprays, and unless the vines are replanted, the soil remains relatively undisturbed compared to the inter-row area. This is also supported by other studies (Frank et al. 1976; Pietrzak and McPhail 2004) which found that the concentration of copper in the soil from the inter-row area was lower compared with the concentration in the undervine area. Whilst it is expected that the distribution of copper within vineyards may vary between regions (e.g. with changes in topography, soil type, rainfall), we believe that it is reasonable to assume from this work and previous studies (Frank et al. 1976; Pietrzak and McPhail 2004) that the highest concentrations in all vineyards are likely to be present in the soil closest to the vine row.

Therefore, we recommended that surface soil samples (top 15 cm) should be collected from the undervine area (no more than 30 cm laterally from the centre line of a row) to have the greatest chance of detecting the highest copper concentrations in Australian vineyard soils.

As copper sprays are directed at the vine canopy, we expected copper concentrations in the soil (at both depths) would decrease sharply with distance from the vine. This was the case with the two 60+ year old vineyards and, to a lesser extent, with the shallow soils in the two new vineyards. However there was no trend with distance in the deeper soils in the new vineyards or in the 30+ year old replanted vineyards, possibly because the disturbance of soil during replanting had redistributed the residues.

It was not an objective of this study to assess the effects of copper concentrations on vineyard soil heath however results showed that with the exception of one sample (63 mg/kg) all samples were below the soil contamination guideline values listed in Table 1. Considering this and the fact that the bioavailable concentrations of copper would be lower than the total amount of copper, it is likely that copper has had little effect on soil organisms in the vineyards studied. However, a detailed ecological investigation would be needed to confirm this.

Our results showed that the variation in copper concentrations between the vineyards was much greater than the variation within the vineyards. Tiller et al. (1975), who investigated a range of sampling schemes for determining metal concentrations in surface soils, also found that the variation between sites was greater than the variation within sites. The high 'between-vineyard variation' needs to be taken into account when developing sampling protocols to compare copper concentrations in vineyards between regions. The estimated standard errors for various sampling schemes indicated that the most precise estimate of the increased copper concentration in older vineyards (and the likely maximum copper concentration in vineyard soils in a region), would be obtained by analysing one soil sample per vineyard, and surveying as many vineyards as possible (including both old and new vineyards). A similar approach was used by Tiller et al. (1975), who also concluded that the best estimate of the mean would be obtained by surveying many sites with one analysis per site. Background concentrations for the region can be checked by also testing non-vineyard virgin soils (i.e. which have not received artificial inputs of copper).

Although the 'within-vineyard variation' found in this study was lower than the 'between- vineyard variation', it is still important to recognise that the within-vineyard variation exists. For the Australia-wide survey, it was therefore recommended that the single soil sample analysed for each vineyard be a composite of sub-samples collected throughout the vineyard to encompass 'within vineyard variation'. Sample depth had a large effect on the copper concentration and careful attention to a sampling depth of 0-15 cm is recommended. Distance from the vines can have a significant effect, and it is recommended that all samples be taken within 30 cm of the vine row.

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References

ANZECC and NHMRC (1992) 'Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites'. Australian and New Zealand Environment and Conservation Council, National Health and Medical Research Council.

Besnard E, Chenu C, Robert M (2001) Influence of organic amendments on copper distribution among particle size and density fractions in Champagne vineyard soils. *Environmental Pollution*. 112, 329 – 337.

Biswas T, Christen E, Quayle W, Beijert M (2002) Copper toxicity associated with viticulture in southeastern New South Wales, Australia. In 'FUTUREsoils, conference proceedings Australian Society of Soil Science national conference, Perth, Western Australia, 2 - 6 December 2002'. (Eds D Williamson, C Tang, A Rate). pp 32 - 33. (Australian Society of Soil Science).

Bogomolov DM, Chen SK, Parmelee RW, Subler S, Edwards CA (1996) An ecosystem approach to soil toxicity testing: a study of copper contamination in laboratory soil microcosms. *Applied Soil Ecology*. 4, 95 - 105.

CCME (2003) 'Canadian Environmental Quality Guidelines'. Canadian Council of Ministers of the Environment, Canada. Available at: http://www.ccme.ca/publications/can_guidelines.html

Chaignon V, Sanchez-Neira I, Herrmann P, Jaillard B, Hinsinger P (2003) Copper bioavailability and extractability as related to chemical propoerties of contaminated soils from a vine-growing area. *Environmental Pollution*. 123, 229 - 238.

Dahlin S, Witter E, Martensson A, Turner A, Baath E (1997) Where's the limit? Changes in the microbiological properties of agricultural soils at low levels of metal contamination. *Soil Biology and Biochemistry*. 29, 1405 - 1415.

Darmendrail D (2003) 'The French approach to contaminated land management - Revision 1: BRGM/RP-51098-FR'. BRGM, France. Available at: http://infoterre.brgm.fr/PDF/RP-52276-FR.pdf

Delusia A, Giandon P, Aichner M., Bortolami P, Bruna L, Lupetti A, Nardelli F, Stringari G (1996) Copper pollution in Italian vineyard soils. *Communications in Soil Science and Plant Analysis*. 27, 1537 – 1548.

Flores-Velez LM, Ducarior J, Jaunet AM, Robert M (1996) Study of the distribution of copper in an acid sandy vineyard soil by three different methods. *European Journal of Soil Science*. 47, 523 – 532.

Frank R, Braun HE, Ishida K, Suda P (1976) Persistent organic and inorganic pesticide residues in orchard soils and vineyards of Southern Ontario. *Canadian Journal of Soil Science*. 56, 463 – 484.

Gardner J (2003) Copper usage controversy heats up in Europe [online]. Ministry of Agriculture and Food, Ontario, Canada. Available at: http://www.gov.on.ca/OMAFRA/english/crops/hort/news/hortmatt/2003/03hrt03a3.htm [accessed 2004].

Johnson S (2005) 'Danish (Zealand) guidelines: classification of polluted soil. Sanaterre Environmental'. Available at: http://www.sanaterre.com/guidelines/zealand.htm

Khalil MA, Abdel-Lateif HM, Bayoumi BM, van Straalen NM (1996) Analysis of separate and combined effects of heavy metals on the growth of Aporrectodea caliginosa (Oligochaeta; Annelida), using the toxic unit approach. *Applied Soil Ecology*. 4, 213 - 219.

Magalhaes MJ, Sequeria EM, Lucas MD (1985) Copper and zinc in vineyards of central Portugal. *Water, Air and Soil Pollution*. 26, 8-24.

McBride MB (1981) Forms and distribution of copper in solid and solution phases of soil. In 'Copper in soils and plants - Proceedings of the Golden Jubilee International Symposium, Murdoch University, Perth, Western Australia'. (Eds JF Loneragan, AD Robson, RD Graham) pp 25 - 45. (Academic Press, Sydney).

McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers SL (2000) Review: A bioavialability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research.* 38, 1037 - 86.

Merrington G, Rogers SL, Van Zwieten L (2002) The potential impact of long-term copper fungicide usage on soil microbial biomass and microbial activity in an avocado orchard. *Australian Journal of Soil Research*. 40, 749 - 759.

NEPC (1999) 'National environment protection (assessment of site contamination) measure'. National Environmental Protection Council Service Corporation, Adelaide, Australia.

O'Halloran K, Booth LH (2000) 'New Zealand ecotoxicity data: Soil invertebrates and terrestrial plants'. In 'Ecological risk assessment at contaminated sites'. Manaaki Whenua Landcare Research, Lincoln, New Zealand. Available at: http://contamsites.landcare.cri.nz/nz_data.htm

Paoletti MG, Sommaggioa D, Favrettoa MR, Petruzzelli B, Pezzarossab B, Barbafieri M (1998) Earthworms as useful bioindicators of agroecosytem sustainability in orchards and vineyards with different inputs. *Applied Soil Ecology*. 10, 137 – 150.

Pietrzak U, McPhail DC (2004) Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. *Geoderma*. 122, 151 - 166.

Sauve S. (2002) Speciation of metals in soils. In 'Bioavailability of metals in terrestrial ecosystems: importance of partitioning for bioavailability to invertebrates, microbes, and plants'. (Ed HE Allen) pp 7 - 37. (Society of Environmental Toxicology and Chemistry (SETAC), Pensacola, Florida).

Snedecor GW, Cochran WG (1989) 'Statistical Methods'. 8th ed. (Iowa State University Press/AMES). pp 237 –241.

Stevenson FJ, Fitch A (1981) Reactions with organic matter. In 'Copper in soils and plants - Proceedings of the Golden Jubilee International Symposium, Murdoch University, Perth, Western Australia'. (Eds JF Loneragan, AD Robson, RD Graham) pp 69 - 95. (Academic Press, Sydney).

Swedish EPA (2002) 'Environmental Quality Criteria - Contaminated Sites'. Swedish Environmental Protection Agency, Sweden. Available at: http://www.internat.enviro.se/documents/legal/assess/assedoc/contdoc/pollevel.htm

Tiller KG, Cunningham RB, Cartwright B, Clayton PM, Merry RH (1975) Sampling and analytical errors in the estimation of copper, cadmium, zinc and lead in surface soils. Commonwealth Scientific and Industrial Research Organisation Division of Soils Divisional Report No. 3/1975, Australia.

Tiller KG, Merry RH (1981) Copper pollution of agricultural soils. In 'Copper in soils and plants - Proceedings of the Golden Jubilee International Symposium, Murdoch University, Perth, Western Australia'. (Eds JF Loneragan, AD Robson, RD Graham) pp 119 - 137. (Academic Press, Sydney).

US National Library of Medicine (2003) Hazardous Substances Data Bank – Copper compounds [online]. US National Library of Medicine. Available from: http://toxnet.nlm.nih.gov/ [accessed 2003].

Van Rhee JA (1976) Effects of soil pollution on earthworms. *Poedobiologia*. 17, 201 – 208.

Van Zwieten L, Rust J, Kingston T, Merrington G, Morris S (2004) Influence of copper fungicide residues on occurrence of earthworms in avocado orchard soils. *Science of the Total Environment*. 329, 29 - 41.

VROM International (2000) 'Circular on target values and intervention values for soil remediation: DBO/1999226863'. Netherlands Ministry of Housing, Spatial Planning and Environment, Netherlands. Available at: http://www2.minvrom.nl/Docs/internationaal/annexS_I2000.pdf

Zarcinas BA, McLaughlin MJ, Smart MK (1996) The effect of acid digestion technique on the performance of nebulization systems used in inductively coupled plasma spectrometry. *Communications in Soil Science and Plant Analysis*. 27, 1331 – 1354.