

Environmental Risks of Fungicides Used in Horticultural Production Systems

Adam Wightwick^{1,2,3}, Robert Walters³, Graeme Allinson^{3,4},
Suzanne Reichman⁵, and Neal Menzies^{1,2}

¹*The University of Queensland*

²*Co-operative Research Centre for Contamination Assessment and
Remediation of the Environment (CRC CARE)*

³*Department of Primary Industries, Victoria*

⁴*Victorian Centre for Aquatic Pollution Identification and Management (CAPIM)*

⁵*Royal Melbourne Institute of Technology (RMIT) University
Australia*

1. Introduction

Fungicide use is arguably the most important component of pest and disease management programs in horticultural production systems, particularly vine and orchard crops. This is because fungal diseases, such as downy mildew and botrytis, have the potential to destroy horticultural crops rendering them unsaleable. However, most fungal diseases are difficult to eradicate as, despite attempts at eradication, disease outbreaks can continue to occur across several growing seasons, often originating from spores that have lain dormant over winter. The devastating and lasting impact fungal diseases can have on horticultural crops has resulted in it being considered best practice to implement preventative agrochemical spray programs (McConnell et al., 2003). This often involves fortnightly fungicide applications during the growing season. However, the regular use of fungicides can potentially pose a risk to the environment, particularly if residues persist in the soil or migrate off-site and enter waterways (e.g. due to spray drift, run-off) (Kookana et al., 1998; Wightwick & Allinson, 2007; Kibria et al., 2010; Komarek et al., 2010). If this occurs it could lead to adverse impacts to the health of terrestrial and aquatic ecosystems. For instance, concerns have been raised over the long term use of copper-based fungicides, which can result in an accumulation of copper in the soil (Wightwick et al., 2008; Komarek et al., 2010). This in turn can have adverse effects on soil organisms (e.g. earthworms, microorganisms) and potentially pose a risk to the long-term fertility of the soil (Wightwick et al., 2008; Komarek et al., 2010).

To ensure the sustainability of horticultural production systems, a balance needs to be found between controlling fungal disease risks to crops and protecting terrestrial and aquatic ecosystems. Research into the potential environmental risks posed by fungicide use is needed so that evidence-based policy decisions can be made on the future management of fungicide use in horticultural crops. This need is driven by an increasing community expectation for governments and industry to implement measures to protect environmental

assets. In addition, from marketing perspectives, there is increasing pressure on agricultural industries to demonstrate their 'clean and green' credentials to address concerns from consumers and to maintain market access.

The risk to the environment posed by the use of fungicides in horticultural production systems has received relatively little attention compared to other types of agrochemicals, such as insecticides and herbicides. For instance, in North America the United States Geological Survey (USGS) has conducted detailed nation-wide surveys of agrochemical residues in surface and ground waters (Gillom et al., 2006). These surveys have produced a wealth of data on agrochemical residues in the environment which scientists and policy makers have used to make decisions on the environmental risks of agrochemicals. However, these large surveys appeared to give cursory consideration to fungicides, with just one fungicide out of 75 different agrochemicals included in the analytical screens (Gillom et al., 2006). Similarly, there is relatively little ecotoxicological data detailing concentrations causing adverse effects to organisms (e.g. effect concentration values, EC_{50}) for even the most widely used fungicides (Frampton et al., 2006; Maltby et al., 2009). Given the current lack of data on their environmental risks, future research needs to give greater consideration to fungicides. In part, this is because fungicides tend to be applied repeatedly over a specific period of the year, and so arguably pose a greater environmental risk than other types of agrochemicals, such as insecticides, which tend to be applied more sporadically to eradicate pest outbreaks when detected. Another important consideration is that there has been a continual evolution of new fungicidal compounds in a race to overcome fungicide resistance, improve the effectiveness of fungicides, and to reduce application rates. As more farmers seek to adopt newer fungicides there is a need to consider the costs and benefits of this adoption, as newer chemicals may not necessarily pose a lower environmental risk than those they replace. For instance, in recent years the use of organophosphate insecticides (e.g. chlorpyrifos) has been restricted in the USA due to the presence of unacceptably high concentrations in some waterways. Subsequently, the use of synthetic pyrethroids has increased, and these in turn are now presenting a sediment contamination issue (Banks et al., 2005; Weston et al., 2004). This is an example of where well intentioned changes to agrochemical use has led to a transfer in risks, rather than the intended reduction in risks.

This chapter provides an overview of the potential environmental risks posed by fungicide use in horticultural crops, including discussion of the main types of fungicides and patterns of use; and the environmental fate and toxicity of these fungicides. Fungicides are discussed within an ecological risk assessment context and perspectives given in relation to linking policy with science in managing ecological risks associated with fungicide use in horticultural crops. Throughout the chapter, fungicide use in Australian viticulture is presented as a case-study. The discussion focuses on risk to the soil environment, particularly in relation to copper-based fungicides, with secondary consideration given to risks to aquatic environments.

2. Types of fungicides and their usage patterns

There are currently 47 different fungicides (active ingredients) registered for use in vineyards in Australia (AWRI, 2010), representing 40% of the total number of agrochemicals registered for use in viticulture. Most of the fungicides registered for use in viticulture are used to control downy mildew (*Plasmopara viticola*) (21) and powdery mildew (*Uncinula necator*) (17). As is the case with most fungal diseases, it is considered best practice to

prevent grapevine disease outbreaks rather than to eradicate once infection has occurred, as reactive spraying is considered less effective (Nicholas et al., 1994; McConnell et al., 2003). Thus, preventative fungicide applications are widely considered to offer the best 'insurance' in protecting against fungal infection (Nicholas et al., 1994). In grapevines, this tends to involve applying around 4 – 6 preventative fungicide applications during periods of rapid foliage growth (i.e. spring/summer; Nicholas et al., 1994).

The fungicides registered for use in Australian viticulture can be categorised into 16 main chemical classes (Table 1), the majority of which are considered to be broad spectrum protectants. Copper-based compounds (to control downy mildew and other diseases) and sulfur (to control powdery mildew) have been in use since the mid to late 1800's and are still widely used (Russell, 2005). Copper (Cu) and sulfur (S) are also the only fungicides permitted for use in organic agriculture (OIECC, 2009). Historically, Cu was applied as a mixture of copper sulphate and lime (Bordeaux mixture), however copper oxychloride and copper hydroxide are now the main forms applied (Pietrzak & McPhail, 2004). Copper and S are contact fungicides with multi-site activity and have traditionally been applied at high rates (up to 50 kg/ha/yr) to achieve effective control. However, lower applications rates are now used. For instance, a recent survey of vineyards in 10 different regions of Australia found that the mean annual Cu usage across the regions was in the range of 5 – 13 kg/ha/yr (Wightwick et al., 2008). Likewise, in Australia, organic standards currently limit annual usage to 8 kg/ha (OIECC, 2009), with similar restrictions in place in other countries.

Synthetic organic fungicide compounds were first introduced during the 1940's, with the main class being the dithiocarbamates (e.g. mancozeb; Table 1). Like the Cu and S formulations, the dithiocarbamates are broad spectrum, contact fungicides with multi-site modes of action (Russell, 2005). During the 1970's, systemic fungicides with greater activity and more specific modes of action were introduced, and these are able to stop fungal development after infection has occurred (Russell, 2005). Significant classes of systemic fungicides are the triazoles (e.g. penconazole), strobilurins (e.g. trifloxystrobin) and phenylamides (e.g. metalaxyl, an effective eradicant). The strobilurins are highly efficacious, having both protective and eradicated action (Russell, 2005). As they are more effective, systemic fungicides can be applied at much lower rates than the older classes of fungicides. For instance, the typical application rates for the strobilurins and triazoles (0.13 to 0.25 kg/ha) are an order of magnitude lower than the dithiocarbamates (1.5 – 3.5 kg/ha) (Russell, 2005). There also many different 'natural' fungicide products available (e.g. beneficial micro-organisms, biosurfactants, phosphoric acid, clay preparations, cow's milk), however, in most cases their effectiveness has not been fully demonstrated (Van Zwieten et al., 2007).

Information on the quantity of individual (or classes of) fungicides being used within a watershed is useful for predicting the fate and risk of these fungicides in the environment. However, as highlighted in recent reviews, there is currently very little information available on the quantity of particular chemicals used in Australian agriculture (Kookana et al., 1998; Radcliffe, 2002; Wightwick & Allinson, 2007). In 2001, agrochemical usage data was collected in a major dairy and horticultural production region in northern Victoria, Australia (Kookana et al., 2003). This study found that 14 different fungicides (active ingredients) were in use, with the dithiocarbamates (45%) and copper-based fungicides (20%) accounting for the majority of the total fungicide used (based on amounts reported to be applied). Ziram (40%) and metriam (32%) accounted for most of the total quantity of dithiocarbamates used. Sulfur (11%), chlorothalonil (a chloronitrile) (11%), and

Chemical class (no. of active ingredients registered)	Range of physical-chemical properties ^a				Half-life in soil (d)
	Molecular weight	Water solubility (mg/L)	Log K _{ow}	Log K _{oc}	
<i>Inorganic (10)</i>					
copper compounds					
Cu sulphate, Cu oxychloride, Cu hydroxide, Cu ammonium acetate, Cu octoanoate, Cu oxide	98 - 427	<1.0 x 10 ⁻⁵ - 2.9	NR	NR	NR
sulfur	32	Insoluble	NR	NR	NR
peroxyacetic acid, phosphorous acid, potassium bicarbonate	NR	NR	NR	NR	NR
<i>Triazole (8)</i>					
flusilazole, hexaconazole, myclobutanil, penconazole, tebuconazole, tetraconazole, triadimefon, triademenol	284 - 315	17 - 260	2.9 - 3.9	2.5 - 3.4	14 - 420
<i>Dithiocarbamate (6)</i>					
mancozeb, metiram, propineb, thiram, zineb, ziram	240 - 1089	1.0 x 10 ⁻⁵ - 65	-0.26 - 1.23	2.6 - 5.7	1 - 30
<i>Carboximide (3)</i>					
boscalid, iprodione, procymidone	274 - 330	4.5 - 13	3.0 - 3.1	2.8 - 3.2	7 - 200
<i>Pyrimidine (3)</i>					
cyprodinil, fenarimol, pyrimethanil	199 - 331	13 - 121	2.8 - 4.0	2.4 - 2.9	20 - 840
<i>Strobilurin (3)</i>					
azoxystrobin, pyraclostrobin, trifloxystrobin	403 - 408	0.6 - 6	2.5 - 4.5	3.4	7 - 70
<i>Amide/amine (2)</i>					
fenhexamide, spiroxamine	298 - 302	20	2.8 - 3.5	NR	< 1 - 64
<i>Phenylamide (2)</i>					
benalaxyl, metalaxyl	279 - 325	37 - 7.1 x 10 ³	3.5	1.7 - 3.5	70 - 77
<i>Quinone/quinoline (2)</i>					
dithianon, quinoxifen	296 - 308	0.12 - 0.14	3.2 - 4.7	NR	123 - 494

Chemical class (no. of active ingredients registered)	Range of physical-chemical properties ^a				Half-life in soil (d)
	Molecular weight	Water solubility (mg/L)	Log K _{ow}	Log K _{oc}	
Anilide (1)					
fluzinam	465	0.07	3.6	NR	33 - 62
Benzimidazole (1)					
carbendazim	191	8	1.8	2.5	NR
Chloronitrile (1)					
chlorothalonil	266	0.6	2.6	3.1	30 - 90
Hydrazide (1)					
oxadixyl	278	NR	0.8	NR	60 - 90
Morpholine (1)					
dimethomorph	388	>50	NR	NR	NR
Phenylpyrrole (1)					
fludioxonil	248	3.9 × 10 ⁻⁴	1.8	4.1	10 - 25
Phthlamide (1)					
captan	300	3.3	2.8	2.3	1 - 10

^a Log K_{ow} – octanol-water partition coefficient, Log K_{oc}, - soil sorption coefficient. NR – not reported Data from Tomlin, 2000; Wauchope, 2005; IUPAC, 2010.

Table 1. Chemical classes of fungicides registered for use in Australian viticulture and their typical physical-chemical properties.

carboximides (iprodione and procymidone; 9%) were the other main classes of fungicides used (Kookana et al., 2003). In the United States the USGS conducted a nation wide study to estimate the annual agrochemical use intensity rates (mass per unit area of agricultural land) based on typical usage patterns from 1999 to 2004 (USGS, 2010). Analysing the available data it was found that sulfur accounted for over 90% of the total amount of fungicide used in grape production. This is consistent with the situation in northern Victoria, Australia, where excluding S, copper (54%) and dithiocarbamates (28%) accounted for the majority of total fungicide use (Fig. 1). Mancozeb accounted for the vast majority (over 70%) of the total amount of dithiocarbamates used; and the triazoles (predominately myclobutanil), pyrimidines (predominately cyprodinil) and strobilurins (predominately azoxystrobin and trifloxystrobin) were the other main fungicides used (USGS, 2010). Whilst this information is now several years old, it shows that many agriculturists in North America and Australia are still predominately using 'old' classes of fungicides, i.e. inorganic formulations (Cu and S) and dithiocarbamates. This is despite a range of newer more effective fungicides, such as the triazoles and strobilurins, being available in the market place for over 10 years. The situation elsewhere may be different. For instance, Gregoire et al. (2010) noted in a study of fungicide use from 2003 to 2006 in a viticultural catchment of France that strobilurins accounted for 36% of the total amount of synthetic organic fungicides applied.

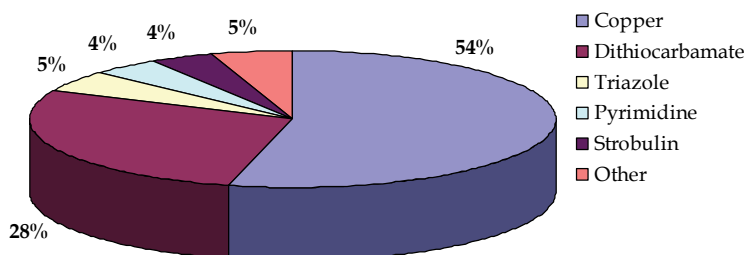


Fig. 1. Contribution (%) of the main fungicide classes, estimated to be used for grape production (excluding sulfur) in the United States, to the total amount of fungicides applied (based on data in USGS, 2010)

3. Environmental fate

Whilst a farmer's objective is to apply fungicides to the agricultural crop/plant, inevitably a proportion of the chemical spray will miss its target. Much of the lost chemical will enter the soil surface where it will persist for a period of time and potentially migrate off-site due to leaching and/or runoff. In addition, some of the agrochemicals applied on farm will migrate off-site due to aerial drift. Once agrochemicals have migrated off-site they can potentially enter nearby waterways and groundwater resources where they can cause adverse effects to aquatic organisms (Wightwick & Allinson, 2007). The fate and behaviour of agrochemicals, including fungicides, in the environment is influenced by the properties of the chemical (e.g. ability to bind to soil, susceptibility to degradation) and environmental factors (e.g. soil type, rainfall, topography, agricultural management practices). These environmental factors, in particular soil type, are widely varied, thus there are many scenarios to consider when assessing the potential for off-site migration and the persistence of agrochemicals in soil (Wightwick & Allinson, 2007; Arias-Estevéz et al., 2008; Komarek et al., 2010). The next section provides an overview of the factors influencing the environmental fate of fungicides and current knowledge on their fate in the environment.

3.1 Persistence, accumulation and availability of fungicides in soil

The two most commonly used inorganic fungicides, Cu and S, are elements and thus do not breakdown in the environment. On the other hand, synthetic organic fungicide compounds do degrade via a number of abiotic and biotic mechanisms, including hydrolysis, volatilisation, oxidation, photolysis, ionisation and microbial degradation. It is generally considered that microbial degradation is the most significant degradation mechanism (Katayama et al., 2010). In the first instance, the persistence (or rate of breakdown) of organic fungicide compounds is related to their chemical structure (e.g. the size, strength of chemical bonds). However, persistence is also influenced by edaphic factors in the environment. Consequently, organic fungicide compounds persist for varying lengths of time in the environment, which is often expressed in terms of their expected half-life (Kookana et al., 1998; Arias-Estevéz et al., 2008; Katayama et al., 2010).

Both inorganic and organic fungicide compounds can be strongly bound within soil (Gevao et al., 2000; Komarek et al., 2010). Cu, being a divalent cation, binds strongly (mostly by specific adsorption) to inorganic and organic material in the soil, and is known to

accumulate in agricultural soils (Wightwick et al., 2008; Komarek et al., 2010). The extent to which organic fungicide compounds are bound within soil is predominately related to their hydrophobicity as indicated by their $\log K_{ow}$ value (a measure of the partitioning of a chemical between octanol and water). Hydrophobicity is also indicated by the $\log K_{oc}$ value, or how readily the chemical adsorbs to soil organic matter. A higher $\log K_{ow}$ and/or $\log K_{oc}$ value indicates that the chemical will have a stronger binding affinity in soil (Gevao et al., 2000; Katayama et al., 2010). The extent to which a fungicide is bound within the soil influences the likelihood that the fungicide will accumulate in the soil. However, it is also related to their bioavailability, defined as "the degree to which chemicals present in soil may be absorbed or metabolised by humans or ecological receptors or are available for interaction with biological systems" (Harmsen, 2007). This is a particularly important consideration for Cu as it is generally considered that the vast majority of Cu in soil is so tightly bound that it is biologically inert (McLaughlin et al., 2000). In the first instance, bioavailability is influenced by the environmental availability of the chemical, defined as the fraction, physico-chemically driven by desorption processes, potentially available to be taken up by organisms (Harmsen, 2007).

The environmental availability of fungicides in soil is related to the extent and type of the adsorption and desorption processes, involving a complex series of soil chemical interactions with both mineral and organic phases in soil (McBride, 1981; Gevao et al., 2000; Komarek et al., 2010). Copper and other fungicides added to the soil partition into three separate pools (Fig. 2). The most available pool being the proportion of the fungicide that is soluble in the soil solution whilst the 'unavailable' pool is the proportion of fungicide very tightly bound within the soil and not easily released. The 'potentially available' pool is considered to be reactive (or labile), as biochemical processes associated with the decomposition of organic material and other dissolutive processes, can release bound fungicide thus making it available (Stevenson & Fitch, 1981; Katayama et al., 2010).

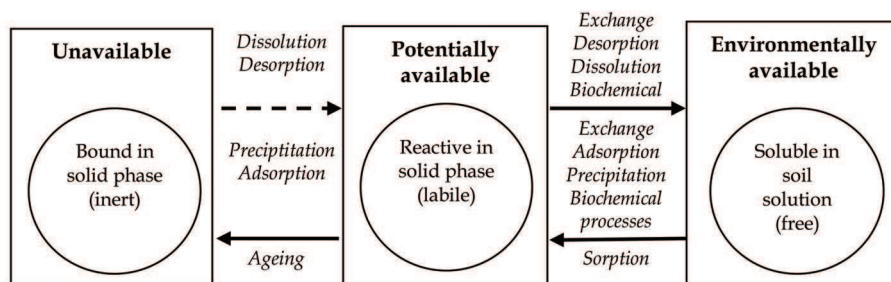


Fig. 2. Diagram illustrating the partitioning of fungicides into the unavailable, available and potentially available pools in soil (adapted from Harmsen, 2007)

A great deal is known about the soil chemical reactions influencing the adsorption of Cu (and other metals) in soil. This is discussed in detail in several reviews (e.g. Pickering, 1979; McBride, 1981; Stevenson & Fitch, 1981; Swift et al., 1995), with only an overview of the main soil-chemical reactions provided here. Copper binds strongly to negatively charged sites on inorganic mineral constituents in soil, with specific adsorption (covalent bonding) to iron (Fe), aluminium (Al), and manganese (Mn) oxides, and exchange on layer silicate clays (electrostatic association) (McBride, 1981). Specifically adsorbed copper is not easily released and is considered to be inert and not biologically available (McBride, 1981). The

environmentally available pool includes Cu which is soluble in the soil solution (as free ions and complexed with organic and inorganic ligands) as well as readily exchangeable forms of Cu. The potentially available or labile pool of Cu in soil is comprised predominately by Cu adsorbed to organic matter. Organically bound Cu has generally been found to represent 20-50% of the total Cu in soil (Stevenson & Fitch, 1981; Pietrzak & McPhail, 2004; Strawn & Baker, 2008). It is important to note that Cu can become very tightly bound in soil due to the formation of three-way complexes with both mineral and organic components of the soil. Copper organically bound in this manner can be considered to be less reactive and associated with the inert pool of Cu in soil (Stevenson & Fitch, 1981; Boudescoque et al., 2007). In this context, it is known that the longer the organically sorbed Cu remains in the soil, the stronger the bond becomes with the soil solid phase. This 'ageing' effect results in the transfer of Cu from the labile 'potentially available' pool into the inert 'unavailable' pool, as adsorbed Cu becomes incorporated into the crystalline structure of soil minerals over time (McLaughlin, 2001; Ma et al., 2006).

Copper adsorption to the solid phase of the soil decreases with increasing soil acidity due to a decrease in the number of negatively charge sites, particular at $\text{pH} < 5$ (Sauve et al., 2000). The proportion of Cu present in the soil solution may also increase with increasing soil alkalinity ($\text{pH} > 8$) due to the formation of complexes with carbonate, hydroxy groups and dissolved organic matter, which reduces Cu sorption to soil solid phases (McBride, 1981; Burton et al., 2005; Fernandez-Calvino et al., 2008). A change in soil pH, particularly a lowering, can cause adsorbed Cu to be released (McLaughlin, 2001). This could occur due to the application of some fertilisers, soil amendments and agrochemicals. Soil pH is also important as it influences the speciation of the Cu in the soil solution (McBride, 1981, Sauve, 2000). In acid soils, soil solution Cu is present mainly as the free Cu^{2+} ion, whereas in alkaline soil the soluble Cu is present mostly as dissolved organic matter complexes (McBride, 1981; Burton et al., 2005; Fernandez-Calvino et al., 2008). It is important to note that the presence of other cationic metals/elements influences Cu adsorption due to competition for binding sites (McBride, 1981; Stevenson & Fitch, 1981). Soil organisms can release organically bound Cu as they utilise organic matter for nutrition and can also modify the chemistry of the surrounding soil; for example by changing pH, ionic strength, and macronutrient cation concentrations, and by excreting organic ligands (Peijnenburg & Jager, 2003).

Increases in the concentration of Cu in the surface soils of vineyards that have received regular inputs of copper fungicides have been reported from many different viticultural regions of the world (Table 2; Komarek et al., 2010). Typically 10 to 20 fold increases in Cu concentrations compared to untreated native soils have been reported in the soils of vineyards with long histories of copper fungicide use (Table 2; Wightwick et al., 2008; Komarek et al., 2010), with the highest reported concentrations in Brazil (up 3216 mg/kg total Cu; Mirlean et al., 2007). As would be expected the extent of Cu accumulation has been found to be influenced not just by the history of copper fungicide use (e.g. years of Cu use) but also soil properties which influence the retention of Cu in soil, such as organic carbon, cation exchange capacity (CEC), and pH (Morgan & Taylor, 2003; Wightwick et al., 2008; Komarek et al., 2010). A number of studies have also sought to characterise the environmental availability of the copper fungicide residues. Overall, the availability of Cu in soil is influenced firstly by the total Cu concentration, with pH, clay, CEC, organic matter being the next most important soil factors (Brun et al., 1998; Sauve et al., 2000; Gray & McClaren, 2006; Fernandez-Calvino et al., 2009; Wightwick et al., 2010). It is generally accepted that the 0.01 M calcium chloride (CaCl_2) extractable concentration provides a useful indication of the environmentally available

proportion of Cu in soil (Harmsen, 2007; Peijnenburg et al., 2007). The CaCl₂ extractable Cu concentrations of vineyard soils have been reported in several viticultural regions of the world, including Southern France (0.10 to 9.24 mg/kg, n = 22; Brun et al., 1998); Roujan region of France (1.00 to 39.0 mg/kg, n = 6; Chaignon et al., 2003); Slovenia (0.04 to 0.07 mg/kg, n = 22; Rusjan et al., 2007); Czech Republic (0.53 to 0.70 mg/kg, n = 5; Komarek et al., 2008); Australia (< 0.1 to 0.94 mg/kg, n = 100; Wightwick et al., 2010); and Brazil (0.20 to 5.00 mg/kg, n = 21; Mirlean et al., 2007). For the most part the CaCl₂ extractable Cu has represented < 1%, and often < 0.5%, of the total Cu concentration in the soil. Even in Brazil, where very high concentrations of accumulated Cu (1214 to 3216 mg/kg total Cu) have been reported in vineyard soils, the CaCl₂ extractable Cu only represented 0.1 to 0.9% of the total Cu (Mirlean et al., 2007). Considerably higher CaCl₂ extractable Cu concentrations (up to 30 mg/kg) have been reported in acidic vineyard soils. For example, Brun et al. (1998) found acidic vineyard soils (pH 4.5 to 5.5) to have much higher and greater variability in CaCl₂ Cu availabilities (0.4 to 9.24 mg/kg; 1.05 to 7.24% of total Cu) than neutral to alkaline soils (pH 6.5 to 8.6) (0.10 to 0.56 mg/kg; 0.13 to 0.54% total Cu). Similarly, relatively high concentrations of ammonium acetate (NH₄OAc) extractable Cu concentrations (which provides a similar indication of availability to CaCl₂ extractable Cu) were reported in a recent study of 170 acidic vineyard soils (mean pH 5.6 (4.0 - 7.9); mean NH₄OAc extractable Cu, 4.9 mg/kg (range, 0.1 - 30.3 mg/kg) (Fernandez-Calvino et al., 2009).

Country	Region	No. of vineyards surveyed	Total Cu (mg/kg)		Years of Cu use	Reference
			Mean	Range		
France	Bordeaux	20	458	305 - 845	NR	Delas (1981)
	Southern France	8	121	47 - 177	50 - 106	Brun et al. (1998)
	Roujan	13	161	75 - 398	NR	Chaignon et al. (2003)
Italy	Northern	NR	297	NR	NR	Deluisa et al. (1996)
	Southern	NR	75	NR	NR	
Germany		NR	1280	NR	NR	Tiller & Merry (1981)
Spain	North-West	20	144	40 - 301	>100	Arias et al. (2004)
Canada	Ontario	16	40	10 - 77	3 - 25	Frank et al. (1976)
Greece	Nemea	24	89	NR	>100	Vavoulidou et al. (2005)
Brazil	Southern	21	2198	1214 - 3216	100	Mirlean et al. (2007)
Croatia	Coastal Croatia	20	200	71 - 626	40 - 100	Vitanovic et al. (2010)
New Zealand	Nationwide	43	35	1 - 259	1 - 100	Morgan & Taylor (2003)
Australia	Victoria	5	59	51 - 77	> 90	Pietrzak & McPhail (2004)
		9	90	9 - 229	20 - 30	
	Nation wide	35	73	24 - 159	40 - 100	Wightwick et al. (2008)
	63	53	6 - 223	1 - 38		

NR - not reported.

Table 2. Summary of copper concentrations reported in the surface soils of vineyards in viticultural regions of the world (adapted from Wightwick et al., 2008).

Understanding the adsorption of synthetic organic fungicides is complex due to the large number of different active ingredients registered for use, all of which have differing physico-chemical properties (Table 1). Moreover, the specific mechanisms controlling the adsorption of different organic chemical compounds are not as well understood (Gevao et al., 2000; Arias-Estevez et al., 2008; Katayama et al., 2010; Komarek et al., 2010). However, in general, it is expected that organic fungicides are adsorbed to organic matter, oxides and clay minerals. This can involve many mechanisms including cation exchange, hydrogen bonding, covalent bonding, van der Waals forces, charge-transfer, ligand exchange, and hydrophobic partitioning (Gevao et al., 2000). The importance of these various mechanisms differs depending on the physico-chemical properties of the chemical, however much of the adsorption is expected to occur with the organic components of the soils (Kookana et al., 1998; Gevao et al., 2000). Adsorption to clay minerals is an important process in soils with low organic matter contents (Gevao et al., 2000; Komarek et al., 2010). It is important to note that hydrophobic agrochemicals may also become adsorbed to dissolved organic matter, and thus remain environmentally available in the soil solution. Like Cu, sorbed fungicides can over time become more tightly bound in the soil due to 'ageing' or 'sequestering' processes, whereby the chemical diffuses into remote microsites within the soil matrix (Gevao et al., 2000; Katayama et al., 2010). Chemicals that are adsorbed in the soil in this manner are likely to persist for longer periods of time due to their decreased availability for microbial degradation (Gevao et al., 2000). Experimentally determined $\log K_{oc}$ values can be used to indicate how strongly chemicals adsorb to organic matter in the soil matrix. Based on published $\log K_{oc}$ values, most of the fungicides registered for use in Australian viticulture have a moderate to high tendency to adsorb to organic carbon, such as the phenylpyroles, chlorothalonil, strobilurins, dithiocarbamates, and triazoles. Other fungicides have lower $\log K_{oc}$ values, such as captan, benzamidazoles, and pyrimidines (Table 1). However, it is important to note that these K_{oc} values tend to be determined using only one soil type, and it is known that the partitioning of chemicals with organic carbon can vary widely across different soil types (Kookana et al., 1998; Katayama et al., 2010). Like Cu, sorbed fungicide compounds can be released from soil binding sites and re-enter the soil solution. This release is most likely to occur for organically bound chemicals due to the activity of micro-organisms, with the release occurring very slowly for aged pesticides (Gevao et al., 2000). Typically, multiple agrochemicals are applied during a growing season, many or all of which can compete for available soil binding sites. This competitive binding can influence the availability of chemicals in soil. For example, Leistra & Matser (2005) reported that the presence of the fungicide carbendazim in soil reduced the adsorption of another fungicide iprodione by 70%. Elevated concentrations of Cu in soil can also react with synthetic organic fungicide compounds. Arias et al. (2006) reported that the adsorption of penconazole is greater in the presence of Cu, possibly due to the formation of Cu-penconazole complexes. Similarly, it has been reported that Cu can form complexes with dithiocarbamate fungicides which can inhibit their rate of degradation (Weissmahr & Sedlak, 2000).

Information on the typical half-lives of synthetic organic fungicides in soil is available (Table 1). Chemicals with a half-life less than 30 days are generally considered to have low persistence, between 30 – 100 days to have moderate persistence, and greater than 100 days to have high persistence (Komarek et al., 2010). The dithiocarbamates, amide/amines, phenylpyroles, phthalamides and strobilurins generally have low persistence in soil; the

phenylamides, anilides, chloronitriles and hydrazides moderate persistence; and the quinones/quinolines high persistence. The persistence of some other classes of fungicides can not be so easily classified. Some triazoles, such as propiconazole (53 days) and triadimefon (14 – 60 days) have moderate persistence, whilst penconazole (133 – 343 days), myclobutanil (306 days) and flusilazole (420 days) have very high persistence. Similarly, with the carboximides, boscalid (200 days) and iprodione (84 days) have much higher persistence than procymidone (7 days). Of the pyrimidines, fenarimol (840 days) is more persistent than cyprodinil (20 – 60 days) and pyrimethanil (55 days). It is important to note however that the published half-lives provide an indication of typical persistence under specific conditions only, i.e. often this is based on laboratory studies undertaken under controlled conditions with a small number of different soil types. However, the persistence of chemicals can vary considerably under different conditions, for example laboratory derived half-lives for myclobutanil have been found to range from 164 – 515 days (IUPAC, 2010). Also synthetic organic fungicide compounds can be degraded to metabolites or transformation products, which may behave differently to their parent compounds. For example, the dithiocarbamate mancozeb is considered to have low persistence in soil (half-life 1 – 7 days), however it is rapidly degraded to ethylenethiourea (ETU) which not only can persist for 5 – 10 weeks but is more soluble than the parent compound (IUPAC, 2010; Komarek et al., 2010). Other dithiocarbamates, such as metiram and zineb, are also rapidly transformed to ETU. Significant metabolites have been identified for many of the other fungicides including the strobilurins, phthalamides, carboximides, pyrimidines and chloronitrile (IUPAC, 2010). In some instances the metabolite has greater persistence in soil whilst for other chemicals the parent compound is more persistent. For example, trifloxystrobin typically has a half-life in soil of seven days, whereas its metabolite ((E,E)-trifloxystrobin acid; EETFA) has a half-life of up to 268 days (IUPAC, 2010). On the other hand, (E)-2-(2-[6-cyanophenoxy]-pyrimidin-4-yloxy)-phenyl-3-methoxyacrylic acid, the metabolite of azoxystrobin, is less persistent (half-life 22 days) than the parent compound (half-life 70 to 180 days; IUPAC, 2010).

There have been few studies to determine the persistence and accumulation of synthetic organic fungicides in horticultural soils, with most of the studies from viticultural regions of Spain (Komarek et al., 2010). The largest of these studies by Bermudez-Cousa et al. (2007) measured the concentrations of cyprodinil, fludioxonil, folpet, metalaxyl, procymidone and penconazole in the soils of 20 vineyards over a two year period. No fungicides were detected in the majority of the soil samples collected, however all fungicides (except folpet) were detected in a number of samples. Procymidone (up to 1124 µg/kg) and metalaxyl (up to 1002 µg/kg) were detected at the highest concentrations, followed by cyprodinil (up to 462 µg/kg), penconazole (up to 411 µg/kg) and fludioxinil (up to 349 µg/kg). In general, the fungicides were only detected in the soils during the seasons that they were being applied (i.e. spring, summer). Whilst fungicides may persist in the soil from one season to the next, there was no clear evidence that they were accumulating in the soil (Bermudez-Cousa et al., 2007). This is perhaps not surprising given that the majority of synthetic organic fungicides are expected to have low to moderate persistence in soil. Similar results have been reported in the other smaller studies conducted in Spain (Komarek et al., 2010). For example, Rial-Otero et al. (2004) detected cyprodinil (260 µg/kg), fludioxinil (991 µg/kg), procymidone (20 µg/kg) and tebuconazole (12 µg/kg) in vineyard soils one month after the final treatment of the crop. Only fludioxinil was detected in the soil nine months later, however this was at a much lower concentration than originally detected (52 µg/kg; Rial-Otero et al., 2004).

3.2 Transport of fungicides from horticultural production systems

Agrochemicals can be transported from agricultural properties due to atmospheric transport (e.g. spray drift, volatilisation), surface run-off and leaching (infiltration through the soil profile) and potentially enter surface and ground waters (Wightwick & Allinson, 2007). The extent of spray drift is influenced largely by the method, type and set-up of the application equipment as well as the weather (i.e. wind) (MacGregor et al., 2004). Whilst the off-site transport via leaching and run-off is related to the adsorption of the chemical to the solid phase of the soil (Kookana et al., 1998). Chemicals dissolved or suspended in the soil pore water are most vulnerable to leaching through the soil profile. These chemically available chemicals can also be transported via surface run-off. However, chemicals strongly sorbed to soil particles are also prone to movement via particle bound surface run-off (Kookana et al., 1998). Given that Cu is strongly bound in surface soils, it is generally considered that Cu has a low likelihood of being transported via leaching but is susceptible to surface run-off of the soil particles to which it is bound (McBride, 1981). The mobility of synthetic organic fungicide compounds in soil can be assessed based on their published log K_{oc} values (Table 1). The majority of the synthetic organic fungicide compounds are likely to be relatively immobile in soil and unlikely to move via leaching. However, if they persist in the soil may move via the surface run-off of soil particles. Once again it is important to note that the published log K_{oc} values are based on a small number of soil types, and fungicides may be more mobile in some types of soils, e.g. particularly porous soils low in organic matter (Kookana et al., 1998; Arias-Estevéz et al., 2008). It is also noted that some fungicide metabolites can have differing mobility in soil relative to their parent compound. For instance, whilst dithiocarbamates are considered to have low mobility in soil (log K_{oc} 2.6 – 5.7) the major metabolite ETU has relatively high mobility (log K_{oc} 1.85; IUPAC, 2010). Similarly, EETFA (log K_{oc} 2.08) is more mobile than its parent compound trifloxystrobin (log K_{oc} 3.38; IUPAC, 2010). It is also important to note that the leaching and surface run-off of chemicals can be accelerated if they are complexed to dissolved organic matter (colloids) in the soil pore water; this is termed 'colloid assisted transport' (Kookana et al., 1998; Komarek et al., 2010).

Over the past decade several studies have sought to determine the extent to which fungicides are transported from horticultural properties to nearby waterways. Ribolzi et al. (2002) and Fernandez-Calvino et al. (2008) reported significant amounts of Cu were transported from vineyard soils to nearby surface waters following storm events. The study of Fernandez-Calvino et al. (2008) reported that total Cu concentrations in sediments increased from 18 mg/kg at an upstream point in the catchment with no productive vineyards to 209 mg/kg at a downstream point of the catchment which represented the largest area of viticultural production. In both studies the readily available fraction of the Cu in sediment/suspended sediment was < 5% and often < 1% of the total Cu (Ribolzi et al., 2002; Fernandez-Calvino et al., 2008). Several recent studies have also studied the movement of synthetic organic fungicides by surface run-off in catchments dominated by viticultural/horticultural production (Hildebrandt et al., 2008; Gregoire et al., 2010; Rabiet et al., 2010). The largest of these studies involved monitoring concentrations of seven fungicides in surface water collected following 58 run-off events (over four years) in a wine-growing catchment in France (Gregoire et al., 2010). Over the four years the chemicals that were detected most frequently (% of samples detected) and at the highest concentrations (maximum concentration detected) were dimethomorph (57 - 98%; 0.66 to 5.7 µg/L), pyrimethanil (39 - 100%; 0.39 to 5.8 µg/L), and azoxystrobin (30 - 41%; 0.36 to 3.4 µg/L). For the most part tetraconazole and penconazole

were detected in less than 10% of the samples at concentrations less than 0.2 µg/L (Gregoire et al., 2010). In a similar study Rabiet et al. (2010), reported that concentrations of fungicides (azoxystrobin, carbendazim, dimethomorph, procymidone, tebuconazole) were found to be highest during the application season. Relatively high concentrations of dimethomorph (up to 3.4 µg/L), procymidone (up to 1.3 µg/L) and tebuconazole (up to 1.9 µg/L) were detected. Contrary to the study of Gregoire et al., (2010) azoxystrobin was detected at much lower concentrations (average of 0.08 µg/L; Rabiet et al., 2010). Hildebrandt et al. (2008) detected metalaxyl in both ground water (8 to 18% of samples; maximum concentration 0.25 to 0.36 µg/L) and surface water (4 to 14% of samples; maximum concentration 0.01 to 0.04 µg/L) in a catchment dominated by horticultural production. Little consideration has been given to assessing spray drift as a source of off-site fungicide movement, although Merli et al. (2010) found that despite up to 11 applications of quinoxifen, very little of this fungicide was detected in sediments of a nearby surface ditch. Similarly in a study of pesticides in irrigation supply channels in a horticultural region in Australia, chlorothalonil, the only fungicide tested for, wasn't detected, despite spray drift being identified as a main source of local surface water contamination (Rose & Kibria, 2007).

4. Environmental toxicology

The presence and persistence of fungicides in agricultural soils can cause adverse effects to soil organisms, such as earthworms and micro-organisms, and the crucial functions these organisms are responsible for (e.g. the breakdown of organic matter, facilitating nutrient cycling). Thus, any negative impacts caused by fungicide residues can have lasting impacts on the fertility and health of agricultural soils. Likewise, fungicide residues, which make their way into surface and ground waters, have the potential to cause adverse effects to the structure (i.e. biodiversity) and functioning of aquatic ecosystems. The environmentally available proportion of fungicides in soil, sediment and water can cause toxic effects to organisms. However, not all of the fungicide will be absorbed by organisms (be environmentally bioavailable to) and react with toxic sites of action within exposed organisms (be toxicologically bioavailable or bioaccessible) (Fairbrother et al., 2007; Harmsen, 2007; Katayama et al., 2010). The environmental and toxicological bioavailability varies between different types (and species) of organisms, thus different organisms/species will have differing sensitivities to the various fungicides. The mechanisms controlling toxicity are complex. For instance the uptake of chemicals by organisms can be reduced if they are complexed with organic matter, as this impedes diffusion across biological membranes, and if cations such as H⁺, Na⁺, Ca²⁺ and Mg²⁺ compete at cell binding sites (Peijnenburg & Vijver, 2007; Katayama et al., 2010). Toxic effect is also related to the whether the chemical reaches a site of toxic action and the rate of detoxification and excretion (Peijnenburg & Vijver, 2007). Organisms can also develop tolerance to chemicals by using defence mechanisms such as regulating the rate at which the chemical is taken up, excreting compounds such as polysaccharides to complex the chemical thus impeding uptake, internal sequestration, and genetic adaptation (Bruins et al., 2000; Peijnenburg & Vijver, 2007). The likely ecotoxicological effect of chemicals can be indicated using controlled dose-response laboratory studies which report toxicity as an effect concentration (e.g. LC₅₀ value, concentration causing mortality to 50% of the test organisms). Such ecotoxicological data can be used to indicate the likely effects of a chemical in the field and the relative potency of different chemicals. This section provides an overview of the known toxicities of Cu and

synthetic organic fungicides to terrestrial and aquatic organisms, based on published laboratory derived ecotoxicological effects data.

4.1 Ecotoxicological effects to terrestrial organisms

Considerable ecotoxicological data has been published describing the effects of Cu to soil organisms (Baath, 1989; Giller et al., 1998; Markich et al., 2002; Frampton et al., 2006; Jansch et al., 2007; IUPAC, 2010; US EPA, 2010). Lethal and sub-lethal (e.g. reproduction, growth, avoidance) toxicity data is reported for over 15 different macro-invertebrate species, with much of the data related to the composting worms *Eisenia fetida* and *E. andrei*. The majority of the ecotoxicological data for soil micro-organisms describes adverse effects to the microbial biomass and indicators of microbial activity, principally rates of respiration and nitrification (Baath, 1989; Giller et al., 1998). There is considerable variation in the reported toxicity values determined by different researchers and using different soils. For example, the reported reproductive EC₅₀ for *E. fetida*/*E. andrei* varies from 8 to 927 mg/kg total Cu (mean 268 mg/kg; CV% 110). Even greater variation has been reported for measures of microbial activity. For example, a study using 19 different European soils found that the total Cu EC₅₀ values for nitrification and respiration varied from <100 to >1000 mg/kg (Oorts et al., 2006b). On first impression it would seem that much of the variation in the reported ecotoxicological data is due to effect concentrations being based on total Cu concentrations rather than the available fraction. However, several studies have reported that effect concentrations represented as the available fraction (e.g. CaCl₂ extractable, free Cu²⁺) are even more variable (Oorts et al., 2006b; Broos et al., 2007; Criel et al., 2008). That said much of the variation in the reported ecotoxicological data can be explained by factors which influence the environmental availability of Cu, such as pH, CEC, clay and organic carbon content of the soil (Oorts et al., 2006b; Broos et al., 2007; Criel et al., 2008). Similarly, toxicity values determined using freshly spiked soils have been reported to be much lower than when using more realistic field aged soils, due to higher Cu availability (Scott-Fordsmand et al., 2000; Oorts et al., 2006a). This presents a significant challenge for ecological risk assessment as much of the ecotoxicological data on Cu has been generated using spiked soils. Using regression equations reported in the literature (Broos et al., 2007; Criel et al., 2008) the Cu concentration expected to cause an ecotoxicological effect (EC₅₀) to *E. fetida* reproduction, substrate induced respiration (SIR) and substrate induced nitrification (SIN) for vineyard soils in 10 different regions of Australia has been predicted (Table 3). Based on these models, accumulated Cu in Australian vineyard soils, (which has typically been reported in the range of 24 - 159 mg/kg total Cu (Table 1)), is unlikely to be causing adverse effects to rate of respiration and nitrification, but could potentially be causing adverse effects to earthworm reproduction.

It is difficult to compare the relative toxicity of Cu across different soil invertebrate species and microbial end points because of the high variability in the reported ecotoxicological data. However, soft bodied invertebrates (e.g. earthworm *Aporrectodea caliginosa*; mean LC₅₀ 226 mg/kg total Cu) are generally more sensitive to Cu than hard bodied invertebrates (e.g. centipede *Lithobius mutabilis*; mean LC₅₀ 1817 mg/kg total Cu). *Aporrectodea caliginosa* appears to be amongst the most sensitive invertebrate species (Frampton et al., 2006), which is of particular relevance as *Aporrectodea sp.* have been reported to be an abundant earthworm species present in vineyard soils (Thomson, 2006). Whilst soil micro-organisms have often been reported to be relatively tolerant to increased soil Cu concentrations, in some instances ecotoxicological effects have been reported at Cu concentrations that could realistically be present in the soils of vineyards (Baath, 1989, Giller et al., 1998). For instance,

Olayinka & Babalola (2001) reported that respiration and nitrogen mineralisation were significantly reduced at a total Cu concentration of 174 mg/kg. Similarly, Bogomolov et al. (1996) reported that litter decomposition was inhibited at total Cu concentration of 100 mg/kg. An increasing number of studies have also reported adverse effects to the activity of soil enzymes at relatively low Cu concentrations (Baath, 1989; Olayinka & Babalola, 2001; Kim et al., 2008). For example, Kim et al. (2008) showed that adverse effects on urease activity began at CaCl₂ extractable Cu concentrations less than 5 mg/kg. Interestingly, fungi seem to be relatively tolerant to Cu whilst nitrifying bacteria are particularly sensitive (Baath, 1989). Frampton et al. (2006) and Jansch et al. (2007) have estimated a lethal hazardous concentration to 5% (HC₅) for soil invertebrates to be 183 mg/kg total Cu (derived using available ecotoxicological LC₅₀ values) and a sub-lethal HC₅ value to soil organisms of 55 mg/kg total Cu (derived using EC₅₀ values for invertebrates, microbial processes and plant species). At these HC₅ values it is assumed that 5% of all species/endpoints will be adversely affected; or, in other words, 5% of species/endpoints will have a value below the HC₅ concentration.

Region	Physical-chemical soil properties mean (range) ^a			Predicted EC ₅₀ (mg/kg total Cu) mean (range) ^b		
	pH	CEC (cmol _e /kg)	Clay (%)	<i>E. fetida</i> rep.	SIR	SIN
Murray Valley	8.7	17	22	353	1119	2165
Southern Highlands	(6.8 - 9.9)	(6.0 - 27)	(7.8 - 34)	(202 - 483)	(811.5 - 1378)	(1329 - 2663)
Riverland	5.6	14	15	331	952.7	813.1
Barossa	(5.1 - 6.3)	(5.1 - 21)	(10 - 20)	(183 - 418)	(870.7 - 1083)	(575.8 - 1097)
southeast, SA	7.7	23	28	439	1253	1717
Riverina	(7.0 - 9.2)	(11 - 31)	(23 - 41)	(295 - 528)	(1074 - 1546)	(1421 - 2370)
Mudgee	7.2	14	17	299	1011	1487
Swan Valley	(6.1 - 8.5)	(<0.1 - 37)	(6.0 - 34)	(9.44 - 583)	(772.5 - 1395)	(1023 - 2058)
Margaret River	7.8	27	31	478	1346	1779
Tasmania	(7.2 - 8.6)	(11 - 36)	(18 - 36)	(288 - 573)	(1260 - 1438)	(1503 - 2102)
	6.6	21	33	418	1356	1252
	(5.9 - 7.2)	(15 - 25)	(24 - 38)	(343 - 468)	(1159 - 1481)	(948.3 - 1498)
	6.0	8.5	17	231	1016	979.1
	(5.6 - 6.4)	(1.5 - 23)	(11 - 29)	(88.4 - 436)	(887.8 - 1277)	(808.0 - 1171)
	5.9	1.6	7.8	76.9	813.8	966.3
	(5.1 - 7.0)	(0.1 - 5.0)	(4.6 - 12)	(18.5 - 207)	(742.5 - 867.0)	(577.9 - 1406)
	5.9	9.0	9.8	250	856.8	936.4
	(5.0 - 7.0)	(3.6 - 17)	(4.7 - 14)	(150 - 374)	(744.4 - 995.4)	(554.4 - 1422)
	6.4	20	18	367	985.4	1181
	(5.7 - 7.7)	(3.6 - 52)	(4.9 - 43)	(149 - 713)	(749.6 - 1588)	(857.0 - 1745)

^a Physical-chemical soil property data from Wightwick et al. (2008).

^b *E. fetida* 28-day reproduction EC₅₀ values predicted using regression equation in Criel et al. (2008); Substrate Induced Respiration (SIR) and Substrate Induced Nitrification (SIN) EC₅₀ values predicted using regression equations in Broos et al. (2007).

n = 10 except for Southern Highlands and Mudgee (*n* = 9), Margaret River (*n* = 13), Tasmania (*n* = 7)

Table 3. The predicted ecotoxicological effects to earthworm reproduction and microbial activity (respiration and nitrification) for 10 viticultural regions of Australia.

A number of field studies have reported adverse effects of Cu fungicides on soil organisms. Paoletti et al. (1998) found that increases in total Cu concentration were correlated ($R^2 = 0.50$) with a decrease in earthworm biomass. A series of controlled field studies in South African vineyards found populations of the earthworms decreased significantly following a series of copper oxychloride spray applications (Maboeta et al., 2003; Eijsackers et al., 2005). Furthermore, a study in avocado orchards reported that accumulated Cu resulted in a decrease in earthworm activity and in decrease in the rate of litter decomposition (Van Zwieten, 2004). In relation to microbial activity, Wang et al. (2009) found a relationship between increased soil Cu concentration and decreased microbial biomass and phosphatase activity in the soils of apple orchards that had received copper-based fungicides for 5 to 45 years. Similarly, Merrington et al (2002) reported a 20% decrease in microbial biomass in avocado orchard soils with 280 - 345 mg/kg total Cu, compared with clean reference soils. Ranjard et al. (2006) found that applications of copper fungicides markedly changed the structure of bacterial and fungal communities in vineyard soils.

Compared to Cu, there is very little published data on the toxicity of the synthetic organic fungicide compounds to soil organisms. Most of the ecotoxicological data has been generated for the earthworm *E. fetida*. Like Cu, most of the fungicide compounds are moderately toxic to earthworms, with LC_{50} values typically in the range of 200 - 1000 mg/kg (Table 4). Carbendazim (LC_{50} 4 mg/kg) and triadimefon (LC_{50} 50 mg/kg) are the most toxic to *E. fetida* (Table 3) (IUPAC, 2010). However, toxicity data has been generated using a limited number of soils, so the variability in toxicity of the fungicides across different soils types is largely unknown. Where toxicity data has been reported from multiple studies, such as with captan (LC_{50} *E. fetida* <89 - 12121 mg/kg, n = 7), there is considerable variability in the reported effect concentrations (US EPA, 2010; Table 3). As

Chemical class	Earthworm LC_{50} (mg/kg)	
	mean	range
Sulfur	> 2000	
Triazole (e.g. myclobutanil)	394	50 - 1381
Dithiocarbamate (e.g. mancozeb)	720	140 - 1262
Carboximide (e.g. iprodione)	> 1000	
Pyrimidine (e.g. pyrimethanil)	252	192 - 313
Strobilurin (e.g. trifloxystrobin)	617	283 - > 1000
Amide/amine (e.g. spiroxamine)	> 1000	
Phenylamide (e.g. metalaxyl)	652	473 - 830
Quinone/quinoline (e.g. dithianon)	751	578 - > 923
Benzamidazole (carbendazim)	4	
Chloronitrile (chlorothalonil)	269	
Hydrazide (oxadixyl)	1000	
Morpholine (dimethomorph)	> 500	
Phenylpyrrole (fludioxinil)	1000	
Phthlamide (captan)	3639	< 89 - 12121

Data from IUPAC, 2010; US EPA 2010; Frampton et al., 2006.

Table 4. Summary of reported data on the acute lethal toxicity (LC_{50}) to earthworm (*Eisenia fetida*) for the different chemical classes of fungicides registered for use.

noted by Bunemann et al. (2006), some studies have shown synthetic organic fungicide compounds to have negative effects on soil organisms. For example, captan and chlorothalonil have been reported to cause reduced respiration, whilst metalaxyl reduced dehydrogenase activity (Bunemann et al., 2006). Carbendazim is also reported to have relatively high toxicity to invertebrates, causing an avoidance response in earthworms at soil concentrations of 10 mg/kg and estimated to have a lethal HC₅ value to soil invertebrates of 0.75 mg/kg (Bunemann et al., 2006; Frampton et al., 2006).

4.2 Ecotoxicological effects of fungicides on aquatic organisms

The effect of Cu on aquatic organisms has been very widely studied, and a large amount of ecotoxicological data is available, most of which relates to fish and invertebrates (Markich et al., 2002; US EPA, 2010). Copper is considered highly toxic to aquatic invertebrates, which is reflected in the Australian and New Zealand Water Quality Guidelines trigger value for Cu of 1.4 µg/L in water (for the protection of 95% of species; ANZECC & ARMCANZ, 2000). There is much less aquatic ecotoxicological data available for synthetic organic fungicides (Maltby et al., 2009; US EPA, 2010). The ANZECC water quality guidelines, and other jurisdictions around the world, do not provide water quality trigger values for any fungicide. The lack of ecotoxicological data for fungicides is surprising given their frequency of use and the fact that most do not have specific modes of action, thus are likely to be toxic to a wide range of organisms, not just fungi (Maltby et al., 2009).

A recent study collected aquatic ecotoxicological data for 42 different fungicides, including ~20 fungicides registered for use in horticulture in Australia (Maltby et al., 2009). This review found that chlorothalonil had the most data available (46 taxa) of all agricultural fungicides, and that most of the fungicide data related to invertebrates (67%). There was no suitable ecotoxicological data available for aquatic fungi or micro-organisms, despite these organisms likely sensitivity to fungicides, and the key role they play in aquatic ecosystems (e.g. decomposition, nutrient cycling; Maltby et al., 2009). In compiling the available ecotoxicological data, Maltby et al. (2009) estimated HC₅ concentrations for the 42 fungicides and compared their relative toxicity to fish, invertebrates and primary producers (e.g. plants). Table 5 summarises these values for the fungicides registered for use in Australian viticulture. Comparing the HC₅ values to the ANZECC & ARMCANZ (2000) water quality trigger value for Cu (1.4 µg/L), it can be seen that although ziram has a comparable low HC₅ value (1 µg/L), on the whole, synthetic organic fungicides appear to be much less toxic to aquatic organisms, particularly the triazoles and dithiocarbamates (Table 5). Fluzinam, carbendazim, and chlorothalonil have relatively high toxicity, whereas the strobilurins, primidines, and captan are moderately toxic (Table 5). The relative toxicity to the three main taxonomic groups (fish, invertebrates, primary producers) varied across the different fungicides. For example the dithiocarbamates and cyprodinil were most toxic to invertebrates, whilst the triazoles, dithanone and captan were least toxic to invertebrates. Fluzinam and carbendazim have relatively low toxicity to primary producers; chlorothalonil has relatively high toxicity to fish, whilst the strobilurins exhibit similar toxicities across the three taxonomic groups (Table 5).

As chemicals are normally present as mixtures in the environment, the issue of mixture toxicity is an important issue to address. This is perhaps particularly important for fungicides given that they are considered general biocides, capable of causing a toxic effect in organisms from different taxonomic groups (Maltby et al., 2009; Norgaard & Cedergreen,

2010). This is supported by a recent study which found that the pyrethroid insecticide α -cypermethrin was up to 12 times more toxic to the aquatic crustacean *Daphnia magna* in the presence of the fungicides prochloraz, epoxiconazole and propiconazole (Norgaard & Cedergreen, 2010). On the other hand, Cu has been reported to have an antagonistic effect on organic pesticide compounds, resulting in them being less toxic (Kungolos et al., 2009).

Chemical class	HC ₅ ($\mu\text{g/L}$) mean (range)	Median EC ₅₀ value ($\mu\text{g/L}$) mean (range)		
		Fish	Invertebrate	Primary Producer
Triazole (myclobutanil, tebuconazole)	229 (220 - 238)	4419 (3137 - 5700)	1710 (720 - 2700)	1628 (1450 - 1805)
Dithiocarbamate (mancozeb, metiram, thiram, zineb, ziram)	51 (1 - 122)	40320 (12 - 180000)	664 (300 - 1125)	1391 (134 - 3250)
Pyrimidine (cyprodinil)	31	2410	660	2600
Strobilurin (azoxystrobin, trifloxystrobin)	25 (8 - 42)	367 (62 - 671)	157 (86 - 228)	235 (17 - 453)
Quinone (dithianon)	14	130	7000	90
Anilide (fluzinam)	8	89	97	1490
Benzamidazole (carbendazim)	8	225	237	27170
Chloronitrile (chlorothalonil)	6	38	183	783
Phenylpyrrole (fludioxonil)	63	740	370	485
Phthlamide (captan)	30	121	8400	320

Data from Maltby et al., 2009.

Table 5. Summary of estimated hazardous concentration (HC₅) values and effect concentrations to aquatic organisms for the different chemical classes of fungicides registered for use in Australian viticulture.

5. Assessment of ecological risks from fungicide use in horticultural production

The information presented on the fate, behaviour and toxicity of fungicides in the environment is useful for understanding the ecological risks posed by the use of fungicides in horticultural production systems. However, to meet the needs of risk managers/decision makers (e.g. policy officers, regulators) this information needs to be considered in a methodical manner that seeks to quantify and describe the risk(s), so that evidence-based decisions can be made. Risk managers/decision makers also require information on the level of confidence in assessments of risks, as they are governed by policies and regulations that often have little flexibility for "if" and "maybe" statements. The widely accepted ecological risk assessment (ERA) framework developed by the United States of America Environment Protection Agency (US EPA) provides structure and guidance for assessing ecological risks, such as those posed by agrochemical use (US EPA, 1998). The ERA framework involves four key steps: (1) problem formulation; (2) analysis (characterise the exposure and effects); (3) risk characterisation (analyse the degree of overlap between the exposure and effect); (4) risk management. In this section information on the fate, behaviour and toxicity of the fungicides registered for use in Australian viticulture is discussed in

relation to the ERA framework and how well this information contributes to describing the environmental risks posed. This is discussed in context of four of the main classes of fungicides used in Australia, these being the traditional copper-based and dithiocarbamates fungicides and the new triazole and strobilurin fungicides.

The reported data on physico-chemical properties (Table 1) can be used to rank the potential for chemicals to leach and persist in the soil. Over 50% of the fungicides registered for use in Australian viticulture theoretically have the potential to leach, including the widely used dithiocarbamates and triazoles. Comparatively, Cu and strobilurins are relatively immobile in soil (Table 6). Next to Cu, the triazole fungicides pose the greatest risks associated with persistence in soil having half-lives in soil of up to 400 days. The dithiocarbamates and strobilurins have much shorter half-lives (typically < 30 days), so are of less concern in relation to risks associated with soil persistence (i.e. toxicity to soil organisms, surface runoff). However, there is a degree of uncertainty around these 'crude' estimates of risk as the behaviour and persistence of chemicals can vary greatly in different soils (e.g. more mobile in sandy soils). Also ETU and EETFA are both more mobile than their parent compounds, which in turn may contribute to an increased risk of leaching (IUPAC, 2010).

	Copper-based	Dithiocarbamates	Triazoles	Strobilurins
Mobility in soil	Low	Medium to low	Medium to low	Low
Persistence in surface soils	High	Low	Moderate to high	Low to moderate
Field data on concentrations in soil	Good	None	Very limited	None
Field data on concentration in aquatic environments	Limited	None	Limited	Limited
Toxicity to earthworms	Moderate to low	Moderate to low	Moderate to low	Moderate to low
Toxicity to aquatic invertebrates	High	Low	Low	Moderate to low
Toxicity to fish	Moderate	Moderate to low	Low	Moderate to low
Toxicity to aquatic primary producers	Moderate	Low	Low	Low

Table 6. Summary of the relative behaviour and toxicity of four key classes of fungicides

A great deal is known about the ecotoxicological effects of Cu to terrestrial and aquatic organisms. However, there is a relatively high degree of uncertainty around the reported terrestrial ecotoxicological data due to the high variability in the data. Much of the data has been generated in the laboratory using freshly spiked soils and risk assessors need to be careful in applying this data as large discrepancies in ecotoxicological effect values have been found between freshly spiked and aged soils (more realistic of the real world). Due to the large degree of variability in reported ecotoxicological effects across different soil, risk assessors need to carefully decide which value to use for a particular species/endpoint. Using the wrong value could cause the risk to be greatly over, or arguably worse, underestimated. Regression models have been developed to predict ecotoxicological effects in specific soil types (e.g. based on clay, CEC, pH; Oorts et al., 2006; Broos et al., 2007; Criel et

al., 2008). These enable ecotoxicological data to be normalised to a specific soil type prior to use in the risk assessment, thus reducing uncertainty. However, at present, predictive regression models have only been generated for a small number of species/endpoints (principally *E. fetida* reproduction, respiration and nitrification). To indicate the likely risk, hazardous concentration (HC₅) values have been estimated for soil organisms (Frampton et al., 2006; Jansch et al., 2007). There is, however, a degree of uncertainty around these HC₅ values as the ecotoxicological data was not normalised before use in the calculations. In Australia both water (1.4 µg/L, protection of 95% of species) and sediment (65 mg/kg, trigger value) guideline values have been derived for Cu for use in ERA (ANZECC & ARMCANZ, 2000). Like Cu, most of the fungicide compounds are moderately toxic to earthworms, including the triazoles, dithiocarbamates, and strobilurins (Table 6). However, toxicity data has been generated using a limited number of soils and species/endpoints (mostly *E. fetida*). So variability in toxicity across different soils and the relative sensitive of different species is largely unknown. Based on the aquatic HC₅ values published by Maltby et al. (2009) it appears that the synthetic organic fungicides are much less toxic than Cu to aquatic organisms, particularly the triazoles. The dithiocarbamates and strobilurins have similar toxicity, although the dithiocarbamates are considerably less toxic to fish (Table 5).

There is sufficient data on the concentrations of Cu in vineyard soils (both total and available) with which to compare to ecotoxicological effect data. In comparison, there is a paucity of field data on the persistence and concentrations of the synthetic organic fungicide compounds in vineyard soils, with no data for Australian vineyards and only a few studies worldwide (Komarek et al., 2010) (Table 6). Whilst these studies did not investigate dithiocarbamates or strobilurins, some triazoles (penconazole and tebuconazole) have been reported to persist in vineyard soils as expected. The more significant finding is that procymidone (up to 1124 µg/kg) and fludioxinil (up to 349 µg/kg) were detected at relatively high concentrations in vineyard soils, despite them being expected to have low persistence in soil. This re-enforces the inherent uncertainty in predictions of the behaviour and fate of chemicals in the environment and the need for field studies to form part of the ERA. No concentrations of fungicides have been reported in surface waters of viticultural/horticultural production regions of Australia, although a paucity of studies have been undertaken (Wightwick & Allinson, 2007). However, some studies in Europe have detected Cu and other synthetic organic fungicide compounds in aquatic environments within viticultural/horticultural catchments (Hildebrandt et al., 2008; Gregoire et al., 2010; Komarek et al., 2010; Rabiet et al., 2010).

The risk characterisation phase of ERA considers the exposure and effect characterisations to formulate a final decision on the risk(s) posed, or in other words the probability of an adverse effect. Ideally the risk characterisation should quantify and describe the nature of the risk and is typically carried out using hazard quotient and/or probabilistic risk assessment method (Urban & Cook, 1986; Solomon et al., 2000). Due to the lack of environmental concentrations and toxicity data on the fungicides used in viticultural production systems of Australia, it is currently not possible to characterise the risks for fungicides other than Cu with any degree of certainty. The data on Cu in vineyards soils in 10 different regions of Australia from the survey of Wightwick et al. (2008) can be compared to the reported hazardous concentration values (Frampton et al., 2006; Jansch et al., 2007). In doing this only one of the 98 vineyards exceeded the lethal HC₅ to soil invertebrates of 183 mg/kg total Cu, whilst 44% of the vineyards exceeded the sub-lethal HC₅ to soil organisms of 55 mg/kg total Cu. Although there is a relatively high degree of uncertainty around these

estimated HC₅ values, for instance the 95% confidence interval for the sub-lethal HC₅ ranges from 28 – 92 mg/kg total. Nonetheless it appears that at present the accumulation of Cu in Australian vineyard soils is unlikely to be causing lethal toxic effects to soil invertebrates in most situations but may be causing sub-lethal effects to invertebrates and microbial processes. Ecotoxicological data for invertebrates suggests that the earthworm *A. caliginosa* is the most sensitive species. This is of significance as it is also one of the most abundant earthworms in Australian vineyard soils, thus representing an important keystone species to protect. Despite the likely risks, at present there is currently insufficient exposure and effect data for which to even attempt to characterise the risks of the synthetic organic fungicides and to the other risk scenarios, such as the transport to surface waters and leaching to groundwater.

From a risk management perspective, the available information on the fate, behaviour and toxicity of fungicides can be used to indicate the relative risks posed by the different chemical classes. This is of importance as there is a trend for horticultural industries to move away from using copper-based and dithiocarbamates fungicides to the newer triazole and strobilurin fungicides. The increased use of dithiocarbamates and strobilurins over copper-based fungicides is likely to result in a decreased risk to soil organisms due to their much lower persistence in soil (Table 6). Furthermore, a move away from copper-based fungicides is likely to result in a decreased risk to aquatic organisms, particularly if dithiocarbamates and triazoles are used.

6. Policy perspectives on assessing and managing ecological risks associated with fungicide use

Scientific information on ecological risks associated with fungicide use needs to be fed back into the wider policy/regulatory frameworks and processes to enable effective management of these risks. This section provides perspectives on the needs and mechanisms for linking science with policy in the management of ecological risks associated with fungicide use.

6.1 Regulatory and policy framework for agricultural chemicals

At the international level, policy development in relation to chemicals dates back to the 1800's, with the St Petersburg Declaration, which marked the need for more information regarding chemicals (Selin, 2010). In 1992, Agenda 21 was adopted at a United National Conference on the Environment thus instigating significant developments in the management of chemicals. This included introducing scientific assessments (risk and hazard) to evaluate the environmental impact of chemicals. More specifically, instruments such as the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade, and the Stockholm Convention on Persistent Organic Pollutants have been introduced to provide for a national decision-making process on the import and export of a range of chemicals including fungicides. Additionally, the Globally Harmonized System for the Classification and Labelling of Chemicals was introduced in 2006 to ensure physical hazards and toxicity information is made available to enhance protection of human health and the environment (UNEP, 2006). More recently, the Strategic Approach to International Chemicals Management 2006 (SAICM) was established, which aims to get the international community to work more co-operatively to protect health and the environment throughout the chemical life cycle. A positive step forward under the SAICM is the requirement for science based approaches to

be applied to new chemicals, existing chemicals, tools and strategies for assessment. Additionally, SAICM outlines the need for civil society and industry to work co-operatively together as well as the need for research into identifying the effects of chemicals to humans and the environment, including technologies to assess these impacts (UNEP, 2006).

The regulation of agricultural chemicals in Australia is complex. In summary, the national government, through the Australian Pesticide and Veterinary Medicines' Authority (APVMA), has responsibility for registration of chemical products through to the point of retail sale. The state and territory governments are responsible for controlling the use of these chemical products. Before registration of a chemical is approved by the APVMA, the chemical product is assessed for its likely impact on human health and the environment. This is a process whereby scientific and hazard assessments are used as part of the policy development aimed at assessing whether a chemical product is 'safe' to be used by industry and the general public, while considering impacts to trade, human health, the environment and animal welfare. The current framework underpinning policy on the management of agricultural chemicals (including fungicides) is focussed on assessing the 'input' standard. That is, understanding the impacts that chemicals have prior to registration and use. However, in Australia there appears to be little or no assessment of the 'performance' standard. For instance, there are essentially no structured ongoing monitoring programs in Australia to determine the presence, concentrations and long term impact of agricultural chemicals in the environment post registration (Wightwick & Allinson, 2007). This represents a significant lack of knowledge in relation to the potential long term impacts of fungicides in the natural environment. The regulatory framework in Australia does recognise that certain chemicals may pose a high risk and where identified individuals are required to undertake specific training and in some cases licensing to be able to use the chemical. From a policy perspective this places a greater emphasis on the need for assessing the 'performance' standards of these chemicals to ensure there is minimal or no impact to chemical users and the environment. At present the triggers for identifying high risk chemicals in Australia occurs in a somewhat ad-hoc fashion predominately being through the APVMA's adverse experience reporting system, those identified in other jurisdictions, and due to concerns raised by community groups.

In Australia, more needs to be undertaken at the national and local levels to not only implement international arrangements, but also further link science and policy through increased research into the longer term effects of chemicals and their presence in the environment (i.e. to assess the 'performance' standard of the chemical product), throughout the chemicals 'life cycle'. The information gathered from this type of research can be used to inform regulators and, where required, change the existing controls on a particular chemical product.

6.2 The pesticide policy debate

Communities are becoming more and more aware that the mis- or overuse of agrochemicals including pesticides may harm aquatic and terrestrial organisms, and potentially change the normal structure and function of ecosystems. As a result, the need to protect the natural environment has become part of the mainstream public policy debate. It is therefore important to understand the external impacts on primary production and the broader community resulting from the use of agricultural chemicals. The externalities and adverse effects of agrochemicals are said to be present when the utility to an individual depends not only on the goods and services the individuals purchase and consume but also on the activity of some

other individual(s), i.e. "where individual A's welfare depends on a range of goods and services which they consume (x_1, x_2, \dots, x_n) as well as on some activity, Y , carried out by another individual, B " (Cullis & Jones, 1992). Moreover, the "distinguishing feature of an externality is that it is an interdependence that occurs outside of the price mechanism that is not compensated" (Cullis & Jones, 1992). The externalities relating to fungicides are where they enter the natural environment from a single or group of primary producers or other land managers, and affect other users of water, resulting in a loss of recreation amenity, drinking water quality/supply and income from commercial activities. These externalities can have adverse human health and environmental impacts. Fungicide pollution can occur: from producers to producers; producers to consumers and consumers to consumers. The most significant type of relationship is the producer-consumer interaction. This 'many to many' interaction is the dominant form for agrochemical pollution (Herath, 1998). Furthermore, fungicide pollution is not easily visible or detected, so the potential environmental risks do not evoke an immediate response, as it can take place over many years and may be as a result of many different land uses within a catchment. It tends to be only when a major incident occurs that the extent of these externalities is recognised. Consequently, the costs of agrochemicals are generally borne by the affected groups who, in the absence of a market, are not compensated by the polluters. Therefore, it is important that more research and assessment of the long term 'performance' standard of fungicides and chemicals in general, throughout their life cycle, is undertaken. This will ensure that there are no further repeats of problems caused by legacy chemicals, such as dichlorodiphenyltrichloroethane (DDT) (APVMA, 2010b), where it has taken a long period of time to fully understand the impact the chemical and its metabolites have had and are having on the natural environment.

It is clear that science needs to be closely linked to policy development and in turn policy needs to inform the science, to improve the management of ecological risks associated with agrochemical use throughout the supply chain (from manufacture to use). This process is referred to as an evidence based policy approach, or an approach that "helps people make well informed decisions about policies, programs and projects by putting the best available evidence from research at the heart of policy development and implementation" (Davies, 1999). Such an approach includes up to eight stages including identifying issues; policy analysis (i.e. using evidence to develop options and make decisions); identifying policy instruments (e.g. advocacy, monetary, legislative); consultation; co-ordination; decision making; implementation; and evaluation (Althaus et al., 2007). Evidence-based approaches differ significantly from opinion-based policy, which relies on selective use of evidence or untested views of individuals or groups, often established by an ideological position or prejudices. Worldwide evidence-based policy approaches have become a major part of many governments' policy and regulatory development as it enhances industry and community confidence in government decisions. The ongoing challenge for governments is to form stronger links between science and policy and to ensure policy assists in determining the science priorities, to ensure that fungicides are managed throughout the chemical life cycle to ensure productivity continues whilst protecting human health and the environment.

Presently, science informs policy on the management of agrochemicals predominately through structured regulatory and policy frameworks that form part of pre-registration assessments. Policy also informs the direction of science where the community has pressured the regulator to undertake further review of the risks a chemical product may be having on the environment or to human health (whether that be real or perceived). Furthermore, in Australia, the APVMA has in place an adverse experience reporting system

and existing chemicals review program to identify priority risk chemicals. This provides a more structured process whereby policy makers can identify and direct scientific research needs, which is crucial given the large number of agricultural chemicals registered for use (i.e. currently in Australia there are over 2000 active ingredients registered for use). Scientific information for environmental risk assessments is then used by policy makers and regulators to assess whether a chemical product needs to be reviewed for registration amendments such as label changes, changes to the method of manufacture, suspension and/or cancellation of registration and approval (APVMA, 2010a). The insecticide DDT and more recently the fungicide quintozene are two contrasting examples of where science has informed the policy debate to instigate management actions to reduce environmental risks associated with agrochemical use.

DDT is a historical example where science and policy did not initially work cohesively enough to manage the ecological risk. DDT was first used in Australian agriculture during the 1950's as a highly effective broad-spectrum insecticide. Ecological and human health concerns about DDT were first raised in Australia during the 1960's. However, despite the known risks of DDT, its use was not phased out until the 1980's (APVMA, 2010b). This was largely due to ongoing economic debate around the benefits of DDT outweighing the disadvantages. The community and subsequent governments are still bearing the costs ('externalities') from the legacy of DDT due to slow uptake of scientific knowledge on the environmental risks of DDT by policy makers. To avoid repeats of legacy chemicals such as DDT, it is clear that science and policy need to work together more closely and take a more proactive approach to understanding and managing environment risks.

In Australia, the recent suspension of the use of the fungicide quintozene (APVMA, 2010a) is an example of where science and policy have communicated more cohesively. Dioxins can be un-intentionally formed during the manufacture of some agricultural chemicals. This may present an environmental concern when the chemicals are used as dioxins are recognised as persistent pollutants of concern (Holt et al., 2010). In recognition of the potential risks, Australian researchers took a somewhat more proactive approach by analysing the concentration of dioxins in 27 different current use agrochemical formulations. This research highlighted that unacceptably high concentrations of dioxins were present in quintozene formulations (Holt et al., 2010). The scientists notified the APVMA of this concern in June 2009 and following results of confirmatory analysis the APVMA initiated regulatory action and suspended the use of quintozene in April 2010. Compared to the DDT example, this more cohesive and timely action between science and policy will help to avert further issues relating to the legacy of dioxins in the environment resulting from use of quintozene. The challenge is for science and policy to identify and action similar issues in a timely and structured manner.

In the future, the pesticide policy debate is likely to be complicated by the large projected increase in the human population, from 6.5 billion people in 2005 to 9 billion people in 2050 (United Nations, 2002). The predicted increase in population will place huge demands on natural resources on which primary production depends for food production. In order to increase food production, it is likely that there will be significant increases in the use of agricultural chemical, including fungicides, to meet this world demand. This will place even further pressure on science and policy to work together to effectively manage the competing pressures on controlling environmental and human health risk, meeting international and national legislative obligations, whilst ensuring pests and disease are controlled to guarantee crop quality and production.

7. Conclusions and future research needs

Fungicides are widely used in horticultural production systems to ensure crop quality and production. However, the use of such fungicides may cause adverse effects to terrestrial and aquatic ecosystems if fungicide residues persist in soil, or if they migrate off-site to surface and ground waters. Whilst a great deal is known about the fate, behaviour and toxicity of Cu in both terrestrial and aquatic environments, comparatively little information has been reported for the synthetic organic fungicide compounds. The accumulation of Cu in surface soils following the use of copper fungicides has been reported in many regions of the world, and there is evidence suggesting adverse effects to earthworms and soil micro-organisms. However, only a small number of studies have measured the persistence of synthetic organic fungicide compounds in the soils of horticultural properties, providing a limited knowledge base on which to assess the likely risks. Similarly, only a few studies have sought to investigate the off-site movement of fungicides and their presence in aquatic environments. Assessments of the behaviour and toxicity of fungicides in the environment are complicated by the environmental and biological availability, which varies greatly across different soils, sediment, and waters (i.e. large influence of pH, clay, organic matter). Using ecological risk assessment principles, it is currently not possible to characterise the environmental risks of fungicides with any degree of certainty. An exception being risks of Cu accumulation to soil organisms, but, even here there is a high degree of uncertainty due to large variability in ecotoxicological effect values across different soil types. The relative risks of different fungicides needs to be considered when making recommendations on the future management of fungicide use.

Current regulatory/policy frameworks both in Australia and worldwide focus on assessment of the 'input' standard of agricultural chemical products prior to their release onto the market. However, significantly more work is needed to assess the 'performance standard' of registered chemicals over the longer term to ensure the environment and human health are not adversely impacted throughout their life cycle. Stronger linkages between science and policy will ensure the more effective and timely assessment and management of ecological risks associated with agricultural chemical use.

Further research into the potential environmental risks posed by fungicide use is needed so that evidence-based policy decisions can be made on the future management of fungicide use in horticultural production systems. This research needs to focus on generating toxicity data for more species/endpoints, in particular aquatic fungi, microbial processes, and earthworms of agricultural relevance to improve the 'input' standard. Research also needs to focus on understanding the influence of differing soil, sediment and water properties and chemical mixtures on the behaviour and toxicity of fungicides in the environment. Field studies to determine environmental concentrations, in particular for synthetic organic fungicide compounds, are also of paramount importance in being able to assess actual environmental risks (i.e. 'performance' standard) throughout the chemicals life cycle. Further information on the types and amounts of fungicides being used is needed to focus this research on priority fungicides of concern.

8. References

ANZECC & ARMCANZ (2000). *Australian and New Zealand guidelines for fresh and marine water quality. National Water Quality Management Strategy paper No.4.* Australian and

- New Zealand Environment and Conservation Council and Agriculture & Resource Management Council of Australia and New Zealand, Canberra, Australia.
- Althaus, C.; Bridgman, P. & Davis, G. (2007). *The Australian Policy Handbook*. Allen & Urwen, Sydney, NSW, Australia.
- APVMA (2010a). *Chemical review program*. Australian Pesticides and Veterinary Medicines Authority, Kingston, ACT, Australia. Available at: <http://www.apvma.gov.au/products/review/index.php>.
- APVMA (2010b). *The history of 'organochlorine' pesticides in Australia*. Australian Pesticides and Veterinary Medicines Authority, Kingston, ACT, Australia.
- Arias, M.; Lopez, E.; Fernandez, D. & Soto, B. (2004). Copper distribution and dynamics in acid vineyard soils treated with copper-based fungicides. *Soil Science*. 169; 796 - 805.
- Arias, M.; Paradelo, M.; Lopez, E. & Simal-Gandara, J. (2006). Influence of pH and soil copper on adsorption of metalaxyl and penconazole by the surface layer of vineyard soils. *Journal of Agricultural and Food Chemistry*. 54; 8155 - 8162.
- Arias-Estevez, M.; Lopez-Periago, E.; Martinez-Carballo, E.; Simal-Gandara, J.; Mejuto, J-C. & Garcia-Rio, L. (2008). The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, Ecosystems & Environment*. 123; 247 - 260.
- AWRI. (2010). *Agrochemicals registered for use in Australian viticulture 10/11*. Australian Wine Research Institute. Glen Osmond, SA, Australia.
- Bååth, E. (1989). Effects of heavy metals in soil on microbial processes and populations (a review). *Water, Air, & Soil Pollution*. 47; 335-379.
- Banks, KE.; Hunter, DH. & Wachal DJ. (2005). Chlorpyrifos in surface waters before and after a federally mandated ban. *Environment International*. 31; 351 - 356.
- Bermudez-Couso, A.; Arias-Estevez, M.; Novoa-Munoz, JC.; Lopez-Periago, E.; Soto-Gonzalez, B. & Simal-Gandara, J. (2007). Seasonal distributions of fungicides in soils and sediments of a small river basin partially devoted to vineyards. *Water Research*. 41; 4515-4525.
- Bogomolov, DM.; Chen, SK.; Parmelee, SS. & 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.
- Boudesocque, S.; Guillon, E.; Aplincourt, M.; Marceau, E. & Stievano, L. (2007). Sorption of Cu(II) onto vineyard soils: Macroscopic and spectroscopic investigations. *Journal of Colloid and Interface Science*. 307; 40-49.
- Broos, K.; Warne, MSJ.; Heemsbergen, DA.; Stevens, D.; Barnes, MB.; Correll, RL. & McLaughlin, MJ. (2007). Soil factors controlling the toxicity of copper and zinc to microbial processes in Australian soils. *Environmental Toxicology & Chemistry*. 26; 583-590.
- Bruins, MR.; Kapil, S. & Oehme, FW. (2000). Microbial resistance to metals in the environment. *Ecotoxicology and Environmental Safety*. 45; 198-207.
- Brun, LA.; Maillat, J.; Richarte, J.; Herrmann, P. & Remy JC. (1998). Relationships between extractable copper, soil properties and copper uptake by wild plants in vineyard soils. *Environmental pollution*. 102; 151-161.
- Bunemann, EK.; Schwenke, GD. & Van Zwieten, L. (2006). Impact of agricultural inputs on soil organisms - a review. *Australian Journal of Soil Research*. 44; 379 - 406.

- Burton, ED.; Phillips, IR.; Hawker, DW. & Lamb, DT, (2005), Copper behaviour in a Podsol. 1. pH-dependent sorption-desorption, sorption isotherm analysis, and aqueous speciation modelling. *Australian Journal of Soil Research*. 43; 491-501.
- Chaignon, V.; Sanchez-Neira, I.; Herrmann, P. & Hinsinger, JB. (2003). Copper bioavailability and extractability as related to chemical properties of contaminated soils from a vine-growing area. *Environmental Pollution*. 123; 229-238.
- Criel, P.; Lock, K.; Van Eeckhout, H.; Oorts, K.; Smolders, E. & Janssen, CR. (2008). Influence of soil properties on copper toxicity for two soil invertebrates. *Environmental Toxicology & Chemistry*. 27, 1748 - 1755.
- Cullis, J & Jones, P. (1992). *Public Finance and Public Choice, Analytical Perspectives*, McGraw-Hill Book Company, London.
- Davies, P. (1999). What is Evidence-Based Education? *British Journal of Educational Studies*. 47; 108 - 121.
- Delas, J. (1981). Copper toxicity in viticultural soils. In *Copper in animal wastes and sewage sludge*. Eds L'Hermite, P. & Dehandtschutter, J. pp. 136-142. D. Reidel Publishing Company, Netherlands.
- Deluisa, 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 & Plant Analysis*. 27; 1537-1548.
- Eijsackers, H.; Beneke, P.; Maboeta, M.; Louw, JPE. & Reinecke, AJ. (2005). The implications of copper fungicide usage in vineyards for earthworm activity and resulting sustainable soil quality. *Ecotoxicology and Environmental Safety*. 62; 99-111.
- Fairbrother, A.; Wenstel, R.; Sappington, K. & Wood, W. (2007). Framework for Metals Risk Assessment. *Ecotoxicology & Environmental Safety*. 68; 145-227
- Fernández-Calviño, D.; Rodríguez-Suárez, JA.; López-Periágo, E.; Arias-Estévez, M. & Simal-Gándara, J. (2008). Copper content of soils and river sediments in a winegrowing area, and its distribution among soil or sediment components. *Geoderma*. 145; 91-97.
- Fernández-Calviño, D.; Nóvoa-Muñoz, JC.; Díaz-Raviña, M. & Arias-Estévez, M. (2009). Copper accumulation and fractionation in vineyard soils from temperate humid zone (NW Iberian Peninsula). *Geoderma*. 153; 119-129.
- Frampton, GK.; Jansch, S.; Scott-Fordsmand, JJ.; Rombke, J. & Van den Brink PJ. (2006). Effects of pesticides on soil invertebrates in laboratory studies: a review and analysis using species sensitivity distributions. *Environmental Toxicology & Chemistry*. 25; 2480 - 2489.
- 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.
- Gevao, B.; Semple, K.T. & Jones, K.C. (2000). Bound pesticide residues in soils: a review. *Environmental Pollution*. 108; 3 - 14.
- Giller, KE.; Witter, E. & McGrath, S. (1998). Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review. *Soil Biology & Biochemistry*. 30; 1389 - 1414.
- Gillom, RJ.; Barbash, JE.; Crawford, CG.; Hamilton, PA.; Martin, JD.; Nakagaki, N.; Nowell, LH.; Scot, JC.; Stackleberg, PE.; Thelin, GP. & Wolock, DM. (2006). *The quality of our nation's waters - pesticides in the nation's streams and groundwater, 1992 - 2001*. U.S

- Geological Survey Circular 1291*. United States Geological Survey, Reston, Virginia, USA.
- Gray, C.W. & McLaren, R.G. (2006). Soil factors affecting heavy metal solubility in some New Zealand soils. *Water Air & Soil Pollution*. 175; 3-14.
- Gregoire, C.; Payraudeau, S. & Domange, N. (2010). Use and fate of 17 pesticides applied on a vineyard catchment. *International Journal of Environmental Analytical Chemistry*. 90; 406 - 420.
- Harmsen, J. (2007). Measuring bioavailability: from a scientific approach to standard methods. *Journal of Environmental Quality*. 36; 1420 - 1428.
- Herath, G. (1998). *Agrochemical use and the environment in Australia*. Department of Business, La Trobe University, Victoria, Australia.
- Hildebrandt, A.; Guillamón, M.; Lacorte, S.; Tauler, R. & Barceló, D. (2008). Impact of pesticides used in agriculture and vineyards to surface and groundwater quality (North Spain). *Water Research*. 42; 3315-3326.
- Holt, E.; Weber, R.; Stevenson, G & Gaus, C. (2010). Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) impurities in pesticides: a neglected source of contemporary relevance. *Environmental Science & Technology*. 44; 5409 - 5415.
- IUPAC (2010). *IUPAC Pesticide properties database*. International Union of Pure and Applied Chemistry. Available at: <http://agrochemicals.iupac.org>
- Jansch, S.; Rombke, J.; Schallanab, H-J. & Terytze, K. (2007). Derivation of soil values for the path 'soil-soil organisms' for metals and selected organic compounds using species sensitivity distributions. *Environmental Science and Pollution Research*. 14; 308 - 318.
- Katayama, A.; Bhula, R.; Burns, G.R.; Carazo, E.; Felsot, A.; Hamilton, D.; Harris, C.; Kim, Y.H.; Kleter, G.; Koedel, W.; Linders, J.; Peijnenburg, J.G.M.W.; Sabljic, A.; Stephenson, R.G.; Racke, D.K.; Rubin, B.; Tanaka, K.; Unsworth, J. & Wauchope, R.D. (2010). Bioavailability of xenobiotics in the soil environment. *Reviews of Environmental Contamination and Toxicology*. 203; 1 - 86.
- Kibria, G.; Yousuf Haroon, A.K.; Nugegoda, D. & Rose, G. (2010). *Climate change and chemicals. Environmental and biological aspects*. New India Publishing Agency, Pitam Pura, New Delhi.
- Kim, B.; McBride, M. & Hay AG (2008) Urease activity in aged copper and zinc soils: relationship to CaCl₂-extractable metals and Cu²⁺ activity. *Environmental Toxicology & Chemistry*. 27; 2469 - 2475.
- Komarek, M.; Cadkova, E.; Chrastny, V.; Bordas, F. & Bollinger, J-C. (2010). Contamination of vineyard soils with fungicides: A review of environmental and toxicological aspects. *Environment International*. 36; 138 - 151.
- Kookana, R.S.; 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 (5); 715 - 764.
- Kookana, R.; Kibria, G., Barnes, M. & Correll, R. (2003). *First tier assessment of the risks associated with pesticides used in Goulburn-Murray irrigation areas*. Goulburn-Murray Rural Water Authority, Victoria and CSIRO, SA, Australia.
- Kungolos, A.; Emmanouil, C.; Tsiroidis, V. & Tsiropoulos, N. (2009). Evaluation of toxic and interactive toxic effects of three agrochemicals and copper using a battery of microbiotests. *Science of the Total Environment*. 407; 4610-4615.

- Leistra, M. & Matser, A.M. (2005). Adsorption, transformation and bioavailability of the fungicides carbendazim and iprodione in soil, alone and in combination. *Journal of Environmental Health and Science Part B – Pesticides, food contaminants, and agricultural wastes*. 39; 1 – 17.
- Ma, Y.; Lombi, E.; Nolan, A. & McLaughlin, MJ. (2006a). Short-term natural attenuation of copper in soils: effects of time, temperature, and soil characteristics. *Environmental Toxicology & Chemistry*. 25; 652 – 658.
- Maboeta, MS.; Reinecke, SA. & Reinecke, AJ. (2003). Linking lysosomal biomarker and population responses in a field population of *Aporrectodea caliginosa* (Oligochaeta) exposed to the fungicide copper oxychloride. *Ecotoxicology & Environmental Safety*. 56; 411-418.
- MacGregor, A.; Mollah, M.I 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. In *Proceedings, Interact 2004, Gold Coast, July 2004*. Australasian Society of Ecotoxicology & Royal Australian Chemical Institute, Australia.
- Maltby, L.; Brock TCM. & Van den Brink PJ. (2009). Fungicide risk assessment for aquatic ecosystems: importance of interspecific variation, toxic mode of action, and exposure regime. *Environmental Science & Technology*. 43; 7556 – 7563.
- Markich, SJ.; Warne, MSJ.; 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.
- 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, May 7 – 9, 1981*. Ed. Loneragan, JF.; Robson, AD. & Graham, RD. pp. 25-45. Academic Press.
- McConnell, S.; Wightwick, A.; Smith, T. & Porteous, C. (2003). *Code of Environmental Best Practice for Viticulture – Sunraysia region. Volume 1 – Environmental best practices*. Department of Primary Industries. ISBN 1 74106 638 7. Victoria, Australia.
- McLaughlin, MJ.; Hamon, RE.; McLaren, RG.; Speir, TW. & Rogers, SL. (2000). Review: a bioavailability based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research*. 38; 1037 - 1086.
- McLaughlin, MJ. (2001). *Fact sheet on environmental risk assessment: Ageing of metals in soils changes bioavailability*. International Council on Metals and the Environment.
- Merli, A.; Reeves, G.; Meregalli, G.; Piccinini, A.; Negri, I.; Carmignano, P.; Balderacchi, M. & Capri, E. (2010). Surface-water exposure to quinoxifen: Assessment in landscape vineyards. *Journal of Hydrology*. 383; 62-72.
- 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.
- Mirlean, N.; Roisenberg, A. & Chies, JO. (2007). Metal contamination of vineyard soils in wet subtropics (southern Brazil). *Environmental Pollution*. 149, 10-17.
- Morgan, RK. & Taylor, E. (2003). Copper accumulation in vineyard soils in New Zealand. *Environmental Sciences*. 1; 139 - 167.

- Nicholas, P.; Magarey, P. & Wachtel, M. (1994). *Grape Production Series No. 1. Diseases and Pests*. Winetitles, Adelaide, SA, Australia.
- OIECC. (2009). *National standard for organic and bio-dynamic produce*. Edition 3.4. Organic Industry Export Consultative Committee, Canberra, ACT, Australia.
- Olayinka, A. & Babalola, GO. (2001). Effects of copper sulphate application on microbial numbers and respiration, nitrifier and urease activities, and nitrogen and phosphorus mineralization in an alfisol. *Biological Agriculture & Horticulture*. 19; 1-8.
- Oorts, K.; Bronckaers, H. & Smolders, E. (2006a) Discrepancy of the microbial response to elevated copper between freshly spiked and long-term contaminated soils. *Environmental Toxicology & Chemistry*. 25; 845-853.
- Oorts, K.; Ghesquiere, U.; Swinnen, K. & Smolders, E. (2006b). Soil properties affecting the toxicity of CuCl_2 and NiCl_2 for soil microbial processes in freshly spiked soils. *Environmental Toxicology & Chemistry*. 25; 836-844.
- Paoletti, MG.; Sommaggio, D.; Favretto, MR.; Petruzzelli, G.; Pezzarossa, B. & Barbafieri, M. (1998). Earthworms as useful bioindicators of agroecosystem sustainability in orchards and vineyards with different inputs. *Applied Soil Ecology*. 10; 137-150.
- Pickering, WF. (1979). Copper retention by soil/sediment components. In *Copper in the environment*. Ed. Nriagu, JO. pp. 217 - 253. John Wiley, New York, USA.
- Pietrzak, U. & McPhail, DC. (2004). Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. *Geoderma*. 122; 151-166
- Peijnenburg, WJGM. & Jager, T. (2003). Monitoring approaches to assess bioaccessibility and bioavailability of metals: Matrix issues. *Ecotoxicology and Environmental Safety*. 56, 63-77.
- Peijnenburg, W. & Vijver, MG. (2007). Metal-specific interactions at the interface of chemistry and biology. *Pure and Applied Chemistry*. 79; 2351-2366.
- Peijnenburg, WJGM.; Zablotkaja, M. & Vijver, MG. (2007). Monitoring metals in terrestrial environments within a bioavailability framework and a focus on soil extraction. *Ecotoxicology and Environmental Safety*. 67; 163-179
- Rabiet, M.; Margoum, C.; Gouy, V.; Carluer, N. & Coquery, M. (2010). Assessing pesticide concentrations and fluxes in the stream of a small vineyard catchment - Effect of sampling frequency. *Environmental Pollution*. 158; 737-748.
- Radcliffe JC. (2002). *Pesticide use in Australia: a review*. Australian Academy of Technological Sciences and Engineering, Victoria, Australia.
- Ranjard, L.; Echairi, A.; Nowak, V.; Lejon, DPH.; Nouaim, R. & Chaussod, R. (2006). Field and microcosm experiments to evaluate the effects of agricultural Cu treatment on the density and genetic structure of microbial communities in two different soils. *Fems Microbiology Ecology*. 58; 303-315.
- Rial-Otero, R.; Gonza lez-Rodriguez, R.; Cancho-Grande, B. & Simal-Gandara, J. (2004). Parameters Affecting Extraction of Selected Fungicides from Vineyard Soils. *Journal of Agricultural & Food Chemistry*. 52; 7227-7234.
- Ribolzi, O.; Valles, V.; Gomez, L. & Voltz, M. (2002). Speciation and origin of particulate copper in runoff water from a Mediterranean vineyard catchment. *Environmental Pollution*. 117; 261 - 271.
- Rose, G. & Kibria, G. (2007). Pesticide and heavy metal residues in Goulburn Murray irrigation water 2004 - 2006. *Australasian Journal of Ecotoxicology*. 13; 65 - 79.

- Russell, PE. (2005). A century of fungicide evolution. *Journal of Agricultural Science*. 143; 11 - 25.
- Sauve, S.; Hendershot, W. & Allen, HE. (2000). Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environmental Science & Technology*. 34; 1125-1131.
- Scott-Fordsmand, 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 & Chemistry*. 19; 1774 - 1780.
- Selin, H. (2010). *Global Governance of Hazardous Chemicals: Challenges of Multilevel Management*. The MIT Press, Cambridge, Massachusetts, London, England.
- Solomon, K.; Giesy, & Jones, P. (2000). Probabilistic risk assessment of agrochemicals in the environment. *Crop Protection*. 19; 649 - 655.
- 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, May 7 - 9, 1981*. Ed. Loneragan, JF.; Robson, AD. & Graham, RD. pp. 69-95. Academic Press.
- Strawn, DG. & Baker, LL. (2008). Speciation of Cu in a contaminated agricultural soil measured by XAFS, μ -XAFS, and μ -XRF. *Environmental Science & Technology*. 42; 37-42.
- Swift, RS.; Rate, AW. & McLaren, RG. (1995). Interactions of copper with soil humic substances. In *Environmental impact of soil component interactions: metals, other inorganics, and microbial activities*. Ed. Huang, PM. pp. 19 - 27. CRC Press.
- 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, May 7 - 9, 1981*. Ed. Loneragan, JF.; Robson, AD. & Graham, RD. pp. 119-137. Academic Press.
- Thomson, LJ. (2006). Influence of reduced irrigation on beneficial invertebrates in vineyards. *Australian Journal of Experimental Agriculture*. 46; 1389 - 1395.
- Tomlin, CDS. (2000). *The pesticide manual (12th ed)*. British Crop Protection Council.
- UNEP. (2006). *Strategic Approach to International Chemical Management*. United Nations Environment Programme.
- United Nations. (2002). *World Population Prospects, the 2002 revision highlights*. United Nations, New York. Available at:
<http://www.un.org/esa/population/publications/wpp2002/WPP2002-HIGHLIGHTSrev1.PDF>
- Urban, DJ & Cook, NJ. (1986). Standard evaluation procedure for ecological risk assessment (EPA-540/9-85-001). United States Environmental Protection Agency, Washington DC, USA.
- US EPA (1998). *Guidelines for Ecological Risk Assessment*. United States Environmental Protection Agency, Washington, DC.
- US EPA (2010). *ECOTOX database*. United States Environmental Protection Agency. Available at: <http://cfpub.epa.gov/ecotox/>.
- USGS (2010). Pesticide national synthesis project: Pesticide use. United States Geological Survey, Reston Virginia, USA. Available at:
<http://water.usgs.gov/nawqa/pnsp/usage/maps/>

- 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.
- Van Zwieten, M.; Stovold, G. & Van Zwieten, L. (2007). *Literature review and inventory of alternatives to copper: for disease control in the Australian organic industry (Publication no. 07/110)*. Rural Industries Research and Development Corporation (RIRDC). ISBN 1 74151 507 6. Kingston, ACT, Australia. Available at <https://rirdc.infoservices.com.au/downloads/07-110.pdf>.
- Vavoulidou, E.; Avramides, EJ.; Papadopoulos, P. & Dimirkou, A. (2005). Copper content in agricultural soils related to cropping systems in different regions of Greece. *Communications in Soil Science & Plant Analysis*. 36; 759 - 773.
- Vitanovic, E.; Vidacek, Z.; Katalinic, M.; Kacic, S. & Milos, B. (2010) Copper in surface soils of Croatian vineyard soils. *Journal of Food, Agriculture & Environment*. 8; 268 - 274.
- Wang, Q-Y.; Zhou, D-M. & Cang, L. (2009). Microbial and enzyme properties of apple orchard soil as affected by long-term application of copper fungicide. *Soil Biology & Biochemistry*. 41; 1504 - 1509.
- Wauchope, D. (2005). *The ARS pesticides properties database*. United States Department of Agriculture.
- Weston, DP.; You, J. & Lydy, MJ. (2004). Distribution and Toxicity of Sediment-Associated Pesticides in Agriculture-Dominated Water Bodies of California's Central Valley *Environmental Science & Technology*. 38; 2752 - 2759.
- Wightwick, A. & Allinson, G. (2007). Pesticide residues in Victorian waterways: a review. *Australasian Journal of Ecotoxicology*. 13; 91 - 112.
- Wightwick, A.; Mollah, M.; Partington, D. & Allinson, G. (2008). Copper fungicide residues in Australian vineyard soils. *Journal of Agricultural & Food Chemistry*. 56; 2457 - 2464.
- Wightwick, AM.; Salzman, S.; Allinson, G.; Reichman, S. & Menzies, NW (2010). Inter-regional variability in environmental availability of fungicide derived copper in vineyard soils: an Australian case study. *Journal of Agricultural & Food Chemistry*. 58; 449 - 457.
- Weissmah, K.W. & Sedlak, DL. (2000). Effect of metal complexation on the degradation of dithiocarbamate fungicides. *Environmental Toxicology & Chemistry*. 19; 820 - 826.



Fungicides

Edited by Odile Carisse

ISBN 978-953-307-266-1

Hard cover, 538 pages

Publisher InTech

Published online 14, December, 2010

Published in print edition December, 2010

Plant and plant products are affected by a large number of plant pathogens among which fungal pathogens. These diseases play a major role in the current deficit of food supply worldwide. Various control strategies were developed to reduce the negative effects of diseases on food, fiber, and forest crops products. For the past fifty years fungicides have played a major role in the increased productivity of several crops in most parts of the world. Although fungicide treatments are a key component of disease management, the emergence of resistance, their introduction into the environment and their toxic effect on human, animal, non-target microorganisms and beneficial organisms has become an important factor in limiting the durability of fungicide effectiveness and usefulness. This book contains 25 chapters on various aspects of fungicide science from efficacy to resistance, toxicology and development of new fungicides that provides a comprehensive and authoritative account for the role of fungicides in modern agriculture.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Adam Wightwick, Robert Walters, Graeme Allinson, Suzanne Reichman and Neal Menzies (2010). Environmental Risks of Fungicides Used in Horticultural Production Systems, *Fungicides*, Odile Carisse (Ed.), ISBN: 978-953-307-266-1, InTech, Available from:
<http://www.intechopen.com/books/fungicides/environmental-risks-of-fungicides-used-in-horticultural-production-systems>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2010 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.