Factors Influencing the Availability of Copper in Australian Vineyard Soils

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Abstract
The regular use of copper-based fungicides in vineyards results in an accumulation of copper (Cu) in the surface soils which may be harmful to soil organisms and plants and have implications for the long-term management of affected land. This study investigated the factors (e.g. soil characteristics) influencing the availability of Cu in vineyard soils from 10 different regions of Australia. Concentrations of 0.01 M calcium chloride extractable Cu measured in surface soils collected from 98 different vineyards ranged from <0.1 to 0.94 mg/kg and accounted for 0.10 to 1.03% of the total Cu concentrations in the soils. Differences in the calcium chloride extractable Cu concentrations were related to the total Cu concentration of the soil. The extractable Cu was also related to soil properties, including pH, cation exchange capacity, exchangeable K, clay, silt, and calcium carbonate. The information generated from this study may prove useful in devising strategies to reduce the availability and toxicity of Cu in agricultural soils.

Key Words
Copper, vineyard, soil, fungicide, availability, risk assessment

Introduction
Copper-based fungicides (e.g. copper sulphate, copper oxychloride) have been used in vineyards throughout the world, including Australia, for many decades to protect against downy mildew (*Plasmopara viticola*). However, their use results in an accumulation of Cu in surface soils which can potentially impact on the biological health of the soil and have implications for the long-term management of affected land. For instance, Cu concentrations in the surface soils of vineyards with histories of Cu-fungicide use have been reported to range from 130 to 1280 mg kg^{-1} in European vineyards and to generally be in the range of 24 to 159 mg kg^{-1} but as high 249 mg kg^{-1} in Australian vineyards (Wightwick *et al.,* 2008). It has been reported that earthworm populations decreased and the structure of microbial communities changed, following applications of Cu-based fungicides (Maboeta *et al.,* 2002; 2003; Ranjard *et al.,* 2006).

Research is needed to understand the risks posed by Cu-fungicide residues in different soils/conditions and to devise appropriate risk management strategies if needed. However, it is not possible to make generic conclusions regarding the likely risks posed by Cu in vineyard soils based on total Cu concentration, since the availability of Cu in soil and toxicity to soil organisms and plants is known to vary greatly across soils with different physical-chemical properties. The availability of Cu in the soil is controlled by the total Cu concentration of the soil and by soil characteristics which influence the extent and strength of Cu adsorption in soil (e.g. pH, cation exchange capacity, clay content, and organic matter content). Accounting for differences in the availability of Cu presents a particular challenge from an Australian perspective, as there are approximately 60 different viticultural production regions with a wide variety of soil types (e.g. in terms of pH, texture, organic matter content). The objectives of this study were to:

- Determine the environmental availability of fungicide derived Cu in the surface soils of vineyards in 10 different viticultural regions of Australia.
- Investigate the factors correlated with differences in Cu availability between regions.

Methods

This study used surface soil (0 - 10cm) samples previously collected from 98 vineyards in 10 different grape-growing regions across five different states of Australia (Victoria, South Australia, New South Wales, Western Australia and Tasmania). Surface soil samples were also collected from areas of remnant vegetation in each region to act as "reference sites" that had not received any artificial inputs of Cu. The environmentally available Cu concentrations of these soils were determined using the 0.01 M calcium chloride ($CaCl_2$) soil extraction method. This method was selected over other approaches (e.g. EDTA extraction, free Cu^{2+} measurements, diffuse gradients in thin films) as it represents an acceptable immediate for determining freely available Cu in terms of ease of use, suitability for a range of different soils, and applicability to biological response. Copper and other elements in soil extracts were analysed by inductively coupled plasma emission spectrometry (ICP-ES). The soil samples had previously been analysed for total Cu and a range of different physical-chemical soil properties. Simple and multiple stepwise regression analysis was used to determine significant relationships between Cu availability and other parameters including total Cu concentration of the soil, physical-chemical soil properties, concentrations of other elements in the soil, and history of Cu-fungicide use.

Results

The $CaCl_2$ extractable Cu concentrations in the vineyard soils ranged from <0.1 to 0.94 mg/kg and accounted for 0.10 to 1.03% of the total Cu concentrations in the soils. With the exception of one site, $CaCl_2$ extractable Cu was not detected in the soil from the reference sites. Differences in the $CaCl_2$ extractable Cu concentrations were generally related to the total Cu concentration of the soil ($R^2 = 0.48$). This regression could be improved by including pH, clay, silt, exchangeable K, and calcium carbonate ($R^2 = 0.70$), with pH and clay content being the greatest contributors to the regression. Using simple linear regression only a weak relationship ($R^2 = 0.06$) could be found between pH and the concentration of $CaCl_2$ extractable Cu. However a polynomial regression indicated a U-shaped trend ($R^2 = 0.39$) suggesting that the $CaCl_2$ extractable Cu concentration increased with increasing soil acidity (pH < 7.5) and to a lesser extent with increasing soil alkalinity (pH > 8.5). Although there is uncertainty around the increase with increasing alkalinity as only 13 out of 62 data points were above pH 8.

Conclusion

The results from this study highlight the wide variation in Cu availability across different soils and the difficulties in adopting a one-size fits all approach to risk assessment and management in an Australian context. This study has identified the key soil properties that appear to be controlling Cu availability in Australian vineyard soils. Information on the influence of soil properties on Cu availability may also prove useful in devising strategies to reduce the availability and toxicity of Cu in agricultural soils, if deemed necessary. For example, controlling soil pH may prove to be a cost effective in-situ remediation strategy, as the pH of agricultural soils can be relatively easily manipulated through the use of lime. Further research underway is investigating the effects of accumulated Cu on soil microbial activity and the extent to which such effects on soil organisms are influenced by soil properties and how closely this is related to the available Cu concentration.

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