Sorption and bioavailability of copper as affected by recycled water sources

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Abstract
Copper (Cu) is applied in vineyards as a fungicide, and these soils are irrigated with recycled water sources that include raw, treated sewage effluent, winery wastewater and farm effluents. These are likely to affect the transformation and mobility of Cu in soils. Batch sorption studies and various microbial characteristics were used to investigate the effect of recycled water sources on Cu in 3 contrasting soils from South Australia varying in pH (4.88-7.83), texture and organic matter (2.5-7.2%). The soils were treated with copper nitrate solutions ranging in concentration from 0 – 400 mg Cu/L, and the adsorption of Cu was measured. The results indicated that adsorption was affected by both the soil type and the origin of recycled water. The adsorption of Cu was less in recycled water sources than in deionised water and decreased with increasing concentration of DOC in the recycled water. An incubation study was also performed to examine the influence of recycled water sources on the bioavailability of Cu as measured by microbial respiration. Respiration decreased significantly with increasing Cu concentration. Respiration, microbial biomass C and metabolic quotient were higher in the presence of recycled water than deionized water, but it varied among the effluents and soils.

Key Words
CO_2 production, qCO_2, substrate induced respiration (SIR), Freundlich isotherm, distribution coefficient.

Introduction
In a number of countries including Australia, the decrease in groundwater levels has been compounded by prolonged periods of drought or seasons of low rainfall. One possible approach by which the pressure on fresh water resources can be mitigated is by the recycled water technology. Recycled water can act both as a source and sink for heavy metals (Martin and Bullock 1994; Singh *et al.* 2005). Recycled water contains a range of heavy metals, and the concentration of these metals depends on the level of treatment; when recycled water is used for irrigation it increases the heavy metal content of soils. However various organic and inorganic components in recycled water immobilize metals through adsorption, complexation and precipitation, thereby affecting their bioavailability (Antoniadis and Alloway 2002). Recycled water sources, such as winery and piggery effluents in particular, contain carbon (dissolved and particulate), which is likely to interfere with metal dynamics in soil. Copper (Cu) enters the agricultural ecosystems through applications of Cu-containing fertilizers, manures (e.g. pig slurry), fungicides and liquid or solid wastes from mining and manufacturing industries (Saria *et al.* 2006).

There is a need to understand the factors such as soil pH, cation exchange capacity, organic matter content, and soil texture affecting Cu concentrations in soils, and its speciation in soils, so that, benefits and potential hazards can be identified. Copper availability to biota (as a nutrient or toxin) and its mobility are the most important factors to be considered when assessing its effect on the soil environment. Sorption measurement is a useful technique to study the retention of metals in soil (Morera *et al.* 2001), and it is a significant process in terms of controlling the distribution of Cu in soils. Sorption of Cu is pH dependent and is attributed to organic matter and iron/manganese oxides (Alloway 1995). Soil microbial biomass has been shown to decrease with the addition of heavy metals (Chaney and Ryan 1993). Microbial biomass size and composition are affected by the changes in the soil management and pollution and hence can be used as an early warning of such changes. Soil microorganisms which are typically associated with the organic fractions of the soil are expected to influence the mobilization-immobilization equilibrium of metals by changing the chemical composition of their immediate microenvironment (Beveridge 1988). The activity of soil microorganisms is measured either by the conventional plate-count technique or by soil respiration and microbial biomass (Jenkinson 1988). The aim of the work reported in this paper is to examine the effect of recycled water on soil physicochemical properties, sorption and microbial respiration process in relation to the interaction of Cu.

Methods

Five recycled water sources [treated sewage water (TS), storm water (SW), farm dairy effluent (FDE), winery effluent (WE) and piggery effluent (PE)] and 3 soil samples varying in texture and organic matter content were used in this study. Soil samples were collected from the surface layer (0-10 cm) of Adelaide Hills (AH; pH_{water} 4.88), Flaxley (FL; pH_{water} 6.07) and Gawler (GL; pH_{water} 7.83) in South Australia.

Sorption of copper in soil

The effect of recycled water on the sorption of Cu was examined using batch experiments. The sorption experiment was carried out by taking one g of soil in Cu solutions of different concentrations in the presence of recycled water. The solution concentrations were 0, 50, 100, 150, 200 and 400 mg/L Cu, prepared from copper nitrate. The samples were then placed in an end-over-end shaker for 24 hours, centrifuged at 2500 rpm for 30 minutes, filtered and analysed for pH and EC. The concentrations of total Cu in the supernatant solution were measured by Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES).

Microbial respiration

An incubation experiment was conducted for 45 days using 3 different soils to examine the effect of recycled water sources on various microbial characteristics as affected by Cu. Basal respiration, substrate induced respiration and microbial biomass carbon were measured in soils spiked with Cu (0-1000 mg/kg) in the presence of three recycled water sources (farm dairy, piggery and winery effluent) differing in DOC and compared with deionized water. Substrate induced (respiratory response on the supply of glucose) and basal respiration rates were determined by trapping evolved CO_2 from soil samples under incubation at 1, 14, 30 and 45 days interval using 0.05 M NaOH. Determination of the amount of evolved CO_2 was done by back-titration of unreacted NaOH with 0.03M HCl. The metabolically active bacterial and fungal biomass was measured by the inhibition of substrate-induced respiration by streptomycin sulphate and actidione, respectively (Wardle and Parkinson 1990). Microbial biomass was calculated using the chloroform-fumigation extraction procedure (Vance *et al.* 1987). 10 g soil were weighed into glass beakers and placed in a desiccator containing about 35 ml ethanol-free $CHCl_3$ in a small beaker. After 24h of fumigation the beaker of $CHCl_3$ was removed and the residual $CHCl_3$ vapor in the soil was removed by repeated evacuations. The fumigated and non-fumigated samples were extracted using 0.5M K_2SO_4 at a solid: solution ratio of 1:4 in an end-over-end shaker. The extract was filtered and analyzed using the TOC analyzer. Microbial biomass C was calculated as E_C/k_{EC}, where E_C= (organic C extracted from fumigated soils - organic C extracted from non-fumigated soils) and k_{EC}=0.45 (Joergensen 1995). Soil microbial basal respiration (R_{mic}) and soil microbial biomass (C_{mic}) ratio were used to calculate the metabolic quotient (qCO_2), which is the amount of CO_2–C produced per unit of microbial biomass carbon (Anderson and Domsch 1978).

Results

Sorption

The difference between the total Cu added and the total concentration remaining in the equilibrium solution gives the adsorbed Cu. The relationship between the Cu concentrations in the equilibrium solution, and the amounts of Cu adsorbed in the solid phase yield an adsorption isotherm. Gawler soil had the highest sorption capacity when compared to other soils (Figure 1A). For all three soils adsorption was less in piggery and winery effluents than in other effluents. The sorption data were fitted to the two most common equilibrium isotherms Langmuir and Freundlich. The Cu sorption isotherms fitted better to the Freundlich equation,

$$S = kC^n \quad (1)$$

where, S is the amount of Cu sorbed (mg/kg), C is the equilibrium Cu concentration (mg/L), k is the equilibrium partition/distribution coefficient, and n is the sorption intensity. The distribution coefficient, k, is positively related to the Cu sorption capacity of soils and provides an index of a metal's potential mobility. Copper sorption, as indicated by k values, was higher in DI water than in the effluents and decreased with increasing concentration of dissolved organic carbon (DOC) in the recycled water (Figure 1B). The sorption of Cu was affected by the origin of recycled water sources, and the effect of effluents on sorption varied between the soils.

Microbial Respiration

Substrate induced respiration was higher than basal respiration (Figure 2A), indicating that basal respiration is limited by carbon substrate. Respiration rates decreased significantly with increasing Cu concentration during the 45 d incubation period and varied between the recycled water sources, which may be attributed to the difference in DOC (Figure 2B). Microbial biomass carbon, bacterial: fungal ratio and metabolic quotient

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also decreased with increasing Cu concentration and varied between the effluents and soils (Figure 2C and 2D). These indices were higher in soils in the presence of recycled water than in the deionized water, indicating that recycled water sources decreased the inhibitory effect of metals on microbial activity as measured by respiration and microbial biomass carbon.

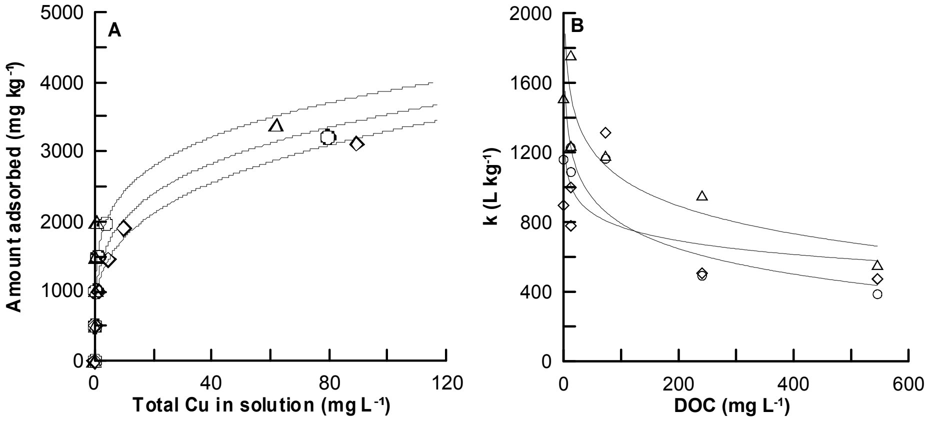

Figure 1. Comparison of Cu sorption between various soil types for DI water (A) and Relationship between DOC in various effluents and k values for Cu sorption (B) (Adelaide Hills Flaxley Gawler).

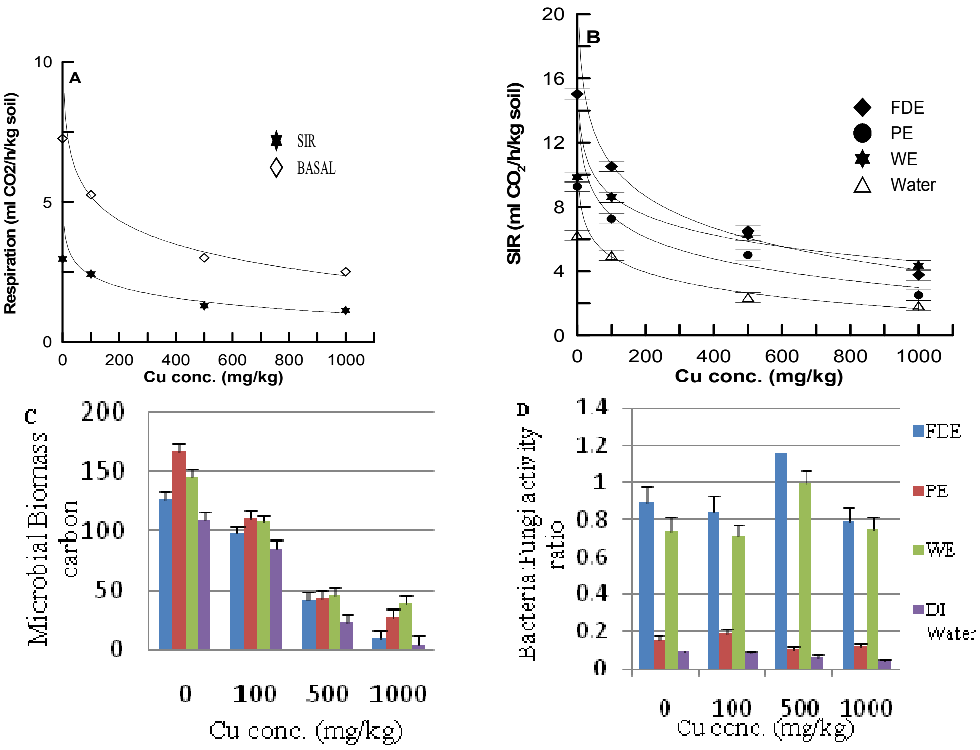

Figure 2. SIR and Basal respiration in Gawler soil in the presence of WE at 30 days interval (A), SIR in Gawler soil in the presence of 3 effluents and water at 30 days interval (B), Difference in microbial biomass carbon (C) and bacterial: fungal ratio among the effluents and water (D).

Conclusions

The results indicated that, DOC in these recycled water sources reduced Cu sorption in soils by forming Cu-DOC complexes. Recycled water resources modify the sorption behaviour of metals in soils, which is attributed to the presence of DOC and other ions such as Al, Fe and Ca in the recycled water. Copper significantly reduced microbial biomass carbon and respiration, indicating that Cu has negative effects on soil microorganisms. Soil disturbance and stress cause a decrease in microbial efficiency and enhance the qCO_2, because the microbial populations need to spend more energy on maintenance limiting the incorporation of added substrate into the cell components. This effect could be explained by the fact that metal sensitive species may be replaced by other more tolerant groups which respire at a higher rate.
Thus when farms, e.g. vineyards and vegetable farms, use recycled water for irrigation, such as winery and piggery effluents that contain high DOC, soluble Cu complexes may affect leaching, plant and microbial uptake.

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