Short Communication

Effects of clay amendment on adsorption and desorption of copper in water repellent soils

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Abstract. Copper is an important micronutrient and trace amounts are essential for crop growth. However, high concentrations of copper will produce toxic effects. Australia is increasingly developing production of crops in water repellent soils. Clay amendment, a common amelioration techniques used in Australia, has demonstrated agronomic benefits in increased crop or pasture production. The sorption and desorption of copper and the effect of clay treatment on copper behaviour in a water repellent soil collected from an experimental farm in South Australia is studied. We found that the water repellent soils amended with clay have an increased adsorption capacity of copper. Also the clay-amended soils had an increased ratio of specific sorption to total sorption of copper. The implications of this study to the sustainable agro-environmental management of water repellent soils is discussed.

Additional keywords: copper, sorption, desorption, water repellent soils, clay amendment.

Introduction

Water repellency is a property of soil that reduces infiltration capacity and crop germination, reduces nutrient and chemical-holding capacity, and promotes erosion (Cann and Lewis 1994). Water repellency is a major problem affecting agricultural properties on almost every continent. In South Australia, up to 2 million ha of potentially productive agricultural lands has been identified has having mild to severe water repellent soils (Cann 2000). In Europe, large areas in the Netherlands, for example, may be water repellent to some degree. The depth, degree, and special variability of water repellent soils in the Netherlands has been extensively investigated (Dekker and Ritsema 2000; Dekker *et al.* 2000).

The processes causing the non-wetting phenomenon are not completely understood. Doerr *et al.* (2000) reviewed water repellency of soil and its causes, characteristics and hydro-geomorphologic significance, and indicated that knowledge about the extent of water repellency among world soils is still comparatively sparse. Its origin by the accumulation of long-chained organic compounds on

or between soil particles is now widely accepted, but understanding the exact chemical composition of these soils and means of attachment to particle surfaces remains incomplete.

The precise causes and characteristics of water repellent soils, as well as the actual extent and effective management practices, are not well understood, although it is known that the coating of the sand particles by plant waxes has a strong repellent effect on water. Current soil and water management practices in water repellent regions are therefore likely to be far from efficient. Many studies aimed at finding cost-effective ameliorative procedures to reduce the potential impacts of water repellency have been conducted (Doerr *et al.* 2002).

A popular treatment for non-wetting soils is by clay amendment. Incorporation of clay into the first 0.10 or 0.15 m layer of non-wetting sands has demonstrable agronomic benefits, such as increased crop or pasture production resulting from increased water-holding capacity and cation-exchange capacity, increased effectiveness of pre-emergent herbicides, and environmental benefits such as

protection of otherwise bare soils from wind and rain-induced erosion (Cann 2000).

Trace elements such as copper are found naturally in the soil environment either as aqueous species or incorporated in the soil structure. Indigenous levels of copper are necessary as a micronutrient for plants, but toxicity may result if elevated levels of copper are introduced into the soil as a result of spillage or wastewater irrigation, the latter being increasingly adopted in Australia as means to augment depleting stores of potable water. Numerous previous studies have quantified the adsorption and bioavailability of copper in various soil types and other materials (e.g. Selim and Iskandar 1999; Arias *et al.* 2002; Maftoun *et al.* 2002; Rodriguez-Rubio *et al.* 2003). The purpose of this note is to provide a comparative study of the effect of clay amendment to water repellent soils on copper adsorption and desorption.

Materials and methods

Experimental site description

The study area is the Myome Farm at Western Flat, approximately 50 km north of the township of Naracoorte, in the south-east of South Australia (36°30′5″S, 140°42′5″E; Fig. 1). The soil description of the site is Basic,
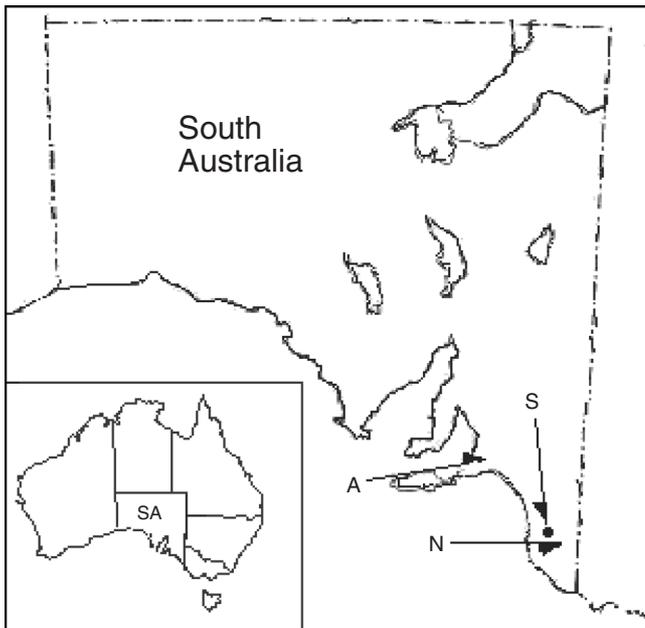

Fig. 1. Location of study area (SA, South Australia; A, Adelaide; N, Naracoorte; S, study area).

Arenic, Orthic, Tenosol; medium, non-gravelly, sandy, very deep and Brown, Mottled-Subnatric, Eutrophic, Sodosol; medium, non-gravelly, sandy, deep (Cann 2000). Soils (0–0.20 m) were sampled from 2 adjacent paddocks. One paddock was treated with 0.03 m equivalent depth of clay approximately 14 years ago. Approximately 338 t/ha of clay was incorporated into the first 0.12–0.15 m of soil. The typical description of the clay is kaolinite ($Si_4Al_4O_{10}(OH)_8$). Its lattice is 1 : 1 (silica layer and alumina layer), CEC 5–15 cmol/kg, and surface area 15 m^2/g— much lower than other clay minerals such as illite, chlorite, vermiculite, and montmorillonite (Yong *et al.* 1996; McKissock *et al.* 2000). The other paddock has not been treated with clay. Approximately 25 kg of soil from the top 0.20 m was collected from a number of random sites in both paddocks.

Soil treatments and characteristics

The soils from the paddock amended by clay will be termed 'treated soils' and the soils from the other paddock that were never amended with clay will be termed 'non-treated' soils. In the laboratory, the soil samples were thoroughly mixed, air-dried for 10 days, allowed to equilibrate with the laboratory atmosphere, and then passed through a 2-mm sieve. Clay aggregates were powdered to assist their passage through the sieve. Potential water repellence on air-dried samples was measured using the water drop penetration time (WDPT). The average WDPT for treated and non-treated soils was 4.8 and 326 s, respectively; the latter result indicating that the soil had strong repellency according the classification by Doerr *et al.* (2002). Clearly, the clay amelioration greatly improved the hydrophilic characteristics of the soil (WDPT = 4.8 s).

The basic properties of the non-treated water repellent soils are presented in Table 1. Not surprisingly, a large proportion of the soil composition is sand (81%). The percent organic matter ranged from 2.5 to 5.1%. The average volumetric water content at the time of collection was 9% for treated soil and 6% for untreated soil.

The dry bulk density for treated soils was 1.5 g/cm^3 and for non-treated soils 1.4 g/cm^3. The average soil porosity was 0.37 (v/v) and 0.47 (v/v) for treated and non-treated soils, respectively. The average indigenous concentration of copper in clay-treated soils collected from the Myome Farm site before treatment with Cu solution was 4.84 mg/kg and for non-treated soils 2.66 mg/kg, indicating that a higher initial concentration of Cu was adsorbed in the clay fraction of treated soils. The concentrations of some of the major cations in the soils are presented in Table 2. Clearly, the clay amendment also resulted in increased retention of other major cations including Ca, Mg, Na, and K.

Adsorption and desorption experiments (performed in triplicate)

This study comprised 2 steps: adsorption and desorption. The adsorption experiment was in the following manner: 2 g of air-dried soil was added to a 20-mL solution of copper in 0.01 M $Ca(NO_3)_2$ electrolyte solution, shaken in an eccentric shaker at 150 r.p.m. for 24 h in a controlled temperature room at 20°C, and then centrifuged at 2500 r.p.m. for a further 0.5 h. The background electrolyte of 0.01 M $Ca(NO_3)_2$ was chosen to minimise any non-specific adsorption of Cu due to

Table 1. Basic properties of non-treated sands at Myome Farm in Naracoorte, South Australia

Soil depth (m)	pH (1 : 5 water)	Per cent organic matter	Particle size (%)[A]			
			Clay	Silt	Fine sand	Coarse sand
Surface	6.2	5.1				
0.10	5.9	3.6	9	10	58	23
0.20	5.9	2.5				

[A] International Soil Science Society classification.

Table 2. Major cation concentrations of non-treated and treated soil collected in Myome Farm soils (mg/kg)

Treatment	Ca	Mg	Na	K
Non-treated soil (A)	340	81	77	172
Treated soil (B)	810	429	110	868
Ratio (B/A)	2.4	5.3	1.4	5.1

ion exchange mechanisms (Care *et al*. 1996). Isothermal adsorption of Cu was determined from batch tests at concentrations of 0, 2.5, 5.0, 10.0, 25.0, and 50.0 mg/L of Cu ($CuCl_2.2H_2O$), respectively. The pH was controlled at 5.5. The concentrations span the typical range of Cu concentrations found in nearby municipal wastewater (potentially used as irrigation). Batch equilibrium tests (i.e. tests an individual samples) are widely used to study the adsorption and desorption of single metals or a combination of heavy metals in soils and other materials (e.g. Lim *et al*. 1997; Jang *et al*. 1998; Elzinga *et al*. 1999; Garcia-Sanchez *et al*. 1999; Phillips 1999; Davranche and Bollinger 2000; Li and Li 2001).

When the supernatant liquid for the adsorption of Cu was removed for the concentration analyses, the residue soil (i.e. the soil phase containing adsorbed Cu) was used for the desorption experiment. Desorption supernatant was created by adding 20 mL 0.01 M $Ca(NO_3)_2$ electrolyte solution at pH 5.5 to the residue soil and then shaking and centrifuging as previously described in the adsorption experiment.

Chemical methods and techniques

The adsorption and desorption capacities of the treated and non-treated water repellent soils were determined in triplicate. The adsorption and desorption supernatants were analysed for Cu using a Hitachi 6000 Atomic Adsorption Spectrophotometer calibrated with standards prepared from a 1.00 g Cu/L⁻ stock solution from AJAX chemicals. The experimental-analytical methods were checked using certified reference material from Analytical Products Group, Inc. Standard: Trace Metals, Order Number 7879, Lot Number 21921-21923. The cation concentrations in Table 2 were determined using an ICP-AES.

Experimental data were statistically analysed to test for significant differences between the non-treated and treated water repellent soil using independent group *t*-tests and 1-way ANOVA (SPSS 11.0 for Windows).

Results and discussion

Sorption

The Cu concentrations in the supernatant liquid and in soils after adorption are presented in Table 3. The mean concentrations of Cu in the supernatant when the sorption experiment was completed were consistently statistically much higher in the non-treated water-repellent sand than the treated clayed sand, indicating that non-treated sand is less capable of absorbing applied Cu. For example, at 50 mg/L of applied Cu, the Cu concentration of non-treated soil was 10.48 mg/L and of treated soil 3.52 mg/L.

From mass balance (i.e. Cu treatment solution concentration minus supernatant liquid concentration), the amount of Cu adsorbed (mg/kg) by the soil can be calculated (Table 3). Copper at low applied concentrations was readily adsorbed in both treated and non-treated soils; however, for higher concentrations of applied Cu, the non-treated soils were first to saturate, resulting in a lower adsorption capacity than the treated soil. For example, at the highest applied concentration of 50 mg/L of Cu, the adsorption capacity was 395 mg/kg for the non-treated soil and 465 mg/kg for the treated soil. The difference is significant.

Desorption

Table 4 presents the Cu concentrations in the supernatant following desorption and also shows, calculated from mass balances, the desorbed amount of Cu extracted from the soil. The supernatant concentration of Cu following desorption in the non-treated sand was more than that for the treated soil, indicating that non-treated soils have greater potential for releasing bound Cu than the clay-treated soil. For example, as demonstrated in Table 4, the non-treated soil at 50 mg/L of Cu applied had a supernatant liquid concentration of 4.53 mg/L of Cu, whereas that for the treated soil was only 2.29 mg/L.

From Table 4, it is apparent that the amounts of Cu released from the soil as a result of desorption were consistently

Table 3. Mean concentration of Cu (mg/L) in the supernatant liquid (after adsorption) and amount of Cu adsorbed (mg/kg) by soil
Values in parentheses indicate the coefficient of variation (%). a and b, Difference significant at $P = 0.001$; c and d, difference significant at $P = 0.01$; e and f, difference significant at $P = 0.05$; mdl, minimum detectable limit of 0.005 mg/L

| | Applied Cu treatment concentration (mg/L): | | | | | |
	0	2.5	5.0	10.0	25.0	50.0
	Concentration of Cu in supernatant					
Treated	<mdl	<mdl	<mdla	0.032c (6)	1.50e (5)	3.52a (8)
Non-treated	<mdl	<mdl	0.053b (9)	0.215d (4)	2.30f (7)	10.49b (8)
	Amount of Cu in soil					
Treated		25.0	50.0a	99.7c (6)	235e (5)	465a (8)
Non-treated		25.0	49.5b (9)	97.9d (4)	227f (7)	395b (8)

Table 4. Mean concentration of Cu (mg/L) in the supernatant liquid, and amount (mg/kg) of Cu desorbed from soil and retained in soil after desorption

Values in parentheses indicate the coefficient of variation (%) c and d, Difference significant at
$P = 0.01$; e and f, difference significant at $P = 0.05$; mdl, minimum detectable limit of 0.005 mg/L

	Applied Cu treatment concentration (mg/L):					
	0	2.5	5.0	10.0	25.0	50.0
Concentration of Cu in supernatant						
Treated	<mdl	<mdl	0c	0.083e (10)	1.09e (8)	2.29e (4)
Non-treated	<mdl	<mdl	0.0096d (4)	0.231f (5)	1.49f (9)	4.53f (3)
Amount of Cu desorbed from soil						
Treated			0c	0.85e (10)	10.9e (8)	27.9e (4)
Non-treated			0.10d (4)	2.30f (5)	14.9f (9)	45.3f (3)
Amount of Cu retained in soil						
Treated		25.0	50.0	98.8	224	437
Non-treated		25.0	49.4	95.6	212	350

statistically much higher in the non-treated soils than the clay-treated soils, indicating that non-treated sand is less capable of tightly binding Cu. For example, at 50 mg/L of applied Cu, the amount of Cu desorbed from the non-treated soil was 45.3 mg/kg and for the treated soil the amount released was only 27.9 mg/kg. The results in the Table 4 also indicate that after desorption, only a small amount of Cu was released from soils into the supernatant liquid and a large proportion of the Cu was still bound in the soil phase. The amount of Cu retained in soil phase after desorption is also presented in Table 4.

Sorption isotherms

Two major techniques commonly used to model soil sorption equilibrium processes are the Freundlich and the Langmuir approaches. Some researchers considered the Freundlich equation more suitable for metal sorption in soil (e.g. Selim and Amacher 1997). The Freundlich equation is given by:

$$S = K_f C^{1/n}$$

where S is the adsorbed metal per unit weight of soil, C is the dissolved concentration of metal in equilibrium solution, K_f is the Freundlich distribution coefficient, and n is a factor dependent on the chemical. The Freundlich sorption isotherms for clay-treated and non-treated soils are summarised in Table 5. Correlation coefficients (r) and coefficients of determination (R^2) are also presented in Table 5.

Table 5. Sorption isotherms for non-treated and clay treated water repellent soils

	K_f (L/kg)	n	r	R^2
Non-treated soil	163	2.591	0.998	0.996
Treated soil	264	3.390	0.959	0.920

The Freundlich distribution coefficient K_f for the treated soil is about 1.6 times higher than for the non-treated soil. For comparative purposes, the coefficient K_f for Cu in a clay-loam soil located in a sewage treatment farm at Werribee in Victoria, Australia, was found to be 629 and 335 L/kg for the A layer (0–0.20 m) and B layer (0.20–0.40 m), respectively (Xiong *et al.* 2001). The clay-treated water repellent sandy soil in South Australia had a distribution coefficient K_f of only 264 L/kg.

Sorption intensity and specific sorption

The sorption intensity is the ratio of the quantity adsorbed in the solid phase to the initial solution quantity. When the applied treatment concentration of Cu was >10 mg/L, the sorption intensity of the clay-treated soil was statistically higher than the non-treated soil. The sorption intensity of the non-treated soil at 50 mg/L of applied Cu fell to 79%, whereas the treated soil still remained high at 93%, as shown in Fig. 2.
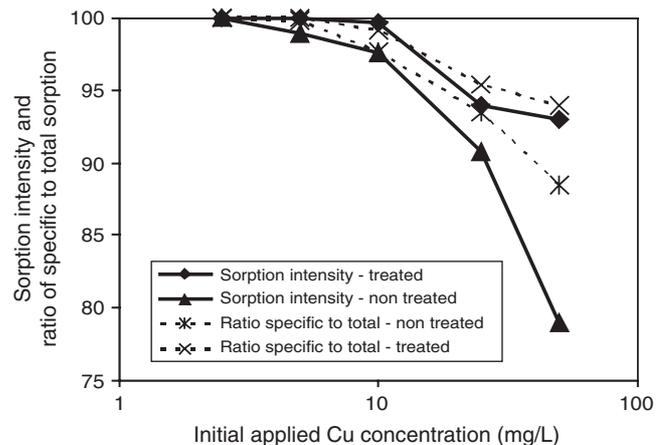

Fig. 2. Sorption intensity and the ratio of specific sorption to total sorption of Cu (%).

The term 'specific sorption' is often encountered in the scientific literature (Alloway 1995) involves the exchange of metal cations with surface ligands to form partly covalent (more or less equal sharing of electrons) bonds with lattice ions. Atanassova (1999) defined metals that are not displaced by more than 24 h of desorption with 0.01 M $Ca(NO_3)_2$ to be *specifically* adsorbed. The amount of Cu in soil (mg/kg) in Table 3 shows the total sorption amount. The amount of Cu retained in soil (mg/kg) in Table 4 is the specific sorption of Cu. The ratio of the specific sorption to the total sorption expressed as a percentage for treated and non-treated is presented in Fig. 2.

Figure 2 illustrates that the specific sorption was a very high proportion of the total sorption. The ratio of the specific sorption to the total sorption at low applied Cu treatment concentration is comparatively higher than that at higher applied Cu treatment concentrations. In addition, the clay-treated soil had a higher ratio than the non-treated soil. This observation has important ramifications when considering application of wastewater to clay-amended water repellent sandy soils.

Conclusions

This study investigated the sorption and desorption potential of surface applied copper in a water repellent soil that had not been previously treated with clay and compared it to a similar soil that had been treated with clay. The water repellent sandy soil amended with clay had a significantly increased sorption capacity for copper. The mechanisms of increased capacity could be physical adsorption, chemical adsorption, and precipitation, which are difficult to fully distinguish. However, the higher concentration of major cations (Ca, Mg, Na, K) in the clay treated soil than the non-treated soil may play an important role in an increased sorption capacity. The clay-treated water repellent soil had a significantly decreased copper desorption and also significantly increased ratio of specific sorption to total sorption of copper compared with the non-treated water repellent soil.

Acknowledgments

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