

Competitive sorption of metals in water repellent soils: Implications for irrigation recycled water

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Abstract. Australia is a water-stressed nation and demand on potable water supply is increasing. Consequently water conservation and reuse are increasingly becoming important. Irrigation of recycled wastewater on water repellent soils is a technology that is being trialled as a means of improving crop production and conserving potable supply. However, recycled water contains potentially harmful heavy metals. This paper reports the competitive sorption and desorption of several common heavy metals found in soils collected from a farm located in the south-east of South Australia. The soil from this location is severely water repellent, but some sites were amended with kaolinite clay ($\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$) about 7 and 15 years ago. The metals studied were Cu, Pb, Cd, Cr, Ni, and Zn. Competitive sorption of the metals was distinctly observed. For all heavy metals, the quantity of metal sorbed was higher in amended soil, and there was a strong correlation between the specific sorption to total sorption ratio and the amount of clay in the soil. The sorption intensities varied with metal, Cr, Pb, and Cu having a high sorption tendencies and Zn, Cd, and Ni having comparatively low sorption tendencies. The total sorption capacity for all metals increased in clay-treated soils compared with non-treated soils. On average, clay-amended water repellent soils had a 20–40% increased capacity to adsorb total metals; however, this increase was largely caused by the increased capacities to adsorb Zn, Cd, and Ni. The effect of clay treatment largely enhanced the sorption capacity of relatively weakly adsorbing heavy metals. The implications for using recycled wastewater on the long-term sustainable agro-environmental management of these soils are discussed.

Additional keywords: sorption, desorption, clay, kaolinite, heavy metal, recycled wastewater, cadmium, chromium, copper, lead, nickel, zinc.

Introduction

In Australia, as in many other parts of the world, increasing regulation covering the delivery and collection of on-farm water and realistic charges being applied for its use are forcing many farmers to seek alternative water sources such as recycled treated municipal sewerage and storm water. Recycled water often contains high levels of nutrients, which can be beneficial to crop production, but it also contains high concentrations of heavy metal metals, which may prove to be toxic. The application of recycled water by irrigation on water repellent soils may provide an attractive means of increasing pasture growth through increased nutrient loading and a cost-effective amelioration technique provided that the

associated environmental risks of contamination of soils and groundwater by heavy metals can be minimised.

Millions of hectares of potentially productive agricultural lands in Australia are subject to water repellency, a property of soil that reduces infiltration capacity and crop germination, reduces nutrient and chemical-holding capacity, and promotes erosion (Cann and Lewis 1994). A popular treatment for water repellent soils is clay amendment. Incorporating clay into the first 0.10 or 0.15 m layer of the soils 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. This ameliorative technique can provide significant improvement of soils even 30 years after initial application (Cann 2000).

The mechanisms of metal cation adsorption onto soil particle surfaces include inner-sphere complex, outer-sphere complex, and diffuse-ion swarm (Sposito 1989). Studies of the competitive adsorption of heavy metals in different types of soils were reported (Atanassova 1999; Phillips 1999; Selim and Iskandar 1999; Ladonin 2000; Voegelin *et al.* 2001; Fontes and Gomes 2003; Veeresh *et al.* 2003). Competitive adsorption of heavy metals on water repellent soils has been studied in this paper. This research is required in order to better understand the possible long-term loading of metals in water repellent soils, particularly if these soils are irrigated with recycled water, a landuse practice increasingly being considered in many parts of the world, including Australia.

Consequently, knowledge of competitive metal sorption of metals in water repellent soils subject to differing treatments of recycled water and as affected by clay will greatly improve the sustainable agro-environmental management of such soils. In this paper, we report the competitive adsorption dynamics of a mixture of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in proportions typically found in municipal sewage (Xiong *et al.* 2001). The differences in competitive sorption are contrasted for water repellent soils that have received no treatment with clay and those with various amounts of clay incorporation.

Materials and methods

Experimental area

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°2'5"E).

Two experimental areas on this farm have been used in this study. The first experimental area contains 2 adjacent paddocks with severely water repellent soils. One paddock was treated with 0.03 m equivalent depth of locally sourced kaolinite clay ($\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$) about 15 years ago. The clayed paddock approximates an application rate of 338 t clay/ha. The other paddock never was amended with clay. The 2 paddocks have a similar cropping and fertilisation history.

The second experimental site was a trial plot established in 1995. Figure 1 presents a diagram of the trial plot. Each trial plot has a dimension of 83 by 20 m. Nine adjacent trial plots were chosen for this study (see Fig. 1). Plots labelled I have never amended with clay and represent control plots. Plots labelled II were amended with 135 t/ha of kaolinite clay in 1995. Similarly, plots labelled III and IV were amended with kaolinite clay at rates of 180 and 240 t/ha, respectively. Apart from the clay amendment, each trial plot has similar soil characteristics and received comparable planting rotations and fertilisation since 1995. The trial plots are located approximately 5 km from the paddock sites.

Soil samples

Soils (0–0.20 m) were sampled with a spade from the 2 adjacent paddocks and from the trial plots. The composites were collected at 20 points of each paddock and plot. The soils collected from the paddock amended with 338 t/ha of clay are termed 'clayed' and the soils from the other paddock that were never amended with clay are termed

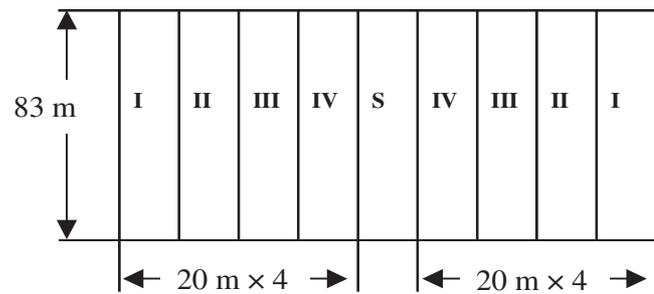


Fig. 1. Trial plots at the Myome Farm: I, non-clayed; II, clayed 135 t/ha; III, clayed 180 t/ha; IV, clayed 240 t/ha; S, separation plot.

'non-clayed'. The control trial plots will also be called 'non-clayed'. 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 clayed and non-clayed soils was 4.8 and 326 s, respectively, the latter result indicating that the soil had strong repellency according to the classification by Doerr *et al.* (2002). Clearly, the clay amelioration greatly improved the hydrophilic characteristics of the soil. At the time of collection, the average soil porosity for soil samples was 37 and 47% for clayed and non-clayed soils, respectively. The basic characteristics and CEC of the non-clayed water repellent soils are presented in Table 1 and Table 2.

Competitive sorption and desorption experiment (performed in triplicate)

The adsorption and desorption capacities of the clayed and non-clayed water repellent soils were determined in triplicate. Competitive sorption of heavy metals was studied in soil samples collected from both the paddock and trial plots. A mixture of heavy metals in a mixed solution was prepared with the following concentrations (mg/L): Cu 10, Pb 5, Cr 5, Cd 0.5, Ni 5, Zn 25. The salts of the cations were $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. The pH was controlled at 5.5. These concentrations were selected based on proportions of heavy metal concentrations typically found in municipal sewage in some Australia cities (e.g. see Xiong *et al.* 2001).

Soil sorption of these metals was investigated in the following manner: 2 g of air-dried soil was added to 20 mL of a mixed solution of the 6 metals in a 0.01 M $\text{Ca}(\text{NO}_3)_2$ electrolyte. This mixture was shaken in an eccentric shaker at 150 r.p.m. for 24 h (equilibrium point achieved) in a controlled temperature room at 20°C. The mixture was separated by centrifugation at 2500 r.p.m. for 0.5 h into supernatant and solid residue. The 0.01 M $\text{Ca}(\text{NO}_3)_2$ was chosen as background electrolyte to minimise non-specific sorption of heavy metals due to ion exchange mechanisms (Carey *et al.* 1996). The remaining solid residue was treated with 20 mL 0.01 M $\text{Ca}(\text{NO}_3)_2$ electrolyte solution to obtain a mixture for the desorption experiment. The mixture was then shaken and centrifuged as above.

Chemical analytical procedures

The adsorption and desorption supernatants were analysed for Cd, Cr, Cu, Ni, Pb, and Zn concentrations using a Hitachi 6000 Polarised Zeeman Atomic Absorption Spectrophotometer. The instrument was calibrated with standards prepared from 1.00 g/L stock solutions of Cd, Cr, Cu, Ni, Pb, and Zn from AJAX Chemicals. The minimum detectable limits (mg/L) were: Cd 0.004, Cr 0.005, Cu 0.006, Ni 0.008, Pb 0.03, Zn 0.002. The instrument calibration was checked using certified

Table 1. Characteristics of non-clayed and clayed soils in the paddock

CS, Coarse sand (0.2–2.0 mm); FS, fine sand (0.02–0.2 mm); silt (0.002–0.02 mm); clay (<0.002 mm); OM, organic matter; OOC, oxidisable organic carbon; TN, total nitrogen; TP, total phosphorus

	pH	Particle size ^A (%)				OM	OOC (%)	TN	TP (mg/kg)	CEC (cmol/kg)
		CS	FS	Silt	Clay					
Non-clayed	5.9	27.6	68.8	1.0	0.4	1.5	0.76	0.06	29	2.5
Clayed	5.9	34.6	54.7	3.5	5.5	2.1	1.1	0.07	120	3.6

^A0.4% of particles lost in acid treatment for both of non-clayed and clayed.**Table 2. Cation exchange capacity of non-clayed and clayed soils in paddock and trial plots (in 1 M NH₄ acetate extractable cations with prewash)**

Values in parentheses indicate the percentage (%) of sum of cations Ca, Mg, Na, and K

	Paddock		Non-clayed	Trial plots		
	Non-clayed	Clayed		135 t/h	180 t/h	240 t/h
Ca	2.0 (79)	2.8 (82)	2.7 (89)	4.0 (81)	5.2 (86)	4.7 (78)
Mg	0.34 (16)	0.57 (14)	0.24 (8.0)	0.79 (16)	0.68 (12)	1.1 (19)
Na	<0.05 (2.0)	<0.05 (2.0)	<0.05 (2.0)	<0.05 (1.0)	<0.05 (1.0)	0.06 (1.0)
K	0.06 (4.0)	0.14 (3.0)	<0.05 (2.0)	0.10 (2.0)	0.11 (2.0)	0.16 (3.0)
Ca : Mg ratio	5.0	5.9	11	5.1	7.7	4.3
Sum of 4 cations	2.5	3.6	3.0	4.9	6.0	6.0

reference material from Analytical Products Group, Inc. Standard: Trace Metals, Order Number 7879, Lot Number 21921-21923. Recoveries obtained for all metals were from 95% to 103%. Experimental data were analysed using independent group *t*-tests and 1-way ANOVA.

Results

Sorption intensity

The concentrations of heavy metal ions in the sorption supernatant are presented in Table 3. As the mixture of heavy metals had initially unequal concentrations, it is difficult to compare absolute percentage change in sorption. Therefore, the relative percentage change (or sorption intensity) is a better measure to compare and contrast sorption between different metal cations. The sorption intensity is calculated by taking the difference between the original treatment concentration of each metal and its supernatant concentration (in Table 3), then dividing the difference by the original treatment concentration, and then expressing this as a

percentage by multiplying by 100. Sorption intensities for each soil are summarised in Table 4.

The competitive sorption of heavy metal cations is obvious in Table 4. It can be seen that Cr, Pb, and Cu show higher adsorption intensities than Zn, Cd, and Ni in both non-clayed and clayed soils of paddock and trial plots. The affinity sequence in water repellent soil is in the order Cr > Pb > Cu ≫ Cd > Zn > Ni.

The initial concentrations of applied Cr, Pb, and Ni in the mixture were the same (5 mg/L). However, their sorption intensities were very different. The sorption intensities of Cr and Pb was almost 100% for both the clay-treated and non-clayed water repellent soils, but the sorption intensity for Ni was much lower, from 20.9 to 38.1% for non-clayed soils and 46.6 to 84.8% for clayed soils (Table 4). Table 4 also shows that Cr, Pb, and Cu have high affinity for sorption sites in soil. The metals Zn, Cd, and Ni have relatively low affinity with ligand in soil. Zn and Cd are located in the

Table 3. Heavy metal concentrations in supernatant following the sorption experimentCoefficient of variation (CV) is given in parentheses (mg/L). The mean different of clayed v. non-clayed is at: c, $P < 0.005$; d, $P < 0.001$; e, $P < 0.0005$; f, $P < 0.0001$

Metal	Original conc. ^A	Paddock		Non-clayed	Trial plots		
		Non-clayed	Clayed		135 t/h	180 t/h	240 t/h
Cd	0.5	0.291 (2)	0.155d (6)	0.193 (4)	0.066f (6)	0.014f (8)	0.008f (8)
Cr	5.0	0.06 (9)	0.003c (11)	0.003 (18)	0f	0f	0f
Cu	10.0	0.346 (9)	0.072c (8)	0.084 (3)	0.003f (6)	0.002f (7)	0.002f (2)
Ni	5.0	3.96 (5)	2.67c (7)	3.10 (4)	1.56f (5)	0.91f (4)	0.76f (9)
Pb	5.0	0.026 (6)	0.003c (8)	0.015 (4)	0.004e (8)	0e	0e
Zn	25	16.80 (4)	12.42c (5)	14.15 (2)	7.02f (10)	4.74f (4)	4.35f (8)

^AOriginal concentration in the mixture (mg/L).

Table 4. Sorption intensities (%)

Metal	Paddock		Non-clayed	Trial plots		
	Non-clayed	Clayed		135 t/ha	180 t/ha	240 t/ha
Cd	41.9	69.1	61.4	86.9	97.3	98.5
Cr	98.8	100	100	100	100	100
Cu	96.5	99.3	99.2	100	100	100
Ni	20.9	46.6	38.1	68.8	81.9	84.8
Pb	99.5	99.9	99.7	99.9	100	100
Zn	32.8	50.3	43.4	71.9	81.0	82.6

same group in the periodic table and have similar chemical characteristics; therefore, they compete for sorption sites. The sorption intensity of Cd is greater than that of Zn; for example, in the non-clayed soil in the paddock, the sorption intensity was 41.9% for Cd and 32.8% for Zn, and in clayed soil in the paddock, sorption intensity was 69.1% for Cd and 50.3% for Zn. Similar results are evident in the trial plots and the results are consistent with findings elsewhere (e.g. Kookana *et al.* 1999; Parkpain *et al.* 2000)

The effect of clay on sorption of metal cations

Table 3 illustrates that there are significant differences in metal sorption between non-clayed and clayed paddock soils for all metal ions ($P < 0.005$ in all cases). In the trial plots there are also significant differences between non-clayed, and for all clayed, soils ($P < 0.0001$ for Cd, Cr, Cu, Ni, and Zn and $P < 0.0005$ for Pb). There were significant differences between the 135 t/ha treatment and the 180 and 240 t/ha treatments ($P < 0.005$ for Cd, Ni, and Pb and $P < 0.001$ for Zn). For Zn there was also a significant difference between 135 and 240 t/ha ($P < 0.0005$). The sorption of each metal cation tends to increase with increasing percentage of clay in the water repellent soil. The effect of clay on sorption of metal cation is related to the increase in cation exchange capacity in the clayed soils as shown in Table 2.

The increase in sorption capacity varies with the type of metal. For example, the data show very little percentage increase in sorption intensity for Cu, Pb, and Cr when compared with the non-clayed soils but very large increases in Cd (61.4–98.5%), Zn (43.4–82.6%), and Ni (38.1–84.8%) for trial plots shown in Table 4. Therefore, not only the application level of heavy metals to the soils and the specific properties of the soil (clay, organic matter, CEC,

and vegetation impact) on metal sorption, but also their competition and relative amounts in solution, critically affect sorption potential, making universal generalisations extremely difficult.

Assimilative capacity of heavy metals affected by clay

The capacity for the clay to increase the sorption of heavy metals is important when designing recycled water irrigation strategies. Mass balances for each metal adsorbed by the soil for each case were calculated from Table 3. The relative sorption capacities for each treatment are presented in Table 5. These capacities are calculated as ratios of the adsorbed amounts of each metal when compared to the non-clay control soils. For example, soil from the 240 t/ha trial plot adsorbed 90% more Zn than the non-clayed water repellent soil.

Competitive desorption

The results of the desorption experiment are shown in Table 6. Again, the patterns of desorption vary according to the metal cations. For example, for the relatively strongly sorbed element Cr, no desorption was observed. For other strongly bound elements Pb and Cu, no desorption was observed in the all clayed soils except for the paddock clayed soil and only at a low Cu concentration (0.027 mg/L). For the relatively weakly sorbing metals Ni and Cd, no statistical differences in desorption concentrations between the non-clayed and clayed paddock soils was found, but very significant differences were found in all trial plots treated with clayed compared with the non-clayed soil ($P < 0.005$). The Zn and Cu desorption concentrations for the clayed paddock soil were found to be significantly different from those of the non-clayed paddock soil ($P < 0.05$ and $P < 0.01$, respectively).

Table 5. Assimilative sorption capacities of each metal as affected by different clay treatments
Numbers are expressed as a ratio of sorption amount relative to non-clayed soil

	Cd	Cr	Cu	Ni	Pb	Zn
Clayed paddock	1.65	1.01	1.03	2.23	1.01	1.53
Clayed trial plots						
135 t/ha	1.42	1.00	1.01	1.81	1.00	1.66
180 t/ha	1.59	1.00	1.01	2.15	1.00	1.87
240 t/ha	1.61	1.00	1.01	2.23	1.00	1.90

Table 6. Concentrations of metals in supernatant (mg/L) following desorption equilibria
 Values in parentheses are the coefficient of variation (CV %). The mean difference of clayed v. non-clayed is at: a, $P < 0.05$; b, $P < 0.01$; c, $P < 0.005$

Metal	Paddock		Non-clayed	Trial plots		
	Non-clayed	Clayed		135 t/h	180 t/h	240 t/h
Cd	0.093 (3)	0.088 (5)	0.094 (5)	0.050c (10)	0.028c (6)	0.026c (13)
Cr	0	0	0	0	0	0
Cu	0.114 (12)	0.027b (6)	0.026 (8)	0c	0c	0c
Ni	0.761 (5)	0.875 (8)	1.052 (10)	0.689c (10)	0.455c (14)	0.109c (11)
Pb	0.037 (9)	0c	0.037 (15)	0c	0c	0c
Zn	4.48 (4)	3.80a (6)	4.46 (5)	2.84c (3)	2.87c (12)	1.72c (9)

Specific sorption

The specific sorption is the exchange of heavy metal cations with surface ligands to form partly covalent bonds with lattice ions (Alloway 1995). Metals that are not displaced by >24 h of desorption with 0.01 M $\text{Ca}(\text{NO}_3)_2$ solution are said to be specifically adsorbed (Atanassova 1999). From Table 3 and Table 6 one can calculate the specific sorption and its ratio. The ratio of the specific sorption to the total sorption expressed as a percentage for each treatment is presented in Table 7. The application of clay to the water repellent soils in all cases increased the specific sorption and the increase is roughly proportional to the amount of applied clay. From Table 7 it can be seen that the strong sorption metal cations, Cr, Pb, and Cu have a high ratio of specific sorption even in the non-clay treated soils. The weak sorption metal cations Zn, Cd, and Ni have low ratios. Clay-treated soils have increased ratios for Zn, Cd, and Ni.

Discussion

Hydrogeology is one of the most important aspects in assessing the feasibility of land disposal of sewage-treatment systems. The assimilative capacity of heavy metals should be considered as a priority for assessing the feasibility of the application of recycled water on repellent soils. Recycled water from sewage treatment often has high concentrations of beneficial nutrients, but it usually has high concentrations of salts and heavy metals.

The application of recycled water to land, including water repellent soils, must be assessed on a local, *in situ*, case-by-case basis. This study demonstrated that metals

in competition preferentially sorb to the soil, and that a host of factors (e.g. pH, per cent organic content, CEC, etc.), which were measured in this study, may dynamically alter the sorption/desorption equilibrium and significantly alter the specific sorption ratios. Further the method of application of the recycled water may also impact critically on the sorption/desorption equilibrium and long-term hydraulic loading of the soils, for example, a rapid rate infiltration system may be more suitable than a slow rate infiltration system.

The use of clays on water repellent soils has been found to be the best way in overcoming water repellency (Cann 2000). At the Myome Farm, the use of kaolinite $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$ greatly improved the hydrophilic characteristics of the soil (e.g. WDPT = 4.8 s for clayed soils and >326 s for non-treated soils). The typical description of the kaolinite is lattice 1:1 (silica layer and alumina layer), CEC 5–15 cmol/kg, and surface area 15 m²/kg. Many of the water repellent soils in South Australia are underlain by kaolinite clay and this provides an excellent *in situ* opportunity for amelioration of water repellent soils (Cann 2000). This study demonstrates that the use of kaolinite clay also has other desirable properties including improving the sorption and retention of heavy metals in the near surface soils. Table 5 illustrates that clayed soils had significantly increased capacity to adsorb heavy metals especially for relative weak sorption metals like Zn, Cd, and Ni. Metal speciation, bioavailability and potential toxicity of metal species on crops, however, have not been investigated in this study.

Table 7. Specific sorption (%) in non-clayed and clayed soils of paddock and trial plots

Metal	Paddock		Non-clayed	Trial plots		
	Non-clayed	Clayed		135 t/ha	180 t/ha	240 t/ha
Cd	55.7	74.9	69.7	88.6	94.3	94.7
Cr	100	100	100	100	100	100
Cu	98.8	99.7	99.7	100	100	100
Ni	27.5	62.5	44.6	80.0	88.9	97.4
Pb	99.7	100	98.6	100	100	100
Zn	45.4	69.8	58.9	83.7	85.8	91.7

Conclusions

Novel amelioration strategies including the application of recycled water on repellent soils are of great significance. For example, the application of treated municipal sewage on water repellent soils can provide nutrition for pasture growth and decrease the repellency. However, sandy soils even with clay amendment have a relative low sorption capacity for heavy metals when compared with loam or clay soil in other studies. Therefore, the application of recycled municipal wastewater on these water repellent soils poses a potential risk of leaching metals to the groundwater, or leaching through the soil into farm dams and water courses, if the hydraulic loadings used in other studies is applied.

It was found that the sorption intensity of heavy metals for a typical solution of recycled wastewater acting in competition produced preferential sorption. The metals Cr, Pb and Cu had a strong propensity for adsorption, and Zn, Cd, and Ni had comparatively weak sorption capacities. The total sorption capacity for all metals increased in clay-treated soils compared with non-treated soils; however, this increase was largely caused by the increased capacities to adsorb Zn, Cd, and Ni; that is, the effect of clay treatment is largely to enhance the sorption capacity of relatively weakly adsorbing heavy metals. The clay-treated water repellent soils also had the effect of increasing the specific sorption of metals, especially for Zn, Cd, and Ni.

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