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ORIGINAL ARTICLE

Competitive sorption of intermixed heavy metals in water repellent soil in Southern Australia

P. J. Li · F. Stagnitti · X. Xiong · P. Li

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Abstract In water repellent soil, Cr, Pb and Cu showed higher adsorption intensities than Zn, Cd and Ni did. Soil water repellency is much more widespread than formerly thought. In order to promote fertility and productivity, the irrigation of recycled water onto water repellent soil may be an applied technology to be used in some areas of Southern Australia. Therefore, heavy metals in recycled water potentially enter into the soil. The competitive sorption and retention capacity of heavy metals in soil are important to be determined, especially considering the special geochemical origin of water repellent soil that was caused by waxes on or between the soil particles. Batch equilibrium sorption experiments on Cd, Cr, Cu, Ni, Pb and Zn in their typical proportion in recycled water were conducted in water repellent soil. The sorption intensity, sorption isotherm in the experiments together showed that Cr, Pb and Cu have higher sorption intensity than those of Zn, Ni and Cd in the competitive system. The risk assessment for the application of recycled water onto water repellent soil is definitely necessary, especially for the metal cations with relatively weak sorption.

Keywords Water repellent soil · Heavy metal · Competitive sorption · Recycled water · Adsorption equation · Australia

Introduction

Since the beginning of last century, water repellent soils have been a topic of study for soil scientists and hydrologists around the world. From the end of 1950s, modification of water repellent soil to improve its hydrophobic characteristics for crop production became a research area of increasing interest. Then a large body of information has been published in a wide range of scientific disciplines throughout the world. This worldwide attention has produced many recent research findings, which have improved the understanding of water repellent soils (DeBano 2000; Dekker et al. 2005).

Soil water repellency is a major problem affecting agricultural properties on almost every continent. Recently, it has become clear that soil water repellency is much more widespread than formerly thought. Water repellency has been reported in most continents of the world for varying land uses and climatic conditions (Ritsema and Dekker 2005). In Australia up to two million hectares of potentially productive agricultural land has been identified in the state of South Australia (Cann 2000) that suffers from water repellency and therefore have reduced infiltration capacity

P. J. Li
Department of Pollution Ecology,
Institute of Applied Ecology,
Chinese Academy of Sciences, PO Box 417,
No. 72, Wenhua Road, Shenyang 110016, China

F. Stagnitti · X. Xiong (✉)
School of Life and Environmental Sciences,
Deakin University, PO Box 423,
Warrnambool, VIC 3280, Australia
e-mail: xiong_x_z@hotmail.com

P. Li
Fujian Institute of Research on the Structure of Matter,
The Chinese Academy Sciences, Fuzhou 350002, China

P. Li
Graduate University of Chinese Academy of Science,
Beijing 100039, China

and crop germination, reduced nutrient and chemical holding capacity, and increased erosion (Cann and Lewis 1994).

The application of recycled water irrigation onto water repellent soils has increasingly been suggested. This may provide an attractive means of increasing pasture growth due to increased nutrient loading and water supply. However, this cost-effective amelioration technique may cause environmental risks of contamination of soils and groundwater by pollutants including heavy metals. Some studies, therefore, paid more attention on the fate and distribution of metals (Cd, Cu, Hg, Pb, Zn, etc.) in the soil. For instance, Yediler et al. (1994) focused on the possible contamination of heavy metals due to recycled effluent irrigation in the slow rate land treatment system. Thus, it is evident that for the feasibility of the application of recycled effluent on water repellent soil will depend upon the behavior of heavy metals. Ritsema and Dekker (2000) indicated that the risks of leaching of surface-applied agrochemicals in water repellent soils can only be quantified to an acceptable degree of accuracy if knowledge of the underlying processes, principles and an appropriate simulation model are available.

Considering the many heavy metals are intermixed in effluents, Morera et al. (2001) studied the competitive sorption isotherms and evaluated the mobility and distribution of Cd, Cu, Ni, Pb and Zn in four soils differing in their physicochemical properties. In general, the soils had a greater number of surface sites and higher affinity for Pb and Cu than for Cd, Ni or Zn. Vega et al. (2006) indicated soil capacities for heavy metal sorption and retention were determined by means of distribution coefficient and selectivity sequences among metals. Gao et al. (1997) assessed nine soils for their adsorption characteristics of Cd, Cu, Ni, Zn, Pb and Cr from mixed solution. The results showed that the distribution coefficient K_d values were Cr > Pb > Cu > Zn > Ni > Cd.

Hitherto there are few reports on competitive metal sorption carried out in water repellent soils. In addition, in many studies of competitive sorption, the different metal cations were used at equivalent concentrations in the experiments. For example, Fontes and Gomes (2003) used same mass concentrations of 0, 5, 15, 25, 35 and 50 mg L^{-1} for the six heavy metal cations (Cr, Ni, Cu, Zn, Cd and Pb) in their experiment. Veeresh et al. (2003) used the same molar concentration at 10, 25, 100, 150 and 200 μM L^{-1} for four heavy metals (Pb, Cu, Zn and Ni) to study competitive adsorption. In fact in recycled water the individual heavy metals have different concentrations. The investigation of simultaneous competitive sorption from dissimilar concentrations of heavy metal is more similar to the practice of the recycled water application to water repellent soils. In this paper, the concentration of every metal cation was chosen of different levels and these concentrations were selected based on the proportions of different metal concentrations found in municipal sewage in some Australian cities (Xiong et al. 2001; Li et al. 2006).

Materials and methods

Location of study area and basic characteristics of soil

The study area is in Clem Obst's Farm (COF) (coordinates Lat. 36°30′5″S and Long. 140°42′5″E) at Mundulla, located in the southeastern part of South Australia. The soil at COF is hydrophobic with average of water drop penetration time (WDPT) of 326 s (second) indicating that the soil had strong repellency according the classification by Doerr et al. (2002). WDPT is a commonly used measurement to quantify the degree of soil water repellency. If a water drop does not enter the soil spontaneously, the soil–water contact angle is greater than 90° and the soil is considered to be water repellent. The time for the drop to enter the soil (WDPT) provides an indication of the stability of the repellency (Letey et al. 2000). The basic attributes of the soils are shown in Tables 1 and 2.

Experiment

The sorption experiments were determined in triplicate. A mixed solution of heavy metals was prepared with five treatments. The salts of the cations were $CuCl_2 \cdot 2H_2O$; $(CH_3COO)_2Pb \cdot 3H_2O$; $CrCl_3 \cdot 6H_2O$; $CdCl_2 \cdot H_2O$; $NiSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot 7H_2O$. The pH of the solution was controlled at 5.5. The solution concentration of treatment 1 was prepared as: Cu 10 mg L^{-1}, Pb 5 mg L^{-1}, Cr 5 mg L^{-1}, Cd 0.5 mg L^{-1}, Ni 5 mg L^{-1}, Zn 25 mg L^{-1}. The highest solution concentration is treatment 5 with triple of the concentration of treatment 1. The five levels of solution concentration for all treatments are shown in Table 3.

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 six metals in a 0.01 M $Ca(NO_3)_2$ electrolyte that was chosen as background electrolyte to minimize non-specific sorption of heavy metals due to ion exchange mechanisms (Carey et al. 1996). This mixture was shaken in an eccentric shaker at 150 RPM for 24 h (equilibrium point achieved) in

Table 1 The characteristics of soil at COF Farm

pH	Particle size[a] (%)				OM (%)	OOC (%)	TN (%)	TP (mg kg^{-1})	CEC (cmol kg^{-1})
	CS	FS	Silt	Clay					
6.2	27.6	68.8	0.6	0.5	0.70	0.36	0.05	20	3.5

Analyses at State Chemical Laboratory (Victoria State, Australia)

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

[a] 0.4% of particles lost in acid treatment

Table 2 The cation exchange capacity at COF Farms (cmol kg^{-1})

Ca	Mg	Na	K	Ca:Mg ratio	Sum of four cations
3.2 (94)	0.13 (4)	0.05 (2)	0.05 (2)	25	3.5

Method: 1 M NH_4OAc, at pH 7 with prewash that is in wide use internationally. Analyses at State Chemical Laboratory (Victoria State, Australia). Figures in parentheses indicate the percentage (%) of sum of cations (Ca, Mg, Na and K)

Table 3 The original concentration of heavy metals in five treatments (mg L^{-1})

Treatment level	Cd	Cr	Cu	Ni	Pb	Zn
1	0.50	5.0	10	5.0	5.0	25.0
2	0.75	7.5	15	7.5	7.5	37.5
3	1.00	10.0	20	10.0	10.0	50.0
4	1.25	12.5	25	12.5	12.5	62.5
5	1.50	15.0	30	15.0	15.0	75.0

a controlled temperature room at 20°C. Then the suspension was separated by centrifugation at 2,500 RPM for 0.5 h into supernatant and solid residue.

Chemical analytical procedures

When adsorption was completed, the Cd, Cr, Cu, Ni, Pb and Zn concentrations in the supernatants were analyzed using a Hitachi 6000 Polarized Zeeman Atomic Absorption Spectrophotometer. The instrument was calibrated with standards prepared from 1.00 g L^{-1} stock solutions of Cd, Cr, Cu, Ni, Pb and Zn from AJAX Chemicals. The determine limits are Cd 0.004 mg L^{-1}; Cr 0.005 mg L^{-1}; Cu 0.006 mg L^{-1}; Ni 0.008 mg L^{-1}; Pb 0.03 mg L^{-1} and Zn 0.002 mg L^{-1}. The instrument calibration was checked using certified reference material from Analytical Products Group, Inc Australia. Standard: Trace Metals—Order Number: 7879, Lot Number: 21921–21923. Recoveries obtained for all metals were from 95 to 103%.

Results and discussion

Competitive sorption among six heavy metals

The concentrations and coefficient of variation (CV%) of six heavy metals in the supernatant after the sorption was completed are shown in Table 4. In order to compare the ability of soil to sorb different metals from the mixed solution the term ‘‘sorption intensity’’ was used.

The ‘‘sorption intensity’’ is calculated by taking the difference between the original treatment concentration of each metal and its supernatant concentration then dividing the difference by the original treatment concentration and then expressing this as a percentage. In water repellent soil, Cr, Pb and Cu showed higher adsorption intensities than Zn, Cd and Ni did. The sorption intensities are showed in Fig. 1. The geochemical origin of water repellent soil is by the accumulation of long-chained organic compounds (waxes) on or between soil particles (Doerr et al. 2002). How-

Table 4 Heavy metal concentrations of supernatant when the adsorption completed (mg L^{-1})

Metal	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
Cd	0.23 (4)	0.44 (5)	0.66 (8)	0.90 (5)	1.15 (3)
Cr	0.04 (9)	0.08 (7)	0.14 (8)	0.25 (6)	0.45 (6)
Cu	0.20 (5)	0.52 (6)	0.89 (3)	1.51 (4)	2.41 (2)
Ni	3.10 (4)	5.35 (7)	7.60 (4)	9.69 (5)	11.8 (3)
Pb	0	0.04 (6)	0.13 (7)	0.24 (4)	0.47 (5)
Zn	16.36 (5)	26.4 (7)	36.82 (8)	46.1 (5)	55.65 (7)

Values in parentheses are the coefficient of variations (CV%)

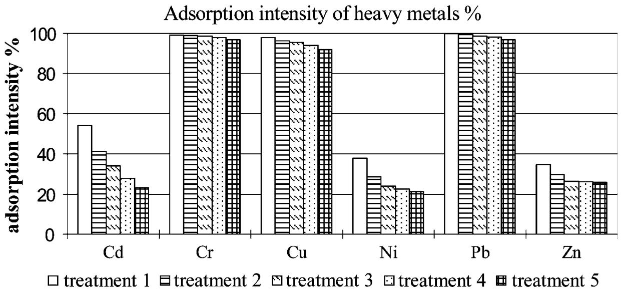

Fig. 1 Sorption intensity of heavy metals in different original concentration treatments

ever, the sequence of adsorption intensity of the soil for different metals is similar to what of most of other soils (Fontes and Gomes 2003; Veeresh et al. 2003). The mechanisms of metal cation adsorption onto soil particle surfaces could include inner-sphere complex, outer-sphere complex and diffuse-ion swarm (Sposito 1989). Texture of soil, content of organic matter, oxidizable organic carbon and CEC are important factors to affect the sorption ability of metals. The effects of long-chained organic compounds in water repellent soil on the sorption behavior and its mechanisms remain to be further studied.

Variation of sorption intensity and sorption amounts from different levels of original heavy metal concentration

Figure 1 shows the sorption intensity for five levels of original concentration treatments. When the original metal concentration increased, the strong sorption metal group (Cr, Pb and Cu) only slightly decreased their sorption intensity. For example in treatment 5, the sorption intensities of Cr, Cu and Pb are still high at 97.0, 92.0 and 96.9%, respectively. In contrast when the original concentration increased, the sorption intensities of relative weak sorption metal group (Cd, Zn and Ni) decreased markedly. The sorption intensities from treatment1: 54.0% (Cd), 38.0% (Ni) and 34.6% (Zn) dropped sharply to 23.3% (Cd), 21.3% (Ni) and 25.8% (Zn) for treatment 5.

Although the sorption intensity of heavy metals decreased with increasing original concentration treatment, the total sorption amounts of heavy metals increased as shown in Table 5. When the original concentrations were at higher levels, the sorbed amounts by the soil of the strong sorption metal group (Cr, Cu and Pb) evidently increased, because the sorption intensity was still high. For example, the sorbed amounts of treatment 5 are up to 2.93, 2.82 and 2.91-fold higher than for treatment 1 for Cr, Cu and Pb, respectively. The above figures (2.93, 2.82 and 2.91-fold) are close to threefold that was designed in the experiment between treatment 5 and treatment 1 for the concentrations of heavy metals. On other hand when the original metal concentrations were at high levels, the sorbed amount of Cd, Ni and Zn increased slightly, because their sorption intensity decreased. The sorbed amounts for treatment 5 was only 1.3, 1.68 and 2.24-fold higher than that for treatment 1 for Cd, Ni and Zn, respectively. The above figures (1.3, 1.68 and 2.24-fold) are much lower than threefold that was designed in the experiment between treatment 5 and treatment 1 for the concentrations of heavy metals.

Sorption isotherms of the six heavy metals

Two common techniques used to model equilibrium processes of soil sorption are Freundlich and Langmuir isotherms. Some researchers considered that the Freundlich equation is more suitable for metal sorption in soil (Selim and Amacher 1997). The Freundlich equation is

$$S = K_{\mathrm{f}} C^{1/n},$$

where S is the sorbed metal per unit weight of soil, C the dissolved concentration of metal in equilibrium solution, K_{f} the Freundlich coefficient, n a parameter dependent on the chemical.

The characteristic shape of adsorption curves for six heavy metals in the designed experimental concentrations was shown individually in Fig. 2, which clearly demonstrated that the adsorption curves of Cd, Cu, Cr

Table 5 Sorbed amounts of heavy metals in soil (mg kg^{-1})

Metal	Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
Cd	2.7	3.1	3.4	3.5	3.5
Cr	49.6	74.2	98.6	122.5	145.5
Cu	98.0	144.8	191.1	234.9	275.9
Ni	19.0	21.5	24.0	28.1	32.0
Pb	50.0	74.6	98.7	122.6	145.3
Zn	86.4	111.0	131.8	164.0	193.5

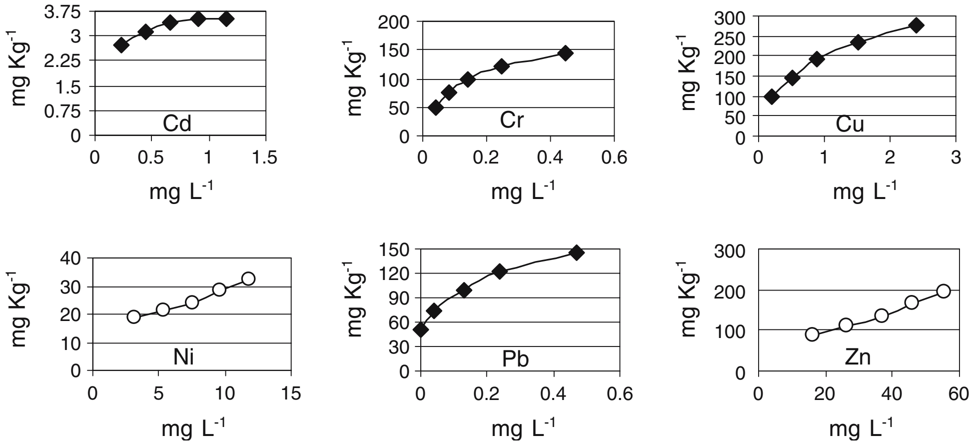

Fig. 2 Adsorption curves of heavy metals. *x-axis* mg L^{-1} of supernatant concentrations of heavy metals and *y-axis* mg kg^{-1} of sorbed amount of heavy metal in soils

and Pb have the Freundich-type isotherms and, in contrast, Ni and Zn do not have the knee of their adsorption curves. Therefore, the Freundlich equation was used for Cd, Cu, Cr and Pb and the parameter values are summarized in Table 6. It was revealed that the Freundlich coefficients K_f are 195, 149 and 221 L kg^{-1} for Cr, Pb and Cu that are much higher than those of 3.51 L kg^{-1} for Cd.

Sorption isotherm analysis is a useful technique to study the retention of metals in soils. Sorption isotherms provide important information about the soil retention capacity and the strength with which the sorbate is held onto the soil. Low values of K_f for Cd in Table 6 indicate that most Cd remains in the solution and is available for transport, chemical processes, and plant uptake; on other hand, large values of K_f of Cr, Pb and Cu reflect a large affinity of solid soil components for these metals.

In the designed experimental concentrations of Ni and Zn, the adsorption curves appear to be a linear equation with very high coefficient of determination shown in Table 6.

Conclusions

Heavy metal cations for typical proportion of concentrations in recycled water act in competition sorption. From the analyses of sorption intensity, sorption isotherm the conclusion is that the six heavy metals in this study can be divided into two groups. The first group of metal cations of Cr, Pb and Cu had a strong propensity for sorption and the second group of Zn, Cd and Ni had comparatively weak sorption capacities. When the original concentration of metal in treatment solution increased, the strong sorption metal group of Cr, Pb and Cu still exhibited high sorption intensity. In contrast, the relative weak sorption metal group of Cd, Zn and Ni exhibited a pronounced drop in sorption intensity. It was found that the particle associated with waxes in water repellent soil does not affect the sequence of sorption intensity for the six metals comparing with most of other types of soils. However, the mechanism of surface coverage for metal adsorption in the water repellent soils should be further studied.

The water repellent soil in this case study has very high sand particle size up to 96.4% and silt and clay only constitute 6 and 0.5% of the total, respectively. According to the underlying principles of land treatment system for the recycled water, the groundwater contamination of pollutants, especially heavy metals, may become the critical factor to be considered for the design and performance of land treatment system. It would be suggested that the slow rate land system of recycled water treatment might be the first choice in

Table 6 Adsorption isotherms for six heavy metals in water repellent soil

Equation	Metal	K_f (L kg^{-1})	*n*	*r*	R^2
Freundlich	Cd	3.51	5.87	0.9727	0.9462
	Cr	221.32	2.25	0.9902	0.9805
	Cu	194.54	2.36	0.9985	0.9969
	Pb	148.81	5.96	0.9681	0.9373
Linear	Ni	$y = 1.4,958x + 13.69$	$R^2 = 0.981$		
	Zn	$y = 2.7,129x + 38.95$	$R^2 = 0.990$		

r correlation coefficients, R^2 coefficient of determination, *x* supernatant concentrations of heavy metals (mg L^{-1}), *y* sorbed amount of heavy metal in soils (mg kg^{-1})

the practical application. However the risk assessment for the application of recycled water onto water repellent soil is definitely necessary, especially for the metal cations with relative weak sorption.

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