

## Competitive adsorption and mobility sequence of heavy metals in urban soils of southeastern China

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**Abstract:** Heavy metals can be introduced into urban soils at the same time. Therefore, their selective retention and competitive adsorption by the soils become of major importance in determining their availability and movement throughout the soil. In this study, the availability and mobility of six heavy metals in eight urban soils collected from different cities of Zhejiang Province, southeastern China were assessed using distribution coefficients ( $K_d$ ) and retardation factor ( $R_f$ ). The results showed that there were great differences in the  $K_d$  and  $R_f$  among the tested soils. The adsorption sequences were  $\text{Cr} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$ , and the  $K_d$  decreased with increasing levels of metal addition. Ni generally has the lowest  $R_f$  values followed closely by Cd, and Zn whereas Cr and Pb reached the highest values. The results suggest that Ni and Zn have the highest mobility associated to the lowest adsorption, Cr and Pb present the opposite behavior. Correlation analysis indicates that soil pH,  $\text{CaCO}_3$  content, and cation exchange capacity (CEC) are key factors controlling the solubility and mobility of the metals in the urban soils.

**Keywords:** competitive adsorption; mobility sequence; heavy metal; urban soil

### Introduction

Urban soils are known to have high concentrations of heavy metals (Manta *et al.*, 2002). As cities are densely populated, the accumulation of heavy metals in the urban soils is closely related to human health (Calabrese *et al.*, 1997). Contaminated urban soils could cause groundwater contamination because metals of the polluted soils tend to be more mobile than those of unpolluted (Manta *et al.*, 2002). Heavy metals in the urban soils can be introduced into soils, mainly by a wide variety of anthropogenic activities such as dumping of waste, smelter stacks, waste incineration, vehicular emissions, application of fertilizers, agricultural waste and sewage sludge (Calabrese *et al.*, 1997; Kock and Rotard, 2001). In this situation, several heavy metal cations can be available at the same time in the soils and, therefore, their selective retention and competitive adsorption by the soil become of major importance in determining their availability to plants and their movements throughout the soil. The risks of environmental toxicity posed by the metals are a function of their mobility and availability. The movement of heavy metals in soil profiles has received considerable attention, since even a slow transport through soil and subsoil materials may result in an increased content of heavy metals in the groundwater (Li and Shuman, 1997). However, up to date, the fate and transport of metals, particularly adsorption-desorption, and physical conditions involved in the soil process are not fully understood. The limited information makes it difficult to predict the mobility of metals in the urban soils. It is required to understand the processes of soil-

heavy metal interactions, in particular, their mobility and retention, since these are essential factors that control groundwater contamination.

The availability and mobility of heavy metals in the soils can be assessed using adsorption-desorption and leaching experiments. Several studies have found that soil properties correlated with adsorption and mobility of heavy metals are pH, organic matter (OM), cation exchange capacity (CEC), specific surface area, free iron oxides, clay, exchangeable Ca. However, the role of soil properties in controlling metal mobility could vary with soils and heavy metals, with most metals being most mobile in acidic, coarse-textured soils (Harter, 1983; Amacher *et al.*, 1986; King, 1988; Slavek and Pickering, 1988; Jopony and Young, 1994). Distribution coefficients ( $K_d$ ) and retardation factor can indicate the capability of a soil to retain a solute and also the extent of movement in a solution phase. The mobility and fate of metals in the soil environment are directly related to their partitioning between soil and soil solution and, therefore, are directly related to their distribution coefficients. The  $K_d$  is a useful parameter for comparing the sorptive capabilities of different soils or materials for any particular ion, when measured under the same experimental conditions. Distribution coefficients have been used in studies of mobility, retention, leaching and solubility of the heavy metals (Reddy and Dunn, 1986; McBride *et al.*, 1997; Alloway, 1995; Lee *et al.*, 1996; Gao *et al.*, 1997; Fontes *et al.*, 2000). The retardation factor of solutes moving through soils, another parameter that expresses the relationship between the speed of solute movement and the water-leaching front speed, is an indicator of

interactions between the solution and the solid phase. It can give an idea about the mobility of cations throughout the soil profile.

The main objectives of the study were to evaluate the retention and mobility sequences of six heavy metals applied together to the urban soils by means of distribution coefficients and retardation factor, and to investigate the relationship between soil properties and adsorption of heavy metals by the urban soils.

1 Materials and methods

1.1 Soil samples

Eight surface soil samples with a wide range of properties were collected at 0–15 cm depth from different cities of Zhejiang Province, southeastern China. S1 is dystric turbi-anthric primosols, S2, S4, and S8 are typic turbi-anthric primosols, S3, S5, S6, and S7 are calcareic turbi-anthric primosols(CGR-CST, 2001). The soil samples were air-dried at 25°C and ground to pass through a 2-mm sieve. Subsamples from each soil were further ground to pass through a 0.15-mm sieve for chemical analysis. Basic properties of the eight urban soils are listed in Table 1.

Table 1 Basic properties of the urban soils

Properties	Soil							
	S1	S2	S3	S4	S5	S6	S7	S8
pH	5.3	7.2	8.6	6.3	8.4	7.9	7.5	6.8
Clay(<2μm), g/kg	306	211	265	143	244	266	293	331
Organic C, g/kg	18.9	13.2	24.5	9.2	19.4	38.9	22.4	29.7
Free Fe, g/kg	22.8	14.3	25	12.2	18.5	13.8	17	30.1
CaCO <sub>3</sub> , g/kg	0	0	53	0	36.4	13.4	0.62	0
CEC, cmol/kg	7.3	8.2	17.3	6.8	13.6	14.2	13.4	10.6

1.2 Determination of soil properties

Soil pH was measured in water at a soil:water ratio of 1 : 1 using a pH meter. Total carbon (C) was determined by wet digestion (Agricultural Chemistry Committee of China, 1983). Particle composition of the soil samples was determined using the micro-pipette method (Miller and Mill, 1987). Free Fe was extracted with citrate-bicarbonate-dithionite(Loeppert and Inskeep, 1996). Carbonate content was determined by back titrating an excess of 0.5 mol/L HCl added to 1 g of sample with 0.5 mol/L NaOH(Allison and Moodie, 1965). Cation exchange capacity(CEC) was estimated using standard methods(Institute of Soil Science, Chinese Academy of Sciences, 1978).

1.3 Sorption experiment

Sorption of Cd, Cr, Cu, Ni, Pb and Zn was performed by equilibrating 1 g air-dried soil with 20 ml 0.01 mol/L CaCl<sub>2</sub> solution containing concentrations of 5, 10, 20, 30, 40, and 50 mg/L of all heavy metals in the same concentration. The soil suspensions were shaken continuously for 8 h at 25°C(equilibrium time was determined by a preliminary experiment). At

the end of the designated period, the suspensions were centrifuged at 6500 × g relative centrifuge force for 30 min and the supernatant was passed through a Whatman # 42 filter paper. The Cd, Cr, Cu, Ni, Pb and Zn concentrations in the filtrates were determined using an inductively coupled plasma atomic emission spectrometry (ICP-AES). The difference between the initial amount of metal in solution and the amount remaining in solution after the reaction period was assumed to be the amount of metal adsorbed by the soil. The distribution coefficients(*K<sub>d</sub>*) were calculated as follows:

$$K_d = \frac{C_{es}}{C_{ea}}$$

(1)

Where, *C<sub>es</sub>* is equilibrium metal concentration adsorbed in soil, mg/kg; *C<sub>ea</sub>* is equilibrium metal concentration in aqueous solution, mg/L.

1.4 Leaching experiment

Effluent breakthrough curves for heavy metals were measured using soil-packed columns. The column (20 cm long and 10 cm inner diameter) was made of a polyvinyl chloride (PVC) tube. The bottom of each column was a polyvinyl chloride plate containing several 5-mm-wide holes and the top of the plate was covered with a nylon cloth glued to the plate. Each column was packed with 1766 g soil sample to a height of 15 cm, with a bulk density of 1.50 g/cm<sup>3</sup>, which is approximated the bulk density in the field (1.45–1.55 g/cm<sup>3</sup>). There were three replications for each soil. Two disks of filter paper were placed on the top of soil column prior to leachings to prevent disturbance by applied solution. Contaminant solutions containing concentrations of 25 mg/L of Cd, Cr, Cu, Pb, Ni, and Zn were ponded on the soil column surface and about 510 ml (1 pore volume) of contaminant solution per day was applied at a rate of 20 ml/min and the leaching lasted for 15 d. This application rate did not cause any ponding on the top of the column. Leachate was collected in a 1000-ml beaker below each soil column, filtered through quantitative filter paper, and stored in a freezer(-4°C) prior to analysis. Cd, Cr, Cu, Pb, Ni, and Zn concentrations in the leachate were determined using the ICP-AES. The retardation factors (*R<sub>f</sub>*) were analytically determined, from regression equations, as the necessary number of pores to make the effluent concentration equal to 50% of the concentration of the concentration solution followed by the procedures of de Matos *et al.* (1999).

2 Results and discussion

2.1 Adsorption selectivity sequence of the heavy metals

There were great differences in metal adsorption capacity among the tested soils. The *K<sub>d</sub>* decreased with increasing levels of metal addition. However, soil

S3 and S5 maintained a relative high  $K_d$  value of Cr and Pb in the whole designed range of metal concentrations. The adsorption capacities of metals decreased generally in the order of  $S3>S5>S6>S7>S2>S8>S4>S1$ . The distribution coefficient( $K_d$ ), a concentration ratio of a substance between a solid phase and a solution phase in a solid-solution system, is usually used to reflect soil capacity to retain the soluble inorganic or organic substance. High values of  $K_d$  indicate that the metal has been retained by the solid phase through sorption, while low values of  $K_d$  indicate that a large fraction of the metal remains in solution. The  $K_d$  values varied with the species of metals(Table 2). Cr and Pb had the highest  $K_d$  values, showing that Cr and Pb were more strongly retained than other metals. The metals with the lowest  $K_d$  values were Cd, Zn, and Ni, showing that they are easily exchanged and substituted by Cr and Pb, when the concentrations of metals in soil solution are high. The result indicated that soil loading of Cd, Zn, and Ni appeared to be of greater environmental concern than Cr, Cu, and Pb and that the first group could be leached into the groundwater. The accelerated decrease of  $K_d$  values for Cd, Zn, and Ni with increasing metal concentrations added suggest the competition among the metal cations decreased significantly the adsorption of Cd, Zn, and Ni by the soils. Competition strongly influenced the adsorption capacity of Cd, Zn, and Ni, indicating a decrease in their adsorption in the more concentrated solutions. The adsorption sequences most found were  $Cr>Pb>Cu>Cd>Zn>Ni$ .

2.2 Retardation factors

The retardation factors for Cd, Cr, Cu, Pb, Ni, and Zn obtained for the eight soils are showed in Table 3. Ni generally has the lowest values followed closely by Cd, and Zn whereas Cr and Pb reached the highest values. It means that Ni and Zn have the highest mobility associated to the lowest adsorption and Cr and Pb present the opposite behavior. Cu present higher values for  $R_f$ , as compared to Ni and Cd, showing that it is more adsorbed and has less mobility than these two metals, in the soil profiles. Cr and Pb presented, consistently, the highest values for retardation factors showing clearly that it is highly immobilized by these soils.

2.3 Effects of soil properties on the  $K_d$  and  $R_f$

The evaluation of the influence of soil properties on the metal-adsorption capacity of the soil was examined by correlation analysis(Tables 4 and 5). The sorption affinity of the metals, represented by the  $K_d$  and  $R_f$  was influenced mainly by pH,  $CaCO_3$  content, and CEC, as shown by the highly significant simple correlation coefficients between these variables. At the same metal rates, the logarithm of the  $K_d$  and  $R_f$  was positively correlated with soil pH (Table 4). The  $K_d$

Table 2 Distribution coefficients ( $K_d$ ) calculated for each added metal concentration for the different soils

	Metal Concentration added, mg/kg	$K_d$							
		S1	S2	S3	S4	S5	S6	S7	S8
Cd	5	28.9	62.0	1234.7	43.7	698.9	146.3	80.0	45.7
	10	16.2	39.7	510.2	21.3	360.4	83.3	74.5	22.0
	20	8.7	27.9	195.8	14.2	165.2	47.1	32.7	18.7
	30	4.5	23.8	184.5	7.3	164.6	38.2	31.3	10.2
	40	1.7	12.6	69.0	3.1	53.0	20.7	15.9	4.5
	50	0.7	5.4	37.7	1.0	33.6	14.0	9.0	1.5
Cr	5	125.6	278.1	1649.4	212.3	1649.4	327.2	286.7	241.1
	10	72.9	119.7	725.4	80.1	784.8	150.8	140.9	92.7
	20	35.5	74.6	590.3	39.1	517.3	88.3	83.0	59.8
	30	29.9	59.3	471.5	32.6	448.7	66.5	65.3	45.6
	40	22.8	46.0	254.5	25.3	236.2	50.0	49.2	32.5
	50	15.5	30.2	195.6	17.6	171.1	41.2	34.2	25.9
Cu	5	56.1	141.2	1412.7	87.1	1096.1	365.4	247.7	234.8
	10	23.7	86.8	360.4	22.2	295.2	171.4	91.6	123.3
	20	18.7	38.0	223.1	9.0	175.0	98.5	61.7	89.8
	30	14.6	18.2	61.5	6.0	45.0	36.2	23.2	30.5
	40	10.1	9.2	34.9	1.8	27.6	23.2	12.7	19.1
	50	8.3	8.3	81.6	1.1	53.0	23.2	11.3	18.1
Pb	5	81.9	197.9	1649.4	160.5	1649.4	316.1	247.7	189.2
	10	55.0	117.1	1522.0	102.7	1522.0	162.0	137.5	110.6
	20	44.4	87.3	1363.6	76.6	1274.9	110.1	97.9	80.5
	30	19.4	44.2	1209.3	24.6	1002.0	82.4	69.7	35.3
	40	12.7	28.8	668.3	16.7	604.5	56.1	49.7	24.2
	50	10.8	20.0	210.9	13.9	197.9	35.4	30.2	16.6
Zn	5	26.3	64.7	698.9	31.3	510.2	189.2	81.9	38.1
	10	15.7	40.9	629.6	20.8	448.7	87.3	77.4	22.1
	20	9.4	24.4	210.6	13.9	184.9	50.4	34.7	19.7
	30	3.8	20.8	199.3	4.8	1096.1	40.8	29.0	10.7
	40	0.8	7.0	39.1	2.8	34.8	14.9	13.1	3.7
	50	0.3	4.5	32.7	1.3	30.0	14.2	10.6	1.3
Ni	5	15.6	33.3	353.4	22.4	177.9	90.4	63.3	34.7
	10	11.3	25.3	285.6	17.8	165.2	65.8	48.1	21.4
	20	8.8	19.3	161.8	11.4	145.5	52.8	32.3	14.2
	30	2.7	11.6	121.8	4.3	113.4	39.2	27.4	8.3
	40	0.9	4.9	92.3	1.5	74.6	28.8	11.0	1.8
	50	0.5	3.0	71.3	0.8	65.1	23.2	5.9	1.1

and  $R_f$  increased exponentially with increasing soil pH(Fig.1), indicating that soil pH has a great influence on metal adsorption. These results indicate that pH is a key factor controlling the solubility of metal in the urban soils. Yong and Phadungchewit (1993) reported that a change in soil solution pH can result in a corresponding change of the dominant retention

Table 3 Retardation factors(Rf) for the six metals of the soils								
Metals	Rf							
	S1	S2	S3	S4	S5	S6	S7	S8
Cd	2.6	7.4	15.6	3.2	13.3	8.9	8.6	4.1
Cr	9.2	14.7	34.2	10.0	30.4	25.8	17.3	11.4
Cu	4.9	8.5	18.3	4.3	16.8	12.7	9.4	7.9
Pb	6.8	11.1	30.4	8.0	28.6	23.8	15.3	10.2
Zn	2.8	7.8	17.6	3.3	15.4	9.6	8.9	5.1
Ni	1.7	5.1	19.3	2.2	14.6	9.4	8.0	3.1

mechanisms of heavy metals in soils. At high soil solution pH, precipitation prevails. As pH decreases, precipitation becomes less important, and cation exchange becomes dominant. The pH effects were

also thought to relate to the exchange of H<sup>+</sup> with heavy metals and the effect of pH on dissolution-precipitation and oxidation of Fe and Mn oxides (King, 1988). As soil pH increased there was an increase in the metals adsorption and there was also an increase of the metals precipitation. This shows that the mobility of all the heavy metals decreased with the pH increase. The phenomenon can be related to both the increasing of the specific and non-specific adsorption and to the precipitation reaction. It seems that the soils with higher pH values adsorbed more metals compared with most of the low pH soils, suggesting that the increase in the hydrolyzed forms of cations and CEC of the soils with the increase in pH was as important as the nature of the adsorbent materials.

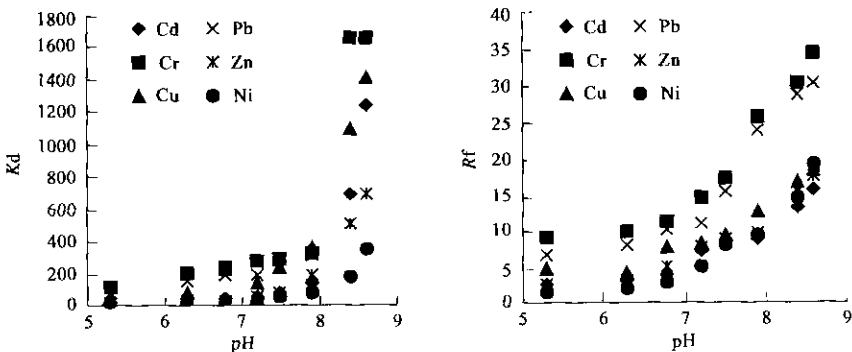


Fig.1 The Kd and Rf varied as a function of soil pH

Table 4 Correlation coefficients between Kd for each metal and soil properties						
Properties	Cd	Cr	Cu	Pb	Zn	Ni
Added metal concentration: 5 mg/L						
pH	0.888**	0.876**	0.942**	0.903**	0.926**	0.944**
Clay	0.006	-0.036	0.055	-0.027	0.005	0.053
Organic C	0.100	0.039	0.184	0.058	0.170	0.211
Free Fe	0.294	0.217	0.284	0.216	0.218	0.278
CaCO <sub>3</sub>	0.983**	0.959**	0.988**	0.963**	0.997**	0.972**
CEC	0.750*	0.703*	0.807*	0.714*	0.794*	0.827**
Added metal concentration: 50 mg/L						
pH	0.967**	0.891**	0.735*	0.887**	0.983**	0.953**
Clay	0.010	0.001	0.152	-0.012	0.019	-0.003
Organic C	0.200	0.084	0.268	0.063	0.234	0.189
Free Fe	0.130	0.244	0.383	0.227	0.091	0.169
CaCO <sub>3</sub>	0.974**	0.978**	0.983**	0.971**	0.957**	0.986**
CEC	0.828**	0.744*	0.819**	0.726*	0.867**	0.783*

Notes: The Kd was logarithmically transformed when it was correlated with pH; \*, \*\* are significant at *P*<0.05 and *P*<0.01 respectively

Table 5 Correlation coefficients between Rf for each metal and soil properties						
Properties	Cd	Cr	Cu	Pb	Zn	Ni
pH	0.974**	0.956**	0.945**	0.961**	0.978**	0.976**
Clay	0.022	0.038	0.137	0.064	0.045	0.054
Organic C	0.241	0.389	0.398	0.427	0.250	0.282
Free Fe	0.043	0.031	0.160	0.043	0.099	0.116
CaCO <sub>3</sub>	0.902**	0.924**	0.921**	0.910**	0.922**	0.950**
CEC	0.879**	0.899**	0.904**	0.907**	0.876**	0.902**

Notes: The Rf was logarithmically transformed when it was correlated with pH; \*, \*\*are significant at *P*<0.05 and *P*<0.01 respectively

### 3 Conclusions

The most frequent heavy metal selectivity sequences were  $\text{Cr} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$ . Ni and Zn have the highest mobility associated to the lowest adsorption and Cr and Pb present the opposite behavior. The soil properties showed significant correlation to the metals retardation factors. pH,  $\text{CaCO}_3$  content, and CEC are key factors controlling the retention and movement of the metals in the urban soils, as measured by the retardation factor. Therefore, keeping high soil pH was an effective measure to reducing risk of metal leaching from the soil.

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