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Monometal and competitive sorption of heavy metals in mine soils: Influence of mine soil characteristics

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ABSTRACT

The environmental and health effects of the contamination of soils by heavy metals depend on the ability of the soils to immobilize these contaminants. This study was conducted to assess the monometallic and competitive sorption of lead, copper, zinc and cadmium in surface samples of four soils from eastern Algeria. Sorption isotherms were characterized using Freundlich and Langmuir equations. Retention selectivity sequences indicate that, in most of the soils, Pb is the preferred retained metal, followed by Cu. The last metals in these sequences are Cd and Zn. All soils showed greater sorption capacity. On the basis of distribution coefficient values for the metal concentration of 100 mg. l^{-1} (Kd_{100}) for each soil and trace element, the two most common adsorption sequences found were Pb>>Cu>Cd>Zn and Pb>>Cu>Zn>Cd. Competition significantly reduced metal Kd, especially that of Cd.   © 2013 Trade Science Inc. - INDIA

KEYWORDS

Competitive adsorption;
Soil;
Heavy metals;
Distribution coefficient.

INTRODUCTION

Assessment of the risk derived from heavy metal contamination in soils requires information about metal interaction and subsequent mobility of metals, which is directly related to their partitioning between soil and soil solution[13]. Soils might be contaminated by heavy metals from various anthropogenic activities, including agricultural practices, transport, industrial activities, and waste disposal or mining activity. These heavy metals are believed to be easily accumulated in the surface soil[5,30]. Some of the elements, such as cadmium (Cd), lead (Pb), zinc (Zn), and copper (Cu) are potentially toxic towards plants and animals and can be accumulated in the food chain[7,29]. Various soils show a very different behavior in sorption of heavy metals[1]. This is due to the fact that the sorption capacity of each heavy metal dependent on factors such as soil pH, iron and aluminium oxide content, clay content, organic matter and cation exchange capacity[19].

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Heavy metals in the soil are to a large extent sorbed on soil particles. Adsorbed heavy metals can be desorbed by soil water, and thus move in dissolved form into plants or move to lower soil horizons and groundwater. The mobility of heavy metals in soil can be characterized by a distribution coefficient, defined as the ratio of metal concentration in the solid phase to that in liquid phase at equilibrium[2,9-11,14,16,22]. Sorption processes and the leaching potential of trace elements by soil depend on factors such as soil pH, the nature of the mineral and organic constituents, the nature of the metal, the ionic strength of the soil solution and the simultaneous presence of competing metals[18,23]. The adsorption of trace elements has been studied and reported in the literature for several different soil components[3,9,10,17,21,26,31,32]. Most trace element sorption has been derived from studies conducted using single metal solutions[28,35]. Sorption of trace elements is a competitive process between ions in solution and those sorbed onto the soil surface. In this situation, single metal solutions have limited practical applications[14].

Batch tests were undertaken with mono and multi metal solutions with equimolar concentrations of the mentioned heavy metals in order to study the sorption equilibrium. The Langmuir isotherm model was adjusted to experimental data, allowing the determination of the soil maximum sorption capacity for each metal, with and without competition.

The present paper aims at studying the effect of competitive and monometal sorption of Pb, Cu, Cd and Zn on four soils of different physicochemical properties. The specific goals were: (1) to determine distribution coefficients Kd of these metals for a range of soils samples and investigate any correlation between distribution coefficients and soil characteristics; (2) to classify the metals and soils according to the Kd values obtained; and (3) to obtain and compare monometal and competitive solution isotherm at 20°C.

MATERIALS AND METHODS

Soil samples used in the study

Four soil samples were taken from the 20 cm deep surface horizon of Amizour, located in Bejaia, east of Algeria. The samples were transported to the laboratory in polyethylene bags, air dried and passed through a 02 mm mesh sieve. Then they were cleaned by deionized water and dried at 50°C during 24h.

Soil analyses

Soil pH in water was determined with a pH meter using 2:1 (v:w) (water:soil) suspensions[39]. Percentages of sand (2–0.05 mm), silt (0.05–0.002 mm) and clay (<0.002 mm) were determined by the wet sieving method and the pipette method. Exchangeable cations were extracted with 0.2M NH_4Cl[38] and measured by atomic absorption spectrophotometry (Ca, Mg, Na and K). Total carbon and organic carbon (C_{org}) contents in soils were determined by elemental analysis[20]. The inorganic carbon content was calculated as the difference between the total carbon and organic carbon contents and expressed as % $CaCO_3$. The X-ray diffraction (XRD) analysis of the sample was carried out via a Powder X-ray Diffractometer (BRUKERAXS) in the 2θ angle ranging from 2° to 65° employing a 0.025° step. The specific surface area was measured by N_2 gas adsorption at -196°C (COULTER-SA3100). BET equation was used to calculate the specific surface area. The physical and chemical characteristics of the samples are shown in TABLE 1.

Sorption stage

Sorption of Cu, Zn, Pb and Cd

Batch sorption studies were conducted to determine the relationship between adsorbent and adsorbate by varying the concentration of the metals. In each experiment, cadmium, copper, lead and zinc were sorbed from a "sorption solution". The initial concentrations of Cd, Cu, Pb and Zn tested were 10, 20, 40, 50, 100 and 200 mg. l^{-1}.

Experimental procedure: 1 g of soil sample was suspended in 100ml of sorption solution and shaked for 24 h at 20 °C in a rotary shaker. Then the suspension was centrifuged at 6000 rmin^{-1} for 5 min, and the supernatant was filtered through slow filter paper (Whatman No. 42). The supernatants metal concentrations were determined by ICP (ICP JY2000). The quantity of the metal sorbed by the soil sample was calculated by using mass balance relationship:

$$qe = \frac{(C0 - Ce)xV}{W} \qquad (1)$$

where qe is the amount of adsorbed species at equilib-

rium (μmol. g^{-1}), C0 is the initial concentration of the species in solution (μmol. l^{-1}), Ce is the measured concentration (μmol. l^{-1}) of metal in solution when the equilibrium is reached. V is the solution volume (L) and W is the weight of air-dried soil (g).

The pH was not controlled during the experiments; it was monitored before filtration and analysis (after equilibrium).

Adsorption from mixtures

The experimental procedure was the same as the monocomponent adsorption (see above). 1 g of soil was mixed with 100 ml of a solution containing copper, zinc, lead and cadmium in 1:1 mg ratio (total concentration range 10–100 mg l^{-1}).

Adsorption isotherms

The equilibrium data were analyzed in accordance with the Langmuir and Freundlich sorption isotherms. These isotherms allow describing adsorption phenomena of metals from aqueous solution onto soil sample. The Langmuir isotherm is expressed by:

$$Ce/qe = 1/(bqm) + Ce/qm \qquad (2)$$

where qe and Ce are the adsorption capacity and concentration, respectively, at the equilibrium. qm is the maximum adsorption capacity at saturation (μmol metal g^{-1}) and b is the affinity coefficient (μmol. l^{-1}) (Langmuir, 1918), qe can be expressed as:

$$qe = Kd.Ce \qquad (3)$$

where Kd is the distribution coefficient that characterizes the affinity of the metal for the sorbent, the Freundlich isotherm, which assumes that different sites with several adsorption energies are involved, is expressed by:

$$qe = K_f C_e^{1/n} \qquad (4)$$

where K_f (lkg^{-1}) is the Freundlich distribution coefficient related to the total adsorption capacity of the solid, and n is the Freundlich sorption exponent.

The goodness-of-fit for all equations was estimated by the regression coefficient. Statistical analysis was performed using the Excel program. In addition, for each stage of each experiment, the distribution of each metal i between soil and solution following equilibration was expressed in terms of the quotient:

$$Kd, i = \frac{Ci, soil}{Ci, solu}$$

where $Ci, soil$ is the concentration of metal i on the soil (mmol kg^{-1}) and $Ci, solu$ is the concentration of metal i in solution (mmol l^{-1})[3,31]. The distribution coefficient at 100mgl^{-1} (Kd_{100}) according to Covelo et al. 2007 was also used to evaluate capacity of soils to adsorb heavy metals.

RESULTS AND DISCUSSION

Soil characteristics

TABLE 1 summarizes the main soil sample characteristics. The four soils were basic (pH 7.5-8.3). pH is one of the main factors controlling metal adsorption, mobility and availability of metals. The organic carbon (Corg) content ranging from 0.96 to 1.34%. The Soil 2 had a highest cation exchange capacity (CEC). Soil 2, Soil 3 and Soil 4 have a clay texture, but Soil1 contains a higher proportion of silt. On the other hand, the soils have a similar surface area except for Soil 1 which has the lowest surface area.

TABLE 1 : Main characteristics of soil samples

Soil property	soil1	soil2	soil3	soil4
Clay (%)	24.6	60.2	51.9	54.7
Sand (%)	28.1	11.1	7.9	10.1
Silt (%)	47.3	28.7	40.2	35.2
pH	7.5	7.9	8.3	7.8
Corg	1.34	1.12	1.08	0.96
CEC cmoles kg^{-1}	13.8	46.3	34.6	37.6
Surface Area (m^2 g^{-1})	12.1	41.8	22.3	29.9
Goethite (%)	28.7	32.2	47.3	18.32
Quartz (%)	3.4	2.65	1.74	1.24
Feldspars (%)	7.2	nd	n. d	nd
Kaolinite (%)	53.4	24.5	31.4	23.8
Mica (%)	7.7	5.5	12.2	12.1
Smectite clay content (%)	28.1	67.3	54.6	62.1

Adsorption isotherms and Kd values

The adsorption isotherms of single metal ions onto soil samples are reported in Figure 1. These isotherms can be subdivided in three parts. At low-concentration, the metal introduced is adsorbed proportionally. At intermediate, there is a pseudo-plateau, which probably corresponds to the saturation of the surface. However in the case of lead, we note that the amount adsorbed increases regularly when the solution concentration
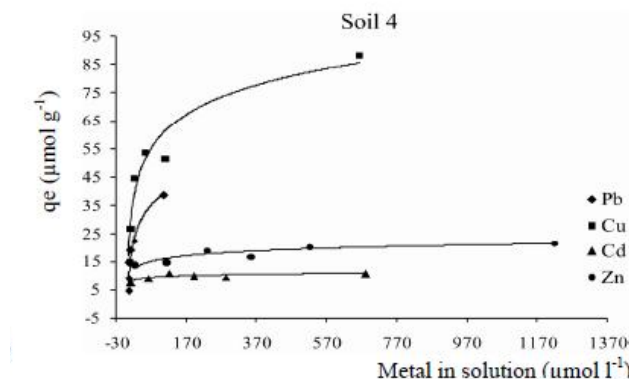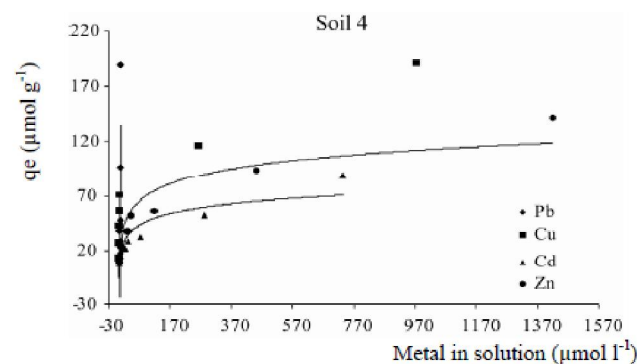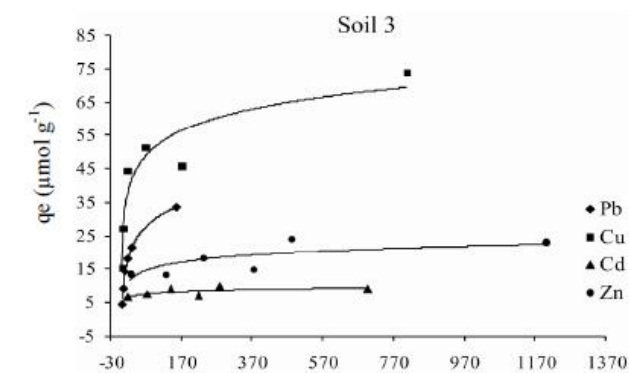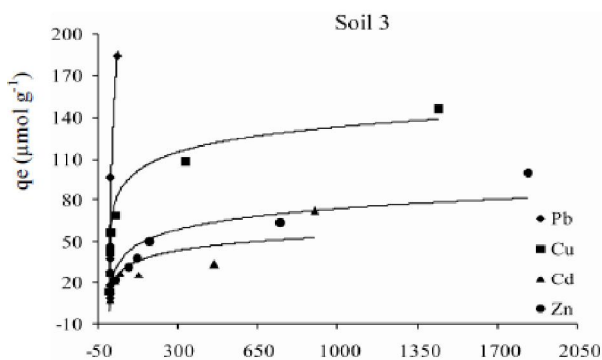
Figure 1 : Monometal sorption isotherms at 20°C for retention of Pb, Cu, Cd and Zn by four soils (soil1, soil2, soil3 and soil4).

increases. This is probably due to a surface precipitation of lead.

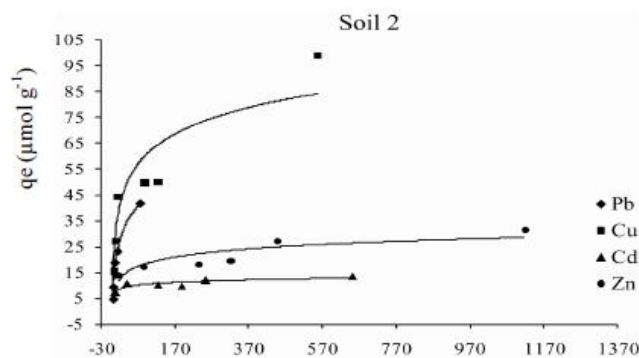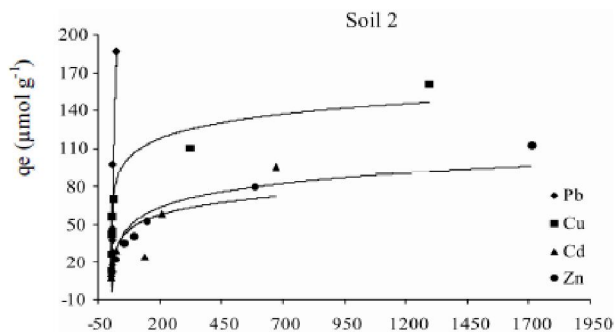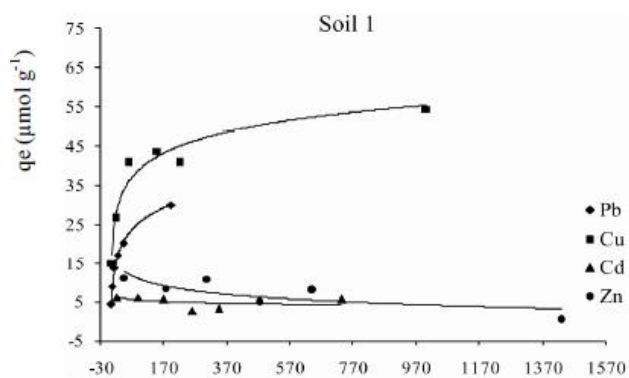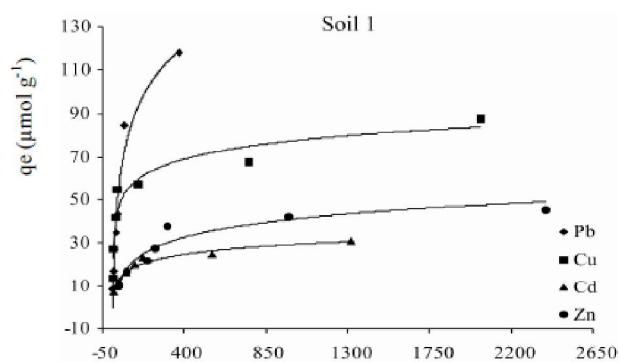TABLE 2 shows values of parameters deduced from the application of Langmuir and Freundlich equa-

Figure 2 : Competitive sorption isotherms at 20°C for retention of Pb, Cu, Cd and Zn by four soils (soil1, soil2, soil3 and soil4).

tions. The maximum adsorption capacity (qm), deduced from the Langmuir equation, may be useful in compar-

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ing the potential adsorption capacity for the studied soils. Langmuir sorption parameters of the studied soils showed differences among the studied heavy metals, as reflected by their sorption maxima (qm) and bonding energy coefficient (b) (TABLE 2). Among all studied metals, Cu showed the highest value of adsorption maxima (qm) in all studied soils Much lower value of adsorption maxima were obtained for Cd. In addition, the bonding energy coefficients (b) for Cd and Zn were lower than those for Cu, suggesting that Cd and Zn could not form much stronger complexes than Cu. Moreover, we note that the data of Pb follow C isotherm. In the other hand, the values for the Freundlich distribution (K$_f$) coefficient were 9.46 and 2.53 litre kg^{-1} for Zn and Pb sorption by Soil 2, respectively. Concerning n parameter, which expresses site heterogeneity, it varied within a wide range of values (0.27–4.83) for the various metal and soil. The amount of Pb and Cu sorbed was greater than that of Zn and Cd.

TABLE 2 : Isotherm parameters of four soils deduced from monometal sorption in solution at 20°C.

Soil	Isotherms					
	Langmuir			Frendlich		
	Qm (μmol g⁻¹)	b (Lμml⁻¹)	R²	Kf (l kg1)	n	R²
Zn						
Soil1	50	0.0062	0.99	3.32	2.74	0.87
Soil2	125	0.0072	0.98	9.46	2.99	0.99
Soil3	111.11	0.0056	0.96	9.15	3.24	0.98
Soil4	166.66	0.0089	0.97	12.44	2.98	0.99
Cd						
Soil1	32.26	0.0148	0.99	4.08	3.33	0.92
Soil2	100	0.010	0.75	8.65	2.94	0.87
Soil3	66.66	0.0098	0.80	7.25	3.3	0.89
Soil4	100	0.012	0.94	7.65	2.77	0.98
Cu						
Soil1	90.9	0.02	0.99	19.45	4.83	0.75
Soil2	166.66	0.04	0.99	32.26	4.21	0.88
Soil3	166.66	0.038	0.99	28.27	4.06	0.89
Soil4	200	0.039	0.97	36.23	4.098	0.78
Pb						
Soil1	142.85	0.016	0.99	4.92	1.68	0.91
Soil2	a	a	a	2.53	0.67	0.77
Soil3	a	a	a	6.72	1.03	0.55
Soil4	a	a	a	0.074	0.27	0.76

ᵃ **: Langmuir equation did not fit to the data.**

The adsorption data were fitted better by the Langmuir equation than by the Freundlich equation. Distribution coefficients (Kd) represent the affinity of the metallic cations in solution towards the solid phase. They can be used to evaluate the sorption and retention of the metallic cations in soils[11]. A distribution coefficient can be related to both plant uptake and environmental pollution.

The low values of distribution coefficients indicate

TABLE 3 : Values of Kd for sorption in four soils deduced from monometal sorption in solution at 20°C.

Initial Concentration (mg/l)	Soil1	Soil2	Soil3	Soil4
Zn				
08.5	282	6000	5237	10575
16.3	211	1200	1006	3019
26.9	115	668	391	1322
33.3	117	453	324	1302
44.6	125	365	291	488
90.9	43	138	86	208
185.8	19	66	55	100
Cd				
09.1	647	5973	3041	5625
18	310	3500	2276	3000
27.2	210	2416	928	1068
36.5	162	1307	563	934
44.9	137	187	206	466
90	45	280	74	185
182.6	23	142	81	121
Cu				
08.86	4190	49111	44200	52058
17.6	11600	10294	18041	24718
27.65	2557	21153	23000	61400
36.45	2447	15739	15083	37142
45.67	407	6818	3112	37916
90.68	90	346	328	448
184.52	43	124	101	197
Pb				
09.84	1934	2381	2333	2333
19.61	1615	4360	3533	2987
30.94	2108	6382	6565	5477
40.34	1666	6198	7870	7631
50.39	1516	7153	9524	9138
101.89	1221	15007	19403	13567
198.01	320	8376	5211	23963

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that most of the metals present in the system remain in the solution and are available for transport, chemical processes, and plant uptake[27]; whereas higher values indicate lower mobility and higher retention of metals in the soil. Therefore, to be able to compare the different metal cations in each different soil, based on the reasoning of Covelo et al 2007, a Kd at a given concentration is considered.

The most used value is $K\mathrm{d}_{100}$, which represents the ratio of metal sorbed to equilibrium concentration at 100 mg l^{-1} metal in the added solution[11]. TABLE 4 shows the value of $K\mathrm{d}_{100}$ for all soils. The Kd values (TABLE 3) obtained for each metal for the concentrations and soils tested (in l kg^{-1}) are as follows: Cd (23–5973), Cu (43–37916), Pb (320–23963) and Zn (19–6000). Zinc showed the lowest Kd values regardless of the soil sample, while Pb Kd were generally the highest. The obtained Kd sequence for both metals showed good agreement with heavy metal Kd data in soils compiled from the literature[9,10,32]. The lowest Kd values were obtained for the Soil1, which correspond to the sample with the highest sand fraction and also the lowest CEC. This can be related to the fact that distribution of trace elements in polluted soils is known to follow particle size distribution[17]. The lowest sorption capacity is related to the sand fraction, due to the lower surface area associated with larger particle size fractions[21]. On the contrary, the highest Kd values corresponded to Soil2, Soil3 and Soil4 for all metals. This is due to the high clay fraction[17]. It means that Zn and Cd have the highest mobility associated to the lowest adsorption. In contrast Cu and Pb present the opposite behaviour. The Kd quantification was extremely dependent on the initial metal concentration. Thus we note a decreases of the Kd values, especially for Cu and Zn, when the initial metal concentration was increased[26]. This decrease reflects the decreasing average binding energy of occupied sites as concentration increases. The sites occupied at high concentration including both high- and low-energy sites, whereas those occupied at low concentration are all of relatively high energy[15]. The higher Kd value that was obtained in the experiment with lower metal concentrations is associated with the sorption sites of high selectivity, which have relatively strong bonding energies[6,33].

TABLE 4 : Values of $K\mathrm{d}_{100}$ (L kg^{-1}) for the different soils and selectivity sequences deduced from monometal sorption in solution at 20°C.

	Pb	Cu	Cd	Zn	Selectivity sequences
Soil1	1222	90	45	43	Pb>Cu>Cd?Zn
Soil2	15007	346	280	138	Pb>>Cu>Cd>Zn
Soil3	19404	329	74	87	Pb>>Cu>Zn>Cd
Soil4	13567	448	186	209	Pb>>Cu>Zn>Cd
Pb					Soil3> Soil4> Soil2> Soil1
Cu					Soil4> Soil2> Soil3>>Soil1
Cd					Soil2> Soil4>> Soil3> Soil1
Zn					Soil4> Soil2> Soil3> Soil1

The most sorbent and retentive soil for the set of heavy metals was Soil4 followed by Soil 2 and Soil 3. The least sorbent and retentive soil was Soil 1. This indicates that the highest adsorption occurs for Soils that have a high cation exchange capacity values (CEC). The lowest adsorption was observed for soil 1 that contains low amount of clay and a low cation exchange capacity value.

According to the Kd_{100} values, the two adsorption sequences most found were Pb>>Cu>Zn>Cd and Pb>>Cu>Cd>Zn. These sequences follow approximately the order of the electronegativity of the metal cations, which is, Pb (2.3) Cu (1.9), Cd (1.7) and Zn (1.6). The electronegativity is an important factor in determining which of the trace metals will chemisorb with the highest preference[25]. These results are in agreement with that found by Arias et al[4]. The adsorption of Pb and Cu, by acid soils, is higher than that of Cd, Ni and Zn. The higher affinity of the four soils for Pb is probably due to the existence of a greater number of active sites (mostly organic matter) with high specificity. When Pb is present these sites would not be occupied by other cations. This affinity can be attributed to: (i) its greater first hydrolysis constant, and therefore, it's more readily hydrolyzed, (ii) its higher atomic weight, (iii) its higher ionic radius, and subsequently smaller hydrated radius, and (iv) its larger Misono softness value, making it a better candidate than other metals for electrostatic and inner-sphere surface complexation reactions. According to the sequences presented by Schwertmann and Taylor 1989, Zn is always adsorbed to a larger extent than Cd on the synthetic samples, which was the case for our study.

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TABLE 5 : Isotherm parameters of four soils deduced from competitive sorption in solution at 20°C.

Soil	Langmuir			Frendlich		
	Qm ($\mu mol\ g^{-1}$)	b ($L\mu ml^{?1}$)	R^2	K_f ($l\ kg^{-1}$)	n	R^2
Zn						
Soil1	0.43	-0.0037	0.84	343.73	-1.37	0.50
Soil2	35.71	0.008	0.96	07.55	5.26	0.84
Soil3	25	0.0011	0.96	07.34	6.33	0.62
Soil4	22.72	0.0178	0.99	08.71	8.00	0.84
Cd						
Soil1	5.31	0.015	0.81	9.12	-7.75	0.20
Soil2	14.29	0.029	0.98	06.02	8.26	0.79
Soil3	09.25	0.056	0.98	05.11	11.11	0.51
Soil4	10.63	0.091	0.99	06.46	12.82	0.76
Cu						
Soil1	55.55	0.032	0.99	09.07	4.56	0.89
Soil2	125	0.015	0.95	14.16	3.35	0.92
Soil3	83.33	0.026	0.98	17.02	4.38	0.88
Soil4	100	0.026	0.99	13.26	3.21	0.86
Pb						
Soil1	33.33	0.05	0.99	3.82	2.32	0.87
Soil2	55.55	0.042	0.91	3.69	1.65	0.8
Soil3	38.45	0.05	0.99	3.92	2.14	0.83
Soil4	50	0.045	0.96	4.075	1.9	0.76

ᵃ **: Langmuir and Frendlich equations did not fit to the data.**

TABLE 6 : Values of Kd_{100} ($L\ kg^{-1}$) for the different soils and selectivity sequences deduced from competitive sorption in solution at 20°C.

	Pb	Cu	Cd	Zn	Selectivity sequences
Soil1	157	54.6	7.5	0.32	Pb>Cu>Cd>Zn
Soil2	537	178.3	21.2	28.2	Pb>>Cu>Zn>Cd
Soil3	213	91.8	13.0	19.06	Pb>>Cu>Zn>Cd
Soil4	368	133.8	15.3	17.6	Pb>>Cu>Zn>Cd
Pb					Soil2> Soil4> Soil3> Soil1
Cu					Soil2> Soil4> Soil3>>Soil1
Cd					Soil2> Soil4>> Soil3> Soil1
Zn					Soil2> Soil3> Soil4> Soil1

Effect of competition on metal adsorption

Comparison of monometal and competitive sorption isotherm parameters (TABLES 2 and 5) reveals that the presence of other cations decreases sorption of all metals. In fact, competition among the four metals reduced their Kd_{100} values significantly for all the soils studied (TABLE 6). This suggests that the metals were competing for the same binding sites. Although Kd_{100} values indicated a reduction in metal adsorption due to competition, metal isotherms (Figure 1) show that the differences in metal sorption were evident mostly at the higher end of equilibrium concentrations. Thus at low metal concentrations, effects of competition were not

TABLE 7 : Desorption ($\mu mol\ g^{-1}$) of Pb and Zn into $NaNO_3$ solution from soils previously loaded by equilibration in solutions with various concentrations of the corresponding metal ($\mu mol\ l^{-1}$) values shown are means ± standard deviations.

Soil	Initial concentration of metal in loading solution ($\mu mol\ l^{-1}$)									
	700		1200		1600		2300		3300	
	Pb	Zn	Pb	Zn	Pb	Zn	Pb	Zn	Pb	Zn
	$\mu mol\ g^{-1}$									
Soil 1	2.2±0.03	6.4±0.01	2.3±0.05	7.2±0.03	3.5±0.03	7.8±0.00	4.5±0.01	8.1±0.03	5.8±0.06	9.2±0.01
Soil 2	3.1±0.05	6.8±0.03	3.6±0.03	7.5±0.01	3.8±0.02	7.4±0.03	4.7±0.02	8.3±0.03	5.9±0.04	9.6±0.02
Soil 3	3.8±0.03	6.3±0.05	3.3±0.03	7.1±0.06	3.9±0.02	7.6±0.05	5.1±0.04	8.6±0.06	5.3±0.02	9.0±0.03

very strong. Although competition reduced sorption of all four metals, the magnitude of these effects was different for each metal. Thus the effect of competition in reducing the sorption of metals followed generally the order Pb>Cu>Cd>Zn.

In soils with high pH the predominance of the metals is in the hydrolyzed (MOH^+) form[16]. In this case, the influence of the metal hydrolysis on metal adsorption becomes more important for the more alkaline range of pH, as suggested by Elliot et al[12], Brümmer et al. (1988), and Schwertmannand Taylor (1989). In general, metal characteristics such as the order of the electronegativity[25], the charge-toradius ratio[16] or metal-ion hydrolysis constants[40], sequences do not always explain metal bonding selectivity to heterogeneous soil systems[35]. Chemical inputs to soils can take several pathways, including rapid leaching into groundwaters, uptake by plants, volatilization to the atmosphere, and storage and retention by soil.

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Desorption

Depending on the concentrations of the solutions from which initial adsorption had occurred, desorption into $NaNO_3$ solution ranged from 2.2 to 5.9 µmol g^{-1} for Pb and from 6.1 to 9.8 µmol g^{-1} for Zn, and for a given concentration of the initial adsorption solution was always greater for Zn than for Pb (TABLE 7). The slight increase in desorption with the concentration of the initial adsorption solution that was observed in this study is attributable to the increased occupancy of binding sites, which reduces binding energy.

ACKNOWLEDGEMENTS

CONCLUSION

A detailed investigation of single and competitive sorption processes was performed in four soils. Most sorption isotherms for trace elements were adequately described by the Langmuir equation. The sorption capacity of the soils for Cu, as measured by the estimated q parameter from the Langmuir equation was greater than for other trace elements. Kd values in monometal followed the two adsorption sequences Pb>>Cu>Zn>Cd and Pb>>Cu>Cd>Zn. These sequences follow approximately the order of the electronegativity of the metal cations. When the studied metals were in competition, this order did not change, although the Kd values of all metals decreased significantly. In general, Cu and Pb were sorbed in greater amounts with binding strength compared to Zn and Cd. This suggests that sorption does not only depend on the element, but also on the soil reactive phase and on the element concentration. The generally greater distribution coefficient (e.g., Kd$_{100}$) led to better retention of trace elements against leaching.

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