CSIRO PUBLISHING
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Adsorption isotherms of copper, lead, nickel, and zinc in two Chilean soils in single- and multi-component systems: sewage sludge impact on the adsorption isotherms of Diguillin soil

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Abstract. The potential impact of the addition of sewage sludge from domestic waste water treatment plants on agricultural soils is a worldwide concern. A proportion of heavy metals in sewage sludge will be present in the soil solution; their equilibria can be modified by the competitive interactions between them, changing not only their mobility but also their adsorption pattern. The competitive adsorption of heavy metals by soils has been studied by several authors in simple model substrates and synthetic minerals, and also in soils but restricted to binary adsorption. In the present paper the modification of the Cu, Pb, Ni, and Zn interactions with soils as a consequence of a competitive adsorption on the available adsorption sites on Andisols were determined.

The single- and multi-component adsorption of Cu, Pb, Ni, and Zn were carried out at constant ionic strength (0.1 M KNO_3). The adsorption was monitored by ICP-OES and the Langmuir model was applied to fit the adsorption isotherms.

Competitive adsorption isotherms indicate a reduction of the adsorption in the control soils when compared to the single adsorption isotherms. The maximum adsorption constants for single- and multi-component isotherms for Diguillín soil were 38.2 and 33.3 mmol/kg for Cu, 48.1 and 30.0 mmol/kg for Pb, 5.4 and 2.1 mmol/kg for Ni, and 18.0 and 8.1 mmol/kg for Zinc, respectively. With Ralun soil, lower values were obtained, but the same tendency was observed.

The maximum adsorption and the affinity constant increased for all cations, after the addition of sewage sludge to Diguillin soil.

Additional keywords: adsorption isotherms, volcanic soils, heavy metals.

Introduction

The use of wastes and residues, especially from industrial and urban sources, needs to be accomplished with the minimum hazardous impact in the environment. A current practice is the application of waste to agricultural lands. Materials such as sewage sludge are being increasingly used in Chilean agriculture and this practice has become a major concern to environmental researchers, because of the input of heavy metals into soils at harmful concentrations (Escudey *et al*. 2007). After the addition of sewage sludge to the soil, heavy metals multi-component soil-solution equilibria may occur, and the competition of heavy metals for the soil active sites may affect their mobility and retention. Competitive adsorption of heavy metals has been indirectly assessed either by single cation equilibrium experiments using pure phases or synthetic minerals (Trivedi and Axe 2000) and soil samples (Polcaro *et al*. 2003). Only few studies involving direct measurement of heavy metal competition on soil samples and considering solutions having more than one component have been reported (Serrano *et al*. 2005; Arias *et al*. 2006). In general, Pb and Cu are more strongly retained compared with Zn, Ni, and Cd.

Fontes *et al*. (2000) and Fontes and Gomes (2003) found that competition strongly influences the adsorptive capacity and mobility of several heavy metals, modifying the fitting of adsorption models. In general the Langmuir model gives the best fit to adsorption data. Gomes *et al*. (2001) reported a Cr > Pb > Cu > Cd > Zn > Ni selectivity sequences. (Fontes and Gomes 2003) found that in competitive adsorption some metals such as Cr, Cu, and Pb maintain their strong affinity with the surface, while others such as Ni, Zn, and Cd were displaced from the surface. Casagrande *et al*. (2004) reported that ionic strength and pH influence cation adsorption due to the variation of the electric charge in soils rich in iron (Fe) and aluminum (Al) oxides and hydroxides.

Adsorption–desorption processes of Pb at contaminated concentrations in 2 variable charge soils were investigated by Yang *et al*. (2004); the maximum adsorptions values (X*m*) were obtained from the simple Langmuir model. Machida *et al*. (2005) reported the maximum number of adsorption sites and adsorption equilibrium constants of Cu(II) and Pb(II) using a Langmuir adsorption model (Van Elteren and Budič 2005; Vandenbruwane *et al*. 2007). Soils in

10.1071/SR07009 0004-9573/08/010053

central and southern Chile are predominantly derived from volcanic parent material. The predominant minerals of their soils are allophone and ferrihydrite in the Andisols. The soils are rich in iron oxides and organic matter content, possess pH-dependent variable surface charge, and high PO_4 accumulation. However, the soils have poor fertility, in the original acidic pH range 4.5–5.8 (Escudey *et al.* 2001).

Heavy metal adsorption on volcanic soils is an interesting challenge due to the interactions of these with soil's organic matter; furthermore ionic strength and pH influence the adsorption of cations due to the variation of the electric charge in soils, in the number and properties of active sites. Thus, the intention in the present paper is to establish the effect of the simultaneous presence of Cu, Zn, Pb, and Ni on the adsorption behaviour on volcanic soils compared with single-component solutions and also determinate how a sewage sludge addition on Diguillin soil affect adsorption.

Materials and methods

Samples

Two volcanic ash-derived soil samples were obtained from uncultivated fields at the 0–0.15 m depth. These 2 soils, classified as Andisols (Ralun, 41°32′S, 73°05′W; and Diguillin, 36°53′S, 72°10′W), are representative of soils which cover the major agricultural regions in South Central Chile. The soils were screened in the field to pass a sieve with 2-mm openings and stored in a cold room at field moisture content.

The sewage sludge was obtained from the El Trebal waste water treatment plant located near Santiago. The Diguillin treated soils were prepared by mixing the soils with the equivalent to 15 t/ha of sewage sludge.

Soil characterisation

The pH was measured in soil suspension with a soil to water ratio of 1 to 2.5 w/v. The pH of the 2 soil samples was also determined in 1 M KCl at the same ratio. The organic carbon content (OC) was determined by the Walkley-Black method. A complete characterisation of the soil samples can be found in Escudey *et al.* (2001).

Determination of heavy metals

Total dissolution

Small subsamples of 100 mg on a dry weight basis of soils at field moisture contents were mixed with 6 mL of HF + 1 mL of a HNO_3–HCl mixture, poured into a teflon Parr bomb, tightly closed, left overnight at 110°C, and then placed into a desiccators for cooling. Once opened, the content was poured over 5.6 g of H_3BO_3 and heated on water bath until dissolution. The solution was placed into a 100-mL flask and the volume completed with double-distilled water, following by filtration through a 0.45-μm nitrocellulose membrane. Heavy metals were measured using a Perkin Elmer Optima 2000 DV ICP-OES.

Extraction with 4 M HNO_3

This procedure has been previously described by Chang *et al.* (1984). Two gram of the sample was treated with 25 mL of 4 M HNO_3 during 16 h at 65°C, after which the suspension was transferred to a 100-mL volumetric flask. The volume was completed with double-distilled water and filtered using a 0.45-μm nitrocellulose membrane, and heavy metals were determined by ICP-OES.

Surface charge determinations

Isoelectric point (IEP)

The IEP values were determined by microelectrophoresis. Electrophoretic mobility was measured with a zeta meter (ZM-77) apparatus. Dilute dispersions (0.05 g/L) were prepared in 10^{-3} M KCl. The pH was adjusted with 10^{-2} M HCl or NaOH. The mobilities were averaged and the zeta potential calculated using the Helmholtz–Smoluchowski equation (Hunter 1981).

Titration data were obtained from a suspension of 3–4 g of solid and 100 mL of KCl of adequate concentration (10^{-1}, 10^{-2}, 10^{-3} M). The K homoionised suspension was equilibrated for 1 h and then titrated from the original pH with 0.1 M KOH or HCl, adding aliquots each 10 min. This procedure was carried out at each ionic strength; blank titrations were performed similarly using 100 mL of KCl solution of appropriate concentration. Titrations were carried out at 25 ± 0.01°C and the pH response of the electrode was calibrated with buffer solutions of pH 4, 7, and 10.

Adsorption isotherms

Single-component isotherms

The adsorption isotherms of the heavy metals by the soils were carried out using a batch method. Subsamples (1 g) of soil were placed in 50-mL centrifuge tubes, and 10 mL of equilibrating solution (in a wide concentration range of 0.5–5 mM) for each cation was added to each tube. All the isotherms were carried out at constant ionic strength (0.1 M KNO_3). The suspension was shaken for 16 h in an orbital shaker, and centrifuged at 10 000 r.p.m. for 10 min, the pH measured on the supernatant, and the concentration of heavy metals determined by ICP-OES. The concentration of metal adsorbed to the soil particles was determined from the difference between the initial amount of metal in solution and that remaining at the end of the equilibrating period. Values below detection limits were considered as zero for calculation purposes.

Multi-component isotherms

The heavy metal solutions were prepared containing Cu, Zn, Pb, and Ni together in the same range of concentrations mentioned before, 0.5–5 mM, used in single-component isotherms. As in the previous case, the ionic strength was kept constant with 0.1 M KNO_3.

For both single- and multi-component isotherms, the program GEOCHEM-PC (Sposito and Mattigod 1980; Parker *et al.* 1994) was used. To obtain the chemical distribution of the species in solution at the working conditions for the studied equilibrium of cation and anions, the data were processed at the molar concentrations and the pH values measured for each equilibrating solution with the GEOCHEM program (Sposito and Mattigod 1980; Parker *et al.* 1994). The program includes a database with the thermodynamics constants and it allows the establishment of the equilibrium reached, and the chemical species for the cations and anions are determined considering the pH effect and the ionic strength. All the chemical species that do not correspond to a cation or an anion species are designated as complex by the program. Therefore, to use the GEOCHEM program, first, data must be entered for the molar concentrations for the cations and anions and the pH at the equilibrium then the ionic strength is calculated by the program. The GEOCHEM program is useful to establish the theoretical concentrations range with the experimental data. No solubility products were exceeded for any possible phase for the 4 elements of interest.

Ionic strength effect on adsorption

Adsorption isotherms, carried out by the same procedure as previously described, were carried out in double distilled water, in 0.001 M KNO_3, and in 0.1 M KNO_3 media.

Kinetics experiments

Kinetics of adsorption was assessed using the same general procedure described for single-component isotherms. In this case only 1 concentration of each metal was used as equilibrating solution (1.4×10^{-3} M for Cu, 1.5×10^{-3} M for Ni, 5.0×10^{-4} M for Pb, 1.3×10^{-3} M for Zn); these are the maximum concentrations allowed for Cu, Ni, Pb, and Zn by The CONAMA Regulations for Non Hazardous Sewage Sludge, generated by the Water Treatments Plants (CONAMA 2000), for heavy metals concentration levels in Chileans soils, and sewage sludge treated soils usually used as agricultural soils, with the exception of Pb, for which concentration range was exceeded in order to obtain a better description of the experimental isotherm. The remaining concentration was determined after 0.5, 3, 7, 16, and 24 h. All the experiments were carried out a 0.1 M KNO_3 constant ionic strength media.

Fitting model

The experimental single- and multi-component data were fitted with the Langmuir isotherm:

$$q = \frac{aXmC}{1 + aC} \qquad (1)$$

where q is the adsorbed heavy metal concentration (mmol/kg), a is the bonding energy coefficient (mmol/L), Xm is the maximum adsorption of metal (mmol/kg), and C is the concentration of heavy metal in solution at equilibrium (mmol/L). The linear expression was used to determine Xm, a. The goodness-of-fit was estimated from the coefficient of determination (R^2), for the linear expressions.

Table 1. Mineralogical composition of soils

+++++, Dominant (>50%); ++++, abundant (20–50%); +++, common (5–20%); ++, present (1–5%); +, trace fraction (<1%)

Mineral	Soil Ralun	 Diguillin
Allphane	+++++	+++++
A-Cristobalite	+	
Chlorite-Al	++	
Ferrihydrite		+
Halloysite		++
Montmorillonite	+	
Organo-allophanic		+
Plagioclase	++	++
Vermiculite		+

Results and discussions

Soil properties

The 2 soils considered, Diguillin and Ralun, are classified as Andisols with mineralogy that consisted predominantly of allophane; a complete description of mineralogical (Table 1) characteristics of both soils can be found in Escudey *et al.* (2001). Both soils have pH in the acidic range. The pH of the Ralun soil (4.5) was considerably lower than that of the Diguillin soil (5.8) (Table 2). The low pH value of Ralun soil may be associated with volcanic eruptions (Osorno and Puntiagudo Volcanos) due to the contribution of SO_2 and NO_x, which combined with the water vapor present in the atmosphere to produce chemical compounds which modify the soil composition, because no acid rain from industrial origin or acidification from cultivation practices around the sampling area exists. A value of –0.5 for ΔpH was observed in both soils ($pH_{KCl} - pH_{H_2O}$), which means that a slight negative charge, from the point of view of H^+ and OH^- interaction with the surface, is present in both soils at the equilibrium pH. Organic carbon, pH, and electrical conductivity of Diguillin soil increased after the addition of sewage sludge, as expected from the properties observed in sludge (Table 2).

The heavy metal contents of Ralun, Diguillin, and sewage sludge were determined using 2 methods: total dissolution and extraction with 4 M HNO_3 (Table 3). Ralun soil has 12.8% of clay content and it is younger than Diguillin, which has a clay content of 10.6%. From the ZP *v.* pH curves (Fig. 1), the IEP is determined, and the overall charge behaviour is observed, not only the H^+ and OH^- interaction as in potentiometric measurements. From the ZP *v.* pH curves it is observed that the Ralun has lower negative charge (Fig. 1) than Diguillin at

Table 2. Humidity, pH (H_2O, KCl 1 M), electrical conductivity (EC), organic carbon content (OC), and exchangeable cations of samples

Diguillin + SS, Sewage sludge treated soil

Sample	Humidity (%)	pH H_2O	 KCl	EC (dS/m)	OC (wt%)	Exchangeable cations (cmol/kg) Na	 K	 Mg	 Ca
Ralun	46.4	4.5	4.3	0.4	4.9	0.1	0.1	0.4	2.5
Diguillin	24.4	5.8	5.3	0.1	3.4	0.2	0.7	1.1	8.4
Sewage sludge	60.4	7.7	–	5.0	17.5	1.5	2.5	10.7	65.9
Diguillin + SS	36.2	6.4	–	0.9	7.6	–	–	–	–

Table 3. Determination of heavy metals (mg/kg) by total dissolution and extraction with 4 M HNO_3

Metal	Total dissolution			Extraction with 4 M HNO_3		
	Ralun	Diguillin	Sewage sludge	Ralun	Diguillin	Sewage sludge
Cu	42.96	14.84	50.21	36.80	9.74	42.50
Zn	78.00	39.00	214.00	41.30	16.70	139.25
Ni	4.47	4.68	11.52	2.12	1.98	7.91
Pb	36.00	34.00	18.00	16.60	14.40	7.75

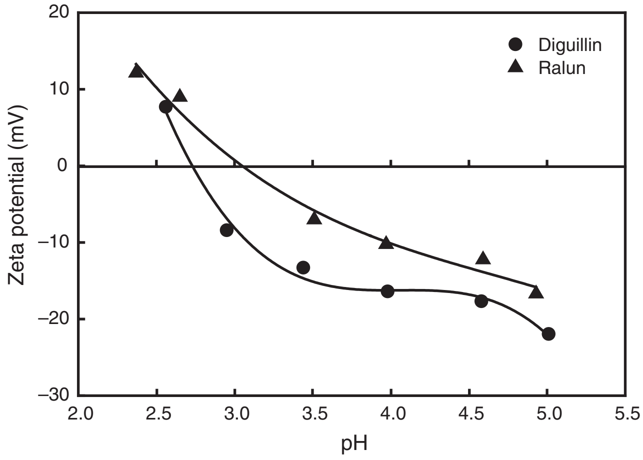

Fig. 1. Zeta potential *v.* pH curves for Diguillin and Ralun soils.

Table 4. Langmuir parameters for Cu, Ni, Pb, and Zn adsorption isotherms carried out on Ralun soil for single- (S) and multi-component (M) equilibria

Cation	Equilibrium pH	*Xm* (mmol/kg)	*a* (L/mmol)	R^2
Cu-S	4.8	6.2	8.46	0.9932
Cu-M	5.3	6.0	12.40	0.9992
Ni-S	5.1	3.6	4.72	0.9842
Ni-M	5.3	2.9	5.36	0.9958
Pb-S	4.9	37.0	10.18	0.9969
Pb-M	5.3	15.0	10.64	0.9985
Zn-S	5.3	13.2	0.53	0.9862
Zn-M	5.3	12.1	0.55	0.9737

the equilibrium pH of isotherms (Tables 4 and 5). Calcium is the most dominant exchangeable base, accounting for about 81% of CEC in both soils (Escudey *et al*. 2001). Sewage sludge has pH of 7.7, which is 2–3 orders of magnitude higher in alkalinity than the soils. The exchangeable base content of the sewage sludge is about 6–20 times those of the soils, with Ca also predominant, accounting for 81% of the total. Judging by their electrical conductivities, the soluble mineral content of sewage sludge is orders of magnitude larger that the soils.

Variable surface charge soil changes the magnitude and sign of its charge with the pH, but a the ionic strength may also modify the magnitude of its charge, which can be easily observed through potentiometric titration curves carried out at different ionic strengths (Fig. 2). The coincidence between the point of zero salt effect (determined through the intersection of the 3 curves), and the point of zero net proton charge (defined on each curve by the pH where the charge equals zero), means that little or no permanent charge is present. As observed in Fig. 2, the surface charge increases when the ionic strength increases, and as a consequence, adsorption controlled by electrostatic interactions will also increase while heavy metal concentration increases throughout the isotherm experiment. Because of that, it is important to carry out adsorption isotherms on variable surface charge soils in constant ionic media.

Because the PIE and ZPSE are physical and chemical methods, respectively, the results appear to be contradictory; however, they are good approximation for this study. To select the adequate ionic strength on adsorption isotherms, double-distilled water, 0.001 M KNO_3, and 0.1 M KNO_3 media was used. Results are presented in Fig. 3; where the effect of ionic strength on adsorption is shown clearly. Adsorption decreased when ionic strength increased; when isotherms were carried out in KNO_3 media, the adsorption also becomes a binary cation

Table 5. Langmuir parameters for heavy metal adsorption isotherms carried out on Diguillin control and sewage sludge treated soil, for single- (S) and multi-component (M) equilibria

Cation	Control				Sewage sludge treated soil			
	Equilibrium pH	*Xm* (mmol/kg)	*a* (L/mmol)	R^2	Equilibrium pH	*Xm* (mmol/kg)	*a* (L/mmol)	R^2
Cu-S	5.1	38.2	22.10	0.9939				
Cu-M	5.5	33.2	14.13	0.9952	5.8	44.1	33.7	0.9973
Ni-S	5.2	5.4	22.20	0.9850				
Ni-M	5.5	2.1	24.58	0.9961	5.8	5.5	85.2	0.9918
Pb-S	5.0	48.1	29.97	0.9808				
Pb-M	5.4	30.0	21.95	0.9975	5.8	30.7	295.6	0.9936
Zn-S	5.3	18.0	4.00	0.9944				
Zn-M	5.4	8.1	3.21	0.9976	5.8	19.0	13.2	0.9974

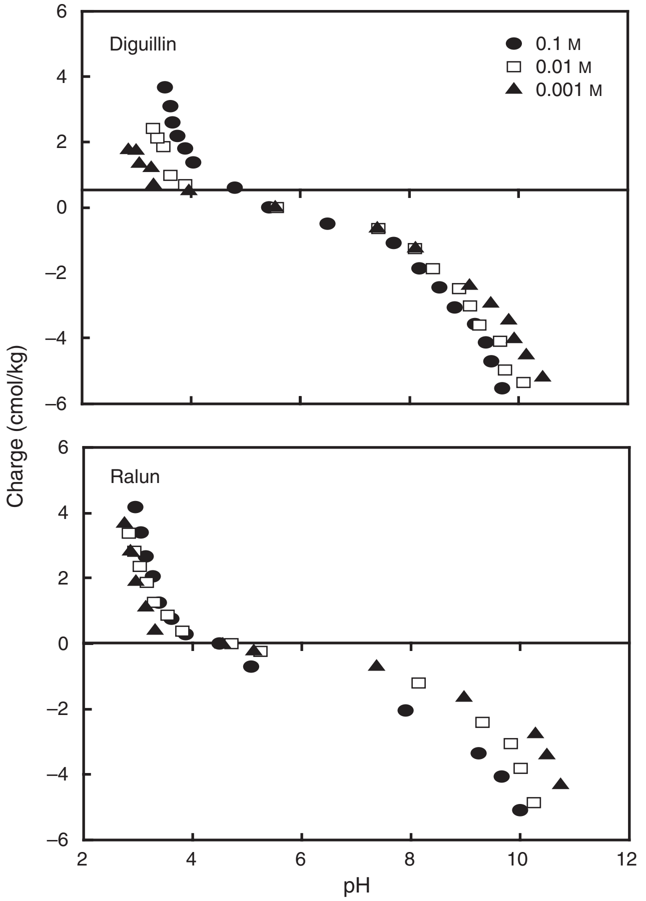

Fig. 2. Titration curves for Diguillin soil carried out at 0.1, 0.01, and 0.001 M KCl.

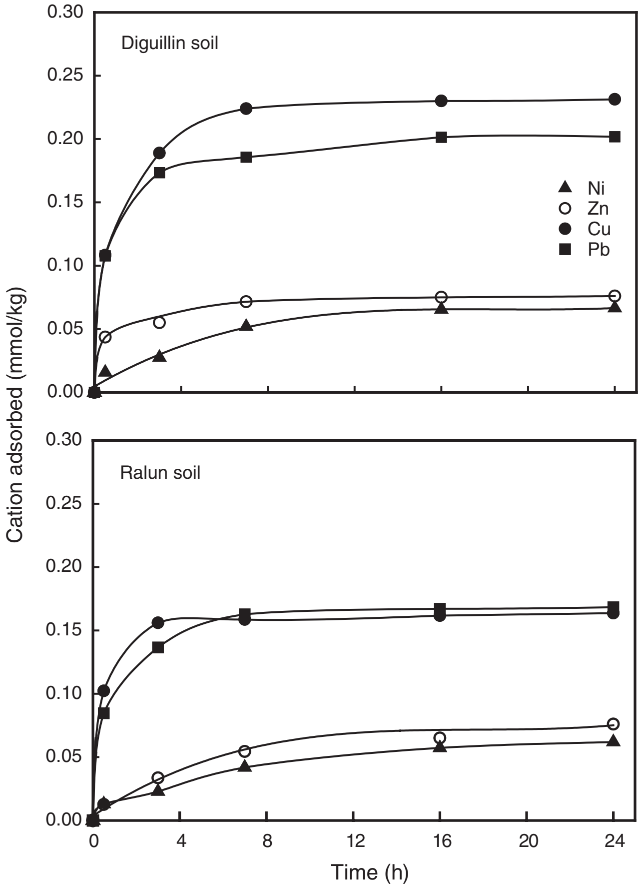

Fig. 4. Adsorption of Cu, Ni, Pb, and Zn on Diguillin and Ralun soils as a function of equilibrium time.

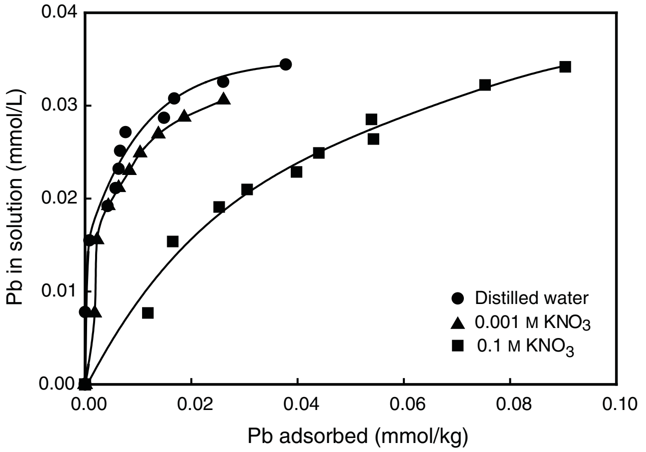

Fig. 3. Adsorption isotherms for Pb on Diguillin soil carried out in double-distilled water, 0.001 M KNO_3 and 0.1 M KNO_3.

exchange isotherm where K and Pb compete for the soil adsorption sites.

The results in Fig. 3 show that as the KNO_3 concentration decreases in the equilibrant media, the cation concentration also decreases; this is an indication of the quantity adsorbed by the soil. This can be explained by the increment of KNO_3 concentration; the K^+ ion competes for the soil active sites, decreasing the adsorbed amount of the metal. The ionic radii could be the cause of the great affinity of monovalent cation allowing the interchange of ions.

To discuss the ionic strength effect in the adsorption phenomena, at least 3 factors may be considered. The hydrated ionic radii of the studied species can explain the fact that the K^+ adsorption increases and then it competes with Pb^{2+}; however, it cannot explain the main preference for Cu^{2+} by soils. On the other hand, as the ionic strength of the system increases, soil charge also increases. Therefore, an increment in total adsorption should occur, having as a final effect a greater adsorption of Pb^{2+} in relation to K^+, but Fig. 3 indicates that this argument is not fulfilled. A possible explanation for this may be that the pH of the equilibrating solutions is dependent on ionic strength of the system; as it increases the soil become more acidic. This result implies a decrease in the negative charge of the soil (or an increment of the positive charges); therefore, the decrease in the total adsorption would be associated with a small number of interchange sites and not to an access problem or competition with K^+.

The analysis of the data obtained from GEOCHEM indicates that when bi-distilled water is used in the equilibrant media, 99% of free Pb(II) ion is in solution and there is no presence of monovalent Pb-complex. A similar result is obtained when the equilibrant media is prepared with KNO_3 0.001 M, approximately 97–98% of free Pb(II) is found in solution. However, when KNO_3 0.1 M is used, free Pb(II) in solution decreases to 60%. This can be a result of the nitrate–Pb monovalent complex formation; this corresponds to an ionic pair of low interaction between the species. This factor also can be associated with a decrease in cation adsorption under the last ionic strength condition. When KNO_3 0.001 M is used, the ionic strength in the equilibrating solution could also change as the cation concentration increases; therefore, the overall effect should alter the surface charge at each point of the isotherm.

Although the ionic strength condition selected in this work (KNO_3 0.1 M) seems to be unfavourable to study Pb(II), this would assure us that the equilibrium conditions in the systems are constant as the concentration of the cations is increased.

Chilean volcanic soils have a high selectivity for K (Escudey *et al.* 2007); thus, the higher the K concentration the lower the Pb adsorption. On the other hand, at 0.1 M KNO_3 any change in ionic strength due to an increasing concentration of metal in solution or due to changes because of adsorption will be negligible with respect to the total ionic strength determined by the supporting electrolyte.

Kinetics experiments

Time is an important parameter in adsorption isotherm studies, and it is necessary to establish the time when equilibrium condition is reached. Results for experiments carried out at a single concentration and in 0.1 M KNO_3 media are presented in Fig. 4; in all cases after 16 h the asymptotic behaviour has been reached and it was set as the equilibration time for all adsorption experiments.

From the results obtained from the GEOCHEM program, all of the cations remain in non-saturated conditions over the whole range of pH and concentrations considered in the present study.

Adsorption isotherms

Single-component isotherms

The adsorption results for single systems for the 4 cations considered, for both soils, are presented in Fig. 5. In all cases the adsorption on Diguillin is more significant than on Ralun soil. This can be explained by the surface charges of the soils soils; Fig. 1 shows that Diguillin presents higher negative charges than Ralun at the equilibrium pH. The selective heavy metal adsorption sequence presented by both soils is similar: Pb > Cu > Zn ≈ Ni in the study concentration range. But the Ralun soil adsorption is very much greater for Pb than Cu, Zn, and Ni.

In all cases the adsorption is well described by the Langmuir isotherm, shown by the fitted curves in Fig. 5, and the

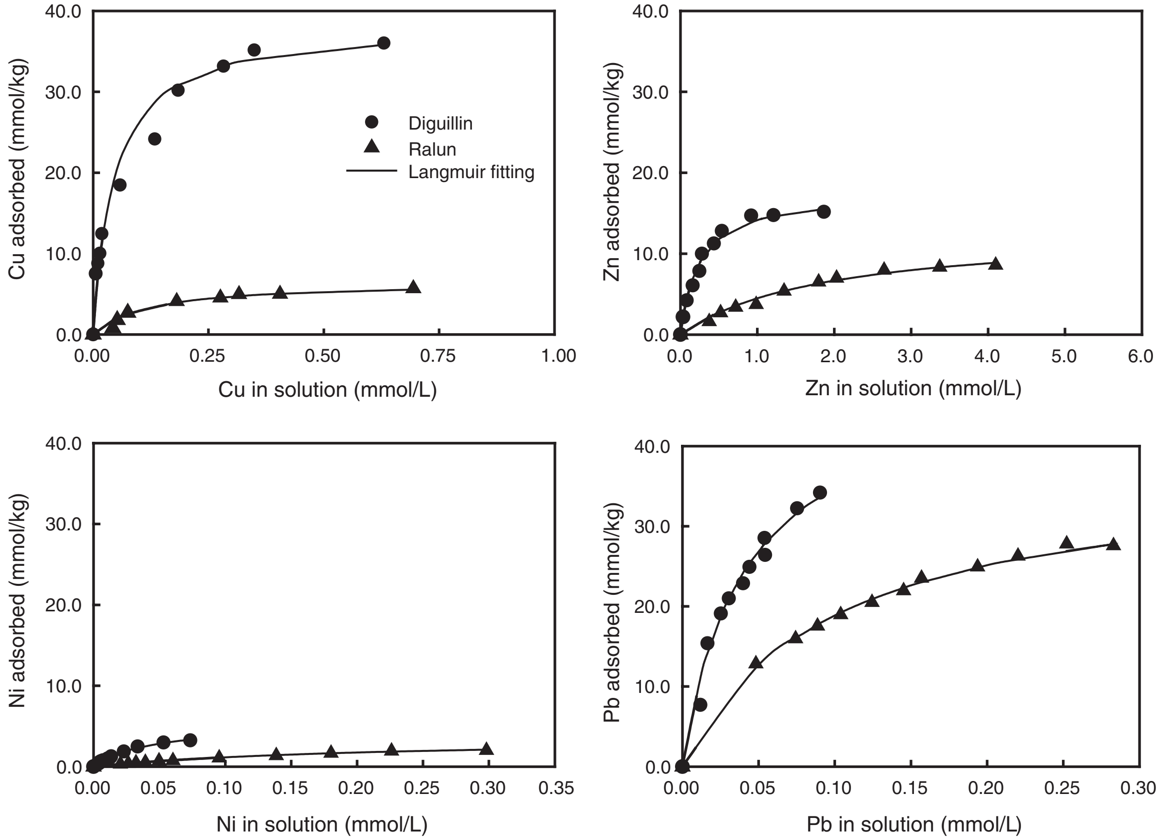

Fig. 5. Experimental results (points) and Langmuir description (lines) of single-component isotherms for Cu, Ni, Pb, and Zn carried out on Ralun and Diguillin soils.

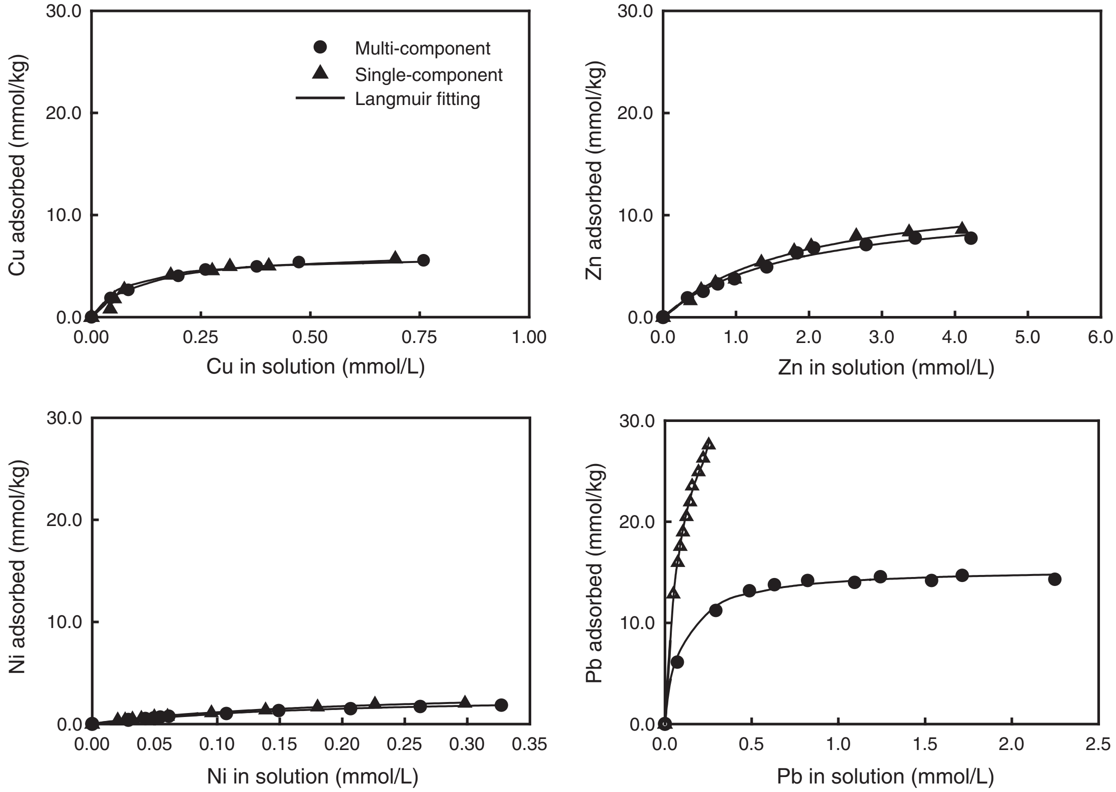

Fig. 6. Experimental results (points) and Langmuir description (lines) of multi-components system (Cu + Ni + Pb + Zn), and comparison with single-component system for isotherms carried out on Ralun soil.

coefficients of determination presented in Tables 4 and 5. From the bonding energy coefficient (*a*), it is possible to establish that in both soils, Pb has the strongest interaction with the surface, with Zn at the end of the sequence. Both, *a* and *Xm* are greater for Diguillin than for Ralun soils.

Multi-component isotherms

The adsorption experiments carried out with the 4 cations competing for the active sites of the soil are presented in Table 4 and Fig. 6 for Ralun soil and in Table 5 and Fig. 7 for Diguillin soil. In all cases, as in single-component results, data are well described by the Langmuir isotherm.

In Ralun soil a significant reduction in the adsorption of Pb, a slight reduction for Ni and Zn, and practically no change for Cu adsorption is observed (Fig. 6). Changes can be quantified if the *Xm* value is considered (Table 4); thus, a significant reduction of 59% in the maximum predicted adsorption of Pb, a reduction of 19% for Ni, 8% for Zn, and a marginal reduction of 3% for Cu is observed. The Cu bonding energy coefficient, *a*, increases with respect to single-component isotherm, slightly increases for Ni, and shows only marginal changes for Pb and Zn. The maximum predicted adsorption in the single-component isotherm reaches 37 mmol/kg, and in the multi-component design the total adsorption reaches 36 mmol/kg; thus, in multi-component isotherms, heavy metals interact over the same total active sites. From these results, it is possible to assume that Cu is adsorbed on very specific sites where none of the others competes for adsorption. The opposite is valid for Pb; most of its adsorption occurs in sites where any cation may also be adsorbed and interaction is the result of a multi-component exchange equilibrium. Zn and Ni represent intermediate situations.

In Diguillin soil the behaviour is rather different, because significant reduction in the adsorption of all heavy metals is observed (Fig. 6) compared with single-component isotherm. A reduction of 13% for Cu, 61% for Ni, 38% for Pb, and 55% for Zn in the predicted maximum adsorption (Table 5) is observed, even though the maximum adsorption reached 73.4 mmol/kg, which corresponds to an increment of 52% with respect to single-component isotherms. The reduction in adsorption is also associated with a reduction in the bonding energy coefficient for all of the heavy metals. From these results it is possible to assign the adsorption to at least 2 types of active sites for each cation, one type associated to very specific adsorption and one where competition occurs.

Impact of sewage sludge on heavy metal adsorption

Previously, to carry out the isotherms on sewage sludge-treated samples, the amount of each heavy metal released by the sewage sludge was determined. Thus, a total of 50 mg/kg of Cu and 27 mg/kg of Zn was released by the sewage sludge; neither Ni nor Pb was detected considering detection limits of 9, 80, 30, and 5 µg/g for Cu, Ni, Pb, and Zn, respectively. The heavy metal released by the sewage sludge considering the total

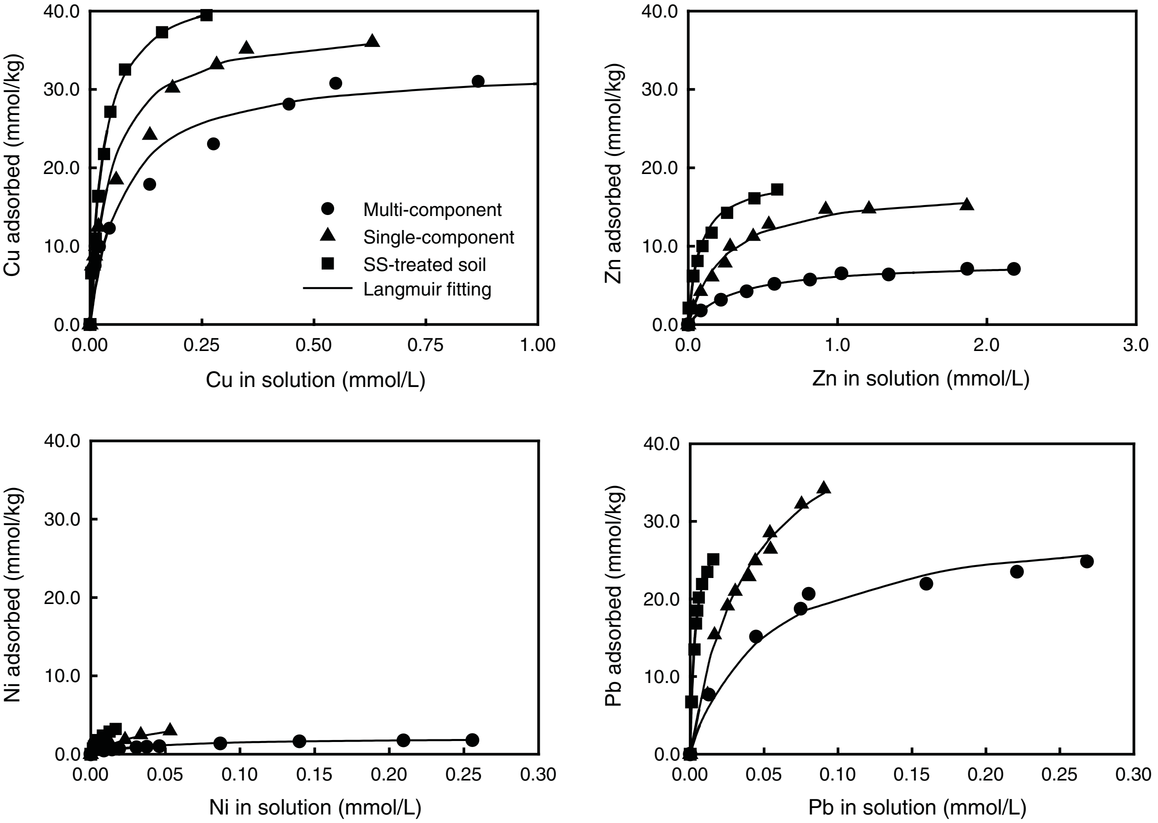

Fig. 7. Experimental results (points) and Langmuir description (lines) of multi-components system (Cu + Ni + Pb + Zn), and comparison with single-component system for isotherms carried out on Diguillin and sewage sludge treated Diguillin soil.

amount added to the soil sample represents <2% for Cu and <0.8% for Zn, of the concentration of the most diluted solution of respective isotherms. Thus, the presence of sewage sludge represents only marginal deviations from the calculated concentration of heavy metals in isotherm equilibrating solutions.

In the sewage sludge-treated soil a higher adsorption of heavy metals is observed (Fig. 7), even when compared to single-component isotherms. Not only the maximum adsorption increases specially for Cu (33%), Ni (61%), and Zn (134%), but also the bonding energy increases significantly (Table 5). More than 35% of the sewage sludge is organic matter (Table 2); consequently, its action may explain the results observed. The adsorption of heavy metals may be associated to the interaction with organic matter active groups.

Conclusions

The adsorption of heavy metals in single-component system for the studied soils indicates the following sequence Pb > Cu > Zn ≈ Ni. However, Ralun showed a greater adsorption capacity for Pb. The maximum adsorption capacity of Ralun and Diguillin soils was modified in a multi-component system due to the heavy metal competitive interactions. The addition of sewage sludge to Diguillin soil not only modified the heavy metals adsorption but also it had increased.

Acknowledgments

This study was supported by DICYT-USACH, FONDECYT (grant 020402CS and 1030778).

References

Arias M, Pérez-Novo C, López E, Soto B (2006) Competitive adsorption and desorption of copper and zinc in acid soils. *Geoderma* **133**, 151–159. doi: 10.1016/j.geoderma.2005.07.002

Casagrande JC, Alleoni LRF, de Camargo OA, Arnone AD (2004) Effects of pH and ionic strength on zinc sorption by a variable charge soil. *Communications in Soil Science and Plant Analysis* **35**, 2087–2095. doi: 10.1081/CSS-200028914

Chang AC, Warneke JE, Page AL, Lund LJ (1984) Accumulation of heavy metals in sewage sludge-treated soils. *Journal of Environmental Quality* **13**, 87–91.

CONAMA (2000) Anteproyecto de reglamento. In 'Manejo de Lodos no peligrosos generados en Plantas de Tratamiento de Aguas'. Anteproyecto publicado en el Diario Oficial del día 29 de Junio de.

Escudey M, Förster JE, Becerra JP, Quinteros M, Torres J, Arancibia N, Galindo G, Chang AC (2007) Disposal of domestic sludge and sludge ash on volcanic soils. *Journal of Hazardous Materials* **139**, 550–555. doi: 10.1016/j.jhazmat.2006.02.062

Escudey M, Galindo G, Förster JE, Briceño M, Díaz P, Chang AC (2001) Chemical forms of phosphorus of volcanic ash-derived soils in Chile. *Communications in Soil Science and Plant Analysis* **32**, 601–616. doi: 10.1081/CSS-100103895

Fontes MPF, Gomes PC (2003) Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils. *Applied Geochemistry* **18**, 795–804. doi: 10.1016/S0883-2927(02)00188-9

Fontes MPF, Matos AT, Costa LM, Neves JCL (2000) Competitive adsorption of zinc, cadmium, copper and lead in the three highly weathered Brazilian soils. *Communications in Soil Science and Plant Analysis* **31**, 2939–2958.

Gomes PC, Fontes MPF, Silva AG, Mendonça ES, Netto AR (2001) Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. *Soil Science Society of America Journal* **65**, 1115–1121.

Hunter RJ (1981) 'Zeta potential in colloid science: Principles and applications.' (Academic Press: London)

Machida M, Aikawa M, Tatsumoto H (2005) Prediction of simultaneous adsorption of Cu (II) and Pb (II) onto activated carbon by conventional Langmuir type equations. *Journal of Hazardous Materials* **120**, 271–275. doi: 10.1016/j.jhazmat.2004.11.029

Parker DR, Norvell WA, Chaney RL (1994) Geochem-PC: a chemical speciation program for IBM and compatible personal computers. In 'Chemical equilibrium and reaction models'. Special Publication No. 42. (Eds Rh Loeppert, AP Schwab, S Goldberg) pp. 253–269. (Soil Science Society of America: Madison, WI)

Polcaro AM, Mascia M, Palmas S, Vacca A, Tola G (2003) Competitive sorption of heavy metal ions by soils. *Environmental Engineering Science* **20**, 607–616. doi: 10.1089/109287503770736122

Serrano S, Garrido F, Campbell CG, García-González MT (2005) Competitive sorption of cadmium and lead in soils of Central Spain. *Geoderma* **124**, 91–104. doi: 10.1016/j.geoderma.2004.04.002

Sposito G, Mattigod SV (1980) 'GEOCHEM: a computer program for the calculation of chemical equilibria in soil solution and other natural water systems.' (Kearney Foundation of Soil Science, University of California: Riverside, CA)

Trivedi P, Axe L (2000) Modelling Cd and Zn sorption to hydrous metal oxides. *Environmental Science & Technology* **34**, 2215–2223. doi: 10.1021/es991110c

Vandenbruwane J, De Neve S, Qualls RG, Sleutel S, Hofman G (2007) Comparison of different isotherm models for dissolved organic carbon (DOC) and nitrogen (DON) sorption to mineral soil. *Geoderma* **139**, 144–153. doi: 10.1016/j.geoderma.2007.01.012

Van Elteren J, Budič B (2005) A solid–liquid extraction approaches to elucidate the chemical availability of metals in soils and sediment assuming Langmuir isotherm behaviour. *Talanta* **66**, 925–930. doi: 10.1016/j.talanta.2004.12.047

Yang JY, Yang XE, He ZL, Chen GC, Shentu JL, Li TQ (2004) Adsorption-desorption characteristics of lead in variable charge soils. *Journal of Environmental Science and Health, Part A* **39**, 1949–1967. doi: 10.1081/ESE-120039367

Manuscript received 17 January 2007, accepted 13 November 2007