

Interactions between Cd, Cu, Pb, and Zn and four different mine soils

Lotfi Mouni¹ · Lazhar Belkhir² · Abdelkrim Bouzaza³ · Jean-Claude Bollinger⁴

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Abstract The chemical associations of Cd, Cu, Pb, and Zn in four mine soil samples from the Amizour-Bejaia Pb/Zn mine (Algeria) have been investigated by a five-step sequential extraction procedure. Although Cd preferentially binds to carbonates, Cu, Pb, and Zn are mainly associated with the organic and reducible fractions. Batch adsorption experiments with either mono- or multi-metallic solutions are described with the Freundlich isotherm model. Whatever the nature of the soil sample, the sorption behavior for each given metal except Pb is very similar, indicating that the binding sites at the soil surface are progressively occupied by the metal from the solution. On each soil sample, the decreasing order of sorption can be established as $Pb \gg Cu > Cd > Zn$. When the four metals are simultaneously applied to each soil sample, their specific behavior is strongly affected by their interactions and/or competition for the available surface sites: we generally observed isotherm curves with a slight maximum before the

plateau at higher solution concentration. Although Cu is only slightly affected by the other metals, in the case of Pb, Cd, and Zn, the sorbed amounts strongly decreased.

Keywords Soil pollution · Metal mobility · Sequential extraction · Sorption

Introduction

Active and abandoned metal mining sites are major sources of metal contamination throughout the world. In metal mining, less than 1% of processed material is recovered as useful metal (Fields 2003). The assessment of metal mobility in a complex system requires knowledge of a range of mobility parameters. The movement of a solute through soils is a complicated process that depends on the physical and chemical properties of both the solid and liquid phases that are in contact with each other. In general, batch experiments are used to obtain equilibrium adsorption isotherms in order to evaluate the solid sorption capacity for any given metal present in the aqueous phase (Evans 1989; Bradl 2004; Violante et al. 2010). The geochemical processes controlling metal lability and bioavailability in solid mine wastes are important.

The adsorption of trace elements has been studied and reported in the literature for several different kinds of soil samples and soil components (Mench et al. 1994; Green-Pedersen et al. 1997; Morera et al. 2001; Covelo et al. 2007a; Covelo et al. 2007b; Covelo et al. 2007c; Sastre et al. 2007; Mouni et al. 2009; Rodriguez et al. 2009; Trakal et al. 2012; Waterlot et al. 2013; Pascaud et al. 2014; Arenas-Lago et al. 2014; Wang et al. 2015). The metal distribution among the different soil components can be estimated using specific chemical reagents in order to discriminate the total metal content over various operationally defined fractions in the solid phase

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✉ Lotfi Mouni
lotfimouni@gmail.com

¹ Laboratoire de Gestion et Valorisation des Ressources Naturelles et Assurance Qualité, Faculté SNVST, Université Akli Mohand Oulhadj, 10000 Bouira, Algeria

² Laboratory of Applied Research in Hydraulics, University of Batna 2, 05000 Batna, Algeria

³ Laboratoire Sciences Chimiques de Rennes—Equipe Chimie et Ingénierie des Procédés, UMR 6226 CNRS, ENSCR, Avenue du Général Leclerc, 35700 Rennes, France

⁴ Groupement de Recherche Eau-Sol-Environnement (GRESE), Université de Limoges, 123 Avenue Albert Thomas, 87060 Limoges, France

(Tessier et al. 1979). Sequential extractions, where the sample is treated with a series of extractants selected on the basis of their ability to release analytes bound to different components of the matrix, are widely used for exploration purposes and to study element speciation in materials such as soils and sediments (Fernandez et al. 2004).

The purpose of this study was to facilitate our understanding of the interaction between soil and metals. Four soil samples from the Amizour-Bejaia mining region (Algeria) were firstly analyzed with a sequential extraction scheme so as to understand their predominant solid fractions. Then, batch equilibrium experiments with Cd, Cu, Pb, and Zn solutions (alone or as mixtures) allowed to discuss the relations between each soil sample and each metal. The results of the present study may be helpful to evaluate the potential for these metals to migrate through this mining soil during raining events.

Materials and methods

Soil samples

Four soil samples, each sample weighing approximately 10 kg, taken from 25 to 50 cm below ground surface in Amizour, located in Bejaia, east of Algeria, were air-dried and passed through a 2-mm sieve and homogenized prior to laboratory analysis and sorption model experiment; they are hereafter designated as SS-1 to SS-4, respectively. Organic matter was determined by wet oxidation (Pansu and Gautheyrou 2003). Soil pH in water was determined with a pH meter (Jenway 3010) using 2:1 (v/w) water/soil suspensions (Pansu and Gautheyrou 2003).

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 0.2 M NH_4Cl (Pansu and Gautheyrou 2003) and measured by atomic absorption spectrophotometry (Ca, Mg, Na, and K) (Shimadzu AA6500). Organic carbon content in soils was determined by elemental analysis (ISO 1995); the inorganic carbon content was calculated as the difference between the total carbon and organic carbon contents and expressed as percent CaCO_3 . The X-ray diffraction (XRD) analysis of the samples was carried out via a Powder X-ray diffractometer (Bruker AXS) in the 2θ angle ranging from 2° to 65° employing a 0.025° step. The specific surface area was obtained from N_2 gas adsorption at -196°C (Coulter SA 3100) using the BET equation. The physical and chemical characteristics of the samples are shown in Table 1.

Soil metal content was measured after inverse *aqua regia* digestion assisted by a microwave system (Anton Paar, Microwave 3000) and analyzed using ICP-OES spectrometry (JY2000). Stock solutions of commercially produced (plasma pure standard solutions, Leeman Labs), multi-element

Table 1 Main characteristics of soil samples

Soil property	SS-1	SS-2	SS-3	SS-4
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
Texture	Loam	Clay	Silty clay	clay
pH _{water}	7.5	7.9	8.3	7.8
Organic C (%)	1.34	1.12	1.08	0.96
CEC (cmol kg ⁻¹)	13.8	46.3	34.6	37.6
Surface area (m ² g ⁻¹)	12.1	41.8	22.3	29.9
CaCO_3 (g kg ⁻¹)	30.6	59.2	64.9	44.2
Fe_2O_3 (g kg ⁻¹)	31.3	24.2	63.7	46.3
Gypsum (g kg ⁻¹)	8.1	10.8	11.3	38.7
Goethite (%)	28.7	32.2	47.3	18.3
Quartz (%)	3.4	2.65	1.74	1.24
Feldspars (%)	7.2	nd	nd	nd
Kaolinite (%)	53.4	24.5	31.4	23.8
Mica (%)	7.7	5.5	12.2	12.1
Smectite (% in clay content)	28.1	67.3	54.6	62.1
Metal elements (total concentration) mg kg ⁻¹				
Cr	84.3	108	93.45	104.70
Mn	2.8	3.6	6.3	7.4
Pb	132.3	102.6	143.8	114.7
Zn	235	206	226	293
Cu	473	342	504	312
Ni	53.8	78.4	64	113
Cd	5.4	2.1	3.6	1.3

nd not determined

standard solutions (100 mg l⁻¹ in 10% nitric acid) were used to prepare appropriate elemental calibration standards for the ICP-OES analysis. Analysis of sample and standard solutions was based on the mean of three readings; standard deviation was always less than 5%. Solutions of HNO_3 (without sample) were used as reagent blanks. All sample concentrations were reported as mg (kg dry weight)⁻¹.

Sequential extractions of metals

The main purpose of the sequential extraction of a soil sample is to investigate the speciation of metal elements. Here, we applied the five-step operationally defined sequential-extraction protocol of Tessier et al. (1979), as described by Delmas et al. (2002). The association of chemical elements with different fractions in soil is investigated through several different dissolution steps: (i) exchangeable fraction (salt-displaceable, agitation with MgCl_2 at pH = 7), (ii) carbonate bound (acid extractable fraction, CH_3COONa adjusted to pH = 5.0 with acetic acid), (iii) Fe/Mn oxide bound (reducible fraction, $\text{NH}_2\text{OH}\cdot\text{HCl}$), (iv) organic matter and sulfide bound

(oxidizable fraction, 30% H₂O₂ in HNO₃, then CH₃COONH₄ in HNO₃), and (v) total extraction (residual, HNO₃, HNO₃ + HClO₄, 6 M HCl). The extracts from each step were filtered through a 0.45- μ m filter, acidified, and analyzed by atomic absorption spectrophotometry AAS (Shimadzu AA6500). The instrument calibration was periodically checked by using standard metal solutions for every 15 readings.

The results of this sequential extraction procedure are reported in Fig. 2 and in Table S1 (Supplementary Information file).

Sorption experiments

Batch sorption studies were conducted to determine the relationship between adsorbent and adsorbate by varying the concentration of the metals. All metal salts of interest were of analytical grade and used without further purification. Stock solutions of single metal ions (1000 mg l⁻¹) were prepared by solubilizing, in deionized water, the corresponding hydrated nitrate salts (Sigma-Aldrich). In each experiment, Cd, Cu, Pb, and Zn were sorbed from a “sorption solution” at pH 6. The initial concentrations of each metal tested were 10, 20, 40, 50, 100, and 200 mg l⁻¹.

In the classical experimental procedure, 1 g of soil sample was suspended in 100 ml of sorption solution and shaken for 24 h at 20 °C in a rotary shaker (Macro Scientific Works, Delhi, India). Then, the suspension was centrifuged at 4146 \times g for 5 min, and the supernatant was filtered through slow filter paper (Whatman No. 42). The metal concentrations in supernatants were determined by ICP-OES (JY2000). The quantity of the metal sorbed by the soil sample was calculated by using a mass balance relationship:

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where q_e is the amount of adsorbed species at equilibrium (mg g⁻¹), C_0 is the initial concentration of the species in solution (mg l⁻¹), C_e is the measured concentration (mg 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 sample (g).

Kinetic data were tentatively modeled according to either the pseudo-first order or the pseudo-second order equations (Limousin et al. 2007). The unknown constants in these model equations are obtained using nonlinear least-squares data processing by the Origin 8.0 software at the 95% confidence level. Experiments and analysis have been carried out three times.

Adsorption isotherms

In order to describe adsorption phenomena of metals from aqueous solution onto soil sample, the equilibrium data were analyzed with the Freundlich model equation (Limousin et al.

2007), which assumes that different sites with several adsorption energies are involved:

$$q_e = K_F C_e^n \quad (2)$$

where K_F (mg^(1-1/n) l^{1/n} g⁻¹) is an affinity coefficient related to the sorptive capacity and n is an estimated sorptive intensity or surface heterogeneity parameter. The unknown constants in this model equation are obtained using nonlinear least-squares data processing by the Origin 8.0 software at the 95% confidence level (Foo and Hameed 2010).

Results and discussion

Soil characteristics

The studied mine is located in the Amizour area of Bejaia, North-East Algeria (Fig. 1), and was set up in 1983. The main ore is Zn and Pb, accompanied by Cu and Fe. The mean Pb and Zn percentages in the ore are 2.6 and 12.7%, respectively. The average depth of the mine is 940 m, and its coverage is 70 km². This area is dominated by a subtropical climate, with rainy mild winter and hot dry summer. The mean annual temperature is 18.3 °C, with extreme temperatures at 29.3 °C in August and 7.6 °C in February. The heavy rain season lasts from November to March, and annual rainfall presents a mean value of 765.5 mm. The dry season extends from June to August and is characterized by low precipitation (mean total value = 35 mm over these 3 months). Prevailing winds are northerly, with an average speed of 7.6 km h⁻¹ (Merabet and Mahtout 1999).

The texture and classification of the four studied soil samples and their main physicochemical and mineralogical (from XRD data) properties are presented in Table 1. These soils have pH values in the slightly alkaline range (7.5–8.3) and low organic matter contents (0.96–1.34 g kg⁻¹). This soil component is of importance because it can complex the metal species and thus influence their circulation within the soil solution.

Their particle size distribution exhibits a substantial variation in clay, silt, and sand contents; they are classified (USDA 1987) as loam (SS-1), clay (SS-2 and SS-4), or silty clay (SS-3). Their cation exchange capacity (CEC) could be generally related to the clay content: therefore, the highest value of CEC (46.3 cmol kg⁻¹) was recorded for SS-2 that was also the richer in clay. Additionally, the main component of clay fraction of soils is smectite, with the exception for SS-1 in which kaolinite is more abundant.

Data indicate that the studied soil samples had values of calcium carbonate in the range of 30.6–64.9 g kg⁻¹; SS-3 had the highest value of calcium carbonate, but SS-1 showed the lowest one, in good correlation with the corresponding pH

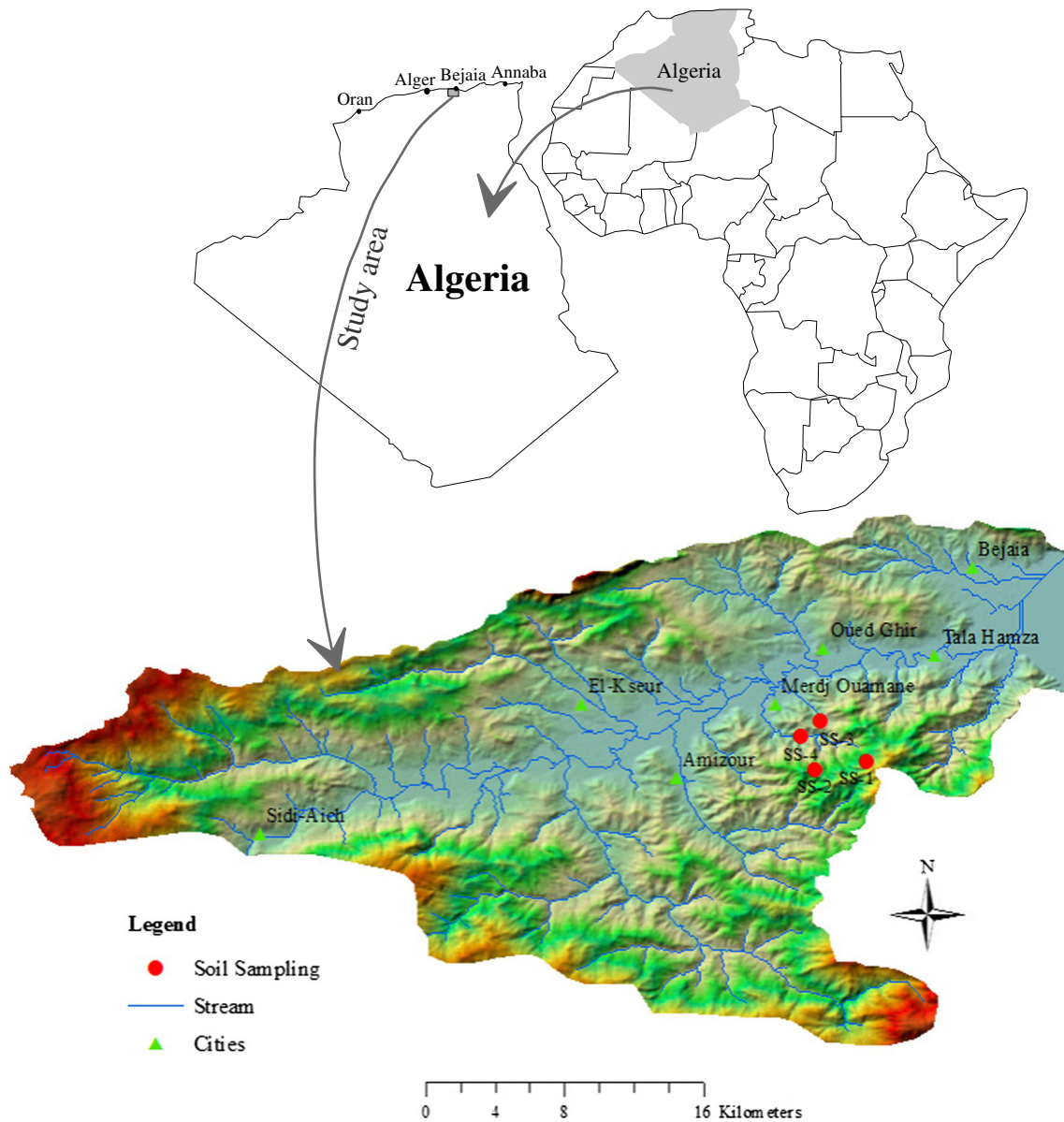


Fig. 1 Map showing soil sampling locations of the studied area

values. Free iron oxide content, expressed as Fe_2O_3 , ranged from 24.2 to 63.3 g kg^{-1} . Moreover, gypsum content was low in all studied soils, as it ranged from 8.1 to 38.7 g kg^{-1} ; the highest gypsum content occurred in SS-4.

Sequential extractions of metals

Although their amounts were different for each metal species and for each soil sample, metal contents are similar and denote slightly contaminated soil samples. The highest amount is for Cu (312–504 mg kg^{-1}), then Zn (206–293 mg kg^{-1}), Pb (102–144 mg kg^{-1}), Cr (84–108 mg kg^{-1}), Ni (54–113 mg kg^{-1}), and Cd (1.3–5.4 mg kg^{-1}).

According to Fig. 2, the high amounts of Pb, Zn, and Cu in the four studied soils (see also Table 1) are mainly associated

with organic and reducible fractions and for less than 20% with the residual fraction. The mobile fraction percentages (exchangeable and carbonate fractions) in the studied soil samples ranged between 1.5–7.2 and 3.8–45.4 for Pb and Cd and between 0.9–11.6 and 1.2–22.5 for Zn and Cu, respectively (Fig. 2; detailed data are available as Table S1 in the Supplementary Material file). This indicates that Cd is more mobile than Pb, Zn, and Cu and perhaps threatens the environment by a larger degree; but Pb, Zn, and Cu are more retained by these soils. One can note that Cd binds preferentially to carbonates, indicating greater mobility and availability to plants. Low amounts of Pb were obtained in exchangeable and carbonate fractions, which are the mobile fractions in the soil. Metal associations with Fe/Mn oxides and organic fractions are less dangerous for the environment than

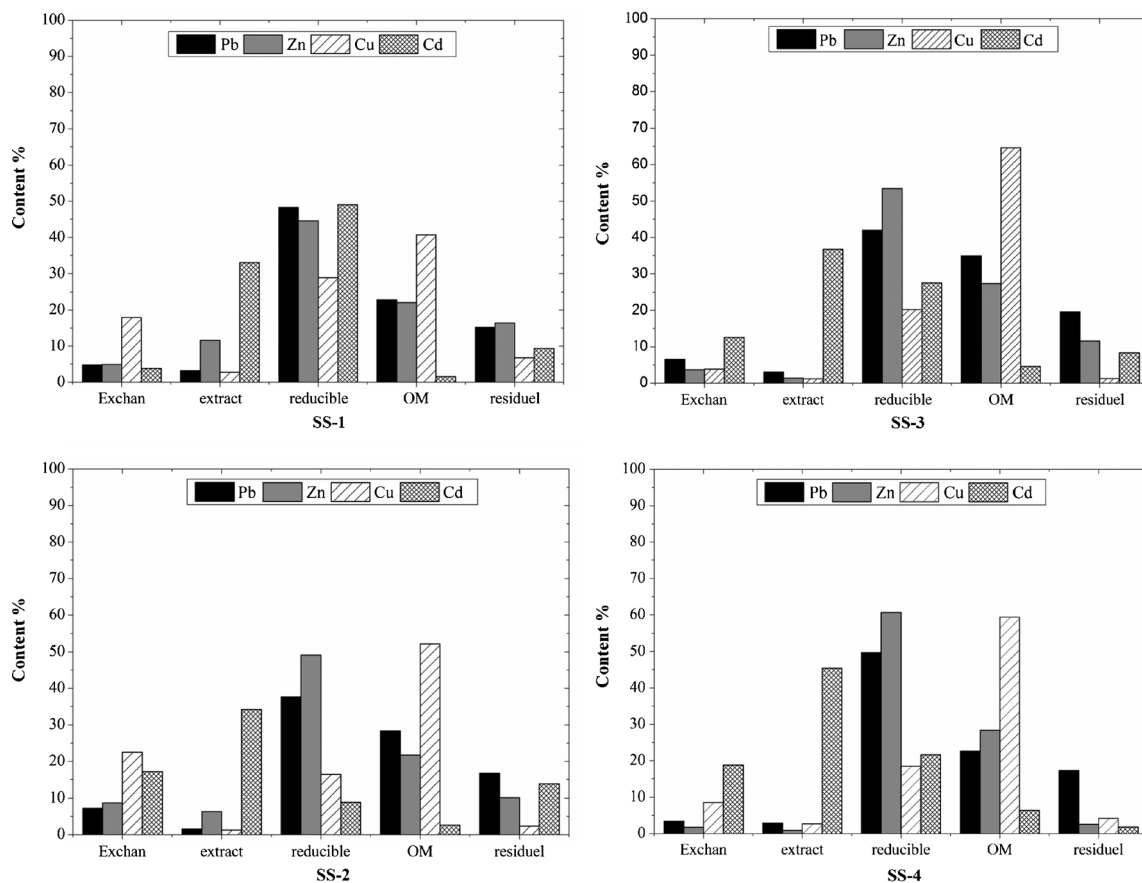


Fig. 2 Results from the five-step sequential extraction procedure applied to each of the four soil samples: percentages of Pb, Zn, Cu, and Cd

exchangeable and carbonate fractions because these fractions are less extractable and less available, but when the environment becomes increasingly reducing or oxidizing, they can be mobilized.

As previously stated, Cu is the first most abundant metal in all of the studied soils (Table 1). The proportion of the total Cu associated with the organic fraction is also the highest, varying between 40.7 and 64.6%, but no direct correlation can be established between Cu amount and organic matter content. The Fe/Mn oxide phases retain between 16.4% (SS-2) and 29% (SS-1) of the total Cu. Although SS-1 has the highest organic matter content (Table 1), the Cu associated with this fraction is the lowest (Fig. 2). This fact is attributable to the soluble complexes that organic matter can form with Cu, and they contribute more to the exchangeable fraction than to the organic matter fraction.

The importance of metal contents in both the reducible (or Fe/Mn oxides) and the organic matter fractions has been also previously observed in various kinds of polluted soil samples. Among others, we can cite the case of Cd and Pb in two different horizons of a contaminated soil with contents similar to our samples (Ash et al. 2015). For an alkaline soil near a smelter, Cu and Zn were mainly in the residual fraction, but Pb is present in both the reducible and oxidizable fractions (Wang

et al. 2015). This is also the case for a series of soil samples from a former mine, where Cd, Pb, and Zn are mainly in the residual fraction, then in the reducible and oxidizable fractions (Arenas-Lago et al. 2014). On the contrary, in the case of a highly carbonated soil, Cd (65%), Pb (99%), and Zn (87%) were mainly extracted as the acid-soluble fraction (Plassard et al. 2000). In a three-step sequential extraction procedure on acid soils near a Pb/Zn mine, Rodriguez et al. (2009) observed that Pb was mainly present in the reducible fraction although Zn was predominant in the residual one. From a five-step sequential extraction procedure applied to carbonated soils near a former Pb/Zn mine, in highly contaminated samples, the metals were mainly in the acid-extractable (carbonate) fraction, but for low-contaminated samples, both metals are mainly associated to Fe/Mn oxides, thus slightly mobile (Iavazzo et al. 2012).

Kinetics of sorption

In order to analyze the adsorption kinetics of metal ions, the pseudo-first- and pseudo-second-order model equations were applied to data (Limousin et al., 2007).

The treatment of experimental data showed that the correlation coefficients for pseudo-first-order were always low

(<0.74): this kinetic model is not convenient for our systems. The case of a second-order kinetic model can be expressed as (Ho and McKay 1999)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant for adsorption and q_e and q_t are the values of the amount adsorbed per unit mass at equilibrium and at any time t , respectively. The results showed straight lines in the plot of t/q_t versus t for all soils and then a good agreement ($0.87 \leq R^2 \leq 0.99$) of experimental data.

Table 2 shows the pseudo-second-order rate constants and correlation coefficients for removal of all four metals at 80 mg l^{-1} from single aqueous solutions. The maximum removal was attained after about 4 h, and final equilibrium was reached after 6 h in all cases. Adsorption of each metal was rapid with more than 80% of total amount removed within the first 5 min of the process.

Batch adsorption experiments

The adsorption isotherms from single metal solutions onto each soil sample are reported in Fig. 3. In the case of Cu, Cd, or Zn, these isotherms can be subdivided in three parts: at low concentration, the metal introduced is sorbed proportionally, but at intermediate concentrations there is a pseudo-plateau, which probably corresponds to the saturation of the surface.

These individual metal sorption isotherms for Cu, Cd, and Zn are well described by the Freundlich model (Eq. 2), with regression coefficients R^2 in the range 0.75–0.99 (Table 3). Whatever the nature of the soil sample, the n power coefficient for each given metal is almost constant: 0.21–0.25 for Cu, 0.30–0.36 for Cd, and 0.31–0.36 for Zn. Such values correspond to convex curves, where the binding sites at the soil surface are progressively occupied by the metal from the solution.

The case of Pb is somewhat different because $n < 1$ for SS-1 and $n \approx 1$ for SS-3. For the two other soil samples, the

power coefficient $n > 1$ (concave curves), with a highest value $n = 4.76$ for SS-4; the sorbed amount is very high from the lowest solution concentrations ($< 5 \text{ mg l}^{-1}$). This specific behavior of SS-1 regarding Pb can perhaps be related to its different physicochemical properties (see Table 1): SS-1 is a loam with 47% silt, and it presents the lowest pH value (7.5), the highest organic carbon content (1.34%), and the lowest CEC and specific surface area values. This is probably due to a surface precipitation of lead.

Although the maximum adsorption capacity (q_m) cannot be directly deduced from the Freundlich model fitting, we can estimate from both the K_F values and the experimental curves (Fig. 3) that Pb showed the maximal sorption capacity on each soil sample. Then, the decreasing order can be established as $\text{Cu} > \text{Cd} > \text{Zn}$. This result suggests that the sorption preference exhibited by these four different soil samples for Pb over the other three metals may be attributed to (i) the greater value of the formation constant of its first hydroxide complex (Stumm and Morgan 1996) and therefore its higher hydrolyzed ratio, (ii) its higher atomic weight, (iii) its higher crystal ionic radius and subsequently smaller Stokes hydrated volumes (Marcus 1985), and (iv) its larger Misono softness value (Misono et al. 1967), making it a better candidate than other metals for electrostatic and inner-sphere surface complexation reactions (see Table S2 in the Supplementary Material file for detailed numerical values).

When the four metals were simultaneously applied to each soil sample, their specific behavior is strongly affected by their interactions and/or competition for the available surface sites. We generally observed isotherm curves with a slight maximum before the plateau at higher solution concentration (Fig. 3). Although the data for Cu are almost similar in values, the other metals showed a very different behavior (Table 4). For SS-2, SS-3, and SS-4, Pb curves presented low sorbed amounts at lower solution concentrations, when during individual experiments these sorbed amounts were very high. In the case of Cd and Zn, the sorbed amounts decreased strongly, due to the competition for the allowable sorption (binding) sites.

When studying contrasted acid soils with heavy contamination in Pb and Zn, Zemanová et al. (2014) observed similar

Table 2 Fitting parameters of the pseudo-second-order kinetic equation for metal sorption on the studied soil samples (initial concentration of each metal is 80 mg l^{-1})

	Cd		Cu		Pb		Zn	
	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
SS-1	0.634	0.94	0.628	0.99	0.375	0.97	0.493	0.98
SS-2	0.469	0.93	0.794	0.99	0.520	0.94	0.632	0.91
SS-3	0.246	0.96	0.653	0.99	0.435	0.99	0.897	0.97
SS-4	0.812	0.87	0.354	0.97	0.467	0.91	0.368	0.99

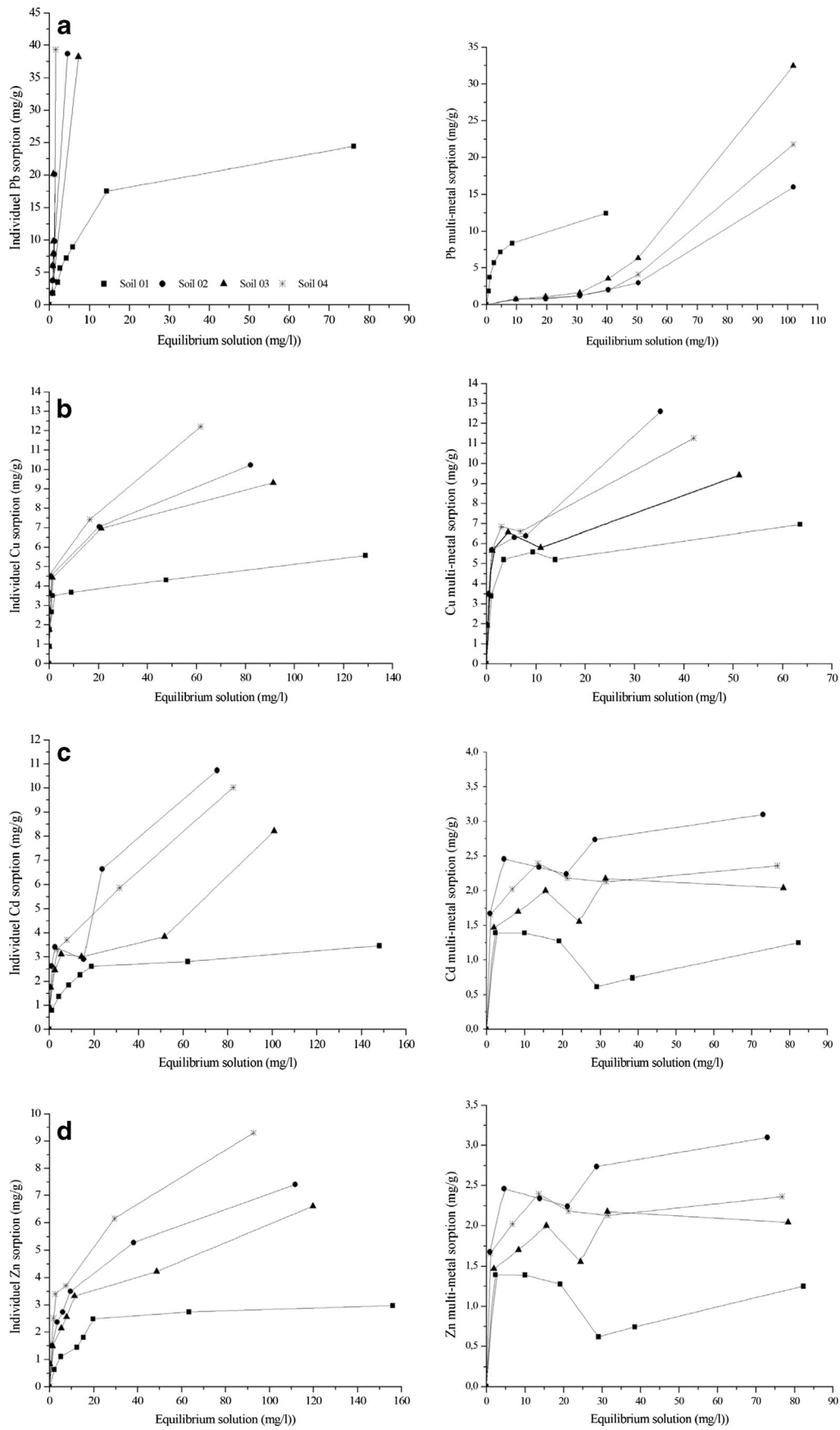


Fig. 3 Individual and multi-metal sorption isotherms of Pb (a), Cu (b), Cd (c), and Zn (d)

Table 3 Values of Freundlich parameters determined in the individual metal experiments

	n	K_F	R^2
Pb			
SS-1	0.59	2.60	0.91
SS-2	1.49	5.47	0.77
SS-3	0.97	6.38	0.54
SS-4	4.76	3.64	0.76
Cu			
SS-1	0.21	2.19	0.75
SS-2	0.24	3.93	0.88
SS-3	0.25	3.54	0.88
SS-4	0.24	4.52	0.78
Cd			
SS-1	0.30	59.10	0.92
SS-2	0.34	18.17	0.87
SS-3	0.30	14.09	0.89
SS-4	0.36	16.81	0.98
Zn			
SS-1	0.36	3.32	0.87
SS-2	0.33	9.46	0.99
SS-3	0.31	9.15	0.98
SS-4	0.33	12.44	0.99

competition effects with the same four metals in solution. With five other kinds of acidic mine soils, Vega et al. (2006) discussed the influence of soil properties on the selective sorption and retention for a six-metal competition (Cd, Cr, Cu, Ni,

Table 4 Values of Freundlich parameters determined in the multi-metal experiments

	n	K_F	R^2
Pb			
SS-1	0.43	3.11	0.87
SS-2	0.61	3.98	0.80
SS-3	0.47	3.38	0.83
SS-4	0.22	3.15	0.89
Cu			
SS-1	0.22	3.15	0.89
SS-2	0.3	4.1	0.91
SS-3	0.23	4.09	0.88
SS-4	0.31	3.97	0.86
Cd			
SS-1	-0.13	1.54	0.20
SS-2	0.121	1.76	0.79
SS-3	0.09	1.41	0.51
SS-4	0.08	1.72	0.76
Zn			
SS-1	-0.73	6.16	0.51
SS-2	0.19	1.66	0.84
SS-3	0.16	1.47	0.62
SS-4	0.13	1.64	0.84

Pb, Zn); they noted the main role of soil organic matter and Fe/Mn oxides. Then, based on the sorption behavior of separate soil minerals (Covelo et al. 2007a), they obtained further information about the order of metal sorption and the role of these soil components (Covelo et al. 2007b; Covelo et al. 2007c).

Morera et al. (2001) discussed the affinity differences between four contrasted soils ($5.0 \leq \text{pH}_{\text{water}} \leq 8.1$) and Cd, Cu, Ni, Pb, and Zn (chloride salts) during a study of both monometal and competitive sorption isotherms; they concluded that “the affinity of inorganic surfaces was larger for Zn than for Cd or Ni, but the affinity of organic surfaces was larger for Cd or Ni than for Zn.” In the case of Cu and Zn sorption on a series of 27 acid soils, all described with the Freundlich model isotherm equation, Arias et al. (2005) established some mathematical relationships indicating the importance of soil pH and CEC. As far as the competitive sorption of Cd and Pb is considered, Serrano et al. (2005) observed the major role of clay mineralogy, in the case of moderately acidic topsoil samples ($5.0 \leq \text{pH}_{\text{water}} \leq 6.1$).

Conclusion

The mobility and bioavailability of toxic metals may be related to their sorption to the surface components of soils. In this paper, the binding of Cd, Cu, Zn, and Pb on a group of four mining soil samples with different characteristics was studied using the batch adsorption method. The Freundlich isotherm model equation allowed to fit the adsorption characteristics for the four metals (alone or as a mixture) onto each soil sample. The four metals examined are associated with various chemical fractions of soils as distinguished by a five-step sequential chemical extraction: the organic matter and Fe/Mn oxide phases dominate for Pb, Cu, and Zn, whereas for Cd, the carbonate phase is the most important. In terms of overall mobility of the metals, the following order is suggested from the results: $\text{Zn} > \text{Cd} > \text{Cu} \gg \text{Pb}$.

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