

Heavy metal sorption and desorption capacity of soils containing endogenous contaminants

Emma Fernández Covelo*, Flora Alonso Vega, M. Luisa Andrade

Departamento de Biología Vegetal e Ciencia do Solo, Facultade de Biología, Universidade de Vigo, 36200 Vigo, Spain

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Abstract

Soils on serpentinites in some regions of northwestern Spain have been the subject of agricultural management practices involving the use of fertilizers and various types of organic waste containing heavy metals. Although such practices have facilitated crop growth, they have also raised the natural contents in heavy metals of the soils.

In this work, three ferralic Cambisols and another three mollic Leptosols with high Cr and Ni contents were used to study competitive sorption and desorption of six heavy metals via K_{d100} , which was employed as a measure of the ability of the soils to adsorb and retain each metal.

Lead was found to be the metal sorbed and retained to the greatest extent, and Cd, Ni and Zn those sorbed and retained in the smallest amounts.

Although the ferralic Cambisols were found to contain greater amounts of natural heavy metals, they exhibited an increased ability to adsorb and retain the body of metals relative to the mollic Leptosols by effect of their increased contents in clay and Fe, Mn and Al oxides, in addition to their higher ion-exchange capacity.

Based on the results, Pb and Cu are strongly bound, and Zn, Cd and Ni weakly bound, to the soils.

The ferralic Cambisols exhibited an increased capacity to adsorb and retain Cd, Ni, Zn and – especially – Cr than the mollic Leptosols; the latter, however, proved more effective in adsorbing and retaining Cu and Pb by virtue of their increased organic matter contents.

Copper sorption and retention, and Pb retention, were found to be correlated with the content in organic matter and that in vermiculite – which was only present in the mollic Leptosols – in the clay fraction.

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1. Introduction

At present, US Soil Taxonomy [1] serpentinite soils at the family level as having magnesian mineralogy “any particle-size class, except for fragmental, with >40% by weight magnesium-silicate minerals, such as serpentinite minerals (antigorite, chrysotile, lizardite) plus talc, olivines, Mg-rich pyroxenes, and Mg-rich amphiboles, in the fine-earth fraction (<2 mm)”. With little substitution of Fe for Mg in serpentinite, Fe in peridotite minerals is incorporated into common accessory minerals such as magnetite and hematite [2].

Therefore, the serpentinitization of basic and ultrabasic rocks produces an especially hypermagnesian environment that causes

the so-called “serpentine syndrome”—a phenomenon that delays soil weathering. Soils on serpentinitized rocks in the poly-metamorphic complex of Mellid (Coruña, Spain) contain high proportions of oxide surfaces where little clay forms owing to the relative scarcity of aluminium. Mollic Leptosols and ferralic Cambisols are among the commonest soil types in the area. These are poorly fertile soils of near-neutral pH (5–6.5) containing little organic matter – particularly the Leptosols – and virtually no exchangeable Al, but large amounts of Mg in addition to Ni, Cr, Mn and – occasionally – Cu in their primary minerals. Their most salient features are their infertility, their low contents in essential nutrients and organic matter, and their high contents in Mg, which result in a nutrient imbalance [3].

There have been attempts at restoring the fertility of these soils in some areas by supplying them with organic waste in combination with large amounts of mineral fertilizer. Replenishment of soil C and N, which is crucial with a view to sustaining vegetation on these soils, may be expedited by using organic

* Corresponding author. Tel.: +34 986 812630; fax: +34 986 812556.

E-mail addresses: emmaf@uvigo.es (E.F. Covelo), florav@uvigo.es (F.A. Vega), mandrade@uvigo.es (M.L. Andrade).

amendments. Thus, organic waste supplies carbon and other biogenic elements in forms that pioneering fauna can in principle make available to plants by metabolization, thereby favouring the development of soil that will be structurally and otherwise suitable for the growth of fauna and flora. However, both mineral fertilizer and industrial, agricultural and domestic waste can contain levels of heavy metals such as Pb, Cr, Ni, Cd and As [4–6], which, while possibly acceptable when applied to normal soils, may be unacceptable when received by, for example, serpentinitic soils—which can contain natural heavy metals at high levels.

Increased anthropogenic inputs of heavy metals in soils have received considerable attention in the past since transport of metals can raise their contents in ground and surface water [7,8].

Exogenous heavy metals can reach soil via commercial fertilizers, liming materials, agrochemicals, and sewage sludge and other types of waste, in addition to soil amendments, irrigation water and atmospheric deposition. Soils repeatedly supplied with organic manure, fungicides and other pesticides usually exhibit high concentrations of extractable heavy metals [9,10]. The mobility of such metals depends not only on their total concentrations in soil, but also on various properties of the metal and soil concerned. Depending on such properties, it may be desirable for organic waste and mineral fertilizer to be applied in combination with natural soil components (e.g. clays, oxides) capable of immobilizing heavy metals in forms that will not be taken up by organisms. Although sorption and desorption tests can be prolonged until equilibrium is reached, predictions of heavy metal fixation and transport in a dynamic environment should not assume equilibrium concentrations [11,12].

Because the threat of heavy metal pollution posed by mine soils generally includes more than one metal, studies of heavy metal sorption and desorption in such soils should consider the potential competition between heavy metals for binding sites. However, few studies have so far examined the simultaneous sorption of more than one heavy metal by any kind of soil [11,13,14]. In fact, more abundant literature has been published on the simultaneous sorption of several heavy metals by isolated silicate minerals [15]; Fe, Al and Mn oxides [13]; humus [16]; and organic and inorganic colloids [17]; however, as with whole soils, the results have been highly contradictory as regards the sequence in which different metals are sorbed and desorbed. In fact, the very relevance of competition between metals has been controversial, possibly as a result of (i) failing to test the importance of competition between cations in many studies; (ii) confounding ionic strength effects by covarying cation concentrations; (iii) the dependence of competing cation effects on pH and loading; and (iv) differences in competitive ability and concentration effects among cations. One useful parameter for the purpose of ranking metals according to their extent of sorption when in competition appears to be K_d (*viz.* the distribution coefficient of the ion concerned between the soil and its solution). In fact, K_d allows one to estimate the mobility and fate of competing metals in soil [18,19].

The primary purposes of this work were to study the competitive sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn in serpentinitic soils from the province of Coruña (Galicia, NW

Spain) in order to establish the selectivity sequences for the sorption and desorption of these metals in the soils from their distribution coefficients and to assess the capacity of the soils to sorb and retain the metals, which were supplied via organic waste and mineral fertilizer.

2. Materials and methods

2.1. Soils

The study was conducted on soils developed on serpentinitic rocks in the province of Coruña (NW Spain). The WRBSR denominations [20] of six soils were determined on the basis of the characteristics of their various horizons. Three are Ferralic cambisols (FC1, FC2, and FC3), and the others are Mollic Leptosols (ML1, ML2 and ML3). Study areas (FC: 42°54'N, 8°1'W, and LM: 42°59'N, 7°54'W) include 136,000 m² each one. Total length of selected transect in each zone is 600 m and it descends in smooth slope (<5%). In each one of them soil samples were taken every 200 m (FC1, FC2, FC3, and LM1, LM2 and LM3, respectively).

2.2. Soil analyses

Five topsoil samples per test site were collected at depths of 0–30 cm with the aid of an Eijkelkamp sampler and stored in polyethylene bags for transfer to the laboratory, where they were air-dried, passed through a 2 mm sieve and homogenized on a Fritsch Laborette 27 rotary sampler divider. Five sub-samples of each composite sample thus obtained were used for analysis for particle size distribution, pH, organic carbon, effective cation-exchange capacity, exchangeable cations, and iron, aluminium and manganese oxides. In addition, the <2 µm fraction was subjected to mineralogical analysis.

Soil reaction was determined with a pH electrode in 2:1 water/soil extracts [21]. Particle size distribution was determined following oxidation of organic matter with hydrogen peroxide, the upper fraction (down to 50 µm) being separated by sieving and the lower one used for subjection to the internationally endorsed procedure [22]. Organic carbon was quantified with the method of Walkley and Black [23]. Organic matter was fractionated using the wet sieving procedure developed by Andriulo et al. [24] and Galantini et al. [25], which facilitated the quantification of humified and non-humified organic matter.

Soil CEC and exchangeable cations (*viz.* Ca²⁺, Mg²⁺, K⁺ and Na⁺) were extracted with 1 M ammonium acetate buffered at pH 7.0, and concentrations determined by inductively coupled plasma atomic emission spectrometry (ICP-OES). Exchangeable acidity was determined by using a 1 M KCl replacing solution and titration to a phenolphthalein end-point [26].

Aluminium, calcium, potassium, magnesium and sodium were extracted with a BaCl₂ solution and quantified by ICP-OES on a Perkin-Elmer Optima 4300 DV instrument.

Oxides were determined using the method of Mehra and Jackson [27]. Samples were shaken in a solution of sodium hydrogen carbonate and sodium citrate, the extract being used to determine Fe, Al and Mn by ICP-OES.

Table 1
Selected chemical characteristics of the studied soils

	FC1	FC2	FC3	ML1	ML2	ML3
pH H ₂ O	6.4a	6.41a	6.39a	4.9b	4.91b	4.89b
CIC ₍₊₎ (cmol kg ⁻¹)	10.92b	11.22a	10.38b	7.92c	7.93c	7.94c
Organic matter (mg kg ⁻¹)	15.8c	14.22d	13.43d	71.12b	71.12b	86.92a
Humified O.M. (mg kg ⁻¹)	1.13d	0.95e	1.06de	25.69b	22.95c	30.05a
Mn oxides (mg kg ⁻¹)	1.41ab	1.3b	1.52a	0.18c	0.16c	0.15c
Fe oxides (mg kg ⁻¹)	68.77b	59.66ab	74.36a	9.76c	9.2cd	8.84d
Al oxides (mg kg ⁻¹)	90.83b	78.8c	98.21a	12.89d	12.15d	11.67e
Total dissolved (mg kg ⁻¹)						
Cd	n.d.	n.d.	n.d.	0.01a	0.01a	n.d.
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	9.67b	10.27a	9.73b	0.63c	0.65c	0.67c
Pb	n.d.	0.03b	0.02b	0.06a	n.d.	0.03b
Zn	n.d.	n.d.	n.d.	n.d.	n.d.	0.12a
DTPA extractable (mg kg ⁻¹)						
Cd	n.d.	n.d.	n.d.	0.01a	0.01a	0.01a
Cr	0.01b	0.02b	0.01b	0.11a	0.10a	0.10a
Cu	4.46a	4.46a	4.51a	0.48c	0.46c	0.53b
Ni	38.62a	39.08a	39a	1.76b	1.69c	1.75b
Pb	0.31a	0.27b	0.3a	0.29a	0.28a	0.32a
Zn	0.18b	0.13c	0.19b	0.2a	0.19ab	0.23a
Total (mg kg ⁻¹)						
Cd	0.75d	1.07c	0.55e	1.86ab	1.78b	2.28a
Cr	2550.18b	2966.43a	2878.87ab	353.41d	366.43d	401.7c
Cu	75.19b	90.53a	86.89ab	26.39d	26.15d	29.88c
Ni	2240.02c	2718.38a	2618.46b	152.63e	158.87e	178.15d
Pb	20.77b	24.73a	23.84ab	14.44d	18.11bc	17.52c
Zn	20.39c	37.44e	42.12a	27.21d	19.46e	29.8c

Means of 15 analyses (three replicate analyses of each of five replicate samples for each soil). Values followed by different letters in each row differ significantly with $p < 0.05$. n.d.: not detectable.

The mineralogical analysis of the clay fraction was done by X-ray diffraction spectroscopy of crystalline powder on a Siemens D-5000 diffractometer, using a $q-2q$ configuration (Bragg–Brentano system) with a Cu anode and 0.05 passes with a time of 10 s per pass [28]. Total dissolved Cd, Cr, Cu, Ni, Pb and Zn were extracted with an acidified 0.1 M solution of calcium chloride, using the method of Houba et al. [29]. Available Cd, Cr, Cu, Ni, Pb and Zn were extracted with diethylenetriamine-pentaacetate (DTPA) as described by Lindsay and Norwell [30]. Total contents were determined following acid digestion with a mixture of concentrated nitric, hydrochloric and hydrofluoric acids (1:3:3, v/v/v) in PTFE bottles placed in a microwave oven [31]. Finally, Cd, Cr, Cu, Ni, Pb and Zn were quantified by ICP-OES.

2.3. Batch experimental methods

Sorption and desorption tests were conducted on five homogenized pooled subsamples per soil, using the method of [32,33]. Sorption isotherms were obtained from solutions containing 5–300 mg L⁻¹ concentrations of Cd, Cr, Cu, Ni, Pb or Zn in nitrate form that were buffered at pH 4.5 with 0.02 M acetic acid and 0.02 M sodium acetate. These buffered solutions mimicked an acid spill and allowed the heavy metal sorption and desorption capacity of the soils to be compared. Soil samples (12 g)

were suspended in 200 mL of sorption solution, equilibrated on a rotary shaker at 25 °C for 24 h [33–35] and centrifuged at 1800 × *g*. The metal concentrations in the supernatant were quantified by ICP-OES and the amounts of metals sorbed by each soil calculated by difference. Each test was performed in triplicate.

Desorption isotherms were constructed as described by Madrid and Díez-Barrientos [36]. The pellets obtained by centrifugation in the sorption tests (following equilibration by shaking for 24 h) were dried at 25 °C, weighed and resuspended in

Table 2
Textural and clay mineralogical analysis of the studied soils

Soil	FC1	FC2	FC3	ML1	ML2	ML3
Sand	26.81b	26.71b	26.91b	60.5a	60.4a	60.6a
Silt	34.31a	34.21a	34.41a	6.97b	6.9b	6.5c
Clay	38.88ab	39.08b	38.68a	32.53b	32.7c	32.9c
Quartz	++	++	++	+	+	+
Mica	–	–	–	tr	tr	tr
Kaolinite	+++	+++	+++	++++	++++	++++
Vermiculite	–	–	–	tr	tr	tr
Hematite	++	++	++	–	–	–

Means of 15 analyses (three replicate analyses of each of five replicate samples for each soil). Values followed by different letters in each row differ significantly with $p < 0.05$. +++++: >50%; +++: 50–30%; ++: 30–10%; +: 10–3%; tr: <3%; –: not identified.

200 mL of 0.02 M acetic acid and 0.02 M sodium acetate prior to equilibration on a rotary shaker at 25 °C for 24 h and centrifugation at 1800 × g. The metal concentrations in the supernatants were determined by ICP-OES and the amounts of metal retained by each soil calculated by difference from the amounts sorbed in the sorption tests. This allowed us to estimate heavy metal retention by the soils. The equilibrium pH after the desorption tests was 4.5 in all samples. Each test was performed in triplicate.

Sorption and desorption data were correlated with the Langmuir and Freundlich models [37]. The sorption and retention distribution coefficients for the metals in each soil at equilibrium were calculated from the previous data [34], using the following expression:

$$K_d = \frac{\text{concentration of metal sorbed or retained } (\mu\text{mol L}^{-1})}{\text{concentration of metal in solution } (\mu\text{mol L}^{-1})}$$

Following Kaplan et al. [38], joint distribution coefficients, $K_{d\Sigma\text{sp}}$, were also calculated for each soil [34,35,39], using the expression

$$K_{d\Sigma\text{sp}} = \frac{\sum C_{M_j,\text{soil}}}{\sum C_{M_j,\text{solution}}}$$

where $C_{M_j,\text{soil}}$ and $C_{M_j,\text{solution}}$ are the concentrations of metal j in the soil ($\mu\text{mol g}^{-1}$) and its solution ($\mu\text{mol L}^{-1}$), respectively.

The heavy metal sorption and retention capacity of each soil was determined from the distribution coefficient corresponding to an added concentration of 100 mg L⁻¹ [34].

All tests were performed in triplicate and the results analysed statistically using the software SPSS v. 14.0 for Windows. The statistical significance of differences was determined by one-way analysis of variance (ANOVA) and the least-significant difference (LSD) test. The influence of soil properties on the metal sorption capacity was determined by correlation analysis. Principal component analysis (PCA) was used to establish relations among the heavy metal sorption and retention capacities of the soils. PCA is one of the simplest and oldest eigenvalue analyses based on ordination methods for quantitative data. Ordination reduces the dimensionality of complex multivariate data from a series of correlated ones. These factors, or axes, are orthogonal linear combinations of the measured variables.

3. Results and discussion

3.1. Soil characteristics

Tables 1 and 2 show the chemical and textural properties of the studied soils, and the results of the mineralogical analysis of

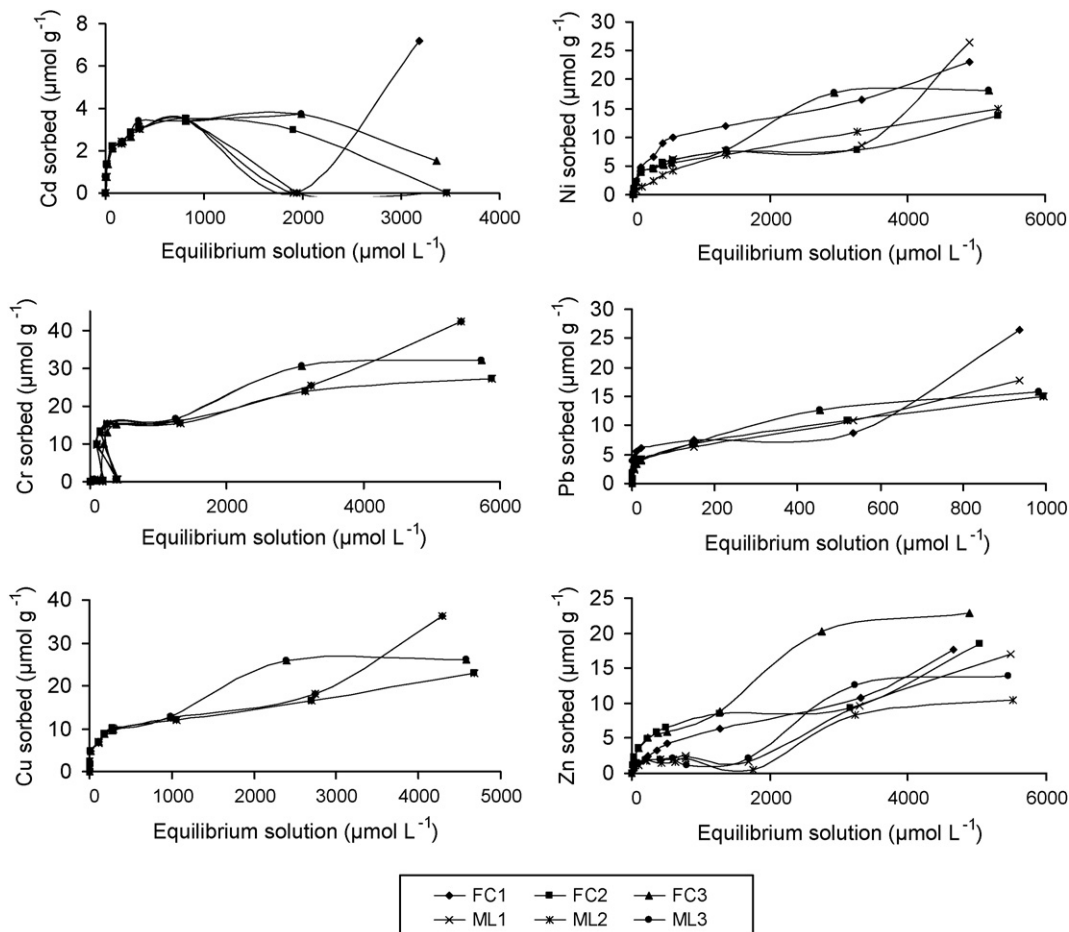


Fig. 1. Sorption isotherms.

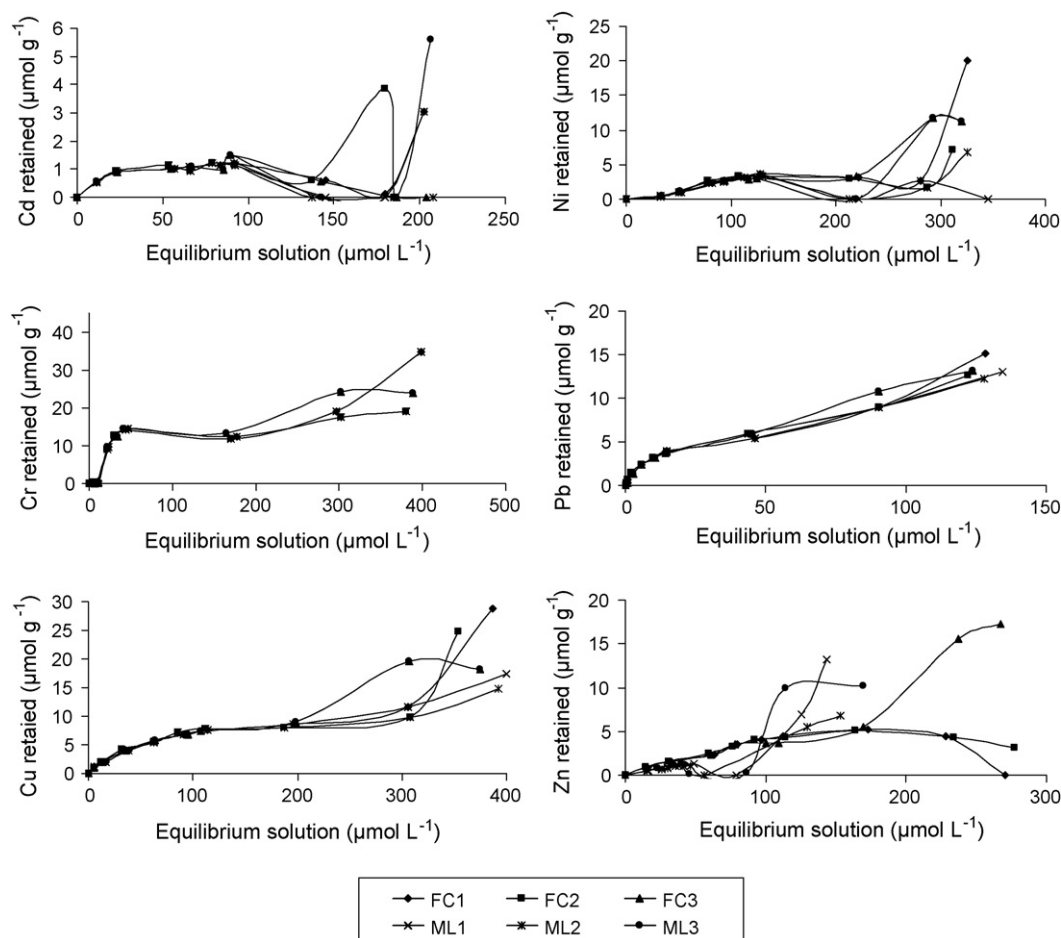


Fig. 2. Desorption isotherms.

their clay fractions. As can be seen, the Mollic Leptosols were more acidic than the Ferralic Cambisols—the latter had more near-neutral pH values.

All soils had a low cation-exchange capacity, the Cambisols exhibiting slightly higher values than the Leptosols. Note the relatively high contents in Fe, Mn, and Al of the ferralic Cambisols relative to the Leptosols—which contained more organic matter than the former (Table 1).

The most salient difference as regards the mineralogical composition of the clay fraction between the two types of soil was the presence of hematite in the Ferralic Cambisols and of vermiculite traces in the Mollic Leptosols.

By virtue of the properties of the original material [40], these soils contain high total concentrations of Cr and Ni, and also high levels of DTPA and CaCl_2 extractable Ni. These contents are higher than the maximum limits established in some reference guides [41,42]. Contents were higher in the Ferralic Cambisols than in the Mollic Leptosols. Copper contents were also high, albeit somewhat lower. Worth special note was the relatively high content in DTPA extractable Cu of the six soils—by contrast the contents in DTPA and CaCl_2 extractable Cr were zero or near-zero.

3.2. Sorption and desorption

Figs. 1 and 2 show the amounts of metals sorbed by the soils and retained upon desorption, as well as the concentrations in the equilibrium solution at each added concentration. Most are irregular because of soil heterogeneity and between-metal competition for binding sites, especially in the case of desorption isotherms and the metals Cd, Ni and Zn.

Tables 3 and 4 list the binding affinity and binding capacity parameters of the Langmuir and Freundlich equations fitted to the sorption and retention data. As rule, the results fitted the latter model more closely than the former.

The Freundlich equation is an empirical sorption model widely used in environmental soil chemistry. However, it has the disadvantage that it cannot predict the maximum sorption. Thus, the single K_d term present in the Freundlich equation implies that the energy of sorption on a homogeneous surface is independent of the surface coverage. While researchers have often used parameters K_d and $1/n$ to draw conclusions about sorption mechanisms and interpreted the presence of multiple slopes in Freundlich isotherms as evidence of the presence of various types of binding sites, such interpretations are purely speculative [12].

Table 3
Freundlich and Langmuir correlations (sorption isotherms)

Metal	Soil	Equation	R^2	n	K_F
Freundlich					
Cd	FC2	$y = 0.29x - 0.27$	0.948	3.41	0.54
	FC1	$y = 0.33x + 0.20$	0.969	3.01	1.57
	FC2	$y = 0.31x + 0.22$	0.984	3.28	1.66
Cu	FC3	$y = 0.35x + 0.16$	0.980	2.89	1.45
	ML1	$y = 0.37x + 0.13$	0.992	2.72	1.35
	ML2	$y = 0.36x + 0.11$	0.991	2.79	1.28
Ni	ML3	$y = 0.37x + 0.10$	0.991	2.68	1.26
	FC1	$y = 0.46x - 0.48$	0.905	2.18	0.34
	FC2	$y = 0.40x - 0.36$	0.920	2.53	0.44
Pb	FC3	$y = 0.48x - 0.51$	0.965	2.10	0.31
	ML1	$y = 0.39x - 0.68$	0.669	2.59	0.21
	ML3	$y = 0.40x - 0.72$	0.670	2.51	0.19
Zn	FC1	$y = 0.35x + 0.13$	0.948	2.82	1.34
	FC2	$y = 0.34x + 0.15$	0.958	2.95	1.41
	FC3	$y = 0.36x + 0.13$	0.953	2.78	1.34
Pb	ML1	$y = 0.46x - 0.18$	0.990	2.19	0.65
	ML2	$y = 0.46x - 0.20$	0.981	2.18	0.64
	ML3	$y = 0.46x - 0.191$	0.987	2.16	0.65
Zn	FC1	$y = 0.43x - 0.32$	0.909	2.34	0.45
	FC2	$y = 0.40x - 0.27$	0.963	2.53	0.53
	FC3	$y = 0.46x - 0.39$	0.972	2.17	0.41
Zn	ML1	$y = 0.48x - 0.91$	0.703	2.07	0.12
	ML3	$y = 0.50x - 0.97$	0.690	1.99	0.11
	Langmuir				
Cd	FC3	$y = 0.59x - 89.19$	0.880	1.70	-6.60
	ML2	$y = 1050.2x - 292006$	0.943	0.001	-3.60
	ML3	$y = 807.61x - 315338$	0.683	0.001	-2.56

Some authors have related varying slopes in a sorption isotherm to differential binding mechanisms depending on the level of metal added [43,44]. However, sorption isotherms provide no detailed information about the sorption processes involved [11,45].

Table 5 lists K_F , $1/n$ and the coefficient of determination, R^2 , for Pb and Cu sorption and desorption by our soils. The sorption and desorption data for Cu and Pb in the six soils fitted the Freundlich model. These two metals were sorbed and retained in greater amounts than Cd, Ni and Zn. On the other hand, the sorption and desorption data for Cd, Ni and Zn in most of the soils failed to fit the Freundlich model, and so did those for Cr in all soils.

The K_F and $1/n$ values for Cu and Pb are quite consistent with the values obtained by Horn [46] in sorption tests on 124 soils of variable compositions, and to those reported by Lair et al. [45] for Cu sorption and desorption in soils under different management regimes.

Both Cu, Pb and Cr were sorbed in greater amounts than Cd, Ni and Zn in all soils.

However, consistent with the results of Lair et al. [45], the constancy in $1/n$ reveals that the buffering capacity of the soils decreased earlier for Cu than it did for Pb (median $1/n$: $Cu_{\text{sorbed}} = 0.35$, $Pb_{\text{sorbed}} = 0.41$, $Cu_{\text{retained}} = 0.63$,

$Pb_{\text{desorbed}} = 0.67$). Also, all soils sorbed Pb in greater amounts than Cu.

Zinc and cadmium exhibited an increased affinity for the soils with the highest organic matter contents and pH. However, an acid soil pH reduced Cd, Ni and Zn sorption [47].

Based on their desorption coefficients, Pb and Cu were strongly sorbed (median: $K_{Fd}Pb \approx K_{Fd}Cu$). Soils FC1, FC2 and FC3 had increased K_{Fd} values for Pb relative to Cu. On the other hand, soils ML1, ML2 and ML3 exhibited the opposite trend.

The ratio K_{Fs}/K_{Fd} is a measure of hysteresis in sorption processes [45]. The results for Pb (1.27–2.20) and Cu (2.00–4.13) reveal that Pb ions were more strongly irreversibly bound than Cu by the studied soils. In those cases where the sorption and desorption data for Zn and Ni fitted the Freundlich model, the K_{Fs}/K_{Fd} ratio varied more markedly. The K_{Fs}/K_{Fd} ratio for Ni was 34, 8.5 and 31 in soil FC1, FC2 and FC3, respectively; and that for Zn 1.8 in FC2 and 8 in FC3. These values suggest reversible binding and a stronger dependence of the sorption behaviour on various soil parameters.

Based on the sorption and desorption data, the amounts of metal sorbed were not linearly related to those added to the soils – at least not throughout the studied range – owing to competition among cations. This precluded using the slopes of the isotherms as distribution coefficients as proposed by

Table 4
Freundlich and Langmuir correlations (desorption isotherms)

Metal	Soil	Equation	R^2	n	K_F
Freundlich					
Cd	FC3	$y = 1048.7x - 57372$	0.686	0.001	-18.28
	ML1	$y = 760.87x - 14215$	0.500	0.001	-53.53
	ML2	$y = 1183.9x - 20696$	0.976	0.001	-57.20
Metal	Soil	Equation	R^2	β ($\mu\text{mol g}^{-1}$)	K ($\times 1000$)
Langmuir					
Cr	FC2	$y = 1.09x - 1.19$	0.703	0.92	0.07
	FC3	$y = 1.09x - 1.14$	0.708	0.92	0.07
Cu	FC1	$y = 0.65x - 0.43$	0.939	1.55	0.38
	FC2	$y = 0.62x - 0.37$	0.925	1.63	0.42
	FC3	$y = 0.65x - 0.43$	0.980	1.54	0.38
	ML1	$y = 0.65x - 0.21$	0.962	1.55	0.62
	ML2	$Y = 0.61x - 0.19$	0.944	1.63	0.64
	ML3	$y = 0.63x - 0.21$	0.974	1.58	0.62
Ni	FC1	$y = 1.14x - 1.93$	0.717	0.88	0.01
	FC2	$y = 0.81x - 1.33$	0.552	1.24	0.05
	FC3	$y = 1.25x - 2.12$	0.910	0.80	0.01
Pb	FC1	$y = 0.64x - 0.21$	0.959	1.57	0.61
	FC2	$y = 0.61x - 0.17$	0.959	1.64	0.68
	FC3	$y = 0.64x - 0.21$	0.971	1.56	0.62
	ML1	$y = 0.73x - 0.33$	0.959	1.37	0.47
	ML2	$y = 0.70x - 0.29$	0.968	1.42	0.52
Zn	ML3	$y = 0.71x - 0.29$	0.976	1.41	0.51
	FC2	$y = 0.52x - 0.54$	0.763	1.93	0.29
	FC3	$y = 0.98x - 1.30$	0.912	1.02	0.05

Gao et al. [19]. The lower metal concentrations used by these authors seemingly failed to induce strong competition between cations. Therefore, based on the reasoning of Sánchez-Martín and Sánchez-Camazano [48], a specific K_d coefficient is an appropriate measure for comparing soils in terms of metal sorption and retention capacity. Such a coefficient represents the ratio of sorbed or retained metal to its concentration in the equilibrium solution. We chose an added concentration of 100 mg L^{-1} for the purpose of establishing an appropriate comparable coefficient (K_{d100}). Following Gomes et al. [33] and Covelo et al. [34], the choice of this concentration was based on the level at

which sorption of the heavy metals sorbed to the smallest extent (*viz.* Cd, Ni and Zn) started to fall.

3.3. Selectivity sequences

Table 6 shows the sorption and retention distribution coefficients for Cd, Cr, Cu, Ni, Pb and Zn at an added concentration of 100 mg L^{-1} in the six studied soils, and the sorption and desorption selectivity sequences established from them. As can be seen, sorption and retention selectivity sequences were very similar in all soils. Thus, Pb was preferentially sorbed and retained by all,

Table 5
Freundlich coefficients for the sorption (K_{Fs}) and desorption (K_{Fd}) isotherms of Pb and Cu in various soils, and K_{Fs}/K_{Fd} ratio

Metal	Soil	Sorption			Desorption			K_{Fs}/K_{Fd}
		K_{Fs} ($\text{L}^{1/n} \mu\text{mol}^{(1-1/n)} \text{g}^{-1}$)	$1/n_s$	R^2	K_{Fd} ($\text{L}^{1/n} \mu\text{mol}^{(1-1/n)} \text{g}^{-1}$)	$1/n_d$	R^2	
Cu	FC1	1.57	0.33	0.969	0.38	0.65	0.939	4.13
	FC2	1.66	0.30	0.984	0.42	0.61	0.925	3.95
	FC3	1.45	0.35	0.980	0.38	0.65	0.980	3.82
	ML1	1.35	0.37	0.992	0.62	0.65	0.962	2.18
	ML2	1.28	0.36	0.991	0.64	0.61	0.944	2.00
	ML3	1.26	0.37	0.991	0.62	0.63	0.974	2.03
Pb	FC1	1.34	0.35	0.948	0.61	0.64	0.959	2.20
	FC2	1.41	0.34	0.958	0.68	0.61	0.959	2.07
	FC3	1.34	0.36	0.953	0.62	0.64	0.971	2.16
	ML1	0.65	0.46	0.990	0.47	0.73	0.959	1.38
	ML2	0.64	0.46	0.981	0.52	0.70	0.968	1.23
	ML3	0.65	0.46	0.987	0.51	0.71	0.976	1.27

Table 6
 K_{d100} values ($L\ kg^{-1}$), and sorption and retention selectivity sequences

Soil	Metal	K_d		Metal	K_d	
		K_d sorption	K_d retention		K_d sorption	K_d retention
FC1	Cd	4.28	4.10	Ni	5.55	14.30
FC2		4.32	4.32		5.51	13.86
FC3		4.19	3.87		5.68	15.02
ML1		0.95	0.00		0.85	0.00
ML2		0.62	0.00		0.33	0.00
ML3		1.11	0.00		1.21	0.00
FC1	Cr	12.50	69.80	Pb	42.35	117.74
FC2		11.63	68.60		45.15	135.29
FC3		13.33	81.10		46.43	131.08
ML1		4.94	58.04		32.03	132.82
ML2		4.18	57.24		32.32	171.54
ML3		5.47	65.65		34.19	137.86
FC1	Cu	12.65	43.80	Zn	6.72	30.07
FC2		11.35	42.43		6.64	30.81
FC3		13.00	44.98		6.93	32.04
ML1		15.36	80.80		0.92	0.00
ML2		14.43	99.72		0.30	0.00
ML3		16.18	84.72		1.24	3.15
Selectivity sequences						
		FC1		FC2		FC3
Sorption		Pb > Cu > Cr > Zn > Ni > Cd		Pb > Cr > Cu > Zn > Ni > Cd		Pb > Cr > Cu > Zn > Ni > Cd
Retention		Pb > Cr > Cu > Zn > Ni > Cd		Pb > Cr > Cu > Zn > Ni > Cd		Pb > Cr > Cu > Zn > Ni > Cd
Selectivity sequences						
		ML1		ML2		ML3
Sorption		Pb > Cu > Cr > Cd > Zn > Ni		Pb > Cu > Cr > Cd > Ni > Zn		Pb > Cu > Cr > Zn > Ni > Cd
Retention		Pb > Cu > Cr > Cd > Zn > Ni		Pb > Cu > Cr > Zn > Cd > Ni		Pb > Cu > Cr > Zn > Cd > Ni

whereas Cd, Ni and Zn were invariably the last in the sorption and retention sequences. Following desorption, soils ML1, ML2 and ML3 retained no Cd, Ni or Zn—which exhibited near-zero K_{d100} values.

The Leptosols were found to adsorb and retain Pb and Cu preferentially; this can be ascribed to their increased organic matter content relative to the Ferralic Cambisols.

Based on the selectivity sequences of Table 6, Pb, Cu and Cr were sorbed and retained in greater amounts than were Cd, Ni and Zn in most cases. The K_{d100} values for Cd, Ni and Zn were very low and suggest that these metals were easily exchanged with, and replaced by, Cr, Cu and Pb when all were in competition. According to Gomes et al. [33], this might strongly suggest why Berti and Jacobs [49] found that soil loading with Cd, Ni and Zn appeared to be of greater environmental concern than loading with Cr, Cu and Pb, and also that the former group of metals might accumulate in the tissues of plants grown on sludge-treated plots. The results for Pb and Cu in relation to Cd and Zn are consistent with increased sorption of the former two relative to the latter in a competitive scenario such as the three high weathered Brazilian soils studied by Fontes et al. [50] and with the lower mobility of Pb and Cu relative to Cd and Zn in a Brazilian Oxisol profile [51].

Some authors [14,52] have found the sorption selectivity sequences for heavy acids in soil to depend on the electronegativity of the cations, which, according to Evans [53], is 1.9 for Cu, 1.8 for Pb, 1.8 for Ni, 1.7 for Cd, 1.6 for Cr and 1.6 for Zn. The fact that Cr was one of the most strongly retained cations despite its low electronegativity seems to be related to its being applied in trivalent form, which is how it occurs predominantly in soils [7].

3.4. Competitive sorption and desorption: soil ranking

Based on parameter $K_{d100\Sigma sp}$ for the joint desorption of several species proposed by Kaplan et al. [38] and adapted to the competitive sorption and desorption of heavy metals by Covelo et al. [34], FC3 was the soil with the highest sorption capacity for the body of metals studied here, and FC1 that exhibiting the highest retention capacity following desorption (see Table 7). Overall, the Ferralic Cambisols exhibited higher sorption and retention capacity for the body of metals than did the Mollic Leptosols, even though the former contained greater amounts of natural heavy metals than the latter. The increased capacity of Ferralic Cambisols to sorb and retain the metals can be ascribed to their higher contents in Fe, Mn, Al and clay, in addition to

Table 7
Sorption and retention $K_{d100\Sigma sp}$ values ($L\ kg^{-1}$)

Soil	Sorption	Retention
FC1	14.33	219.8
FC2	14.29	211.68
FC3	15.06	157.41
ML1	4.16	85.99
ML2	3.59	88.41
ML3	4.63	54.87

their increased cation-exchange capacity (see Tables 1 and 2). Also, the clay fraction of these soils has been shown to contain hematite and metal concentrations in the soil solution are known to be strongly influenced by the presence of iron hydrous oxides [54,14], the most frequently detected of which in soils and sediments are ferrihydrite, goethite and hematite [13,55]. In addition, goethite and hematite have been shown to fix various metals [56].

3.5. Principal component analysis

The sorption and retention K_{d100} values for each metal in the soils were subjected to principal component analysis. A sorption PC and a retention PC (Table 8) were found to account for 95.423 and 85.065%, respectively, of the total variance.

The sorption component (SPC1) reveals an increased sorption of all metals except Cu. The retention component (RPC1) indicates an increased retention capacity for all metals except Pb

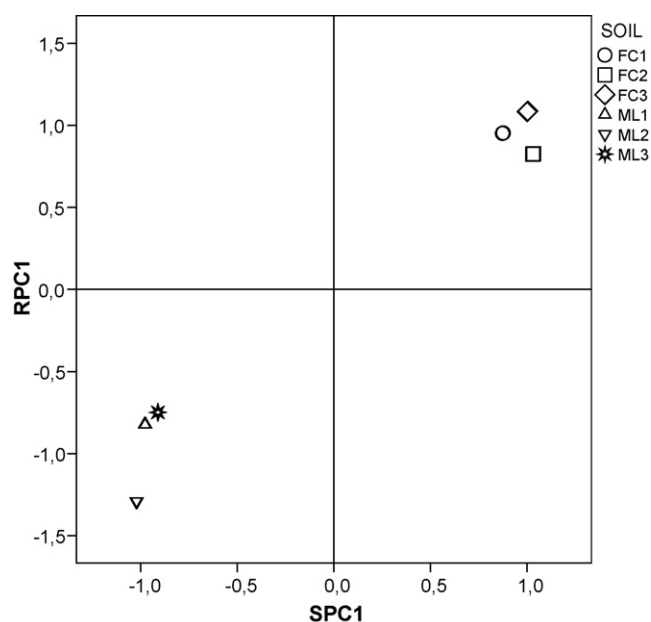


Fig. 3. Principal component analysis.

and Cu, which were the metals most strongly retained in most instances.

As can be seen in the plot the soils against the two PCs (SPC1 and RPC1), Fig. 3, the Ferralic Cambisols clustered in the first quadrant and the Mollic Leptosols in the third. Therefore the Leptosols possess a higher Cu sorption capacity, and an also higher Cu and Pb retention capacity, than the Cambisols;

Table 8
Principal component analyses

Total variance explained						
PC	Initial eigenvalues			Extraction sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
Sorption						
1	5.725	95.423	95.423	5.725	95.423	95.423
2	0.234	3.901	99.324			
3	0.034	0.574	99.898			
4	0.006	0.102	99.999			
5	3.06E-005	0.001	100			
6	1.01E-006	1.69E-005	100			
Retention following desorption process						
1	5.104	85.065	85.065	5.104	85.065	85.065
2	0.577	9.621	94.686			
3	0.307	5.122	99.808			
4	0.010	0.162	99.970			
5	0.002	0.030	100			
6	1.67E-007	2.79E-006	100			
Metal						
			PC1 sorption			PC1 retention
Cd			0.997			0.975
Cr			0.987			0.860
Cu			-0.897			-0.987
Ni			0.996			0.984
Pb			0.984			-0.710
Zn			0.997			0.983

Extraction method: principal component analysis.

Table 9
Pearson correlation analyses

	Cd sorbed	Cd retained	Cr sorbed	Cr retained	Cu sorbed	Cu retained	Ni sorbed	Ni retained	Pb sorbed	Pb retained	Zn sorbed	Zn retained	Sorption $K_{d100\Sigma P}$	Retention $K_{d100\Sigma P}$
OM														
Humified OM					0.932**	0.954**			0.478*	0.527*				0.984**
CEC(+)					0.939**	0.944**		0.977**	0.466*	0.495*		0.981**	0.961**	0.981**
Vermiculite					0.596**	0.909**			0.945**	0.492*		0.981**	0.553*	0.482*
Gibbsite	0.996**	0.997**	0.980**	0.780**			0.992**		0.561*	0.811**	0.993**	0.997**	0.983**	0.879**
Chlorite	0.992**	0.998**	0.964**	0.741**			0.984**		0.970**		0.985**	0.989**	0.971**	
Hematite	0.994**	0.999**	0.973**	0.772**			0.989**		0.959**		0.989**	0.995**	0.978**	
Mn oxides	0.988**	0.986**	0.994**	0.839**			0.991**		0.973**		0.993**	0.996**	0.991**	
Fe oxides	0.982**	0.978**	0.995**	0.851**			0.998**		0.973**		0.988**	0.991**	0.989**	
Al oxides	0.982**	0.978**	0.995**	0.851**			0.995**		0.967**		0.988**	0.991**	0.989**	
							0.986	0.995**	0.967**	0.811**	0.988**	0.991**	0.989**	
							0.986	0.995**	0.967**	0.811**	0.988**	0.991**	0.989**	

* Correlation was significant at the 0.05 level (two-tailed).

** Correlation was significant at the 0.01 level (two-tailed).

by contrast, the latter possess higher capacities for the other metals.

The fact that the Leptosols studied contain more organic matter than the Cambisols can be the origin of the higher Pb and Cu sorption and retention capacity of the former. Stevenson [57] noted that copper has a relatively high charge-to-radius ratio and is known to bind strongly to humic substances. Also, Bradl [58] concluded that the chemistry of Pb in soils is affected by the formation of relatively stable complexes or chelates that result from interaction with organic matter, and Pinheiro et al. [59] showed the presence of organic matter in soil to also play a prominent role in Pb sorption because it can mobilize the metal via specific sorption reactions.

3.6. Correlation analysis

The influence of soil properties on the sorption and retention capacity for the studied heavy metals was examined via bivariate correlation analysis. The sorption and retention of Cd, Ni and Zn, and the sorption of Pb and the body of metals, were found to be correlated with the contents in Fe, Mn and Al oxides, and those in gibbsite, chlorite and hematite. Also, the sorption of Pb and the body of metals, and the retention of Ni and Zn, were correlated with the cation-exchange capacity of the soils. The sorption and retention of Cu, and the retention of Pb and the body of metals as established from $K_{d100\Sigma P}$, were correlated with the content in organic matter and also with that in vermiculite of the clay fraction (Table 9).

4. Conclusions

The studied soils have high contents of natural Cr and Ni by virtue of their developing on serpentinitic rocks. Despite their high content in natural Cr, they adsorb Cr, Cu and Pb in larger amounts than they adsorb Cd, Ni and Zn.

The results suggest that Pb and Cu bind strongly, and Zn, Cd and Ni more weakly, to the studied soils.

The Mollic Leptosols sorb and retain Pb and Cu preferentially by effect of their high contents in organic matter—where the previous two metals are predominantly sorbed. A correlation analysis confirmed the influence of organic matter and vermiculite on the ability of the soils to sorb and retain the metals.

The Ferralic Cambisols possess a higher sorption and retention capacity for the metals than do the Mollic Leptosols. This can be ascribed to the increased contents in Fe, Mn and Al oxides of the former, their also increased cation-exchange capacity, and their clay being more abundant and mineralogically varied.

The results obtained in this work suggest the need to control the contents in heavy metals of amendments and fertilizers supplied to the soils in order to avoid their being transferred to, and contaminating, surface and subsurface waters.

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