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Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region

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ABSTRACT

The sorption and mobility of trace metals in calcareous soils (calcaric Fluvisols) were studied in experimental columns using nine soil samples extracted from Ap and AC horizons, under laboratory conditions. A contaminating solution with six heavy metals at identical concentrations (350 mg kg^{-1} for each metal) was used to saturate the soil columns, and after the contamination assay two successive washes with de-ionized water were performed. Sorption rates were high for all the metals, higher than 90%. However, competition between metals resulted in greater retention of Cr, Cu and Pb than Ni, Zn and Cd. The data on mobility showed that Cr and Pb (values of K_d 5.6×10^4 and 8.1×10^4, respectively) were the least mobile metals, Cu and Zn had intermediate values (values of K_d 6.9×10^3 and 4.8×10^3, respectively), and Ni and Cd were the most mobile (values of K_d 8.2×10^2 and 7.2×10^2, respectively).

The mineralogy of the soil constituents was the main factor determining the retention of the metals applied. The differences observed between the soil samples, in both the retention and liberation phases, could not be linked to the properties used to characterize them.

1. Introduction

Fertilizers, especially ones originating from urban and industrial waste, contain small quantities of metals that are toxic for plants and animals. The use of waste rich in carbon, nitrogen and phosphorus has increased its standing as a fertilizer, but it has given rise to a significant increase in heavy metal content in agricultural soil (Smith, 1996). Many industrial activities, especially the burning of fossil fuels, make an additional contribution. The heavy metals most frequently found in the soil are lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), chromium (Cr) and nickel (Ni).

The mobility of the metals deposited in soil depends on interaction with the solid phases during transport by water through open spaces. Both water circulation and the chemical processes that act on charged species of metals are dependent on the hydrological, mineralogical and chemical properties of the soil (Tyler and McBride, 1982). The main sorption surfaces are clay particles and organic matter (Römkens and Salmons, 1999; Kaschl et al., 2002). In the last three decades the mobility of many heavy metals has been studied in a wide range of soils, including acid (Simard et al., 1999; Cornu et al., 2001) and alkaline soils (Walter and Cuevas, 1999; Navarro-Pedreño et al., 2003).

Several laboratory studies, using samples of disturbed soils, have been done to identify soil characteristics that can be correlated with the retention and mobility of heavy metals. The studies came to a variety of conclusions, due mainly to the different chemical and mineralogical characteristics of the soils and to the relative selectivity of the active sites in retaining the different metals.

Multiple regression analysis correlated the retention of Cd, Zn, Ni and Cr with clay content, the specific surface area, and the iron oxide and carbonate contents (Korte et al., 1976). However, Amarcher et al. (1986) were not able to correlate the retention of Cd, Cu, Zn and Pb with iron oxide content. Sidle and Kardos (1997) found a correlation between Cd retention and organic matter content while Harter (1983) could not tie total organic matter content to metal sorption.

Independent of the correlations found in each of the particular cases studied, data available in the bibliography indicates that pH, organic matter content, cation exchange capacity, specific surface area, carbonate content and iron oxide content (de Matos et al., 2001) are the principal soil characteristics that determine the capacity to retain heavy metal pollutants.

Two mechanisms participate in the adsorption of heavy metals. One is non-selective adsorption, in which the metallic cations act as counter-ions in the diffuse layer. The other is selective adsorption, in which surface complexes are formed (Msaky and Calvet, 1990). The importance of each of these mechanisms depends on the metal and the type of soil in which the study is carried out (Gomes et al., 2001).

At elevated pH, the presence of carbonates in the soil leads to an increase in the retention of heavy metals. When the carbonate content and the pH are high, heavy metals are retained in the soil mainly as

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carbonate salts. When the pH of the soil decreases, carbonate dissolution increases and ionic exchange is the principal retention mechanism of heavy metals (Plassard et al., 2000; Elzahabi and Yong, 2001).

When the dissolution medium is a multi-component mixture of metals, the metals should compete to attach to different active sites in the soil. This competition between heavy metals affects their retention and their mobility. Studies set up to characterize the competitive adsorption of heavy metals have been done with both direct and indirect measurements. Indirect measurements have been performed studying individual and binary retention of the different ions (King, 1988). Less frequent are measurements that use multi-component solutions to directly measure the competition between different metallic ions (Gao et al., 1997; Fontes and Gomes, 2003). Both research methodologies reveal the capacity of the soil to react to the incorporation of these contaminants and they produce similar results. Pb and Cu are retained with greater strength than Ni, Zn, and Cd. The behavior of Cr varied, showing both strong and weak adsorption, which can be attributed to different ionic forms (Fontes and Gomes, 2003).

Distribution coefficients characterize the capacity of the soil to retain a solute and the capacity of a solution phase to mobilize it when it is retained (Reddy and Dunn, 1986). To examine the mobility of heavy metals in the laboratory, different studies have used batches (Howard, 1990) and small columns (Giusquiani et al., 1992) in an attempt to reflect field conditions. Discontinuous studies seek to detect the distribution of the metals in both solid and solute phases, but they are not always representative of soil conditions or the contact between phases (Darban, 1997). Column measurements set up to study thermodynamic equilibrium avoid these problems but they are more complicated and less easy to reproduce. For these reasons, assays in columns are more valuable than those done in batch experiments. Nevertheless, some authors (Allen et al., 1995) have not found differences between batches and columns when studying desorption of metals. Plassard et al. (2000) compared both techniques and concluded that discontinuous experiments can be used to simulate metal–soil interactions only if the infiltration speed in the soil is very slow. The retention of metals by the non-saturated zone of the soil is slightly inferior to what discontinuous experiments predict.

The objective of this study has been to determine the retention and mobility of a cocktail of six heavy metals in nine soil samples extracted from the Ap and AC horizons, of different calcareous soils by characterizing the metals distribution in solid and liquid phases through assays performed in columns with disturbed soil. The data obtained could show the relationship between the chemical and mineralogical characteristics of the soil and the retention and mobility of each of the metals studied.

2. Materials and methods

The study area lies in the central region of the Iberian Peninsula. According to data from the National Weather Institute of Spain, the area has a semiarid Mediterranean climate with average annual precipitation of 447.4 mm and average annual temperature of 13.58 °C. The area is quite flat, with abundant river terraces — a typical feature of the Mediterranean region. The selected soils were collected at “El Encín”, an agricultural research station with an area of about 706 ha, on which grain crops traditionally have been grown.

The studied soils developed on recent alluvial calcareous deposits formed from abandoned river meanders. The study area had high pedodiversity, which was lowest in the most recent river terraces (Saldaña & Ibáñez, 2004). The water table lies 1–3 m below ground level. These soils were poorly developed, with little genetic differences and no horizons other than the Ap horizon, which was somewhat darker as a result of its higher organic matter content. All profiles exhibited an either mollic or ochric epipedon depending on their organic matter content, thickness and color (Moreno Merino et al., 1995). The soils were calcareous throughout their thickness, so they were classified as calcaric Fluvisols (FLca) as per the WRB system (1998). Calcareous Fluvisols are abundant throughout the Mediterranean Basin and in Spain. This is a type of soil that develops the basins of the main rivers that traverse limestone material, which is the dominant material in the eastern half of the Iberian Peninsula. Fluvisols have very important agronomic traits like high fertility and good drainage, although they have a high rockiness and easily lose their structure.

2.1. Soil samples

Duplicates of all tests were conducted on the <2 mm fraction of eight agricultural soil profiles, randomly distributed in the area selected. These profiles were sampled every 10 cm down to the end of the profile, in order to record the full variety of the physical–chemical characteristics of the soil. The total number of samples analyzed was 56. Analytical parameters were determined in accordance with ISRIC (1993). Organic carbon was quantified by wet oxidation, using the method of Walkley and Black (1974); total nitrogen by the Kjeldahl method; pH in a 1:2.5 soil/water suspension; the $CaCO_3$ equivalent with a Bernard calcimeter; the cation exchange capacity was measured by extracting samples with 1 M ammonium acetate at pH 7.0, individual exchangeable cations being analyzed by atomic absorption (Ca, Mg) and flame atomic emission spectroscopy (Na, K); and bulk density and moisture content in unaltered samples at a pressure of −33 kPa (Soil Survey Staff, 1984). Particle size distribution was determined by the pipette method.

The mineralogical composition of the soil samples (fine earth and clay fractions) were examined by X-ray diffraction (XRD) using a Philips X PERTMPD diffractometer with Cu-K radiation. Soils were examined on randomly-orientated powders. The clay fraction in air-dried samples after saturation with Mg was calcinated at 550 °C for 2 h and after an ethylene glycol solvation.

A total of 56 soil samples were subjected to cluster analysis, using the variables that determined the interactions between these soil and metal contaminants (pH, electrical conductivity, nitrogen and organic carbon contents, cation exchange capacity, and silt and clay contents). This cluster analysis allowed us to select nine samples that encompassed the wide range of variations encompassed in these soil properties. The soil samples were packed in experimental columns and treated with a solution containing a cocktail of heavy metals of known concentrations.

2.2. Contaminant experiment

Six heavy metals, chromium, copper, lead, zinc, nickel and cadmium, were selected as the most representative of soil contamination due to their high toxicity or their abundance in rainwater.

In order to increase the response of the soils, the concentration used in the assay was greater than that which is found under natural conditions. A preliminary study was carried out to ascertain the maximum concentration of the metals in the cocktail. The obtained result, the upper limit of the concentration of each metal, was 500 mg L^{-1}, since at greater concentrations precipitates formed in the mixtures.

To avoid anionic interactions, the cocktail of metals was prepared as NO_3^- or Cl^- salts in the following forms: $CdCl_2$, $CrCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}H_2O$, $NiCl_2{\cdot}6H_2O$, $Pb(NO_3)_2$ and $Zn(NO_3)_2{\cdot}4H_2O$, dissolved in de-ionized Milli-Q water.

The PVC (polyvinyl chloride) columns measured 30 cm high by 7.5 cm in diameter. The ends of the columns had perforated covers so that the upper end could be hooked to a peristaltic feeder pump and the lower end to vacuum extraction pump.

Before use, the pumps were washed with a diluted ultra-pure nitric acid solution (0.1%) and rinsed with de-ionized Milli-Q water to eliminate traces of soluble substances that could interfere with the analysis.

Each column was uniformly packed with disturbed soil samples, air-dried, with a bulk density equal to the undisturbed soils (1.05–1.40 Mg m^{-3}). Each column also had a diameter-height relationship of 1:2.5 to reduce the formation of preferential flows between the soil and the wall of the column.

A solution with a mixture of heavy metals was added to each column in a concentration equal to 350 mg kg^{-1} of each of the metals. The solution was added at flow rate of 0.1 mL min^{-1} at the upper end of the column until reaching a moisture level equivalent to field capacity.

Once moisture field capacity was attained, the samples were kept in contact for 24 h, the period of time necessary to assure sorption of the metals in the conditions assayed (Hooda and Alloway, 1998; Gray et al., 1999). Next, the soil solution was recovered at the bottom of the column using a water extraction pump with a water potential of 50 cm. The metals retention in the column was determined by comparing the concentration of each of the metals in the starting solution and in the soil solution.

The liberation of contaminants in the polluted columns of soil was conducted by simulating periods of rain. De-ionized water was added to each of the soil columns until the moisture reached field capacity. The columns were left in contact for 24 h. After this period of time, the solution was extracted in the same way as in the contamination assay. This process was performed two times, with no interval between the successive washes. From the concentration obtained in the second wash, the amount of metal liberated per unit of soil mass was determined.

The effluents from the columns, in both the retention and liberation process, were collected directly in inert containers and immediately refrigerated at 2±1 °C; they were passed through Millex cellulose acetate filters of 0.45 μm pore size (Millipore Corp, Bedford, MS) prior to analysis. The metals were determined by Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma–Mass Spectrometry (ICP-MS).

The distribution coefficients (K_d) were calculated according to Anderson and Christensen (1988) and Alloway (1995):

$$(K_\mathrm{d}) = \frac{M_\mathrm{sorbed}}{M_\mathrm{solution}}$$

where M_sorbed is the amount of sorbed metal per unit weight of soil (mg kg^{-1}), and M_solution is the amount of heavy metal in solution per unit volume of liquid (mg L^{-1}).

The Student-*t* test was done to observe whether significant differences existed between the behavior of the Ap and AC horizons in the sorption and desorption processes, using the software SPSS for Windows v. 11. Cluster analysis was done using the Euclidean distance squared, following Ward's Method.

In addition, we have performed a direct gradient analysis based on constrained ordination methods. The analyses performed were Redundancy Analysis (RDA) (Rao, 1984). In this analysis the canonical axis obtained in the ordination is a linear combination of the environment variables. We have performed 1 RDA analyses. As species data, or response variables, we have used the concentrations of Cr, Pb, Cu, Zn, Ni and Cd sorbed in the contaminant treatment (CT). As environmental data, or explanatory variables, we have started in all cases with the 36 available variables characterizing the soil properties of each sample. The multivariate analyses were carried out with CANOCO 4.5 (ter Braak and Smilauer, 2002).

We used the Forward Selection method to rank the soil property variables according to their importance in determining the mobility of heavy metals data and in reducing the large set of available soil property variables. Nevertheless, the low number of samples ($n=9$) in relation to the available soil property variables may lead to weak constraints in direct gradient methods (ter Braak and Smilauer, 2002). We performed a standardized RDA, based on a correlation matrix, which was obtained by centering and standardizing the response variables (mobility of heavy metals). We selected correlation biplots to evaluate the relationships between the mobility of heavy metals and the soil characteristics. In this way the ordination diagram obtained allows visualizing the correlation between variables (ter Braak, 1994). Samples were also displayed in the same canonical space. The multivariate analysis was carried out with CANOCO 4.5 (ter Braak and Smilauer, 2002).

3. Results

3.1. Characterization of the soil samples in the experimental system of columns

The physical and chemical properties selected to characterize the soil samples are: pH, organic carbon, total nitrogen, calcium carbonate equivalent, cation exchange capacity and water retention. The values of each of these properties for the different soil samples are collected in Table 1. The first five soil samples correspond to surface horizons and the next four to subsurface horizons. All of the samples were slightly alkaline (pH 7.4–8.0) and had very similar pH values. Differences in the pH parameter were not observed in the different horizons.

The surface horizon samples showed high organic carbon contents, in a range between 36.4 g kg^{-1} (sample 2) and 195.9 g kg^{-1} (sample 1). Those corresponding to the subsurface horizons showed less organic carbon content, with values ranging between 4.5 and 18.3 g kg^{-1}. The total N content in surface horizons was determined to be between 2.2 and 7.3 g kg^{-1} and in subsurface horizons between 0.6 and 1.2 g kg^{-1}. The relationship observed between the organic matter content and nitrogen content in the different soil samples suggests that organic forms of nitrogen predominate.

The content in calcium carbonate equivalent was approximately 10% and significant differences were not observed between the nine samples (5.9–12.3%). The cation exchange capacity varied between 6.1 and 36.4 cmol kg^{-1} and showed some relationship with organic matter content. The amount of water retained in the soil was very similar in all the samples studied.

Variations in some of the measured properties were too small to explain the differences noted between separate soil samples in both retention and liberation experiments.

The soil texture was coarse, loamy or sandy loam in surface horizons and sandy in the AC horizons. Fine sand was the most abundant grain size fraction. The values for bulk density were less in the surface horizons than in the AC horizons due to organic matter content.

Table 1
Selected physical and chemical properties of soil samples packed into the experimental column system and experimental conditions used

Samples	Horz.	pH	Organic C	Total N	Equivl. $CaCO_3$	CEC[a]	Water retention
		H_2O	g kg^{-1}	g kg^{-1}	%	cmol kg^{-1}	gkg^{-1}
1	Ap	7.4	195.9	6.2	10.7	26.1	605.0
2	Ap	7.7	36.4	2.2	9.1	6.1	545.2
3	Ap	7.8	161.4	7.3	12.3	36.4	584.0
4	Ap	7.7	62.1	5.8	9.1	31.1	350.2
5	Ap	7.8	84.3	5.6	7.3	10.1	550.3
6	AC	7.7	5.7	0.6	12.0	18.4	585.8
7	AC	7.4	18.3	1.1	10.9	19.1	585.8
8	AC	7.8	14.5	1.2	8.0	12.3	520.2
9	AC	8.0	4.5	0.9	5.9	12.6	510.3

[a] CEC, cation exchange capacity.

Table 2
Descriptive statistics of semi-quantitative mineralogical composition (relative % between samples) of soil samples (n=9)

Minerals	Mean	S.E.	Min.	Max.
Fraction <2 mm				
Quartz	37.6	5.5	20	70
Feldspars	2.9	0.9	1	9
Calcite	13.9	1.9	8	23
Dolomite	2.3	0.7	0	6
Phyllosilicates	43.3	6.2	16	65
Fraction <2 µm				
Illite	76.0	1.4	70	83
Kaolinite	14.6	0.9	10	20
Chlorite	0.4	0.3	0	2
I-S[a]	5.7	1.4	0	13
I-C[b]	3.3	2.2	0	17

[a] I-S, interstratifieds illite–smectite.
[b] I-C, interstratifieds illite–chlorite.

The mineralogical composition of the samples of fine earth is shown in Table 2. It was formed mostly of layer minerals (16–65%), and quartz in percentages that oscillated between 20% in sample 3 to 70% in sample 5. These components were accompanied by variable percentages of calcite and dolomite. The content in feldspars was always very low (1–9%).

The mineralogical composition of the clay fraction (Table 2) was very similar in all cases. The most common mineral was illite, in very high proportions that oscillated between 70% in sample 7 and 83% in sample 9. The minerals 1:1 of the koalinite group displayed lower percentages that ranged from 10% to 20%. The illite–smectite interstratified minerals were found in proportions that varied between 0% and 13%. Chlorites and illite–chlorite interstratified were occasionally present, in low proportions. The mineralogical differences were significant enough to distinguish between the individual soil samples (González et al., 2007).

3.2. The sorption of heavy metals

The amount of metal retained for each metal and each soil sample is depicted in Table 3. The soil samples were characterized by the elevated amount of metal they retain, although differences were observed in the behavior of metals and soil samples. While Cr, Cu and Pb were retained in similar amounts in the nine samples studied, Zn, Ni and Cd showed significant differences. Soil samples 1, 2 and 9 retained lower amounts of Zn, Ni and Cd than the other samples.

3.3. The mobility of heavy metals

Table 4 depicts the amount of metal liberated by each of the soil samples in the second wash. The mobility of the six metals was very low. However, significant differences divided the metals into three groups, Cr and Pb, which were the metals most difficult to liberate, Ni and Cd, the most easily liberated, and Cu and Zn, which had an intermediate behavior. Cadmium was the metal with the most irregular results from the second wash. A comparison can be made between these results, seen in Table 4, and results from the first wash, not shown because of the inability to repeat the experiment with quantitative reliability. Such comparison reveals that Cd showed great differences while the rest of the metals, except Ni, which showed slight differences, behaved in a similar way in both washes.

Table 3
Metal cation sorbed in mg kg^{-1} into the experimental soil columns

Samples	Cr	Cu	Pb	Zn	Ni	Cd
	mg kg^{-1}					
1	349.79	348.14	347.13	323.50	311.04	288.29
2	348.80	344.80	344.38	255.25	221.30	243.38
3	349.88	349.82	347.61	348.89	347.00	345.92
4	349.89	349.80	347.98	344.48	344.08	338.68
5	349.81	349.71	347.52	349.14	348.26	347.65
6	349.82	349.84	348.12	348.13	347.02	344.79
7	349.90	349.82	347.65	346.81	344.58	342.50
8	349.91	349.49	347.37	340.91	340.91	331.16
9	349.93	345.45	342.53	273.14	273.14	244.36

Table 4
Effluent heavy metal concentration after second leaching treatment

Samples	Cr	Cu	Pb	Zn	Ni	Cd
	mg kg^{-1}					
1	0.07	0.28	0.05	0.21	1.06	1.31
2	0.02	0.14	0.02	0.23	0.80	0.94
3	0.05	0.39	0.07	0.12	0.80	0.38
4	0.02	0.15	0.02	0.18	0.70	0.34
5	0.08	0.56	0.06	0.58	1.42	2.68
6	0.02	0.14	0.02	0.22	1.17	1.92
7	0.03	0.12	0.03	0.33	1.24	1.40
8	0.02	0.12	0.02	0.14	0.72	2.01
9	0.03	0.02	0.02	0.06	0.32	0.62

4. Discussion

All of the soil samples (FLca) retained more than 90% of each of the six metals in solution, and no significant differences arose between the two types of horizons studied (Student-*t*) (Fig. 1). Fontes and Gomes (2003), studying competitive sorption of these same metals in tropical soils, observed that Cr, Cu and Pb have greater affinity for the surface of sorbates than Ni, Zn and Cd. This behavior became even more evident when the total concentration of added metals was increased. In our case, the carbonated soils studied had the same sorption sequence in conditions of competition. Although all of the metals had high retention values, significant differences did emerge. Cr, Cu and Pb were retained in amounts close to 100% both in the Ap and AC horizons. The rest of the metals, Zn, Ni, and Cd had lower values of sorption and greater variability between samples. In spite of major differences in soil properties between the two types of soils (acid tropical soils and calcareous soils), the order of retention of these metals was similar.

The washing process done in soil columns with high metal concentrations can provide information about the difficulties each of the added metals has to dissolve. In Table 4 it is observed that Cr and Pb had a similar behavior in the wash. Of all six metals, they liberated

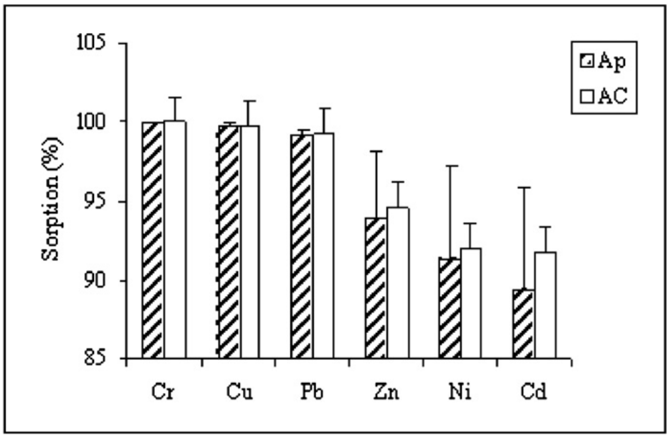

Fig. 1. Mean heavy metal sorption at the Ap and AC horizons. Bars represent standard error of mean.

Table 5
Distribution coefficients (K_d) calculated for the second leaching treatment

Samples	Cr	Cu	Pb	Zn	Ni	Cd
	L mg^{-1}					
K_d	5.58×10^4	6.90×10^3	8.11×10^4	4.85×10^3	8.17×10^2	7.24×10^2

Mean of different samples.

with the greatest difficulty and did so in a similar way in all the soil samples (on the order of 0.03 mg/kg) except sample 5 (three times higher liberation). Cu and Zn also formed a pair with similar behavior. The amount of Cu and Zn liberated was on the order of 0.25 mg/kg in all the soil samples, except in number 9, where it was much lower, 0.04 mg/kg. Finally, Ni and Cd were the metals which were liberated with the greatest ease in all cases, with an average concentration of 0.91 mg kg^{-1} for Ni and 1.29 mg kg^{-1} for Cd. These results agree with those obtained by other authors studying the mobility of heavy metals in different soils. Atanossova (1999), analyzing the sorption and desorption of metals in clays in acid soils, obtained the same desorption sequence: Cd > Ni > Zn > Cu. Richards et al. (2000), studying the washing of soils to which sewage sludge had been applied, found Ni, Cd and Zn to be the most mobile.

It is interesting to compare the behavior of the six metals in the retention process with how they behaved in the liberation process. As the experimental procedure for both processes was carried out in the same column of soil, differences were due exclusively to differences between retention and liberation behavior. Chromium and lead had similar behavior in the calcareous soils studied. Both metals were retained in elevated amounts (Table 3) and were liberated with great difficulty (Table 4). Both behaved in the same way in all nine columns.

Nickel and cadmium, which acted the same way in the liberation process, mobilized very easily and did so in similar amounts in eight of the soil samples. Nevertheless, liberation in one of the soil samples, sample 9, was almost one order of magnitude less than in the rest of the soils. In the retention process (Table 3), both metals behaved in the same way with respect to amount retained, since they, along with zinc, were retained in amounts that were similar to or less than the rest of the metals. For both metals (Ni and Cd) samples 1, 2 and 9 had retention values that were less than the rest of the analyzed samples.

The remaining two metals, copper and zinc, behaved similarly in the liberation process but differently in the retention process. These two metals were liberated in soils in intermediate amounts, with liberation values that fell between the values of the other two groups of metals. However, in the retention process copper behaved in a similar way to chromium and lead, while the behavior of zinc was closer to that of nickel and cadmium, both because the amounts retained were smaller and because of differences observed in soil samples 1, 2 and 9.

Table 5 collects the distribution coefficients of each of the six metals, obtained in the nine samples analyzed.

Distribution coefficients represent the affinity of the solid phase of the soil to retain the metallic cations in solutions. Following Anderson and Christensen (1988), high K_d values indicate that the metal has been retained by the solid phase through sorption reactions, while low K_d values mean that high concentrations of metals remain in solution. In Table 5, Cr, Pb and Cu present high K_d values, indicating greater retention of these cations. Cr and Pb were more strongly retained than Cu. The metals with the lowest K_d values were Cd, Ni and Zn, demonstrating that when these cations form part of a multi-component system they are easily exchangeable and substitutable by Cr, Pb and Cu. These results agree with those of Fontes et al. (2000) and Gomes et al. (2001) obtained by analyzing competitive adsorption processes in Oxisols, Ultisols and Alfisols.

The elevated sorption of metals in carbonated, alkaline soils is regulated by three different mechanisms: surface adsorption of colloids, complexation with surface functional groups, and the precipitation with hydroxides, phosphates and carbonates (Plassard et al., 2000; Veeresh, et al., 2003).

It can be seen in our results that the retention process behaved similarly in six samples and notable differences occurred in samples 1, 2 and 9. Sample 1 was characterized by the lowest pH value as well as the highest organic matter content. Sample 2 had the lowest cation exchange capacity. Sample 9 presented the lowest content in organic matter and calcium carbonate. Samples 2 and 9 had the lowest sorption capacity for Cd, Ni and Zn. To analyze this behavior we conducted a multivariant analysis (Fig. 2) that related the soil characteristics (Tables 1 and 2) with the adsorption of metals (Table 3). In the graph, we observed the dispersion of these samples and the absence of a relationship with any edaphic property. Nevertheless, the mobility of metals with the least affinity for sorbates (Cd, Ni, Zn and Cu) is conditioned by the mineralogical characteristics of the soil (Fig. 2).

The principal retention process of chromium and lead is a product of the metal–surface interaction of the solute. For these cations the process is mainly regulated by strong covalent bonds (McBride, 1994), as well as the possibility to form salts (Bradl, 2004). All of the soil samples studied had a sufficient amount of constituents to be able to form strong bonds that permitted the retention of these two metals regardless of the presence of other metals. This type of low soluble, stable salt has been proposed in the bibliography as retaining Pb in these media (phosphates and carbonates) and suggests that the carbonated minerals fraction (calcite, dolomite) in the soil samples have been largely responsible for their retention. At pH higher than 7, chromium anions form that give rise to salts insoluble to other metals. These compounds immobilize chromium.

Copper and zinc are also immobilized in the soil by forming low soluble, stable compounds (McGrath et al., 1988) and have a greater adsorption in the exchange complex (de Matos et al., 2001). Both behave similarly to lead and chromium in the liberation phase, although the compounds formed are more soluble.

The lowest observed retention for zinc, in samples 2 and 9, could be due to the lower cation exchange capacity and to the lower

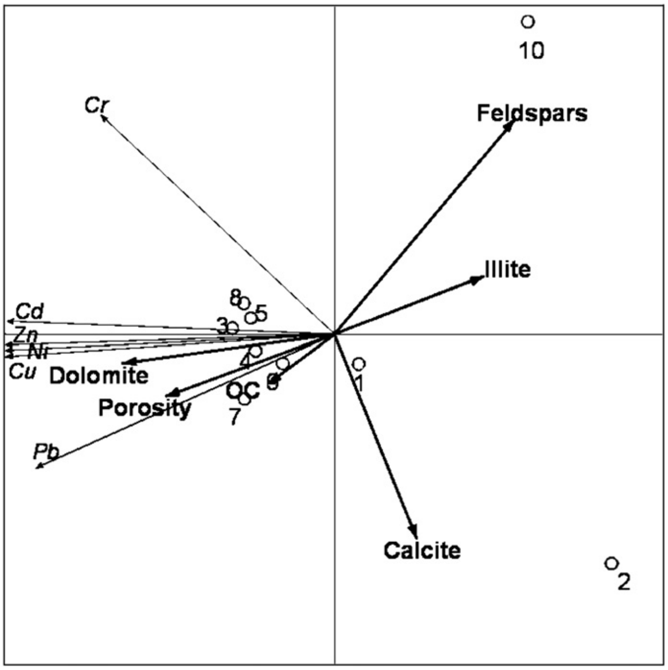

Fig. 2. Ordination diagrams from correlation-based RDA with the first two axes for the heavy metal sorption. Samples are represented as circles, heavy metal concentrations as thin arrows and variable names in italic and the selected soil characteristics represented as arrows. In the diagram there are three types of scores: species (heavy metal concentrations), environmental variables (soil characteristics), and samples.

carbonate content in the samples. As the number of retention sites decreases, the metals with greater capacity to form stable compounds, Cr, Pb and Cu (Table 3), caused the other metals, Zn, Ni and Cd, to be retained at a lesser rate than in the other six soil samples.

The retention of nickel and cadmium is regulated fundamentally by adsorption processes. Both metals showed similar behavior in all the soil samples, which was not the case with the other metals. The cadmium liberated into solution in the first wash was up to ten times greater than that liberated in the second. Significant differences were also observed with nickel, although not so elevated as with cadmium. These anomalies, with respect to the behavior of the rest of the metals, could be due to competition between them. Those that have the least capacity to form insoluble compounds in the solid matrix have to occupy different sites when Cr, Pb, Cu and Zn have occupied the sorption positions. The sites that retain cadmium and nickel are characterized by the greatest lability of all the compounds formed. Thus, the liberation of Cd and Ni occurred almost exclusively in the first wash. The other unique circumstance observed with these two metals was the low value for the amount of each of the metals liberated in the second wash in soil sample 9, the only time this low value appeared.

Zn behaved similarly to Ni and Cd in the retention phase and to Cu during liberation. Following the previous interpretation, it can be concluded that Zn was retained only by forming insoluble compounds. In a state of competition, Cr, Pb and Cu formed these insoluble compounds with greater effectiveness than Zn, while Ni and Cd were the least effective.

5. Conclusions

All the metals studied have high sorption in calcareous soil columns, but Cr, Pb and Cu have a greater affinity than Zn, Ni and Cd. The studies on liberation in the same columns show that the mobility of the metals is very low in this type of soil. However, the K_d values obtained demonstrate that mobility varies between metals. For example, Cr and Pb are the metals that have the greatest difficulty in transfer into the soil solution; Ni and Cd are the ones that reach the greatest concentrations in the aqueous phase, and Cu and Zn have an intermediate behavior. Significant differences have not been observed in the liberation of the six metals in nine soil samples with different physical–chemical properties. Nevertheless, it has been observed that the mobility of the metals that show less affinity for sorbates (Cu, Zn, Ni and Cd) is conditioned by the mineral characteristics of the soil.

According to the mobility sequence, it seems clear that in soils carbonated by sorption sites competition between metals is a major risk for groundwater contamination in the short run and raises the probability of absorption by plants, especially of the most mobile and toxic metals.

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