Cd²⁺, Cu²⁺, and Pb²⁺ sorption, desorption and migration in Fluvisols

Sorción, desorción y migración de Cd²⁺, Cu²⁺ y Pb²⁺ en Fluvisoles
Sorção, dessorção e migração de Cd²⁺, Cu²⁺ e Pb²⁺ em Fluvissolos

AUTHORS

Arenas-Lago D.[@, 1]
darenas@uvigo.es

Rodríguez-Seijo A. [1]

Cerqueira B.[1]

Andrade M. L. [1]

Vega F. A.[1]

@ Corresponding Author

[1] Department of Plant Biology and Soil Science, Faculty of Biology, University of Vigo. Lagoas, Marcosende. 36310 Vigo, Pontevedra, Spain.

ABSTRACT

The aim of this work was to assess and compare the mono and bimetallic Cd²⁺, Cu²⁺ and Pb²⁺ sorption and desorption capacities as well as the sorption hysteresis in two different types of Fluvisols. The migration of cations through the profiles was evaluated, along with the dependence on soil properties of mono and bimetallic Cd²⁺, Cu²⁺ and Pb²⁺ fixation, hysteresis and mobility. Sorption irreversibility and migration of the studied cations through the profiles were evaluated, by means of hysteresis and migration indexes calculated from retention capacity values (Kr) proposed and validated in a previous work. The results showed that the sorption and retention capacities of the A horizons were higher than those of C and that the individual sorption and retention capacities were greater than the competitive capacities. The highest values of sorption and retention capacities were those for Pb²⁺, followed by Cu²⁺ and Cd²⁺. Mn oxides, organic matter and, consequently, ECEC were the components and properties that most highly influenced Pb²⁺ monometal and competitive sorption and retention. Cd²⁺ did not interfere with Pb²⁺ or Cu²⁺ sorption and retention. Organic matter content was only correlated with the sorption hysteresis of Pb²⁺, in accordance with the high Pb²⁺ fixation capacity of in this component and its lower capacity to retain Cu²⁺ and Cd²⁺. Tidalic Fluvisols retained only 0.4 and 0.2% of added Cd²⁺ when competing with Cu²⁺ and Pb²⁺, respectively. However, more than 60% of the added Pb2+, and over 47% of the added Cu²⁺ were retained. The Pb²⁺ retained in competition with Cu²⁺ was 98.2 in TF and 47% in the Umbric Fluvisol, whereas the retained Cu²⁺ was 93.8 and 29.9% respectively. These retention and Cd²⁺ mobility indicated that there is a possibility of heavy metals transferring to subsurface waters and, through these, of contamination and even of these metals entering the food chain.

RESUMEN

El objetivo de este trabajo fue evaluar y comparar la capacidad de sorción y desorción, individual y bimetálica, y la histéresis de Cd²⁺, Cu²⁺ y Pb²⁺ en dos tipos diferentes de Fluvisoles. Se evaluó la migración de los cationes a través del perfil, y la influencia de las propiedades del suelo en la fijación mono y bimetálica, la histéresis y la movilidad. La irreversibilidad de sorción y la migración a través del perfil de los cationes estudiados se determinó, por medio de índices de histéresis y de migración, calculados a partir de los valores de capacidad de retención (Kr) propuestos y validados en un trabajo anterior. Los resultados mostraron que las capacidades de sorción y retención de los horizontes A fueron mayores que las de los C y que las individuales fueron mayores que las competitivas. Los suelos mostraron mayor capacidad de sorción y retención de Pb²⁺, seguido de Cu²⁺ y Cd²⁺. Los óxidos de Mn, materia orgánica y la CIC son los componentes y propiedades con mayor influencia en la sorción y retención individual y competitiva de Pb²⁺. El Cd²⁺ no afecta a la sorción y retención de Pb²⁺ o Cu²⁺. El contenido de materia orgánica solamente se correlacionó con la histéresis de la sorción de Pb2+ debido a que este componente tiene alta capacidad de fijación de este ion y menor de Cu²⁺ y Cd²⁺. Los Fluvisoles Tidálicos retuvieron solamente el 0,4 y el 0,2% del Cd²⁺ añadido en

competencia con Cu²⁺ o Pb²⁺, respectivamente. Sin embargo, más del 60% del Pb²⁺ y más del 47% del Cu²⁺ añadidos fueron retenidos. El Pb²⁺ retenido en competencia con Cu²⁺ fue un 98,2% del añadido en los Fluvisoles Tidálicos y un 47% en los Fluvisoles Úmbricos, mientras que el Cu²⁺ retenido fue de un 93,8 y 29,9%, respectivamente, del añadido. Esta retención y la movilidad de Cd²⁺ mostró la posibilidad de transferencia de metales pesados a las aguas subsuperficiales y, a través de éstas, de contaminación e incluso de que estos metales entren en la cadena alimentaria.

RESUMO

O objetivo deste trabalho foi avaliar e comparar a capacidade de sorção e dessorção, individual e bimetálica e a histerese de Cd²⁺, Cu²⁺ y Pb²⁺ em dois diferentes tipos de fluvissolos. Avaliou-se a migração dos catiões através dos perfis bem como a influência nas propriedades do solo da fixação mono e bimetálica Cd²⁺, Cu²⁺ e Pb²⁺, a histerese e a mobilidade. Avaliou-se a irreversibilidade de sorção e a migração através dos perfis dos catiões estudados, por meio de índices de histerese e de migração, calculados a partir dos valores de capacidade de retenção (Kr) propostos e validados em trabalho anterior. Os resultados mostraram que as capacidades de sorção e retenção dos horizontes A foram maiores que as dos C, e que as capacidades de sorção e retenção individuais foram maiores que as capacidades competitivas. Os solos mostraram maiores capacidades de sorção e retenção de Pb²⁺, seguido de Cu²⁺ e Cd²⁺. Os óxidos de Mn, matéria orgânica, e consequentemente, a CTC são os componentes e propriedades com maior influência na sorção e retenção individual e competitiva de Pb²⁺. O Cd²⁺ não afeta a sorção e retenção de Pb²⁺ ou Cu²⁺. O teor de matéria orgânica somente se correlacionou com a histerese da sorção de Pb²⁺ devido à alta capacidade de fixação de Pb²⁺ deste componente e à sua menor capacidade de reter Cu²⁺ e Cd²⁺. Os Fluvissolos Tidálicos retiveram somente 0,4 e 0,2% do Cd²⁺ adicionado em competição com o Cu²⁺ ou o Pb²⁺, respectivamente. Entretanto, mais de 60% do Pb²⁺ e mais de 47% do Cu²⁺ adicionados foram retidos. O Pb²⁺ retido em competição com o Cu²⁺ foi de 98,2% do adicionado aos Fluvissolos Tidálicos e 47% nos Fluvissolos Úmbricos, enquanto que o Cu²⁺ retido foi de 93,8 e 29,9%, respectivamente, do adicionado. Esta retenção e a mobilidade de Cd²⁺ mostra a possibilidade de transferência de metais pesadospara as água subsuperficiais e através destas, de contaminação, ou mesmo de que estes metais entrem na cadeia alimentar.

1. Introduction

Cd, Cu and Pb reach soils via fertilizers, pesticides, liming agents, acid water drainage from mining activities, sewage sludge and urban and industrial waste (Nagajyoti et al. 2010; Loganathan et al. 2012). Additionally, Pb reaches soils through emissions from the combustion of coal and petrol and through the dumping of industrial wastewater (Denaix et al. 2001; Zhi-Yong et al. 2012). On the other hand, Cd mainly reaches the environment through atmospheric deposits. Finally, Cu accumulation in soils is mainly due to the production of alloys, to the manufacture of electrical and fiber optic cables and to its use in water pipes, in biocides for treating wood, and in agriculture, paints manufacture and smelting procedures (D'Emilio et al. 2013).

Soils can act as sinks for metals and contamination problems can arise once their sorption capacity has been exceeded (Fontes and Gomes 2003). The mobility and bioavailability of metals and the possibility of their transfer to other compartments of the ecosystem mainly depend on the sorption and desorption capacities of the different components of the soil (OECD 2004; Vega et al. 2008; Diagboya et al. 2015; Fernández et al. 2015).

The term sorption was used to encompass adsorption, precipitation on soil particle surfaces and fixation (Vega et al. 2009a). Furthermore, since the threat of heavy metal pollution generally involves more than one metal, sorption and retention (retained after desorption experiments) studies should take into account competition among metals for binding sites, which can lead to a metal being sorbed to a much lesser extent than in the absence of other metals (Diagboya et al. 2015). Desorption implies the release of sorbed species into the environment surrounding the soil particles (Covelo et al. 2008). The distribution of metals among soil components depends on the intrinsic properties of the types of metals involved, on soil properties and also on the amount of metal added (Fontes and Gomes 2003; Bradl 2004; Cerqueira et al. 2011; Shaheen et al. 2013; Fernández et al. 2015).

In recent years, sorption processes have been studied in order to determine the influence of soil components on metal fixation (Lair et al. 2007; Covelo et al. 2008; Vega et al. 2009a; Diagboya et al. 2015; Fernández et al. 2015).

Studies on the behaviour of Cd^{2+}, Cu^{2+}, and Pb^{2+} in soils have largely focused on interactions with solutions containing one metal, and have therefore ignored the potential effects of their mutual competition (Diagboya et al. 2015).

The migration of a heavy metal through a soil profile is a complex process that depends on multiple factors, such as soil pH, Fe and Mn oxide contents, clay and carbonate contents, clay mineral type and the amount of organic matter, texture and structure, as well as on the intrinsic properties of the metal, its concentration in the soil solution and the presence of other metals (Vega et al. 2011).

The heterogeneity of soil makes it very difficult to predict the potential mobility and distribution of even single metals, so experimental data are usually essential for this purpose (Fernández et al. 2015). Consequently, sorption tests on soils should invariably be followed by desorption tests. Sorption and desorption isotherms reveal whether sorption is reversible or wholly or partially irreversible (hysteretic) (Uchimiya et al. 2011; Sahu et al. 2014).

As described in previous studies by Vega and co-workers (Vega et al. 2009b) in two locations in the province of Pontevedra (Galicia NW, Spain), soils formed from recent alluvial deposits are affected by various inputs (waste, fertilizers, etc.) that contain metals. One of these areas is located in an estuary (Miñor River, Ramallosa marsh) and the other in the terraces of the lower Miño River basin. Soils from these areas are predominantly Fluvisols: tidalic (sodic) in the first site and umbric (alumic) in the second. Their location near the river bed and the coast means that metal transfer to the surrounding waters is highly likely, contaminating other ecosystem compartments, even those far afield.

Therefore, the objectives of this work were: a) to assess and compare the mono and bimetallic Cd^{2+}, Cu^{2+} and Pb^{2+} sorption and desorption capacities and the sorption hysteresis in two different Fluvisol types, b) to study the migration of cations through the profiles, and c) to determine the dependence of Cd^{2+}, Cu^{2+} and Pb^{2+} fixation, hysteresis and mobility on soil properties.

2. Materials and Methods

2.1. Study areas

The study was conducted in two areas in the province of Pontevedra: the Miñor River estuary (MRE: 42º 06´ 52´´ N, 8º 49´ 25.2´´ W), and the Miño River terraces (MRT: 42º 00´ 37´´ N, 8º 40´ 15´´ W) (Figure 1).

The MRE is a natural area included in the European Union Natura 2000 network because of its environmental and landscape quality. It is
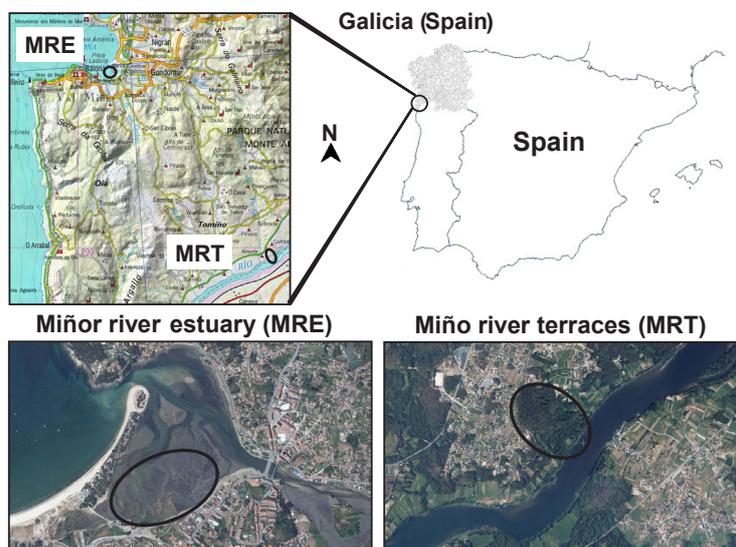
Figure 1. Studied zones (SIGPAC 2015).

also a nesting area for many different birds. This estuary comprises a tidal plain and marsh area with an EW direction.

It is located in the southwest of the province of Pontevedra (NW Spain) in the Ría of Vigo, the southernmost of the Rías Baixas. The geology of the area is dominated by igneous and metamorphic rocks from the Precambrian-Paleozoic period. The only younger rocks present are Miocene-Quaternary continental sediments.

It is an area with a high population density (especially in summer, due to tourism). It is also a horticultural area and fertilizer, manure and slurry inputs leach into the soil and are capable of polluting the estuary (Vega et al. 2009b; Ullah et al. 2013; Sungur and Özcan 2014). In addition, the Miñor River receives a number of discharges with the potential of contaminating the estuary.

The bottom of the estuary presents incipient coastal soils associated with tidal range and fluvio-marine sedimentary dynamics: muddy soils and subsequent evolutionary stages associated with marsh areas with Salic, Thionic and Tidalic Fluvisols. The vegetation is mainly

rushes and saline plants and the area is bordered by riparian forest, except next to the beach, where pines are abundant.

The MRT, in which there are nine levels from +5 m to +100 m over the current course of the river, comprises large accumulations of heterometric, rounded quartzite boulders, supported by a sandy silt matrix of quartzitic lithology on which significant levels of sandy loam have developed, typical of floodplain facies. They support important pedogenic processes. Soils developed on level T1 (+5 m) were chosen for this study. These soils may transfer stored pollutants into the river.

Each study area covers about 280,000 m². At each site, a transect with a total length of 900 m was selected, descending in a smooth slope (< 2%, almost flat) and soil samples were taken every 300 m. At MRE, the surface (A: from 0 to 15 cm approximately) and subsurface horizons (Cg: more than 15 cm) of the selected site (TF1, TF2 and TF3) were sampled and transported to the lab for further characterization. In the MRT area the surface (A: approximately from 3-20 cm) and subsurface (C1: approximately from 20-50 cm) horizons of the soils from the selected

sites (UF1, UF2 and UF3) were also sampled. The WRBSR (IUSS Working Group WRB 2006) denominations of all six soils were determined on the basis of the characteristics of their different horizons. Three soils (from the Miñor River estuary) are Tidalic Fluvisols (sodic): (TF1, TF2, and TF3), and the others (from the Miño River terraces) are Umbric Fluvisols (alumic) (UF1, UF2 and UF3).

At each selected site, three soil horizon samples (less than 0.5 m distance) were collected with an Eijkelkamp sampler and immediately stored in polyethylene bags. In the laboratory, they were air-dried, passed through a 2 mm sieve, mixed to form a composite sample, and homogenized with a Fritsch Laborette 27 rotary sample divider. The composite sample of each site (TF1, TF2, TF3, UF1, UF2 and UF3) was labelled and stored for further analysis.

2.2. Soil analyses

The different soil horizons from each selected site were analysed. Soil analyses were performed in representative subsamples of the previously indicated composite sample of the sampled site. Soil pH was determined with a pH electrode in 2:1 water/soil extracts (Slattery et al. 1999). Particle size distributions were determined after oxidising the organic matter with hydrogen peroxide; the > 50 µm fraction was further fractionated using sieves, and the < 50 µm fraction using the international procedure (Day 1965). Organic carbon was quantified using the Walkley and Black method (Walkley and Black 1934).

Specific surface area was determined by drying the samples at 110 ºC for 48 h, degassing under a vacuum for 4 h and using approximately 1 g of degassed sample to obtain N_2 sorption– desorption isotherms at -196 ºC and subatmospheric pressures, in a Quantachrome Autosorb-6B apparatus; specific surface area was calculated by fitting the three-parameter BET equation (Murray and Quirk 1990) to the relative pressure (P/P_0) region 0.05-0.30 of the sorption isotherms.

Soil effective cation exchange capacity (ECEC) and exchangeable cations (Al^{+3}, Ca^{2+}, Mg^{2+}, K^+ and Na^+) were extracted at soil pH with a $BaCl_2$ solution and quantified by ICP-OES on a Perkin-Elmer Optima 4300 DV instrument.

Iron and Mn oxide contents were determined using the dithionite-citrate method (Soil Conservation Service 1972; Sherdrick and McKeague 1975). Al oxide content was determined by the ammonium oxalate - oxalic acid method (McKeague and Day 1966). Fe, Mn, and Al concentrations in their extracts were determined by ICP-OES.

The soil mineralogical analysis was performed using a Philips-type powder diffractometer fitted with a Philips PW1710 control unit, Vertical Philips PW1820/00 goniometer, and an FR590 Enraf Nonius generator. The X-Ray powder diffraction pattern (XRPD) was collected and the determination was done using the RIR procedure (Reference method Intensity/Radium) (Chung 1975), with corundum as the reference material. The identification and quantification of the crystalline phases were performed using the programme "High Score Plus Version 3.0d" (2011).

Dissolved Cd, Cu and Pb were extracted with an acidified 0.01M solution of calcium chloride, using the method proposed by Houba et al. (2000). Available Cd, Cu and Pb were extracted with diethylenetriaminepentaacetate (DTPA) as described by Lindsay and Norwell (1978).

The pseudo-total Cd, Cu and Pb contents were determined following acid digestion with a mixture of HNO_3 and HCl (1:3v/v) in polytetrafluoroethylene bottles placed in a microwave oven. In all of the extracts, the metal concentrations were analysed by ICP-OES.

2.3. Batch experimental methods

Sorption and desorption experiments were performed using the batch method. Soil samples (6 g of each composite sample of each soil horizon) were added to 100 mL of "sorption solutions" containing 0.01M $NaNO_3$ as a background electrolyte and 0.01, 0.05, 0.10,

0.50, 1.00 or 3.00 mmol L^{-1} of cadmium nitrate, copper nitrate and/or lead nitrate ("single-metal solutions" contained just one heavy metal at one of these concentrations; "bi-metal solutions" contained two of the three metals at the same concentration in each of the six solutions).

The soil-and-solution mixtures were shaken in polyethylene centrifuge tubes for 24 h at 25 ºC in a rotary orbital shaker and were then centrifuged at 5 000 rpm as preliminary experiments showed that 24 h shaking was sufficient for the equilibration (Vega et al. 2009a). The resulting pellet was set aside for the desorption phase of the experiment (see below), and the supernatant was filtered through Whatman 42 paper prior to ICP-OES analysis, which determined Cd^{2+}, Cu^{2+} and/or Pb^{2+}.

Data for desorption isotherms were obtained as described by Cerqueira et al. (2011). The pellets obtained in the sorption phase of the experiments were dried at 45 ºC according to Vega et al. (2009a), weighed, mixed with 100 mL of a background electrolyte solution (0.01M NaNO$_3$) in polyethylene centrifuge tubes, shaken for 24 h at 25 ºC and centrifuged at 5 000 rpm; the supernatant was then filtered through Whatman 42 paper and the Cd^{2+}, Cu^{2+} and/or Pb^{2+} contents determined by ICP-OES. Together with the quantity sorbed (determined in the sorption experiment), the concentration of metals released into the solution following desorption was used to determine the quantity retained (the concentration of Cd^{2+}, Cu^{2+} and/or Pb^{2+} that had been retained on the soil sample).

In all the sorption/desorption experiments, soil-less controls were run and showed no interference. The sorption of metals by filter paper was negligible.

2.4. Construction of isotherms

Sorption isotherms were constructed by plotting the amount of metal sorbed after the 24 h equilibration period (in µmol per gram of dry soil) against the equilibrium concentration of metal in solution (in µmol L^{-1}). In turn, desorption

isotherms were constructed by plotting the amount of retained metal (sorbed metal retained following desorption, in mol per gram of dry soil) against the concentration of metal in solution following desorption (in µmol L^{-1}).

2.5. Overall sorption and retention capacities and hysteresis

The overall capacity of the soil from each site to sorb a given metal, or two of them, was evaluated as the K$_{r,s}$ slope (Vega et al. 2008) of the regression equation C$_{s,i}$ = K$_{r,s}$ C$_{p,i}$, where C$_{s,i}$ is sorbed metal i (µmol) per gram of soil at equilibrium, and C$_{p,i}$ is potentially sorbable metal i, namely, the amount of metal i in the solution before contact with the soil, likewise per gram of soil.

K$_{r,s}$ is adimensional and varies from 0 for totally non-sorbent soils to 1 for an ideal sorbent that completely eliminates the metal i from the solution (Vega et al. 2008). The retention capacity of the soil after desorption experiments (K$_{r,r}$) was calculated in the same way, except that sorbed metal was replaced by metal retained at equilibrium.

The irreversibility of sorption was measured by a hysteresis index (HI) defined as the ratio between the K$_r$ values for retention and sorption (Vega et al. 2009a). HI would be unity if sorption was totally irreversible, and zero if all the sorbed metal were released.

The migration and mobility of the metals were studied in terms of the K$_{r,r}$ coefficient for mono and bimetallic retention. The migration capacity of each soil was evaluated as the migration indices (MI) for their horizons, which were calculated from the corresponding K$_{r,r}$ retention values (Vega et al. 2009a). It was necessary to determine the amount of metal fixed by each gram of soil per µmol of added metal.

Finally, based on the MI, the percentage of the amount added that would be retained by each soil was calculated for each horizon and treatment.

2.6. Statistical analyses

All tests were performed in triplicate and the results analysed statistically using the software IBM-SPSS for Windows version 19. Different analyses of variance (ANOVA) were carried out, together with homogeneity of variance tests for the variables found. In case of homogeneity of variance, the minimum significant distance test among soil properties was carried out as a post-hoc test, or otherwise Dunnett's T3 test. The influence of soil characteristics on sorption and retention capacities was investigated by means of the Pearson pairwise correlation, as well as a correlation analysis between the horizon characteristics and hysteresis indices. It was performed a multiple regression analyses. The independent variables were the values of Kr for sorption or retention and they were selected as dependent ones those soil properties or components that the correlation analysis revealed as with high influence in the fixation of the metals studied.

3. Results and Discussion

3.1. Soil characteristics

Table 1 shows the most relevant characteristics of the studied soils. As can be seen, the Umbric Fluvisols (UF) were more acidic than the Tidalic Fluvisols (TF) – the latter had more near-neutral pH values.

The A horizons, from the TF soils, exhibited significantly higher values for effective cation-exchange capacity than the UF soils, and this is attributable to their higher pH together with the higher contents of both exchangeable Ca and Mg and also Na. These contents determined the highest percent base saturation of TF wherein the predominant cation was Na⁺. In the case of UF, these soils were desaturated and the most abundant exchangeable cation was Al³⁺.

It is worth highlighting the relatively high contents of Fe and Al oxides in the UF soils in comparison to TF (Table 1).

The most noteworthy difference with regards to the mineralogical composition between the two types of soils was the higher abundance of kaolinite and gibbsite in UF than in the TF soils, where quartz and mica predominated (it was the only mineral detected in the Cg horizon). The higher specific surface area of UF with regard to TF was due to a higher clay content in the former, particularly gibbsite and kaolinite, while in the latter, the most abundant minerals were quartz and mica.

These studied soils contained low pseudo-total concentrations of Cu and Pb, and an undetectable level of Cd. These contents were lower than the maximum limits established in some reference guides (NMHPPE 2000; CCME 2007) and in the generic reference levels in Galician soils for the protection of ecosystems (Macías and Calvo de Anta 2009). Cu contents were higher in TF.A than in UF.A while in the subsurface horizons were similar. Pb contents were similar in the surface horizons of both type of soils but comparing subsurface horizons it was higher in those from UF soils, therefore the overall content of pseudo-total Pb content is higher in the soils from MRT.

3.2. Individual and competitive sorption and desorption isotherms

Figures 2 and 3 show the monometal and competitive sorption and desorption isotherms. The individual sorption isotherms of Cu²⁺ and Pb²⁺ were L type (Giles et al. 1974) for horizons TF.Cg, UF.A and UF.C1 (typical of soils with a high affinity for the solute), with an initial slope that remained unchanged whatever the metal concentration in the equilibrium solution. On the other hand, the monometal sorption and desorption isotherms of Cu²⁺ and Pb²⁺ in the TF.A horizons were L type, with a typically high initial slope reflecting the high affinity of the soil solid phase for the sorbate. The individual and competitive sorption and desorption of Cd²⁺ for

Table 1. Soil characteristics

	Units	Miñor river estuary (MRE)						Miño river terraces (MRT)					
		Soil/horizon						Soil/horizon					
		TF.A(1)	TF.A(2)	TF.A(3)	TF.Cg(1)	TF.Cg(2)	TF.Cg(3)	UF.A(1)	UF.A(2)	UF.A(3)	UF.C1(1)	UF.C1(2)	UF.C1(3)
pH H_2O		6.81b	6.79b	6.83b	7.56a	7.48a	7.64a	4.74c	4.81c	4.67c	4.94bc	4.85c	5.03bc
OM	%	9.76a	9.80a	9.71a	0.69d	0.73d	0.65d	9.59b	9.60b	9.50b	2.03c	1.97c	2.19c
Aluminium, Iron, and Manganese oxides content													
AlOx		8.93d	9.01cd	10.08c	1.29e	1.17e	1.20e	19.17a	19.63a	19.50a	12.90b	13.04b	13.26b
FeOx	g kg^{-1}	11.11c	11.34c	11.98c	3.71d	3.54d	3.40d	19.48ab	19.18c	19.92ab	20.64ab	21.06a	21.17a
MnOx		0.10a	0.08a	0.09a	0.04bc	0.03c	0.04bc	0.06b	0.05b	0.07ab	0.02d	0.02d	0.01d
Effective cationic exchange capacity and exchangeable cation content													
ECEC		19.25a	19.47a	19.03a	2.94c	2.80c	3.09c	5.22b	5.28b	5.19b	2.70cd	2.61d	2.51d
Na^+		7.91ab	7.56b	8.26a	1.14c	1.02c	1.26c	0.15d	0.13de	0.17d	0.12e	0.09e	0.15cd
K^+		1.32ab	1.45a	1.19b	0.20c	0.18cd	0.24c	0.11e	0.09f	0.1d5	0.08f	0.09f	0.07f
Ca^{2+}	cmol$_{(+)}$ kg^{-1}	4.19ab	4.50a	3.88b	0.12de	0.09e	0.15d	0.15d	0.09e	0.13de	0.79c	0.82c	0.74c
Mg^{2+}		5.82a	5.95a	5.69b	1.34cd	1.22d	1.46c	0.24ef	0.19f	0.27e	0.10g	0.08g	0.12g
Al^{3+}		0.01e	0.01e	0.01e	0.00	0.00	0.00	4.61ab	4.72a	4.50b	1.85cd	1.77d	1.93c
Pseudo-total heavy metal content													
Cd		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	mg kg^{-1}	13.00ab	14.60a	12.20b	3.00e	6.00cd	5.00d	6.00cd	5.00d	5.00d	7.00c	6.00cd	5.00d
Pb		32.78a	34.01a	35.63a	3.85c	7.82c	4.67c	33.36a	33.01a	31.97a	27.29b	28.59b	28.12b
Particle size distribution													
Sand		60.00b	60.00b	61.00b	91.00a	91.00a	90.00a	49.00c	49.00c	50.00c	49.00c	49.00c	49.00c
Silt	%	27.00a	27.00a	27.00a	6.00c	4.00d	5.00cd	24.00b	24.00b	24.00b	25.00b	24.00b	24.00b
Clay		13.00b	13.00b	12.00b	4.00c	5.00c	5.00c	27.00a	27.00a	26.00a	26.00a	27.00a	27.00a
Soil mineralogical analysis													
Mica		XX	XX	XX	-	-	-	X	X	X	X	X	X
Kaolinite	%	XXX	XXX	XXX	-	-	-	XXXX	XXXX	XXXX	XXXX	XXXX	XXXX
Quartz		XXX	XXX	XXX	XXXX	XXXX	XXXX	XXX	XXX	XXX	XX	XX	XX
Gibbsite		X	X	X	-	-	-	XX	XX	XX	XX	XX	XX
Specific surface area	m² g^{-1}	4.00c	3.80c	4.02c	1.00d	1.00d	0.90d	12.60b	12.00b	12.20b	20.50a	20.00a	20.30a

Mean of 9 analyses (three replicate analyses of each of three replicate samples for each soil horizon). In each row values followed by different letters differ significantly with $p < 0.05$, according to the ANOVA performed. OM: Organic matter; ECEC: Effective cation exchange capacity; X: 3-10%; XX: 10-30%; XXX: 30-50%; XXXX: > 50%; n.d.: not detectable.

most horizons were irregular; therefore, they were not comparable with the types of curves described by Giles et al. (1974). As a result of these irregularities, some isotherms did not fit the empirical models (Langmuir and Freundlich) and the calculations for the sorption and retention capacity using the distribution coefficients K_d (L kg^{-1})

made it impossible to clearly discriminate and compare the individual and competitive sorption capacities.

As a result the best parameter to estimate the sorption and retention capacity was the parameter Kr proposed by Vega et al. (2008).
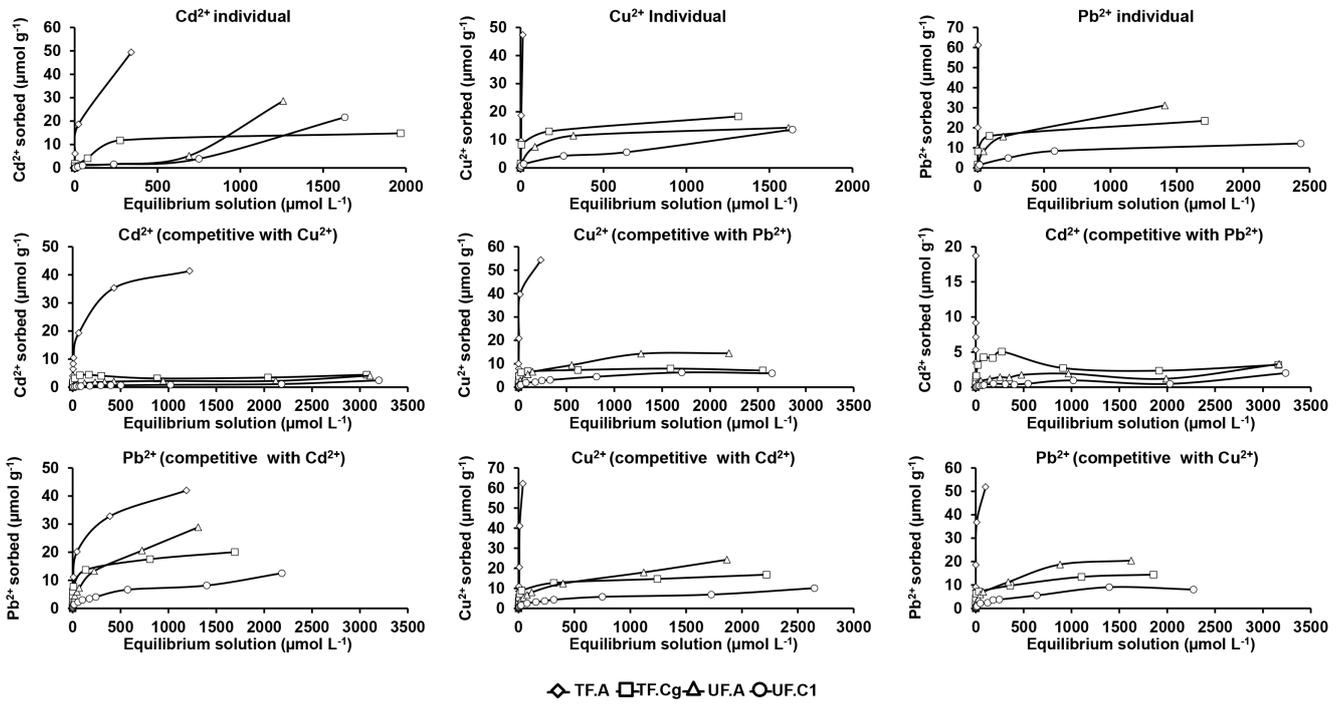
Figure 2. Individual and competitive sorption isotherms of Cd²⁺, Cu²⁺ and Pb²⁺ in TF and UF soils.
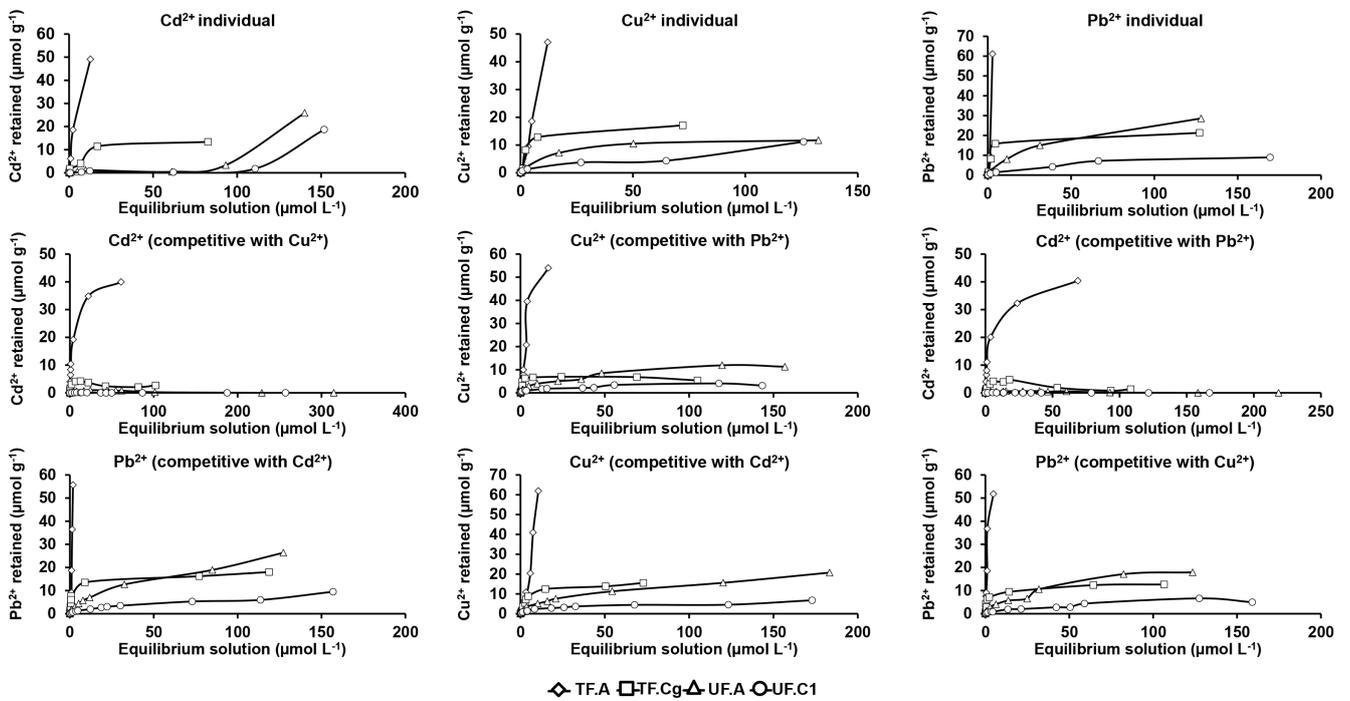
Figure 3. Individual and competitive desorption isotherms of Cd²⁺, Cu²⁺ and Pb²⁺ in TF and UF soils.

Table 2. Kr and HI

	Kr sorption								
Soil	Cd^{2+} individual	Cu^{2+} individual	Pb^{2+} individual	Cd^{2+} (competitive with Cu^{2+})	Cu^{2+} (competitive with Cd^{2+})	Cd^{2+} (competitive with Pb^{2+})	Pb^{2+} (competitive with Cd^{2+})	Cu^{2+} (competitive with Pb^{2+})	Pb^{2+} (competitive with Cu^{2+})
TF.A	0.891a	0.994a	0.999a	0.670a	0.990a	0.683a	0.994a	0.932a	0.967a
TF.Cg	0.357d	0.521b	0.510c	0.097b	0.366c	0.078b	0.469c	0.191c	0.366c
UF.A	0.525b	0.397c	0.583b	0.078c	0.452b	0.061b	0.573b	0.298b	0.440b
UF.C1	0.405c	0.326d	0.251d	0.042d	0.197d	0.036c	0.263d	0.132d	0.191d
	Kr retention								
Soil	Cd^{2+} individual	Cu^{2+} individual	Pb^{2+} individual	Cd^{2+} (competitive with Cu^{2+})	Cu^{2+} (competitive with Cd^{2+})	Cd^{2+} (competitive with Pb^{2+})	Pb^{2+} (competitive with Cd^{2+})	Cu^{2+} (competitive with Pb^{2+})	Pb^{2+} (competitive with Cu^{2+})
TF.A	0.886a	0.988a	0.998a	0.650a	0.984a	0.661a	0.993a	0.926a	0.965a
TF.Cg	0.329c	0.494b	0.473c	0.065b	0.344c	0.044b	0.431c	0.158c	0.330c
UF.A	0.465b	0.333c	0.540b	0.004c	0.392b	0.002c	0.528b	0.240b	0.394b
UF.C1	0.339c	0.267d	0.191c	0.001d	0.138d	0.000d	0.202d	0.078d	0.125c
	Hysteresis indices								
Soil	Cd^{2+} individual	Cu^{2+} individual	Pb^{2+} individual	Cd^{2+} (competitive with Cu^{2+})	Cu^{2+} (competitive with Cd^{2+})	Cd^{2+} (competitive with Pb^{2+})	Pb^{2+} (competitive with Cd^{2+})	Cu^{2+} (competitive with Pb^{2+})	Pb^{2+} (competitive with Cu^{2+})
TF.A	0.994a	0.994a	0.999a	0.970a	0.996a	0.968a	0.999a	0.994a	0.998a
TF.Cg	0.921b	0.949b	0.928b	0.668b	0.941b	0.561b	0.920b	0.826b	0.902b
UF.A	0.885c	0.852c	0.927b	0.047c	0.868c	0.038c	0.920b	0.807c	0.895c
UF.C1	0.836d	0.819d	0.760c	0.002d	0.700d	0.000d	0.769c	0.592d	0.654d

The curves obtained by plotting the concentrations of metal(s) added, (μmol g^{-1}) against those sorbed (or retained) at equilibrium, in each horizon (μmol g^{-1}), or the amounts added against those not sorbed (or not retained) by the soils, were all straight lines and fitted to an equation of $y = ax$, with $R^2 > 0.90$, $Kr = a$. Kr and IH values are the means of 9 data, three replicate of each of three replicate samples each horizon (three TF and three UF). In each column (for each treatment), values of sorption, retention or hysteresis indices followed by different letters differ significantly ($P < 0.05$).

Table 2 shows the values for the individual and competitive (bimetallic) sorption and retention capacities.

Based on data presented in Table 2, it was found that the sorption and retention capacities of the A horizons were significantly higher than those of C; the individual sorption and retention capacities were greater than the competitive capacities. Moreover, the highest values of sorption and retention capacities were those corresponding to Pb^{2+}, except TF.Cg and UF.C1 for both sorption and retention, followed by Cu^{2+} and Cd^{2+}. It is also noteworthy that the horizons with the highest sorption and retention capacities were the A horizons from the TF

soils. Due to the relatively high pH (Table 1) of the soil samples from the Miñor river site (TF.A and TF.G), precipitation of heavy metals during sorption and desorption experiments probably occurred. Nevertheless, the extent of this process was not possible to evaluate with the experiments performed, and the terms sorption (after sorption experiments) and retention (after desorption experiments) were used to encompass adsorption, precipitation on soil particle surfaces and fixation (Vega et al. 2009a).

Furthermore, the soil sorption and retention capacities of Pb^{2+}, Cu^{2+} and Cd^{2+} decreased in the following sequences: TF.A > UF.A > TF.Cg > UF.C1, except for the individual sorption and retention of Cd^{2+},

whose sequence was: TF.A > UF.A > UF.C1 > TF.Cg, and for the competitive sorption and retention of Cd, whose sequence was TF.A > TF.Cg > UF.A > UF.C1, proving the competence for sorption sites, favourable for Cu or Pb.

A statistical analysis was carried out to study the correlations between the properties and components of the six horizons and the individual and competitive (bimetallic) sorption and retention capacities (Table 3). It was revealed that the individual sorption and retention of Cu²⁺ were strongly correlated with the Mn oxide content and ECEC and also with the pH and organic matter content, albeit less markedly. Cu²⁺ is known to be preferentially fixed by soils with a moderately acidic to slightly alkaline pH, especially in the presence of Mn oxides (Covelo et al. 2008; Vega et al. 2009a; Arenas-Lago et al. 2014a).

In addition to the known influence of the characteristics of each soil horizon, one should also consider the widely accepted fact that Cu²⁺ and Pb²⁺ in soil compete with each other for sorption sites (Benjamin and Leckie 1981; Arias et al. 2005; Vega et al. 2009a; Diagboya et al. 2015). The horizons with the highest competitive sorption and retention capacities of Cu²⁺ were the A horizons with the highest pH, ECEC, and Mn oxide content (Table 1).

Therefore, soil properties with a highly significant and positive correlation to the sorption and retention of Cu²⁺ enhance the ability of soils to sorb and retain this cation.

Table 3. Pearson correlation coefficients between soil characteristics and Kr and HI

| | $K_{r,s}$ (monometal) | | | $K_{r,s}$ (competitive) | | | | | |
	Cd²⁺	Cu²⁺	Pb²⁺	Cd²⁺ (Cu²⁺)	Cd²⁺ (Pb²⁺)	Cu²⁺ (Cd²⁺)	Cu²⁺ (Pb²⁺)	Pb²⁺ (Cd²⁺)	Pb²⁺ (Cu²⁺)
pH		0.596*							
OM	0.767**	0.492*	0.728**	0.584*	0.583*	0.722**	0.707*	0.755**	0.714**
MnOx	0.698*	0.922**	0.906**	0.840*	0.827*	0.878**	0.831**	0.883**	0.887**
ECEC	0.949**	0.943**	0.919**	0.988*	0.988*	0.973**	0.996**	0.940**	0.970**
	$K_{r,r}$ (monometal)			$K_{r,r}$ (competitive)					
	Cd²⁺	Cu²⁺	Pb²⁺	Cd²⁺ (Cu²⁺)	Cd²⁺ (Pb²⁺)	Cu²⁺ (Cd²⁺)	Cu²⁺ (Pb²⁺)	Pb²⁺ (Cd²⁺)	Pb²⁺ (Cu²⁺)
pH		0.619*							
OM	0.736**		0.718**			0.689*	0.686*	0.741**	0.753**
MnOx	0.748**	0.929**	0.911**	0.844*	0.827**	0.896**	0.844**	0.890**	0.898**
ECEC	0.960**	0.934**	0.921**	0.979**	0.983**	0.969**	0.995**	0.941**	0.967**
	HI (monometal)			HI (competitive)					
	Cd²⁺	Cu²⁺	Pb²⁺	Cd²⁺ (Cu²⁺)	Cd²⁺ (Pb²⁺)	Cu²⁺ (Cd²⁺)	Cu²⁺ (Pb²⁺)	Pb²⁺ (Cd²⁺)	Pb²⁺ (Cu²⁺)
pH	0.604*	0.870**	0.561*	0.880**	0.825**	0.734**	0.589*	0.558*	0.620*
OM		0.601*					0.608*	0.619*	0.540*
MnOx	0.915**	0.952**	0.886**	0.940**	0.948**	0.929**	0.940**	0.900**	0.627*
ECEC	0.834**	0.694*	0.672*	0.717**	0.787**	0.633*	0.791**	0.713**	0.466*

OM: Organic matter; MnOx: Manganese oxides; ECEC: Effective cation exchange capacity. ** The correlation is significant at the level of 0.01 (bilateral). * The correlation is significant at the level of 0.05 (bilateral).

The horizons with the highest sorption and retention capacities of Pb^{2+}, as revealed by Kr (sorption and retention), were also the A horizons from the TF soils. As a rule, the horizons with the highest Pb^{2+} fixation capacity were those with the highest ECEC, organic matter and Mn oxide content, and the horizons with the lowest Pb^{2+} fixation capacity were those with the lowest ECEC and pH and with low Mn oxide concentrations. These facts suggest the formation of insoluble organic complexes with added Pb^{2+} although precipitation was probably due to the pH of the horizon. This was confirmed by the correlation analysis between the characteristics of the studied horizons and the Kr value for the competitive sorption and retention of Pb^{2+} (Table 3).

Kr values for the individual and competitive sorption and retention of Pb^{2+} were correlated with ECEC, organic matter, and Mn oxide content (Table 3).

These results were consistent with those of other authors (Arias et al. 2005; Cerqueira et al. 2011; Fonseca et al. 2011), who found that Pb^{2+} ions possess a high affinity for organic matter. Moreover, the presence of Mn oxides may have a prominent effect on Pb^{2+} sorption by soil. Covelo et al. (2008), Arenas-Lago et al. (2014b) and Kabata-Pendias (2010) found that Mn oxides exhibited the highest affinity for Pb^{2+} among the most abundant oxides in soil.

Therefore, Mn oxides, organic matter, and consequently, ECEC are the components that most highly influence Pb^{2+} monometal and competitive sorption and retention (Businelli and Tombesi 2009; Cerqueira et al. 2011; Mayanna et al. 2015).

Kr values for non-competitive and competitive Pb^{2+} sorption (with Cd^{2+}), as well as for retention, were similar; suggesting that Cd^{2+} did not interfere with Pb^{2+} sorption and retention; in fact, Pb^{2+} sorption and retention capacities were practically independent of Cd^{2+} competition. A similar pattern was shown by Cu^{2+} in competition with Cd^{2+} (Bradl 2004; Kabata-Pendias 2010; Vega et al. 2011; Diagboya et al. 2015). This

pattern is attributable in both cases to the organic matter and Mn oxide content. These authors found that these components have a higher affinity for Pb^{2+} or Cu^{2+} than for Cd^{2+}.

Moreover, the soils studied showed a lower Cd^{2+} sorption and retention capacity than for Cu^{2+} and Pb^{2+}, which is attributable to the low affinity of horizon components for Cd^{2+} and to competition with Cu^{2+} and Pb^{2+} for sorption sites (Diagboya et al. 2015); in this case, the organic matter and Mn oxide contents and the ECEC (Tables 1, 2, and 3) also favoured the sorption of Cd^{2+} (Shaheen 2009).

Cd^{2+} exhibited a different pattern. Under non-competitive conditions, the retention of Cd^{2+} was influenced by the organic matter and Mn oxide content, as they have a marked affinity for this ion. These results were consistent with those obtained previously in different soils (Arenas-Lago et al. 2013); however, Cd^{2+} was much less sorbed and retained in competition with Cu^{2+} and Pb^{2+} because Cd^{2+} is a poor competitor for sorption sites (Denaix et al. 2001; Vega et al. 2011).

It was found that under non-competitive conditions, the TF-A horizons had a relatively high Cd^{2+} sorption and retention. This is possibly because of their ECEC and their organic matter and Mn oxide content, according to Arenas-Lago et al. (2013).

3.3. Hysteresis

Table 2 shows the hysteresis indices calculated from Kr,r and Kr,s. Differences between metal fixation and the degree of monometal and competitive fixation irreversibility of the different horizons were established using ANOVA and LSD analysis. The results show that the sequence of individual sorption irreversibility was $Pb^{2+} > Cu^{2+} = Cd^{2+}$ and $Pb^{2+} > Cd^{2+} > Cu^{2+}$ for the A horizons of TF and UF, respectively. These results were consistent with those obtained by several authors (Shaheen 2009; Vega et al. 2009a, 2011; Shaheen et al. 2009, 2013) from different soil types, who found high affinity of Pb

sorption and retention, and consequently lower mobility. Those horizons are also the ones with the highest organic matter content and as Strawn and Sparks (2000) and Fonseca et al. (2011) indicated, Pb forms strong complexes with soil organic matter and can compete with most other metals for sorption sites (Strawn and Sparks 2000; Fonseca et al. 2011). These results are also in agreement with the results obtained after competitive experiments were studied in detail; in all the horizons the competitive sorption irreversibility was $Cu^{2+} > Cd^{2+}$, $Pb^{2+} > Cd^{2+}$ and $Pb^{2+} > Cu^{2+}$. Although a less direct interpretation, the low organic matter content of the subsurface horizons also determined the results obtained. The sequences calculated for the C horizons studied revealed an increase of the Pb mobility compared to the one for surface ($Cu^{2+} > Pb^{2+} > Cd^{2+}$ and $Cd^{2+} > Cu^{2+} > Pb^{2+}$ for TF.Cg and UF.C1 horizons, respectively).

Attending to each experiment (individual or competitive sorption and desorption) the horizons with the highest sorption irreversibility are always the TF.A followed by TF.Cg, UF.A and UF.C1. Only in the case of Pb individual sorption and Pb competitive sorpion with Cd, there were no significant differences between the hysteresis indices of TF.Cg and UF.A. This indicates that the greater fixing capacity of the studied ions occurred in TF, which is attributable to the higher pH, ECEC, and organic matter and Mn content.

The horizons exhibiting the lowest sorption irreversibility (UF.A and particularly UF.C) had an acidic pH and the lowest ECEC values and Mn oxide content (Table 1).

In order to reliably identify the specific soil properties that most strongly influenced sorption irreversibility, the soil characteristics and hysteresis indices for all the horizons (Table 3) were correlated.

It was found that the aforementioned components and properties had a highly significant and positive correlation with the hysteresis indices (Table 3).

However, the organic content was only correlated with the Pb^{2+} sorption hysteresis (monometal and competitive), which proved the specific fixation of this cation by organic matter, and the low capacity of this component to retain Cu^{2+} and Cd^{2+} (Table 3). This was confirmed by the non-correlation obtained between organic matter contents and the individual or competitive hysteresis indices of Cu^{2+} and Cd^{2+}.

ECEC and especially Mn oxide content were closely related to hysteresis in the competitive sorption (Table 3).

As a result, irreversibility in the competitive sorption of these metals (Table 2) was especially strong in the neutral or slightly alkaline horizons that contained the largest amounts of Mn oxides (Table 1). Therefore, irreversibility in individual and competitive Pb^{2+} sorption was mainly governed by organic matter, ECEC and Mn oxide content; however, the hysteresis in competitive Cu^{2+} or Cd^{2+} sorption was not correlated with organic matter (Table 3). These results were consistent with those obtained by several authors who found that the sorption of Cd^{2+}, Cu^{2+} and Pb^{2+} is most irreversible in the more basic soils with high ECEC and Mn oxide contents (Vega et al. 2009a; Cerqueira et al. 2011; Shaheen et al. 2013).

Based on the above, not all horizons could efficiently fix these metals under the same conditions. In fact, the characteristics of each soil had a crucial influence on its ability to retain the metals that were added individually or in pairs.

3.4. Metal migration through soil profiles

Table 4 summarizes the results of the monometal and competitive migration in different soils, horizons and profiles.

According to the MI values for monometal experiments, Pb^{2+} migrated to a lesser extent through the TF than the UF profiles. In the first soils, Pb^{2+} migrated to a lesser extent than Cu^{2+} and Cd^{2+}, while in UF, the sequence of migration

was $Cu^{2+} > Pb^{2+} \approx Cd^{2+}$. This was attributable to the higher organic matter content in C1 than in the Cg horizons. This component was highly correlated with individual Cd^{2+} retention, and uncorrelated with monometallic Cu^{2+} fixation (Table 3), which was probably due to the fact that organic matter tends to form soluble complexes with Cu^{2+} that can migrate through the profile (Cao et al. 2004; Arenas-Lago et al. 2014a).

Therefore, for the experiments with a single metal, and in the TF soils, more than 90% of each ion was retained (Figure 4). However, due to the aforementioned characteristics, the UF soils retained 64.6, 51.0 and 62.8% of Cd^{2+}, Cu^{2+} and Pb^{2+} respectively (Table 4), much less than TF; this indicates that there is a possibility of heavy metals transferring to subsurface waters and, through these, of contamination and even of these metals entering the food chain.
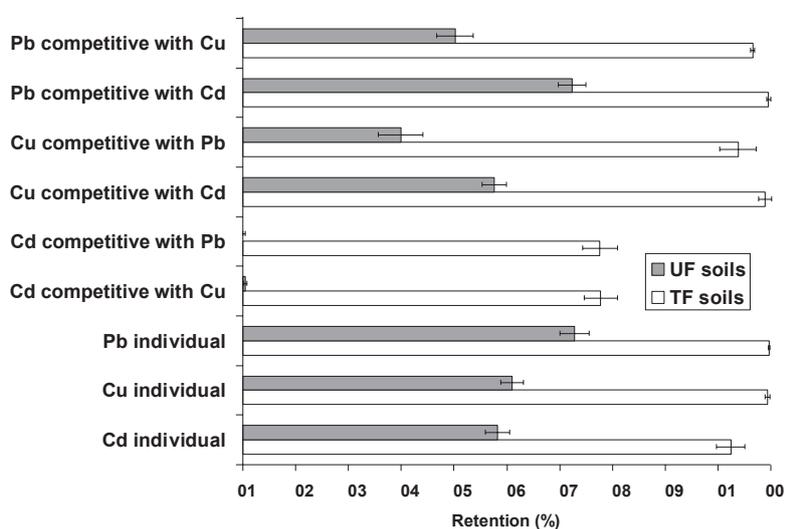
Figure 4. Retention percentage of Cd^{2+}, Cu^{2+} and Pb^{2+} in TF and UF soils.

Regarding competitive migration and retention (Table 4 and Figure 4), the results show that Cd^{2+} competed unfavourably with Cu^{2+} or Pb^{2+} for sorption sites, especially in the UF soils, where there was a clear antagonism and in which competition brought about the migration of almost all the added Cd^{2+} (Table 4).

The above was confirmed by the values of Cu^{2+} or Pb^{2+} migration indices when competing with Cd^{2+} (Table 4) for the sorption sites. These values indicated very little migration of the first two metals, especially in the TF soils (migration index: 0.011, 0.004, respectively). When competing

with Cd^{2+} in the UF soils, migration indices of Cu^{2+} and Pb^{2+} were higher than in the TF soils (0.524 and 0.376) but those of Cd^{2+} were 0.996 and 0.998 respectively, indicating almost total migration.

Therefore, in so far as the competitive sorption of Cd^{2+} with Cu^{2+} or Pb^{2+}, the antagonism mentioned above between the first ion and the other two in the TF soils was obvious. These soils retained only 0.4% of added Cd^{2+} when it competed with Cu^{2+}, and 0.2% with Pb^{2+}; however, these two ions were retained to a much greater extent (Figure 4).

Table 4. Migration through soil profiles

		Individual migration indices					
Soil	Horizon	Cd^{2+}		Cu^{2+}		Pb^{2+}	
		RI	MI	RI	MI	RI	MI
TF	A	0.886	↓	0.988	↓	0.997	↓
			0.114		0.012		0.003
	Cg	0.038	↓	0.006	↓	0.0001	↓
			$MI_{Cd}= 0.076$		$MI_{Cu} = 0.006$		$MI_{Pb} = 0.003$
UF	A	0.465	↓	0.333	↓	0.540	↓
			0.536		0.667		0.460
	C1	0.181	↓	0.178	↓	0.088	↓
			$MI_{Cd} = 0.354$		$MI_{Cu} = 0.489$		$MI_{Pb} = 0.372$

		Competitive migration indices					
Soil	Horizon	Cd^{2+} in competence with Cu^{2+}		Cd^{2+} in competence with Pb^{2+}		Cu^{2+} in competence with Cd^{2+}	
		RI	MI	RI	MI	RI	MI
TF	A	0.650	↓	0.661	↓	0.984	↓
			0.350		0.339		0.016
	Cg	0.023	↓	0.015	↓	0.005	↓
			$MI_{Cd} = 0.327$		$MI_{Cd} = 0.324$		$MI_{Cu} = 0.011$
UF	A	0.004	↓	0.002	↓	0.392	↓
			0.996		0.998		0.608
	C1	0.0001	↓	0.000	↓	0.084	↓
			$MI_{Cd} = 0.996$		$MI_{Cd} = 0.998$		$MI_{Cu} = 0.524$

		Competitive migration indices					
Soil	Horizon	Pb^{2+} in competence with Cd^{2+}		Pb^{2+} in competence with Cu^{2+}		Cu^{2+} in competence with Pb^{2+}	
		RI	MI	RI	MI	RI	MI
TF	A	0.993	↓	0.965	↓	0.926	↓
			0.007		0.035		0.0745
	Cg	0.003	↓	0.012	↓	0.012	↓
			$MI_{Pb} = 0.004$		$MI_{Pb} = 0.018$		$MI_{Cu} = 0.062$
UF	A	0.528	↓	0.394	↓	0.240	↓
			0.4724		0.606		0.760
	C1	0.096	↓	0.0769	↓	0.059	↓
			$MI_{Pb} = 0.376$		$MI_{Pb} = 0.530$		$MI_{Cu} = 0.701$

RI: retention in the horizon. MI: migration from the horizon, *MI*: soil migration index (Vega et al. 2009a). Means of 9 data, three replicate of each of three replicate samples each horizon (three TF and three UF).

In any case, when it competed with Cd^{2+}, more than 60% of the added Pb^{2+} was retained and it reached 99.6% in the TF soils. Cu^{2+} competed somewhat less effectively with Cd^{2+}, although in the TF soils 98.9% of the added Cu^{2+} was retained and in UF, 47.6%; whereas the retention rates for Cd^{2+} in this case were 67.8 and 0.4% respectively (Figure 4).

These results confirmed that the horizons have a high affinity for Pb^{2+} followed by Cu^{2+}, and they were consistent with the aforementioned correlations between the characteristics of each horizon and the $K_{r,r}$ slope used to estimate their retention capacity for the metal ions.

Cu^{2+} in competition with Pb^{2+} also favoured the latter, although to a lesser extent than with Cd^{2+}. Table 4 shows a Cu^{2+} migration index higher than that of Pb^{2+} (MI: 0.062 and 0.018 respectively in TF, and 0.701 and 0.530 in the UF soils).

These results (Figure 4) revealed that the retained percentage of the added Pb^{2+}, in competition with Cu^{2+}, was 98.2 in TF and 47% in the UF soils, whereas the proportion for Cu^{2+} was 93.8 and 29.9% respectively.

The studied soils retained Pb^{2+} more efficiently than Cu^{2+}, particularly in the A horizon because Pb^{2+} is known to form strong insoluble complexes with organic matter (Covelo et al. 2008) and to advantageously compete with Cu^{2+}.

According to the results obtained, Cd^{2+} can cause pollution problems in surface and subsurface waters due to its lower retention in the selected soils, especially in the UF Soils.

3.5. Modelling sorption and retention capacities

As already mentioned, the correlation analysis measured the relationship between the sorption or retention soil capacities and other physicochemical properties and components of the soils studied. Attending to these results, in all cases there is a high, positive and significant relationship with the Mn oxide content and the ECEC of the soils. They were the independent

variables selected to perform the multiple regression analysis in order to predict the sorption and retention capacities assessed.

For sorption capacities the goodness-of-fit (R^2) of the models fitted ranges from 0.91 to 1.00 (Table 5). In all the equations the sign and intensity of the values of ECEC are very low and similar (ranging from 0.02 to 0.04). This means that ECEC influences the sorption capacities but no differences among all the cases were revealed.

When focussing on the influence of the oxide Mn contents more differences among sorption capacities are observed. The coefficients in each equation for the oxide Mn contents are different, thus their sign and intensity will influence the most the sorption capacities, as the ones of ECEC are very similar in all models for sorption capacities.

The coefficients for oxide Mn contents in the equations obtained for individual sorption of Cd^{2+}, Cu^{2+} and Pb^{2+} are -2.62, 9.74 and 10.10, respectively (Table 5). This means that these oxides have great influence in the sorption of the metals studied, especially in Pb^{2+} sorption and in a lesser extent, in Cu^{2+} sorption.

The influence of the Mn oxides becomes clearer in the equations obtained after the results from bimetallic sorption data were regressed. These coefficients in the equations for Pb^{2+} sorption when Cd^{2+} and Cu^{2+} are also in the environment are still high compared to the ones for individual Pb^{2+} sorption (10.10) and very similar (7.90 and 7.18, respectively). This fact suggests that the Mn oxides play an important role on Pb^{2+} fixation, although there is a small influence on its sorption when one of the other metals evaluated are present, especially Cu^{2+}. This influence is even clearer when focussing on Cu^{2+} sorption as those coefficients for the bimetallic sorption equations are lower than the one obtained in the equation for the individual Cu^{2+} sorption (9.74). The one for Cu^{2+} sorption when Cd^{2+} is present is 6.72. The strong competition among Pb^{2+} and Cu^{2+} and high affinity of the Mn oxides for the sorption of Pb^{2+} is shown, as the coefficient in

Table 5. Multiple linear regression

		Determination coefficient (R^2)	Interception	Coefficients		
				MnOx	ECEC	OM
Individual sorption	Cd	0.91	0.38	-2.62	0.03	-
	Cu	0.97	0.04	9.74	0.02	-
	Pb	0.93	0.06	10.10	0.02	-
Competitive sorption	Cd(Cu)	0.99	-0.14	3.24	0.03	-
	Cd(Pb)	0.98	-0.15	2.53	0.04	-
	Cu(Cd)	0.98	0.01	6.72	0.03	-
	Cu(Pb)	1.00	-0.03	2.79	0.04	-
	Pb(Cd)	0.93	0.10	7.90	0.02	-
	Pb(Cu)	0.98	0.00	7.18	0.03	-
Individual retention	Cd	0.93	0.22	0.46	0.03	0.01
	Cu	0.99	0.02	9.67	0.03	0.02
	Pb	0.98	-0.14	13.96	0.01	0.02
Competitive retention	Cd(Cu)	1.00	-0.13	1.98	0.04	-0.02
	Cd(Pb)	1.00	-0.11	0.85	0.05	-0.02
	Cu(Cd)	0.99	-0.15	10.07	0.03	0.01
	Cu(Pb)	1.00	-0.13	4.25	0.04	0.00
	Pb(Cd)	0.99	-0.10	11.55	0.01	0.02
	Pb(Cu)	0.99	-0.17	10.53	0.02	0.01

MnOx: Manganese oxides; ECEC: Effective cation exchange capacity; OM: Organic matter.

this case is 2.79. These results suggest that the Mn oxides of the soils are important components in terms of sorption and they have specific sorption sites for Pb^{2+} fixation.

In the regression analysis performed with the retention data the organic matter content was also included as an independent variable in order to increase the goodness-of-fit (R^2). The R^2 obtained ranges between 0.93 and 1.00 (Table 5) and, as in the case for sorption capacities, the sign and intensity of the values of ECEC are very low and similar (ranging from 0.01 to 0.05). Although the sign of the coefficients obtained for the organic matter contents is not the same in all equations, these results are similar to the ones of ECEC as the values of these coefficients are even closer (values between -0.015 and 0.022). Therefore both ECEC and organic matter contents influenced the retention capacities of the soils although the extent is not revealed.

The strong influence on retention capacities of the three metals studied and the high affinity of the Mn oxides content for Pb^{2+} fixation is also shown in the equations obtained for retention capacities. The coefficients of the Mn oxides in the equations for Pb^{2+} retention are the highest and when Pb^{2+} is present the ones for Cu^{2+} retention are lower than when it is not. Therefore, the Mn oxides have high affinity for heavy metals sorption and retention, especially Cu^{2+} and Pb^{2+}, but when both are present in the environment Pb^{2+} competes favourably and specific fixation sites for Pb^{2+} may exist in the Mn oxides of the soils.

4. Conclusions

The highest sorption and retention capacities were for Pb^{2+}, followed by Cu^{2+} and Cd^{2+}. The individual sorption and retention capacities were greater than the competitive sorption and retention capacities.

The lowest Cd^{2+} sorption and retention capacities were due to the low affinity of horizon components for Cd^{2+} and to the competence with Cu^{2+} and Pb^{2+} for sorption sites.

Mn oxides, organic matter, and consequently ECEC, were the components that in general most highly influenced Pb^{2+} monometal and competitive sorption and retention.

The greatest fixation capacity occurred in Tidalic Fluvisols due to their high pH, ECEC, and organic matter and manganese contents.

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