Evidence of Physical and Chemical Nonequilibrium in Lead and Cadmium Transport and Sorption in Acid Soils

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Environmental issues regarding soil trace metals often center on mobility and bioavailability. Transport of metals through the soil system could be affected by physical or chemical nonequilibrium processes. In this study, the physiochemical factors involved in Pb and Cd transport and sorption in soils were examined to determine the fate of metal pollutants. A series of metal miscible displacement experiments were executed following a full factorial statistical design including five sources of variability: soil (S1 and S2), metal (Pb and Cd), metal initial concentration (C_0), water flux rate (J_w), and depth (0–4 and 4–8 cm). Temporal moment analysis of the measured breakthrough curves (BTCs) revealed that Cd transport is characterized by larger mass recovery values and lower estimated values of the transport timing—mean travel time (μ) and vertical solute spreading (σ^2)—than Pb. This indicates the high affinity and retention of Pb in the soil and the high mobility of Cd. On the other hand, the sorption parameters for both Pb and Cd were estimated from a sequential chemical extraction of the metal retained in the soil column. The effect of the sources of variability on both transport and sorption parameters were determined. The functional relationship between sorption and transport parameters was also estimated through a linear regression and canonical correlation analysis. Physical and chemical nonequilibrium in transport processes were demonstrated by BTC tailing, changing BTC characteristics (μ and σ^2) with J_w and C_0, and semi-irreversible sorption identified by sequential extraction.

Abbreviations: BTC, breakthrough curve; ICP–AES, inductively coupled plasma–atomic emission spectrometry.

Industrial discharges, fertilizer application, sewage and sludge disposal, as well as mining activities have resulted in the deposition and accumulation of trace metals in soils (Förstner, 1995). For example, accidents such as the mining spill at Aznalcóllar in Andalusia, southern Spain, in April 1998 continue to occur and degrade large areas of agricultural soils (Aguilar et al., 2004). Metal contaminants either accumulate in soils or leach and percolate into local groundwater, polluting aquifers and potential drinking water supplies. Among these metal contaminants, two of the most toxic are Cd and Pb. Classified as soluble and strongly hydrating cations (McBride, 1994), both metals are particularly toxic to higher animals, producing kidney and blood diseases among other health disorders (Adriano, 2001).

Environmental issues regarding soil trace metals often center on mobility and bioavailability. Transport of metals in groundwater systems could be affected by physical nonequilibrium processes (e.g., soil heterogeneity, preferential flow, and kinetic diffusion) or chemical nonequilibrium processes (e.g., caused by kinetic sorption or ion exchange and hysteretic sorption) (Pang et al., 2002). Local equilibrium conditions are only

Table 1. Physical, chemical, and mineralogical properties of the soils.

Soil	pH_w†	pH_k‡	Organic C	Ca	Mg	Na	K	Al	ECEC§	Sand	Silt	Clay
			g kg⁻¹				cmol_c kg⁻¹				g kg⁻¹	
S1	5.2 (0.02)¶	4.2 (0.03)	17 (1.0)	0.32 (0.02)	0.08 (0.00)	0.04 (0.00)	0.09 (0.00)	1.26 (0.08)	1.79 (0.11)	675 (38)	250 (15)	75 (5)
S2	5.0 (0.02)	3.8 (0.01)	3 (0.1)	0.06 (0.00)	0.20 (0.02)	0.02 (0.00)	0.11 (0.01)	0.7 (0.03)	1.09 (0.05)	710 (42)	245 (16)	45 (6)

† pH measured in deionized water.

‡ pH measured in 1 mol L⁻¹ KCl.

§ Effective capacity of the exchange complex.

¶ Mean values with standard deviations in parentheses (n = 3).

valid when solute transport occurs in a homogeneous porous medium and sorption is linear, reversible, and not kinetically limited. Therefore, most natural systems are rarely homogeneous and sorption is not established instantaneously during solute transport in soils (Brusseau et al., 1989; Kookana and Naidu, 1998). Consequently, the metal retention processes in the soil matrix should be studied under nonequilibrium conditions to correctly establish the risks associated with the presence of these elements in soils.

The complexity of the soil matrix, the simultaneous presence of contaminant elements in the soil solutions (resulting in competitive sorption), the variability of the geochemical conditions, and wide range of initial metal concentrations results in difficulty in determining sorption mechanisms under nonequilibrium conditions. An approach commonly used to study the mobility of metals in soils is a sequential chemical extraction procedure such as those developed by Tessier et al. (1979) and Shuman (1985). The accuracy and validity of these methods for the purpose of metal speciation has been questioned due to nonselectivity of the reagents in the sequential steps and to the possibility of metal readsorption during the extraction (Kim and McBride, 2006). Through the determination of the element distribution in the different soil solid fractions as a function of its chemical extractability, however, the availability of the element for transport and biological uptake may be inferred (Chlopecka and Adriano, 1996).

A complementary approach to examining transport processes is the application of temporal moment analysis to concentration breakthrough curves (BTCs) in contaminant transport studies (Valocchi, 1990; Campbell et al., 2006). This method may be used to estimate the transport parameters associated with a pollution element (Pang et al., 2003) and thus characterize its movement under different experimental conditions.

This study had three objectives designed to examine nonequilibrium heavy metal transport. The first was the study of the effect of the initial conditions including: soil type (S1 and S2), metal (Pb and Cd), initial metal concentration (C_0), and water flux rate (J_w) on physical and chemical nonequilibrium transport. The second objective was to examine the depth distribution (0–4 and 4–8 cm) and mobility in the Pb and Cd transport using a sequential metal extraction procedure. Finally, the third objective was to determine the functional relationship between sorption and transport parameters through linear regression and canonical correlation analysis.

MATERIALS AND METHODS
Soil Characteristics and Sample Collection

Two weathered acidic soils, developed from Pliocene–Quaternary aged formations in central Spain and classified as a Plinthic Palexerult (S1) and an Arenic Pachic Palexerult (S2) (Soil Survey Staff, 1999), were used for this study. Soil columns were collected from two level field sites. A total of 12 undisturbed columns of soil (8-cm diameter by 20-cm length) were taken from the Ap horizon by pressing beveled polyvinyl chloride cylinders into the soil on a uniform grid at 50-cm intervals. Once the cylinders were placed in the soil at the desired depth, the surrounding soil was carefully excavated and the columns were removed from the ground, capped, and transported to the laboratory. The moisture content (averaging a gravimetric water content of 0.20 ± 0.01) of the soil at the sampling time minimized compaction and disturbance. The columns were kept wet with deionized water until their subsequent use on trays filled with bulk soil. In addition, samples of the Ap horizon of each soil were collected at various locations surrounding the zone used for column extractions, air dried, crushed, sieved through a 2-mm mesh, and bulked before general characterization.

Selected physical, chemical, and mineralogical properties of the horizon are summarized in Tables 1 and 2. Soil pH was measured in deionized water (pH_w) and in 1 mol L⁻¹ KCl (pH_K, in a 1:2.5 suspension), and organic C was determined by wet digestion (Walkley and Black, 1934). The exchangeable bases were extracted with 1 mol L⁻¹ NH₄OAc (pH 7; Thomas, 1982), and the exchangeable Al (Al_K) was determined with 1 mol L⁻¹ KCl (Barnhisel and Bertsch, 1982). The effective capacity of the exchange complex was calculated as the sum of Al_K and the amounts of Ca, Mg, Na, and K extracted by 1 mol L⁻¹ NH₄OAc at pH 7 (Shuman, 1990). The supernatants from each extraction were separated by centrifugation and stored in polyethylene containers at 4°C until analysis. Analyses were performed in triplicate. The Ca, Mg, K, Na, and Al contents were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES) on a PerkinElmer OPTIMA 4300DV (PerkinElmer Corp.,

Table 2. Semiquantitative mineralogical composition† of the soils.

Soil	Fraction	Q	F_{Ca-Na}	F_K	G	H	Ph	S	V	I	K
					relative % between samples						
S1	≤2 mm	74	tr‡	tr	4	3	19	–§	–	–	–
	≤2 µm	12	ND¶	ND	6	6	76	ND	8	11	57
S2	≤2 mm	52	8	31	ND	ND	9	–	–	–	–
	≤2 µm	13	5	4	ND	ND	78	ND	ND	52	26

† Q = quartz, F_{Ca-Na} = Ca- and Na-rich feldspars, F_K = K-rich feldspars, G = goethite, H = hematite, Ph = phyllosilicates, V = vermiculite, S = smectite, I = illite, K = kaolinite.

‡ Trace.

§ Not determined.

¶ Not detected.

Table 3. Initial metal concentration (C_0) and water flux rate (J_w) in the transport experiments.

Parameter	Soil S1		Soil S2	
	Pb	Cd	Pb	Cd
High C_0, mg L^{-1}	4950	3233	3600	2800
Low C_0, mg L^{-1}	2300	1560	2900	1800
Fast J_w, cm h^{-1}	0.81	0.81	0.81	0.81
Slow J_w, cm h^{-1}	0.43	0.43	0.43	0.43

Norwalk, CT). The mineralogical compositions of the total (≤2-mm) and clay ≤2-µm) fractions were identified by x-ray powder diffraction on a Philips X'Pert diffractometer with graphite-monochromated CuKα radiation (PANalytical, Amelo, the Netherlands). We obtained semiquantitative estimates of the minerals from random powder and oriented aggregate patterns.

For all metal concentration determinations performed by ICP–AES, calibration curves for elemental analyses were run before and after each sample series (20 samples including matrix-matched blanks and in-between calibration checks). The calibration solutions covered the range of the concentrations in the samples and were prepared in the same matrix as the extracting reagents from certified stock solutions. Sample blanks were analyzed for correction of background effect on instrument response. Trace metal standards were used to assess instrument precision. We calculated metal concentrations in unknown solutions on the basis of the external calibration, averaging the concentrations from two repetitions for each experimental replication. The limits of detection were calculated as three standard deviations of the instrument response from 10 repeated analyses of sample matrix-matched blank solutions. The detection limits showed that a concentration of a few micrograms per liter of the two metals could be analyzed.

Leaching Experiments
Experimental Conditions

All metal leaching experiments were performed following a full factorial statistical design, including four sources of variability, each one with two response values, and three replicates for each experimental case. These sources of variability were: soil, metal, metal initial concentration, and water flux rate. The values of the metal pulse initial concentration and water flux rate are shown in Table 3.

Miscible Displacement Studies

All leaching experiments were done under unsaturated steady-state flow conditions (averaging a volumetric water content of 0.34 ± 0.02) and at room temperature (24 ± 2°C). The soil columns were initially eluted with 1 mmol L^{-1} CaCl$_2$ as the background solution from the top boundary of the column at the desired constant flow rate, ensured by using an adjustable-speed peristaltic pump. After steady-state water flow was achieved, a 400-mL pulse of a Pb and Cd solution containing the concentrations of both metals indicated in Table 3 for each experimental case was applied to the surface of the columns using the same irrigation system. These metal concentrations were believed to be necessary to assure metal migration through the soil columns in a workable period of time to achieve breakthrough. All metal solutions were prepared from their Cl$^-$ salts in the background solution. Theoretical calculations by MINTEQA2 (Allison et al., 1991) indicated that the solutions were not saturated with respect to any Cd species at the pH of the solution; however, Pb was found to be saturated with respect to laurionite at a concentration <0.29% in

all metal solutions. Thus, all solutions were filtered before their use in the experiments to ensure the total solubilization of the metal species.

Immediately following the pulse of metals, leaching was resumed with the background solution displacing the pulse through the soil columns until the metal concentrations in the effluent were reduced to zero. In all experiments, an air gap was left between the background and metal solutions to prevent dispersion in the irrigation tubes. Samples of effluent were collected at regular time intervals with an automatic fraction collector and analyzed for pH, electrical conductivity, Cl$^-$ (measured by an ion-selective electrode), and Cd, Pb, Ca, and Al (by ICP–AES).

Moment Analyses

Temporal moment analysis is a method to quantitatively represent a statistical probability distribution (in this case the metal BTCs) using characteristic values (Valocchi, 1990). Calculation of these moments and details on the transfer function approach may be found in Jury and Roth (1990) and Valocchi (1990). The BTCs from all the soil columns were analyzed by calculating the first (µ) and second (σ^2) temporal moments as the times corresponding to the statistical mean and variance of this distribution. The first temporal moment (µ) is defined as

$$\mu = \int_0^\infty t f(t) \, dt \tag{1}$$

where t is time on the x axis of the BTC and $f(t)$ is the probability distributions of tracer travel times, also called the transfer function. This temporal moment characterizes the mean displacement time of the solute or mean travel time expressed in time units. The second temporal moment or variance (σ^2) represents the spreading of the distribution along the x axis expressed in units of time squared. This value is defined as

$$\sigma^2 = \int_0^\infty (t-\mu)^2 f(t) \, dt \tag{2}$$

where µ is the first temporal moment and t is again time on the x axis (Mallants et al., 1994).

Additionally, mass recovery of the metal exiting each soil column was calculated using the BTCs. The tracer mass is commonly presented as the mass measured vs. the mass applied, or mass recovery (M_r), given by

$$M_r = \sum \left[\left(C_{(t)}^f / C_0 \right) V_w(t) \right] \tag{3}$$

where $C_{(t)}^f/C_0$ is the flux (f) metal concentration exiting the soil columns measured in each sample divided by the initial concentration of the metal in the metal pulse added to the column; $V_w(t)$ is the volume of water in each glass tube of the fraction collector for each sampling period. This value is therefore the total normalized metal mass per unit time exiting the soil column.

Sequential Extraction Procedure, Metal Fractionation

Following the end of miscible displacement studies, all columns were dismantled and the soil sectioned at approximately 4-cm intervals. The portions obtained at 0 to 4 and 4 to 8 cm from the surface (discarding the first 0.5 cm from the surface) were air dried, crushed, and sieved through a 2-mm mesh for subsequent analysis of metal in the solid phase. Duplicate 10-g subsamples from each soil portion and column (considered pseudo-replicates) were used to fraction the metals in the solid phase into the following operational fractions according to the method proposed by Shuman (1985):

1. Exchangeable metal fraction extracted with 1 mol L^{-1} $Mg(NO_3)_2$ at pH 7 (F^I)

2. Metal bound to organic matter extracted with 0.7 mol L^{-1} NaOCl at pH 8.5 (F^{II})

3. Metal fraction bound to Mn oxides extracted with 0.1 mol L^{-1} $NH_2OH \times HCl$ at pH 2 (F^{III})

4. Metal fraction bound to amorphous Fe oxides extracted with 0.2 mol L^{-1} $(NH_4)_2C_2O_4 \times H_2O$ + 0.2 mol L^{-1} $H_2C_2O_4$ at pH 3 (F^{IV})

5. Metal fraction bound to crystalline Fe oxides following an extraction procedure similar to that for Step 4 plus an additional extraction with 0.1 mol L^{-1} ascorbic acid (F^V)

In addition, we determined the total metal content (F^{Tot}) in duplicate subsamples (pseudo-replicates) by digestion in aqua regia (3:1 v/v 12 mol L^{-1} HCl/14 mol L^{-1} HNO_3) as described by Vercoutere et al. (1995). All metal concentration values obtained for each extraction step (fractions) mentioned above were converted into percentages with respect to the total metal content. All extracts and digests were stored in polyethylene tubes at 4°C for analysis and metal concentrations were determined by ICP–AES. We followed the same quality control system as described above.

Statistical Analysis
Statistical Design

The effect of the above-mentioned variability factors (except depth) on the characteristic metal transport parameters (M_r, μ, and σ^2) was studied based on a 2^n (n = 4) experimental design with two response levels (i = 2) for each variability factor (soil, metal, J_w, and C_0) and three replicates (j = 3). This way, for each combination of three variability factors, the differences found in the transport parameters were contrasted by means of one-way ANOVA. On the other hand, to study the effect of soil (S1 and S2), metal (Pb and Cd), metal initial concentration (C_0), water flux rate (J_w) on the sorption patterns as described by the group of fractions obtained from the sequential extraction procedure {k = 5; F^I, F^{II}, F^{III}, F^{IV}, F^V} and total metal content {F^{Tot}}, the same statistical model was applied, this time considering the nested effect of the depth factor with two measurement levels: 0 to 4 and 4 to 8 cm. Thus, given the sources of variability considered (n = 5; soil, metal, depth, J_w, and C_0) with two response levels (i = 2) and three replicates (j = 3; obtained from the mean of the corresponding pseudo-replicates after verifying the absence of statistical differences among them), for each combination of four variability factors, the differences in each of the k fractions (k = 5) as a result of the fifth variability factor were studied by means of an one-way ANOVA including the fraction (k – 1) as a covariable. Both ANOVA procedures were performed using the statistical program SPSS Version 14.0 (SPSS Inc., Chicago, IL).

Functional Relationships between Sorption and Transport Parameters

Linear Regression Analysis. Given both transport {μ, σ^2, M_r} and sorption {F^I, F^{II}, F^{III}, F^{IV}, F^V} parameters, the best combination of sorption parameters to explain each transport parameter was sequentially selected by means of a stepwise multiple linear regression analysis. This procedure was done for the all the possible combinations of soil × metal, not taking into account the existing differences in the values of sorption parameters produced by the other three variability factors considered in this study (J_w, C_0, and depth). These analyses were done using the statistical program SPSS Version 14.0.

Canonical Correlation Analysis. Last, a canonical correlation analysis was performed for studying the linear relationships between transport and sorption parameters without considering any sort of dependency between them. By means of this procedure, the Pearson correlation coefficient matrix of transport and sorption parameters was interpreted for each metal, evaluating the maximum global multivariate relationship between both groups of parameters. These analyses were done using the statistical program SAS 8.2 in Windows XP (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION
Initial Conditions and Transport Patterns

The mean BTCs for Pb and Cd (calculated from the three replicated BTCs) obtained for the different experimental conditions are shown in Fig. 1 and the corresponding estimated mean values of the transport parameters are shown in Fig. 2. The Cd transport pattern observed in both soils is characterized by larger mass recoveries and lower first and second temporal moments (μ and σ^2) than observed in the Pb transport. This different behavior is illustrated by significant differences (data not shown) between the mean transport parameters values estimated for each metal in most of the experiments performed in this study. The explanation for the observed differences in transport lies in the greater mobility of Cd compared with Pb (Camobreco et al., 1996; Voegelin et al., 2003) and the greater tendency of Pb to be strongly retained in the soil matrix through the formation of inner sphere complexes (Papelis and Hayes, 1996; Chen and Hayes, 1999; Strawn and Sparks, 1999). Contrary to Pb, Cd has been demonstrated to have a lower tendency to hydrolyze, tends to form outer sphere complexes on exchange positions of the mineral surfaces (Bradbury and Baeyens, 2005), and thus is more readily displaced to the soil solution (Hooda and Alloway, 1998; Voegelin et al., 2003). This different sorption behavior leads to longer residence times for Pb than for Cd (Pang et al., 2002).

The soil type did not produce remarkable differences between the transport patterns of each metal although, in general, greater mass recovery values and shorter mean travel times were estimated for both metals in Soil S2 than in S1, probably as a result of the coarser texture of S2 (Table 1) and greater sorption capacity of S1 (Serrano et al., 2005); however, these differences were more noticeable for the case of Pb than Cd. For instance, at rapid water flux (J_w^{fast}) and high initial metal concentration (C_0^{high}), the estimated Pb mean values of M_r and μ were 8 ± 2% and 62 ± 14 h^{-1}, respectively, for Soil S1, while for Soil S2, these values were 22 ± 8% and 25 ± 2 h^{-1}, respectively. Under the same experimental conditions, Cd M_r and μ values varied from 72 ± 2% and 19 ± 1 h^{-1}, respectively, in Soil S1 to 89 ± 1% and 23 ± 2 h^{-1}, respectively, in Soil S2. This different effect of the soil properties on the metal transport patterns might be explained by the greater affinity for Pb of Fe oxides and the greater Fe oxide content in the clay fraction of Soil S1 than Soil S2 (Table 2); however, Cd also shows affinity for sorption positions on Fe oxides (Cowen et al., 1991), so the effect of soil properties should have been apparent also in the case of this metal. The existence of competitive sorption processes between Pb and Cd for high-affinity sorption sites on Fe oxides could explain the different effect of the soil factor, as the greater affinity of Pb by these surface sorption sites pro-
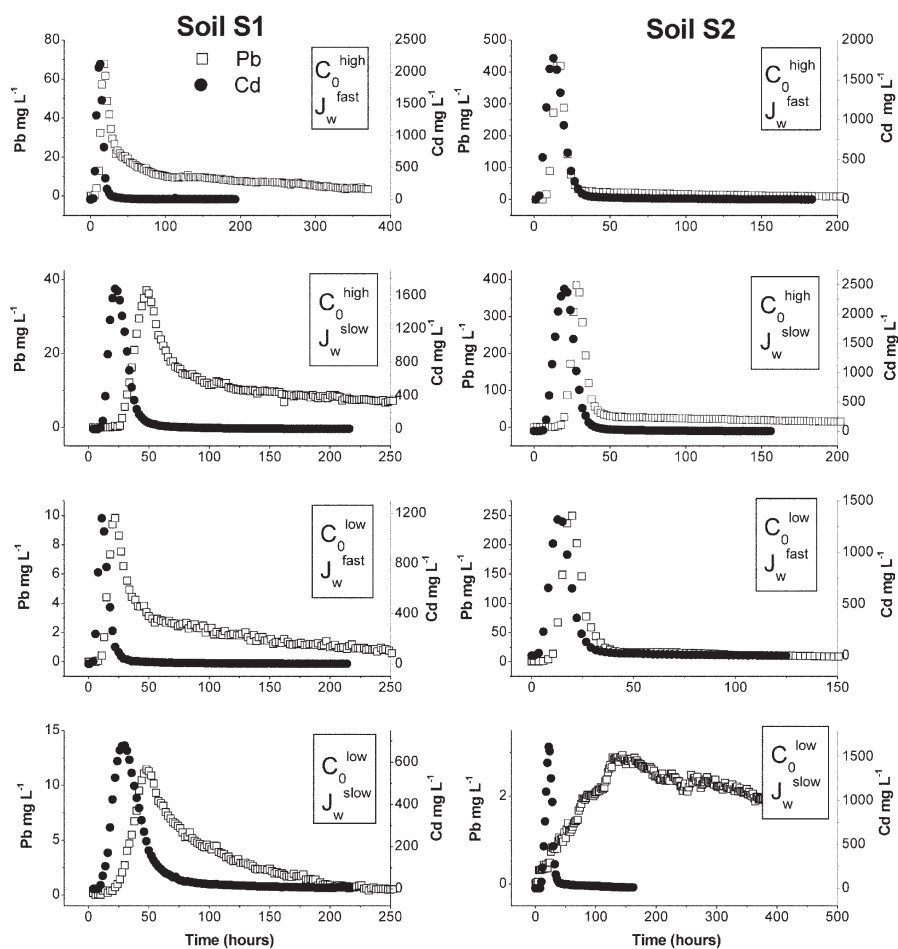
Fig. 1. Breakthrough curve data for Pb and Cd in soil columns under different water flux rates (J_w) and initial metal concentration (C_0). Values of J_w and C_0 are shown in Table 3.

motes the displacement of Cd from these positions, resulting in Cd transport patterns that were less sensitive to the Fe oxide content of the soils.

The effect of water flux on metal retention has already been studied, with contradictory results (Bajracharya et al., 1996; Tran et al., 1998). As theoretically deduced by Nkedi-Kizza et al. (1984) and similar to the experimental results of Bajracharya et al. (1996) with respect to Cd and Miretzky et al. (2006) for Zn, our results show a significant decrease in the estimated M_r values for Cd resulting from a decrease in J_w in all experimental cases. Other researchers, however, have observed increasing mass recovery rates of Cd as a result of an increment in water flux (Akratanakul et al., 1983) or an inconclusive relationship between pore water velocity and the mass of metal retained in the soil matrix (Bajracharya et al., 1996). A similar dependency of M_r on J_w was found with respect to Pb although the differences were not significant in all cases.

This effect of J_w on M_r might be a direct result of a decrease of the mean travel time of the metals, as estimated by the significant increment in the μ mean values, as well as an increase in dispersion estimated by σ^2. High values of μ and σ^2 facilitate metal diffusion into micropores, promoting greater contact between the metals and the reactive surface of the soil matrix. In addition, low flow rates increase the participation of kinetic-dependent sorption reactions or others, with greater activation energy producing more stable sorption mechanisms,

such as the formation of inner sphere complexes that overall induce the retention of metals within the soil matrix.

The effect of the initial metal concentration on Pb and Cd transport depends on the experimental conditions established by the other experimental variables considered. In Soil S1, lower values of Cd mass recovery (M_r) were found at C_0^{high} and at both J_w^{fast} and J_w^{slow}. These results concur with those of Alesii et al. (1980) but they are not in agreement with Miretzky et al. (2006), who found a lower fraction of Zn adsorbed in the soil at a higher initial metal concentration than at a lower one. On the other hand, the effect of the initial metal concentration in Soil S2 seemed to depend on the water flow conditions: at J_w^{fast}, Cd M_r decreased as C_0 increased, while at J_w^{slow}, the values of M_r obtained at C_0^{high} and C_0^{low} did not show significant differences. Nevertheless, the absolute mass of metal retained in both S1 and S2 was always greater at higher C_0 (for instance, 363 ± 34 and 541 ± 84 mg at slow and fast rates of flow, respectively, in Soil S1) than at low C_0 (68 ± 18 and 146 ± 48 mg at slow and fast rates of flow, respectively, also in Soil S1). A similar tendency was found for Pb, which suggests some metal precipitation process or the formation of multinuclear complexes at C_0^{high} values (Sposito, 1984).

Figure 2 shows greater Pb M_r values at C_0^{high} than those observed at C_0^{low}, however, for most of the experimental conditions. This different behavior in the mass balance as a result of the initial metal concentration of the pulse could be related to the maximum sorption capacity of the soils, greater in S1 than in S2. While the M_r value at J_w^{slow} and C_0^{high} was 6 ± 0.9 and 15 ± 2% in Soils S1 and S2, respectively, at C_0^{low}, M_r values were similar in both soils (1.7 ± 1.8 and 1.7 ± 0.5% in Soils S1 and S2, respectively).

The effect of C_0 on the transport parameters μ and σ^2 was different for Pb and Cd and depended on the experimental conditions. While no significant differences were found in the μ values between the two initial Cd concentrations in either soil, the μ values for Pb in Soil S2 were higher at C_0^{low} than at C_0^{high}, which means that low mean travel times are associated with a high initial Pb concentration of the pulses. Also, higher values of the second temporal moment (σ^2) were found to be associated with a lower initial Pb concentration in Soil S2 , resulting in greater spreading of the distribution along the x axis. These results were corroborated by Murali and Aylmore (1980), who observed the influence of the initial metal concentration on the transport characteristics and metal retention. Therefore, if the metal mass retained in the soil is high with respect to the sorption capacity of the soil, then high C_0 values are related to low μ values. This effect is attributed to the nonlinearity of the sorp-

tion processes that induce an increase in the metal displacement as the initial metal concentration increases and thus a lower dispersion of the BTC (Naidu et al., 1997).

Initial Conditions and Sorption Patterns

The effect of the initial conditions (soil, metal, C_0, and J_w) on the sorption patterns at two depths as described by the group of fractions obtained from the sequential extraction procedure (F^I, F^{II}, F^{III}, F^{IV}, F^V, and F^{Tot}) are shown in Table 4 for Soils S1 and S2. The results reveal a metal distribution in the soils that was highly dependent on the experimental conditions established by the different variables considered in this study, so that we were not able to describe a consistent sorption pattern. Some interesting conclusions were possible from the statistical analysis, however, and are shown below.

Influence of Soil Type and Mineralogy

The different physical, chemical, and mineralogical characteristics of both soils induced significant differences between the total metal concentrations retained in each soil (Table 4). The higher Pb and Cd total fraction adsorbed in Soil S1 than in Soil S2 corroborate the higher sorption capacity of the first soil with respect to the second one, as was shown by Serrano et al. (2005).

The metal mass observed in the different chemical extraction fractions in both soils were influenced by the experimental conditions, so that not all the fractions showed significant differences between Soils S1 and S2. For instance, the Cd fraction retained in the exchangeable metal fraction (F^I) was higher in Soil S2 than in Soil S1 at J_w^{fast}. At lower water flow, however, the Cd fractions retained in F^I of both Soils S1 and S2 did not show significant differences (Table 4).

The Pb fraction sorbed in F^I was higher in Soil S2 than in Soil S1 at both J_w^{fast} and J_w^{slow}, which suggests an easier metal displacement from the exchange sites in Soil S1. The composition of phyllosilicates present in the soils, the kaolinite and illite in Soils S1 and S2, respectively, are characterized by the absence of isomorphic substitutions that promote the formation of weak electrostatic and reversible bonding between metals and the sites associated with the ditrigonal cavity of siloxane (Sposito, 1984). Our results indicate a higher global reactivity of the exchange sites in Soil S2 than in Soil S1; however, this hypothesis cannot be verified.

The metal fraction bound to Mn oxides (F^{III}) was significantly different for Cd between soils, being higher in S1 than in S2 under all experimental conditions. Not all the experimental cases showed significant differences for Pb between Soil S1 and Soil S2; however, in those cases where significant differences were found, the Pb fraction was greater in Soil S1 than in Soil S2. Because Soil S1 is characterized by a higher fraction of Mn oxides than Soil S2, these results would be initially unexpected. As we saw above, however, the displacement velocity and the metal recovery fraction were higher in S2 than in S1, which suggests less interactive metal displacement in S2 than in S1 and so a lower retention in F^{III} in Soil S2.

Last, no significant differences were found for Cd in either F^{IV} or F^V, defined as the fractions bound to amorphous and crystalline Fe oxides, respectively. For Pb, while the fraction retained in F^{IV} was generally higher in Soil S1 than in Soil S2,
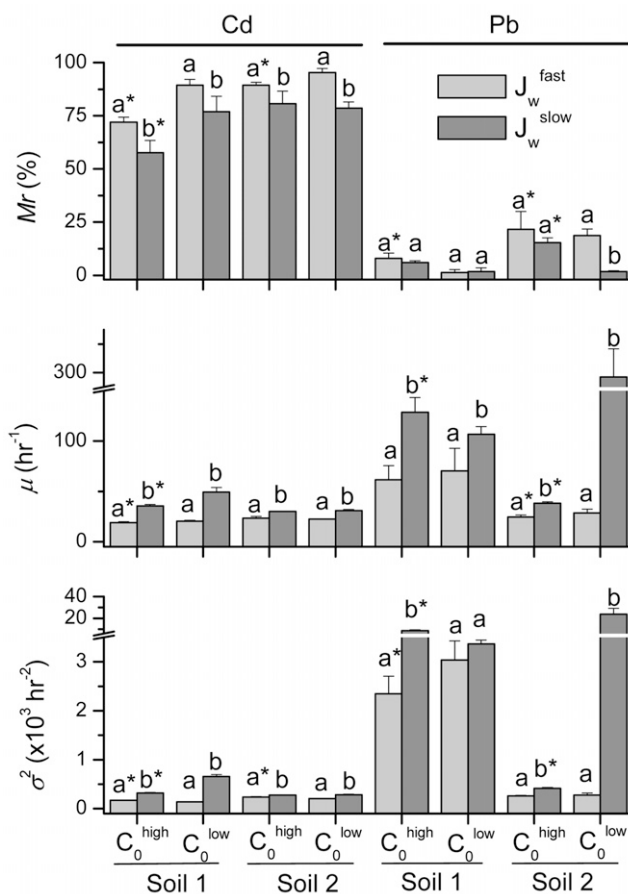

Fig. 2. Mass recovery (M_r), mean travel time (μ), and vertical solute spreading (σ^2) for Pb and Cd in two soils under different water flux rates (J_w) and initial metal concentration (C_0). For each metal, soil, and C_0, different letters indicate statistically significant differences ($P = 0.05$) of the corresponding mean values as a result of different J_w. For each metal, soil, and J_w, columns with an asterisk beside the letter indicate statistically significant differences ($P = 0.05$) of the corresponding mean values as a result of different C_0. Values of J_w and C_0 are shown in Table 3.

the one adsorbed in F^V was higher in Soil S2 than in Soil S1, showing significant differences between the soils.

Influence of Metal Type

The different sorption behavior of the two metals in this study was revealed in the analysis of the sequential extraction results. The metal type was one of the sources of variability considered in this study that showed more significant differences in both the total metal retention and the metal distribution along the different fractions defined in the chemical extractions (Fig. 2). The greatest total concentration retained in the soils for all the experimental conditions corresponded to Pb, which once again reflects the higher affinity of the soils for Pb than Cd. This result was also observed in the higher Cd displacement along the soil profile respective to Pb, corroborated by the higher Cd mass recovery relative to Pb. Due largely to its lower tendency to hydrolyze, Cd is adsorbed on the mineral surface in unstable surface complexes. In addition, studies have revealed that competition among various species for adsorption sites can significantly affect the activity of Cd in soil solution, and therefore its leaching potential through a soil profile (Serrano et al., 2005). Research has shown that Ca^{2+}

Table 4. Metal distribution on the soil solid fractions (F^I–F^V) and total metal content (F^{Tot})as determined by the sequential extraction procedure.

Depth	J_w†	C_0‡	Cd						Pb					
			F^I	F^{II}	F^{III}	F^{IV}	F^V	F^{Tot}	F^I	F^{II}	F^{III}	F^{IV}	F^V	F^{Tot}
cm			—————— % ——————					mg kg^{-1}	—————— % ——————					mg kg^{-1}
								Soil S1						
0–4	fast	high	0.7	0.3	4.9	0.2	97.6	408.3	6.4	0.7	58.7	11.2	17.6	2871.2
		low	1.9	0.6	10.2	0.4	88.8	252.8	8	1	45.7	19.4	16.6	2288.7
	slow	high	3.9	0.2	6.1	0.2	90.2	520.9	3.9	0.7	44.3	20.6	20.7	3414.2
		low	1.3	0.5	6.2	0.3	83.4	374.4	6.1	0.9	44.0	18.1	22.2	2696.2
PSE§			0.4	0.1	0.5	0.1	3.5	28.2	0.4	0.1	2.3	0.8	0.4	135.1
4–8	fast	high	0.7	0.4	3.0	0.3	80	388.6	4.4	0.9	39.9	17.1	30.8	1765.3
		low	2.5	1.0	6.4	0.9	90	102.3	7.2	1	38.0	14.5	26.8	1235.1
	slow	high	0.6	0.4	4.2	0.2	88.2	660.7	5.5	0.9	51.1	14.2	14.5	2477.2
		low	0.7	0.6	5.4	0.6	79.4	222.9	3.5	0.7	41.7	19.2	26.3	1769.2
PSE			0.4	0.1	0.5	0.0	5.3	30.6	0.3	0.1	1.6	1.8	0.8	79.2
								Soil S2						
0–4	fast	high	4.9	1.7	0.9	0.3	92.9	246.6	0.7	2.4	45.0	5.9	29.9	2098.2
		low	9.2	1.4	1.4	0.3	81.7	81.5	17.8	1.6	41.3	5.8	30	1713.4
	slow	high	2.5	2.1	1.0	0.4	93.6	278	16.0	4.1	44.3	7.5	22.5	2099.7
		low	4.3	2.1	1.8	0.5	85.6	306.3	11.1	1.9	47.2	8.5	28.1	1920.0
PSE			1.5	0.1	0.4	0.1	3.9	27.3	1.5	0.4	1.0	0.5	0.9	37.9
4–8	fast	high	1.3	4.4	0.6	0.5	90.6	117.1	15.0	3.9	6.0	18.4	59.0	620.9
		low	5.1	10.3	1.5	0.5	98.4	19.2	10.0	3.9	29.0	11.2	45.3	582.1
	slow	high	0.3	6.2	0.4	0.7	87.4	193	10.0	2.7	21.1	4.6	50.7	967.0
		low	0.8	5.9	0.6	0.7	91.2	132.5	7.8	5.6	20.0	19.6	42.4	742.3
PSE			1.1	2.9	0.3	0.1	6.1	26.5	1.2	0.6	2.3	1.4	1.1	18.9

† Water flux rate as described in Table 3.

‡ Initial metal concentration as described in Table 3.

§ Pooled standard error for all combinations of $J_w \times C_0$ and each soil, depth, metal, and fraction.

strongly competes with Cd^{2+} for exchange sites in soils (Naidu et al., 1994). Consequently, the marked effect of the $CaCl_2$ background electrolyte on Cd displacement was observed for all the chemical extraction fractions. The percentage of Cd adsorbed in the fractions F^I, F^{III}, and F^{IV} was lower than that of the Pb. Instead, Cd in F^V was higher than Pb. This indicates that competitive sorption was occurring between Ca and Cd except in the fraction corresponding to crystalline Fe oxides, where Cd is strongly retained through specific sorption reactions (Table 4).

Influence of Initial Metal Concentration

The effect of the initial metal concentration on the metal total retention on the soils is shown in Table 4. As can be observed, an increase in the Pb and Cd total mass adsorbed in the soils was observed as a result of the increase in the initial metal concentration values. Higher significant differences were found for Cd at Depth 2 (4–8 cm) than at Depth 1 (0–4 cm) at both J_w^{fast} and J_w^{slow} in Soil S1. While the concentration of Cd retained in the soils increased from C_0^{high} to C_0^{low} 1.5 times and 3.2 times at Depths 1 and 2, respectively, the total Pb adsorbed increased 1.2 and 1.4 times at Depths 1 and 2, respectively. These results could be attributed to the more homogeneous water flow distribution at Depth 2, and so a higher contact between the metal in the soil solution and the mineral surface than at Depth 1 (Garrido et al., 2001). In the same way, the higher Cd mobility and the lower affinity for the specific sites with respect to the Pb resulted in greater differences between depths for Cd than for Pb.

On the other hand, the Pb and Cd distribution along the chemical fractions as a function of the initial metal concentration may depend on the experimental conditions and, in most cases, did not show significant differences; however, the effect of the initial concentration on the metal retained in the F^I fraction is noticeable (Table 4). The estimated ionic strength (I) of the metal pulses is 125.2 and 60.8 mmol L^{-1} for C_0^{high} and C_0^{low}, respectively, in the case of Soil S1. For Soil S2, these values are 100.9 and 72.3 mmol L^{-1} for C_0^{high} and C_0^{low}, respectively. The effect of I on metal sorption is difficult to assess. On the one hand, increasing I may yield an increment of surface charge in variable-charge soils (Naidu et al., 1997), which provides these soils with greater sorption capacity. On the other hand, increasing I may also decrease metal sorption through changes in metal activities (depending on the background electrolyte), competition for the sorption sites (depending on the index cation), and changes in the electrostatic potential of the plan of sorption (depending on pH and soil mineral properties) (Naidu et al., 1994). While insensitivity to I has been understood as an indication of inner sphere surface complexation, however, a decrease of sorption with increasing I has been associated with outer sphere surface complexation sorption processes (Lützenkirchen, 1997). Attending to the results of the sequential chemical extraction (Table 4), the concentration of Cd in F^I (ascribable to outer sphere sorption mechanisms) is lower at C_0^{high} (high I) than at C_0^{low} (low I) at both depths for both soils. This tendency was not found for Pb. The higher tendency of Cd to be retained in nonspecific sites compared with Pb could explain the higher

Table 5. Regression coefficients associated with the sorption parameters as independent variables selected to describe the first and second temporal moments (mean travel time μ and vertical solute spreading σ^2, respectively) and mass recovery (M_r) for soil solid fractions F^I through F^V from the sequential extraction procedure.

Parameter	Soil	Metal	Regression coefficients ± SE					R
			F^I	F^{II}	F^{III}	F^{IV}	F^V	
μ	S1	Cd		−6.7 ± 8.9			−0.6 ± 0.3	0.41
		Pb	−18.8 ± 4.6	90.1 ± 44.5	−1.7 ± 0.9		−5.1 ± 1.3	0.74
	S2	Cd	−0.9 ± 0.3		2.9 ± 1.4			0.56
		Pb	−15.4 ± 4.6		5.0 ± 1.5	13.1 ± 3.8		0.74
σ^2	S1	Cd	−32.4 ± 38.7	−89.4 ± 168.7	12.6 ± 24.6		−9.9 ± 5.2	0.82
		Pb	−1514.0 ± 331.1	6663 ± 3229	−151.1 ± 70.1		−518 ± 97	0.73
	S2	Cd	−8.7 ± 2.3	−3.3 ± 1.3	17.5 ± 11.0	36.5 ± 25.2		0.74
		Pb	−1426.8 ± 433.9	−1085 ± 1523	469 ± 143	1425 ± 453	0.1 ± 0.3	0.76
M_r	S1	Cd	−4.4 ± 1.4		3.1 ± 0.8	30.9 ± 6.8		0.83
		Pb	−1.1 ± 0.3		0.1 ± 0.1	−0.4 ± 0.2		0.67
	S2	Cd	1.7 ± 0.4	0.9 ± 0.3		−4.0 ± 5.5	0.1 ± 0.1	0.74
		Pb	0.8 ± 0.4		−0.2 ± 0.3	−0.9 ± 0.4	0.1 ± 0.3	0.61

influence of C_0 (i.e., I) on Cd retention on the ionic exchange sites compared with that of Pb.

Influence of Flow Rate

The total metal mass retained in the soils was greatly influenced by the water flux rate used in the displacement experiments. In general, higher values of the metal mass adsorbed were found at lower water flux (Table 4). At slow water flow velocity, the equilibrium conditions could be reached more easily than at higher flow rates, and thus the metal can be retained on specific sites through very stable complexes that are not easily displaced (Sparks, 1984). This result, therefore, suggests chemical non-equilibrium transport conditions at the higher flow rate.

In addition, faster flow velocities may favor transport in fast flow pathways (like macropores) and slower transport velocities may allow a greater influence of the soil matrix (smaller pores) (Dyson and White, 1989). So at the slower flow rate, the solute is actually physically interacting with a larger proportion of the total soil volume or effective porosity. This effect could also result in physical nonequilibrium transport conditions at the higher flow rate.

The effect of water flux on metal adsorption in the different sequential soil fractions was not conclusive. The more important effect was found in F^I. In general, both Pb and Cd retained in F^I were higher at J_w^{fast} than at J_w^{slow}. These results are consistent with Pang et al. (2002), who showed an increase in the Pb and Cd sorption phenomena and the metal mass recovered with increasing water flow in soil columns (Table 4).

Depth Differences in Sorption

Last, the depth variable showed the greatest influence on the total metal mass retained in the soils. As can be seen in Table 4, for most of the experimental conditions a higher Pb and Cd metal fraction was found at Depth 1 (0–4 cm) than at Depth 2 (4–8 cm). It has been shown that, in structured soils, uniformly applied solutes tend to be focused into preferential flow pathways (Fluehler et al., 1996). If this focusing were to occur, it would result in a greater contact between the solute and soil at Depth 1 than at Depth 2, where less contact with the soil could affect mass retention deeper in the soil.

Statistical Relationships between Initial Conditions and Transport
Linear Regression: Sorption and Transport Parameters

The result of the regression analysis for studying the linear relationships between each transport parameter (μ, σ^2, and M_r) and the whole sorption parameters (F^I, F^{II}, F^{III}, F^{IV}, and F^V) is shown in Table 5. This procedure does not consider the effect of the variability factors J_w, C_0, and depth, thus the model adjustment level for each transport parameter depends on the experimental conditions established by the combination metal × soil. As can be observed in the tables, the model does not provide a complete representation of transport for all the experimental cases. The lack of adjustment level could be due to variables not taken into account in this regression analysis. While a complete model was not possible, some conclusions were possible and are discussed here.

First Temporal Moment. The results of the regression model for the first temporal moment (μ) showed a higher adjusting level for Pb than for Cd. With the exception of one result corresponding to Cd in Soil S1, the model coefficients associated with F^I were negative and significant for all experimental conditions (Table 5). These results suggest that, independent of the initial metal concentration or the flow rate, the mean displacement time of the metals was greatly influenced by the exchange reactions between the metals and the soil matrix.

It is also interesting that in Soil S2, both Pb and Cd were observed to have high positive model coefficients for the F^{III} fractions associated with high values of μ (i.e., slower metal travel time). In addition, the Pb retention on the amorphous Fe oxides (F^{IV}) contributed to predicted first temporal moments, similar to that observed with F^{III} (Table 5). These results suggest that the semi-irreversible character of the Pb sorption process on the Mn and Fe oxides is related to a slow metal transport phenomenon.

In Soil S1 for Pb, besides F^I, the F^{II} and F^V appear as predictive variables to explain μ. The first temporal moment is related positively to the F^{II} coefficient and negatively to the F^V coefficient. The high affinity of Pb for the specific sites associated with organic matter (Sposito, 1984; Basta et al., 1993) resulted in a low metal displacement time. We are unable to

Table 6. Canonical correlation analysis for Cd.

Function	Canonical correlation	Eigenvalue	Difference	Proportion	Cumulative
1	0.684	0.878	0.741	0.859	0.859
2	0.347	0.136	0.130	0.133	0.993
3	0.082	0.006		0.006	1.000

offer any good explanation for the negative coefficient associated with F^V (Table 5); however, the fact that Pb has a high affinity for Fe oxides could suggest that an important concentration of this metal does not participate in the transport processes and consequently the BTC area decreases, producing a decrease in μ as a result of a collateral effect.

Second Temporal Moment. The model results for the second temporal moment were similar for both metals in Soil S2 (Table 5). In this soil, the coefficients associated to F^I and F^{II} were negative, while those associated with F^{III} and F^{IV} were positive. The metal retention on the exchange sites associated with phyllosilicates and organic matter may be described by assuming instantaneous equilibrium and nonchemical hysteresis (Seuntjens et al., 2001). Consequently, a greater tendency for sorption on these sites is associated with a more convective transport and more symmetrical (low σ^2 values) shapes of the BTC. On the other hand, metal retention on the specific sites occurs through semi-irreversible sorption processes under physical or chemical nonequilibrium conditions. The metal retention on these specific sites promotes more dispersive BTCs and thus higher σ^2 values. Assuming that it is not easy to establish differences between chemical and physical nonequilibrium conditions, the fact that most of the variance associated with σ^2 can be explained by these sorption parameters could indicate that the metal behavior during the transport processes was more affected by the sorption processes (chemical nonequilibrium) than by the diffusion processes that were taking place in the micropores of the soil structure (physical nonequilibrium).

Since low R values were obtained in the regression analysis for Cd in Soil S1, no conclusions could be extracted from the results. The analysis results for Pb, however, showed that all the sorption variables (with the exception of F^{IV}) took part in the description of the second temporal moment (σ^2). Once again, the coefficient associated with F^I was negatively related to σ^2, while the one associated with F^{II} was positive. This result corroborates the study of Basta et al. (1993), which showed a tendency for Pb to be retained on organic matter through inner sphere complexes, which induces asymmetric leaching curves characterized by high σ^2 values.

Mass Balance. The model results for the mass balance (M_r) for all the experimental conditions established by the combination metal × soil showed higher R values than the ones obtained for the two previous temporal moments. In Soil S1, the fractions F^I, F^{III}, and F^{IV} appear as predictive variables, with significant coefficients for both Pb and Cd metals (Table 5). The inconclusive results obtained can be attributed to the effect of the variability factors that have not been taken into account in the leaching experiments. For instance, while it would be expected that higher mass balances would be associated with a larger fraction of metal retained on the exchange sites, the negative coefficient associated with F^I for both metals showed the contrary. These results could suggest a metal displacement process by the Ca cation present in

the solution that increased the values of the mass of metal recovered in the leachate with respect to the initial mass added to the soil column.

Canonical Correlation Analysis

The statistical relationship between the whole sorption parameter group and the transport parameters was studied in a multivariant way through a canonical correlation analysis. This analysis provides the best combination of sorption parameters that explains the whole transport phenomenon as defined by the three transport parameters that jointly represent the metal BTCs.

This procedure defines as many double canonical functions (canonical variables) as the least number of variables within each variable group—in this case, three. In the case of Cd, the first canonical function, which describes 86% of the variance (Table 6), can be interpreted by the correlations between the variables from both groups of parameters and their first canonical variable (Table 7). Each of these coefficients provides information on the multivariant functional relationship that operates between both variable groups. This way, the sorption variables F^I, F^{II}, and F^{IV} and the transport variable M_r showed the highest weight in the canonical correlation and both groups of variables are positively related. On the other hand, the sorption variable group is also negatively related to the first and second temporal moments. Overall, the relationship between both sorption and transport variable groups could be represented as

$$\left\{F^I, F^{II}, F^{IV}\right\}^+ \leftrightarrow \left\{M_r\right\}^+ \cup \left\{\mu, \sigma^2\right\}^- \qquad [4]$$

These multivariant relationships indicate the inverse relation between both μ and σ^2 temporal moments and the mass balance (M_r). Therefore, as the mass of metal in the leachate increases, the mean displacement time of the solute increases and the spreading of the distribution of the BTC decreases. These results indicate that Cd transport is convective and is regulated by the sorption parameters F^I, F^{II}, and F^{IV}.

The second component explains 14% of the variance (Table 6) and the sorption F^V variable is related to the first and second temporal moments through the expression (Table 7)

$$\left\{F^V\right\}^- \leftrightarrow \left\{\mu, \sigma^2\right\}^+ \qquad [5]$$

This expression indicates that low values associated with F^V are related to high values of μ and σ^2, which suggest the irreversible character of the sorption processes on F^V. The metals retained though irreversible sorption are not easily displaced from the sorption sites, making the BTCs more compressed and thus decreasing the values of the temporal moments.

The results of the canonical analysis correlation for Pb showed two canonical functions that represent 98% of the variance (Table 8). The first canonical function, which describes 86.6% of the variance, can be interpreted by the correlation between the variables from both groups of parameters and their own first canonical variable (Table 9). Attending to these correlations, the following interparametric expression is suggested:

$$\left\{F^I, F^{II}, F^V\right\}^+ \cup \left\{F^{III}, F^{IV}\right\}^- \leftrightarrow \left\{M_r\right\}^+ \cup \left\{\mu, \sigma^2\right\}^- \qquad [6]$$

Table 7. Correlations between the soil solid fraction from sequential fractionation (F^I, F^{II}, F^{III}, F^{IV}, and F^V) and moments variables of mean travel time (μ), vertical solute spreading (σ²) and mass recovery (M_r) and their canonical variables for Cd.

Fraction or moment variable	Correlation	
	First canonical variable	Second canonical variable
F^I	0.636	−0.138
F^{II}	0.563	0.035
F^{III}	−0.279	0.282
F^{IV}	0.583	0.366
F^V	0.100	−0.904
M_r	0.917	−0.025
μ	−0.393	0.919
σ²	−0.395	0.871

The Pb transport is mainly regulated by the sorption fractions F^I, F^{II}, and F^V, which are related to high values of the metal mass leached (M_r) and transport conditions close to the physical or chemical equilibrium (low μ and σ² values). Opposite to these fractions, F^{III} and F^{IV}, associated with semi-irreversible sorption mechanisms, are related to a lower mass balance (low M_r values), a lower mean displacement time (high μ values), and a higher dispersion level (high σ² values).

Last, it should be mentioned that the expression corresponding to the second canonical function (Table 9) can be represented by

$$\left\{F^{II}\right\}^+ \leftrightarrow \left\{\mu, \sigma^2\right\}^+ \qquad [7]$$

This interparametric relationship indicates the semi-irreversible sorption mechanism of Pb on the organic matter fraction related to a slow mean displacement time and high dispersion levels.

CONCLUSIONS

This study investigated the sorption behavior of Pb and Cd during nonequilibrium transport in undisturbed columns of two acidic soils. We examined the effect of initial conditions including soil (S1 and S2), metal (Pb and Cd), metal initial concentration (C_0), and water flux rate (J_w) on Pb and Cd transport and sorption processes at two depths (0–4 and 4–8 cm). In addition, statistical relationships between both sorption and transport phenomena were examined in detail.

The transport parameters obtained from the BTC's temporal moments analysis indicated that Cd transport is characterized by larger mass recovery values (M_r) and lower estimated values of the transport travel time (μ) and solute spreading with time (σ²) than those observed for Pb. This indicates the higher affinity for Pb to be retained in the soil matrix with respect to Cd and the higher mobility of Cd relative to Pb. In addition, lower metal mass recovery values (M_r) were obtained when the metal transport occurred at low water flow rates.

On the other hand, the initial conditions of soil type and metal species produced significant differences in the mass fractions obtained from the chemical sequential extraction. The initial concentration (C_0) was directly related to the total metal mass retained; however, the effect of C_0 on the sorption fractions was dependent on the metal species, so a sorption pattern cannot be established.

Table 8. Canonical correlation analysis for Pb.

Function	Canonical correlation	Eigenvalue	Difference	Proportion	Cumulative
1	0.762	1.387	1.198	0.866	0.866
2	0.398	0.188	0.162	0.117	0.983
3	0.159	0.026		0.016	1.000

In addition, the results of the statistical study showed a relationship between sorption and transport parameters, indicating that Cd transport was regulated by F^I, F^{II}, and F^{IV}, which are inversely related to M_r and directly related to μ and σ². In the case of Pb, the fractions that regulate transport are F^I, F^{II}, and F^V, which were also directly related to μ and σ² and inversely to M_r. The different experimental approaches in this study, including BTC analysis and sequential extraction performed in combination with statistical analyses, revealed complicated patterns in Pb and Cd reactive transport, indicating physical and chemical nonequilibrium. These results demonstrate that characterization and modeling of Pb and Cd transport in heterogeneous soils require techniques that do not assume physical and chemical equilibrium.

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Table 9. Correlations between the soil solid fraction from sequential fractionation (F^I, F^{II}, F^{III}, F^{IV} and F^V) and moments variables of mean travel time (μ), vertical solute spreading (σ²) and mass recovery (M_r) and their canonical variables for Pb.

Fraction or moment variable	Correlation	
	First canonical variable	Second canonical variable
F^I	0.792	−0.102
F^{II}	0.673	0.632
F^{III}	−0.577	0.010
F^{IV}	−0.739	0.096
F^V	0.734	0.063
M_r	0.982	−0.155
μ	−0.454	0.881
σ²	−0.312	0.947

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