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Applying Freundlich, Langmuir and Temkim Models in Cu and Pb Soil Sorption Experiments

Uso de los modelos de Freundlich, Langmuir y Temkin en experimentos de sorción de Cu y Pb en suelos

Aplicação dos modelos de Freundlich, Langmuir e Temkin em ensaios de sorção de Cu e Pb no solo

AUTHORS

Vega, F.A.[1@]
florav@uvigo.es

Covelo, E.F.[1]

Andrade, M.L.[1]

[@] Corresponding Author

[1] Departamento de Bioloxía Vexetal e Ciencia do Solo. Facultade de Bioloxía. Universidade de Vigo. 36310. Vigo. Spain.

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ABSTRACT

In acid soils, inputs of Cu and Pb of various origins create a high risk of environmental pollution. For this reason, batch experiments on Cu and Pb sorption and desorption in various horizons of three acid soils were performed on soil pH with 0.01 M $NaNO_3$ as background electrolyte. The objectives were to evaluate Cu and Pb sorption and retention capacity through the Langmuir, Freundlich and Temkin equations parameters fitted to the sorption/desorption data; to determine the coherence of the implications of these parameters; and to estimate the role of various soil characteristics in the Cu and Pb immobilization soil capacity. The results confirmed the suitability of the models parameters for studying Cu and Pb sorption and retention by acid soils. The greatest maximum sorption and retention capacities, indicated by the Langmuir parameter β_L, corresponded to the lowest energy values required for fixation, indicated by the Temkin parameter b'. Together with the Freundlich parameter K_F, which indicates sorption and retention capacity, they made it possible to infer that the acid soil component that most influences Cu and Pb immobilization was the organic matter, followed by the Al-oxide content. High organic matter and Al-oxide contents, especially the former, gave rise to a lower energy requirement for the immobilization of metal cations, since they increased the soils' sorption and retention capacities. Al^{3+}, the dominant cation in the exchange complex in the horizons studied, and K^+ are responsible for the influence of CEC_e on Cu and Pb immobilization in the acid soils studied.

RESUMEN

El aporte de Cu y Pb a través de diversas fuentes a suelos ácidos supone un alto riesgo de contaminación medioambiental. Por ello, usando el método batch y con $NaNO_3$ *0,01 M como electrolito de fondo, se llevaron a cabo, al pH del suelo, experimentos de sorción y desorción de ambos elementos en muestras de todos los horizontes de tres suelos ácidos. Los objetivos fueron evaluar la capacidad de sorción y retención de Cu y Pb a través de los parámetros derivados de los ajustes a los modelos de Langmuir, Freundlich y Temkin; determinar la coherencia de las conclusiones deducidas de dichos parámetros, y estimar el papel de las características de todos los horizontes de esos suelos ácidos en la capacidad de fijación de Cu y Pb. Los resultados confirmaron la idoneidad del uso de los parámetros de las ecuaciones de Langmuir, Freundlich y Temkin para estudiar la sorción y retención de Cu y Pb por los suelos ácidos, ya que permitieron deducir que los mayores valores de la máxima capacidad de sorción o retención de ambos metales, deducidos de la* β_L *de Langmuir, se corresponden con los menores valores de la energía requerida para la fijación, indicados por la b' de Temkin. Estos parámetros, junto con la* K_F *derivada de los ajustes a la ecuación de Freundlich indicativa de la capacidad de sorción y retención, permitieron evaluar que las características de los suelos ácidos con mayor influencia en la fijación de Cu y Pb fueron el contenido de materia orgánica, seguido del*

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contenido en óxidos de Al. Altos contenidos de ambos componentes, especialmente de materia orgánica, influyeron en un menor requerimiento de energía para la fijación de cationes metálicos ya que aumentaron la capacidad de sorción y retención de los suelos. El Al^{+3}, catión mayoritario en el complejo de cambio de los horizontes estudiados, y el K^{+} fueron los responsables de la influencia de la CIC_e en la fijación de Cu y Pb en los horizontes de los suelos ácidos objeto de este trabajo.

RESUMO

Em solos ácidos, as entradas de Cu e Pb de diferentes origens pressupõem um elevado risco de poluição ambiental. Por esta razão, usando a metodologia "batch" e o $NaNO_3$ 0,01 M como electrólito de fundo realizaram-se, no pH do solo, ensaios de sorção e desorção de ambos os elementos em amostras de todos os horizontes de três solos ácidos. Os objectivos foram avaliar a capacidade de sorção e retenção de Cu e Pb através dos parâmetros derivados do ajustamento dos modelos de Langmuir, Freundlich e Temkin; determinar a coerência das conclusões deduzidas a partir desses parâmetros e estimar o papel das várias características do solo na sua capacidade imobilização do Cu e Pb. Os resultados confirmaram a adequação dos parâmetros daqueles modelos para estudos de sorção e retenção de Pb de Cu por solos ácidos. A sorção máxima e a maior capacidade de retenção, indicada pelo parâmetro de Langmuir β_L, correspondeu aos valores mais baixos de energia necessária para fixação, indicados pelo parâmetro Temkin b'. Juntamente com o parâmetro de Freundlich K_F, indicativo da capacidade de sorção e de retenção, foi possível inferir que o componente do solo ácido que mais influenciou a imobilização de Cu e Pb foi a matéria orgânica, seguido do conteúdo em óxidos – Al. O alto teor de matéria orgânica e de óxidos – Al, em particular o primeiro, deram origem a uma menor necessidade de energia para a imobilização de catiões metálicos, uma vez que conduziram a um aumento das capacidades de sorção dos solos. O ião Al^{+3}, catião dominante no complexo de troca nos horizontes estudados, e o ião K^{+} são responsáveis pela influência da CTC na imobilização do Cu e do Pb nos solos ácidos estudados.

KEY WORDS
Acid soils, sorption and desorption capacity, soil characteristics

PALABRAS CLAVE
Suelos ácidos, capacidad de sorción y desorción, características de los suelos

PALAVRAS-CHAVE
Solos ácidos, capacidade de sorção e desorção, características dos solos

1. Introduction

Soils are increasingly burdened with Cu and Pb originating in emissions from industries and motor vehicles, agrochemicals (fertilizers, pesticides, liming agents, manure, slurry and agriculturally applied sewage sludge), wastewaters, and industrial and urban solid wastes. Both Cu and Pb are more soluble in acid than in basic soils; therefore, their mobility and bioavailability in acid soils mainly depend on the ability of solid soil components to capture and immobilize them in different forms. In principle, the extent of these sorption processes, which include both adsorption and complexation (Sparks et al. 1999), depends in turn on factors such as pH, the composition and age of the soil, the metal in question, and competition with other metals (Kerndorf and Schnitzer 1980). However, many authors have found that the predominant factors are not such particular characteristics of the heavy metal in question, as there are other influential soil properties such as organic matter content, Al, Fe and Mn oxide contents, calcium carbonate content, cation exchange capacity and, of course, pH (Gomes et al. 2001; Vega et al. 2006; Covelo et al. 2007b).

In a number of studies, pH has been the best predictor of heavy metal ion mobility (García-Miragaya and Page 1978; Ram and Verloo 1985; Elliott et al. 1986; Basta and Tabatabai 1992): in general, heavy metal sorption is only slight in acid soils, increasing with soil pH (Semu et al. 1987; Barrow and Cox 1992; Temminghoff et al. 1994 and 1995; Covelo et al. 2007b), and has been reported to be practically total at pH > 6 (Farrah and Pickering 1979). Other studies have found that the main determining factors of the capacity of soils to retain heavy metals are the quantity and nature of their organic matter (Lair et al. 2007). Finally, a major contribution to heavy metal retention is often made by Al, Fe and Mn oxyhydroxides; these substances possess surface hydroxyl groups that can exchange hydrogen ions for heavy metal cations (Covelo et al. 2007a); accordingly, like organic matter, they tend to sorb more heavy metal as the pH rises (Tessier et al. 1989; Kooner 1993). Thus, the effect of pH is partially explained by the pK_as of acidic groups on soil oxyhydroxides and organic matter. Nonetheless, an additional contribution to this effect derives from the hydrolysis of metals at high pH, which facilitates their complexation by other dissolved species to form insoluble hydroxycomplexes (Farrah and Pickering 1979; Elliott et al. 1986; Basta and Tabatabai 1992). Conversely, at a low pH, hydrated oxides may dissolve (Elliott et al. 1986).

Much of our imperfect understanding of the fixation of heavy metal ions by soils originates from studies of their interaction with relatively homogeneous soil components such as clay minerals, humic substances or Fe, Al or Mn oxides (Covelo et al. 2007a) or with whole soils from which organic matter, etc., have been removed with appropriate extractants (Bibak 1997; Yuan and Lavkulich 1997; Vega et al. 2007). These studies have shown, for example, that both Al hydroxides and humic substances sorb more Cu than Pb (Schnitzer 1969; Hsu 1989; Covelo et al. 2008). However, we are far from being able to accurately predict a given soil sorption capacity for a given ion based on the knowledge we have of the soil's components, especially if the ion in question is competing with others for binding sites. Experimental measurements are still essential.

Cu and Pb sorption and desorption by eight soil horizons from three soils (two Humic Umbrisols and an Umbric Cambisol) were investigated. They are the most common soil types found in Galicia (NW Spain). The experimental data were compared with Langmuir, Freundlich and Temkin models, since well-fitting isotherm models shed light on the nature of sorption processes (Abusafa and Yücel 2002). The capacity and strength of metal sorption and retention were examined by the fitted equations parameters, as well as their mutual coherence. The influence of soil properties on Cu and Pb sorption and retention capacities was also studied.

2. Material and Methods

Soils and sampling

The three soils studied were two Humic Umbrisols (HU1 with 4 horizons: HU1.A, HU1.AB, HU1.Bt and HU1.Bw and HU2 with 2 horizons: HU2.A and HU2.Bw) and one Umbric Cambisol (UC with 2 horizons: UC.A and UC.Bw). Samples were collected using an Eijkelkamp model A sampler and were transported in polyethylene bags to the laboratory where they were air dried, passed through a 2 mm mesh sieve, pooled, and homogenized in a Fritsch Laborette 27 vibratory solid sample homogenizer. Three subsamples of the homogenized sample were used for the soil analyses and three for the sorption/desorption experiments. All experiments were performed in triplicate.

Soil analyses

Soil pH was determined with a pH electrode in 2:1 water:soil suspensions (Guitián and Carballas 1976). Particle size distribution was determined following oxidation of organic matter with hydrogen peroxide, separating the coarse fraction (down to 50 µm) by sieving and the finer material by the pipette method (Day 1965). Organic carbon was quantified by the method of Walkley and Black (1934). Exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) were extracted with 0.2 M ammonium chloride buffered at soil pH (Reeve and Sumner 1971; Sumner and Miller 1996; Rodríguez and Rodríguez 2002), and their concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-OES). Exchangeable acidity was determined using a 1 M KCl replacing solution and titration to a phenolphthalein endpoint (Thomas 1982). Oxides were determined by the method of Mehra and Jackson (1960): samples were shaken in a solution of sodium hydrogen carbonate and sodium citrate, and Fe, Al and Mn were determined in the extract by ICP-OES.

Sorption and desorption experiments

The sorption of Cu^{2+} and Pb^{2+} by each horizon was determined using the method of Alberti et al. (1997) and Gomes et al. (2001) as modified by Harter and Naidu (2001). Soil samples (6 g) were added to 100 mL of "sorption solutions" containing 0.01 M $NaNO_3$ as a background electrolyte and 0.01, 0.03, 0.05, 0.08, 0.10, 0.20, 0.30, 0.40, 0.50, 1.00, 2.00 or 3.00 mmol L^{-1} copper nitrate or lead nitrate. Nitrates were used on account of their solubility in water. The concentrations chosen were such that if the metal contents of the solutions were totally sorbed by the soil samples, the resulting soil metal contents would reach values representative of severe pollution.

The above mixtures were shaken for 24 h at 25ºC in polyethylene centrifuge tubes in a rotary shaker, and then centrifuged at 5000 rpm. The supernatant was filtered through Whatman 42 paper and analyzed by ICP-OES for Cu or Pb, calculating the sorbed metal based on the difference in relation to the initial solution.

The desorption isotherm data were obtained as per Madrid and Díaz-Barrientos (1992). The pellets obtained in the sorption phase of the experiments were dried at 45ºC, weighed, mixed with 100 mL of the background electrolyte solution (0.01 M $NaNO_3$) in polyethylene centrifuge tubes, shaken for 24 h at 25ºC, and centrifuged at 5000 rpm. The supernatant was filtered through Whatman 42 paper and the concentration of Cu or Pb was determined by ICP-OES. The amount of Cu or Pb retained on the soil was calculated by subtracting from sorption results.

Construction of isotherms and model fitting

Sorption isotherms were constructed by plotting the amount of metal sorbed after the 24 h equilibration period (in µmol per gramme of dry soil) against the concentration of metal in solution at equilibrium (in µmol L^{-1}); and desorption isotherms by plotting the amount of sorbed metal retained following desorption (in µmol per gramme of dry soil) against the concentration of metal in solution following desorption (in µmol L^{-1}). Linearized forms of the following models were fitted to the sorption or desorption isotherm data as in Günay et al. (2007):

• The Langmuir equation

The unlinearized Langmuir equation is
$x/m = \beta_L K_L C/(1+K_L C)$
where C is the concentration of metal in solution at equilibrium (µmol L^{-1}), x is the amount of sorbed metal (µmol), m is the mass of sorbent (g), and β_L and K_L are the Langmuir parameters that characterize the sorption process in question.

This equation can be derived under the assumptions that all sorption sites in the sorbent particle bind a single molecule of sorbate, all are identical (particularly as regards binding energy), and all are mutually independent (so that the affinity of any site for the sorbate is independent of the amount of sorbate already sorbed).

The parameter β_L is the maximum sorption capacity (µmol g^{-1}) which under the above assumptions measures the number of sorption sites per gramme of sorbent. The Langmuir constant K_L (L µmol^{-1}) is an equilibrium constant which increases exponentially with the sorption energy.

The assumption that all sorption sites are identical is, of course, strictly untenable for a heterogeneous material such as whole soil. Nevertheless, this does not prevent the Langmuir equation from being used on an empirical basis, taking the necessary caution when interpreting its parameters. A good fit may suggest that the population of all the sorption sites is dominated by just one type. The linearized form fitted in this study was:
$C/(x/m) = 1/(\beta_L K_L) + C/\beta_L$

• The Freundlich equation

The Freundlich equation is the most widely used equation to model sorption from an aqueous solution (Taqvi et al. 2006).
$x/m = K_F C^{1/n}$

It is essentially an empirical power law that can only hold for small C (since sorption cannot increase indefinitely). Nevertheless, from the assumptions that sorption sites are mutually independent but heterogeneous as regards binding energy Q, it can be derived (for small C and small $1/n$), that the occupation of the population of sites with binding energy Q is governed by the Langmuir equation with parameters $\beta_L = 1$ and $K_L(Q) = b_0 \exp(Q/RT)$ (where T is the absolute temperature, R is the universal gas constant, and b_0 is a constant that is the same for all Q), and that the proportion $N(Q)$ of those sites with binding energy Q is given by $N(Q) = (nRT)^{-1} [K_L(Q)/b_0]^{-(1/n)}$ (Silva da Rocha et al. 1997).

Given these assumptions, the adimensional parameter n can be considered to reflect both the average binding energy and the energetic heterogeneity of the sorbent binding sites (specifically, nRT is the mean of the distribution $N(Q)$, and $(nRT)^2$ is its variance).

The Freundlich constant K_F (µmol$^{1-1/n}$ L$^{1/n}$ g^{-1}), which is the value of x/m for $C = 1$, allows a comparison to be made of different sorbent sorption capacities. The linearized Freundlich equation fitted was:
$\log C_s = \log K_F + (\log C)/n$

• The Temkin equation

The Temkin equation is:
$\Theta = (RT/b) \ln(K_T C)$
where Θ is the proportion of occupied sorption sites, and is similar to the Freundlich equation in that it can only hold for small enough C. It predicts that total occupation ($\Theta = 1$) will occur at a finite equilibrium concentration C_{max}.

Like the Langmuir equation, its derivation assumes that all the sorption sites are identical but, unlike the Langmuir equation, it also assumes that, due to the influence of the particles sorbed at neighbouring sites, the sorption energy of each unoccupied site decreases proportionally with the increase in Θ: $Q = Q_0(1–\alpha\Theta$, where α is a constant (Vannice and Joyce 2005). This assumption implies that when all the sites are occupied, the distribution of sorption energies is uniform on

the interval $[(1-\alpha)Q_0,Q_0]$. Additionally, it is assumed that Θ does not approach either zero or unity (more specifically, that $|\ln(\Theta/(1-\Theta))|$ is very small in comparison with $|\alpha Q_0\Theta/RT|$). Given these assumptions, K_T is the sorption equilibrium constant when $\Theta = 0$, and $b = \alpha Q_0$ is the width of the range of sorption energies. The Temkin equation is linearized to
$\Theta = A + B_1 \ln(C)$
where:
$B_1 = RT/b$ and
$A = B_1 \ln K_T$

However, in the present context in which the measured dependent variable is x/m, fitting the equation
$x/m = A' + B_1' \ln(C)$
implies the inclusion of a constant β_T that represent the number of sorption sites per gramme of sorbent:
$B_1' = \beta_T RT/b$, $A' = B_1' \ln K_T$, and $b' = RT/B_1' = b/\beta_T$. Yet the number of sorption sites per gramme of sorbent is what is measured by the Langmuir parameter β_L. β_T may therefore be identified with β_L which makes it possible to calculate the width of the range of sorption energies: $b = \beta_L b'$.

Statistical analyses

The significance of differences among means was estimated by an analysis of variance (ANOVA) followed by least significant difference (LSD) tests, when variances were not seen to be heterogeneous, or by Dunnett's T3 test if they were. The dependence of β_L, K_F and b' on soil properties was investigated for each metal by means of pair-wise Pearson's correlation analyses. All the statistical calculations were performed using SPSS for Windows, version 14.0.

3. Results

Table 1 lists the relevant properties of the horizons studied, and **Figure 1** shows the isotherms of Cu and Pb sorption or desorption on these horizons. In general, for both metals, the sorption curves are smoother than the desorption curves. In any case, most of them are L-type curves exhibiting a tendency to saturation (Giles et al. 1974; Sposito 1984).

All the fits of the model equations to experimental data presented acceptable coefficients of determination R^2, ranging from 0.66 (Temkin equation for copper sorption and retention on HU1.Bw) to 0.986 (Langmuir equation for sorption of copper on HU2.A) (**Tables 2 and 3**). In general, for a given horizon, R^2 increased in the order Temkin < Freundlich < Langmuir for Cu and Pb sorption and retention of Pb, whereas the model equations behaved more erratically in Cu retention data.

Table 1: Characteristics of the horizons studied

Soil	Humic Umbrisol 1				Humic Umbrisol 2		Umbric Cambisol	
Horizon	A	AB	Bt	Bw	A	Bw	A	Bw
pH$_{H2O}$	4.67a	4.93a	4.83a	5.13a	4.77a	4.90a	4.60a	4.73a
OM (g kg^{-1})	39.27c	38.35c	10.51e	3.67f	60.83b	22.74d	92.40a	40.18c
Al oxides (g kg^{-1})	7.66d	12.95b	6.89d	2.37e	17.14a	11.35c	13.07b	12.84b
Fe oxides (g kg^{-1})	3.78g	5.32e	4.36f	2.33h	20.61a	16.64c	13.67e	17.03b
Mn oxides (g kg^{-1})	0.12c	0.31a	0.30b	0.02d	0.13c	0.02d	0.01e	0.01e
CEC$_e$ (cmol kg^{-1})	2.81ab	1.97ab	1.72bcd	1.23cd	1.90bc	0.88d	4.54a	3.14ab
Na$_{exch.}$ (cmol kg^{-1})	0.12c	0.12c	0.10c	0.15b	0.15b	0.15b	0.19a	0.16b
K$_{exch.}$ (cmol kg^{-1})	0.25ab	0.17bc	0.13cd	0.05d	0.16c	0.09d	0.37a	0.24b
Ca$_{exch.}$ (cmol kg^{-1})	0.10a	0.07a	0.06a	0.06a	0.04a	0.04a	0.15a	0.10a
Mg$_{exch.}$ (cmol kg^{-1})	0.07a	0.03ab	0.04ab	0.04ab	0.02b	0.01b	0.09a	0.06a
Al$_{exch.}$ (cmol kg^{-1})	0.70c	0.49d	0.43d	0.28e	0.49d	0.18f	1.17a	0.81b
Sand %	69.65a	61.06b	57.06bc	70.81a	52.94c	62.09b	48.04cd	45.64d
Silt %	18.43c	24.89b	24.54b	17.11c	30.16a	27.08ab	31.42a	23.92b
Clay %	11.92de	14.05d	18.40bc	12.08de	16.90c	10.83e	20.54b	30.44a

OM: organic matter, CEC$_e$: effective cation exchange capacity, exch.: exchangeable. Within each row, values associated with the same letter do not differ significantly at the *p* = 0.05 level.

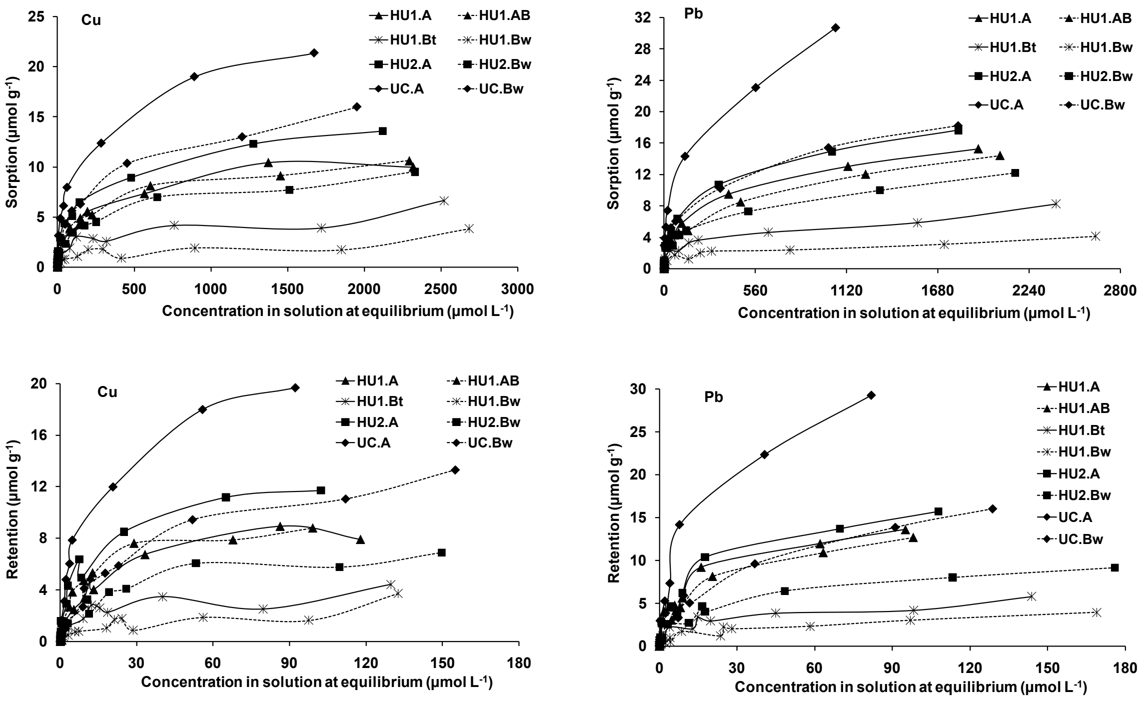

Figure 1. Isotherms for Cu and Pb sorption and desorption in soil horizons.

Table 2: Parameters of the equations fitted to the sorption data with the corresponding coefficients of determination

Soil/Horizon	Cu					
	LANGMUIR		TEMKIN		FREUNDLICH	
	R^2	β_L	R^2	b’	R^2	K_F
HU1.A	0.985	10.41cd	0.897	20.18d	0.919	0.37d
HU1.AB	0.985	10.49c	0.897	22.8cd	0.953	0.52b
HU1.Bt	0.892	5.65e	0.826	38.7b	0.945	0.29e
HU1.Bw	0.740	2.94f	0.664	68.46a	0.886	0.15f
HU2.A	0.986	13.58c	0.905	17.79de	0.912	0.64b
HU2.Bw	0.975	9.28d	0.867	25.57c	0.971	0.39cd
UC.A	0.987	21.49a	0.901	10.69f	0.908	0.75a
UC.Bw	0.977	15.81b	0.883	14.08f	0.945	0.43c
	Pb					
HU1.A	0.981	15.15bc	0.859	17.04b	0.936	0.52c
HU1.AB	0.968	14.33c	0.815	44.23ab	0.916	0.39d
HU1.Bt	0.940	7.58e	0.831	35.28b	0.935	0.28e
HU1.Bw	0.945	3.87f	0.848	62.67a	0.929	0.16f
HU2.A	0.982	17.37b	0.863	15.68b	0.919	0.73b
HU2.Bw	0.971	11.89d	0.833	23.85b	0.918	0.42d
UC.A	0.970	29.71a	0.849	9.07b	0.898	1.15a
UC.Bw	0.978	18.06b	0.843	14.79b	0.890	0.53c

Within each column, of each metal, values associated with the same letter do not differ significantly at the $p = 0.05$ level.

Table 3: Parameters of the equations fitted to the desorption data with the corresponding coefficients of determination

Soil/Horizon	Cu					
	LANGMUIR		TEMKIN		FREUNDLICH	
	R^2	β_L	R^2	b’	R^2	K_F
HU1.A	0.882	9.35c	0.920	17.852dc	0.771	0.839d
HU1.AB	0.986	9.23c	0.968	17.529dc	0.859	1.028c
HU1.Bt	0.878	3.85d	0.843	42.721b	0.900	0.577f
HU1.Bw	0.672	2.96d	0.655	54.142a	0.903	0.247e
HU2.A	0.874	12.97b	0.946	14.149c	0.743	1.410b
HU2.Bw	0.979	7.09c	0.916	23.790c	0.930	0.599e
UC.A	0.749	23.14a	0.958	7.754d	0.806	1.552a
UC.Bw	0.973	14.75b	0.893	12.308c	0.944	0.622e

	Pb					
HU1.A	0.974	14.33c	0.899	14df	0.879	1.32c
HU1.AB	0.975	13.37d	0.832	16.84d	0.924	1.08d
HU1.Bt	0.937	5.45f	0.876	35.91b	0.897	0.51f
HU1.Bw	0.902	4.11g	0.779	52a	0.938	0.26g
HU2.A	0.955	16.53b	0.861	13.34f	0.870	1.48b
HU2.Bw	0.979	9.47e	0.875	22.85c	0.909	0.66e
UC.A	0.949	31.32a	0.815	7.65g	0.905	2.47a
UC.Bw	0.952	16.74b	0.788	14.68df	0.951	1.05d

Within each column, of each metal, values associated with the same letter do not differ significantly at the $p = 0.05$ level.

4. Discussion

According to the parameter $ß_L$ from Langmuir equations (**Tables 2 and 3**), the horizon with the greatest Cu and Pb sorption and retention capacity is UC.A. In keeping with this, UC.A is the horizon with the highest K_F values, i.e. the largest relative sorption and retention capacities when the concentration of metal in solution at equilibrium is 1 µmol L^{-1}. At the other end of the scale, HU1.Bw, followed by HU1.Bt are the horizons with the lowest $ß_L$ and K_F values.

UC.A and HU1.Bw also respectively present the lowest and highest values of the Temkin-related parameter *b'* (except for HU1.AB, which has a higher *b'* value than HU1.Bt for Cu sorption) (Tables 2 and 3). For Cu, the *b* values calculated from the fitted $ß_L$ and *b'* values range from 201 to 242 J mol^{-1} and from 160 to 184 J mol^{-1} when calculated with the data from the sorption and desorption experiments, respectively. The corresponding ranges for Pb are 243-634 J mol^{-1} (243-284 J mol^{-1} if horizon HU1.AB is excluded) and 196-246 J mol^{-1}. These *b* values and the width of the range of sorption energies between zero and total sorption site occupation are very low when compared, for example, with typical sorption energies of the order of several, or several tens, of kJ mol^{-1}. In keeping with the generally good fit of the Langmuir, these narrow energy ranges suggest that in each horizon, sorption fundamentally involves only a single type of sorbent material, although the slightly higher values obtained for Pb suggest that it is somewhat broader than Cu in this respect. That *b* values obtained from the desorption experiment data are lower than those obtained from the sorption experiment data, suggesting that the binding of some of the sorbed metal becomes irreversible, which is in keeping with the concomitant decrease in $ß_L$.

UC.A and HU1.Bw are the horizons with the highest and lowest organic matter contents (Table 1). Indeed, the ratio of the UC.A content to that of HU1.Bw is much greater for organic matter, 25.1, than for any other of the possible sorption-determining factors considered: the next largest ratios are for exchangeable K (7.4), Fe oxides (5.9) and Al oxides (5.5). This suggests that organic matter is the dominant sorption-determining factor, whose existence is suggested by the generally good fit of the Langmuir equation and the results for the Temkin parameter *b'*. To support this hypothesis, Pearson's correlations between soil characteristics and fitted model equations parameters were calculated (**Table 4**, the parameter *b'* was used for the Temkin equation).

Table 4: Pearson correlations between soil characteristics and the parameters of the model equations fitted

	Sorption					
Property	Cu			Pb		
	$ß_L$	$b´$	K_F	$ß_L$	$b’$	K_F
Organic matter	0.935(**)	-0.763(**)	0.946(**)	0.965(**)	-0.587(**)	0.971(**)
Al oxides	0.726(**)	-0.820(**)	0.856(**)	0.683(**)	-0.547(**)	0.637(**)
Fe oxides	0.626(**)	-0.609(**)	0.617(**)	0.534(**)	-0.546(**)	0.557(**)
CEC$_e$	0.827(**)	-0.603(**)	0.622(**)	0.848(**)	-0.479(*)	0.791(**)
Na$_{exch.}$	0.653(**)		0.526(**)	0.624(**)		0.638(**)
K$_{exch.}$	0.880(**)	-0.742(**)	0.723(**)	0.914(**)	-0.556(**)	0.845(**)
Ca$_{exch.}$						
Mg$_{exch.}$	0.497(*)			0.539(**)		0.516(**)
Al$_{exch.}$	0.840(**)	-0.614(**)	0.638(**)	0.855(**)	-0.497(*)	0.799(**)
Sand	-0.761(**)	0.643(**)	-0.663(**)	-0.676(**)	0.480(*)	-0.631(**)
Silt	0.680(**)	-0.638(**)	0.837(**)	0.671(**)	-0.441(*)	0.719(**)
Clay	0.564(**)	-0.426(*)		0.448(*)		

	Retention					
Property	Cu			Pb		
	$ß_L$	$b´$	K_F	$ß_L$	$b’$	K_F
Organic matter	0.951(**)	-0.824(**)	0.926(**)	0.971(**)	-0.821(**)	0.979(**)
Al oxides	0.656(**)	-0.832(**)	0.760(**)	0.621(**)	-0.814(**)	0.615(**)
Fe oxides	0.566(**)	-0.620(**)	0.467(*)	0.474(*)	-0.565(**)	0.407(*)
CEC$_e$	0.860(**)	-0.623(**)	0.595(**)	0.871(**)	-0.633(**)	0.825(**)
Na$_{exch.}$	0.697(**)	-0.428(*)	0.419(*)	0.655(**)		0.539(**)
K$_{exch.}$	0.891(**)	-0.756(**)	0.694(**)	0.917(**)	-0.771(**)	0.897(**)
Ca$_{exch.}$				0.407(*)		
Mg$_{exch.}$	0.558(**)			0.589(**)		0.575(**)
Al$_{exch.}$	0.872(**)	-0.633(**)	0.612(**)	0.877(**)	-0.640(**)	0.835(**)
Sand	-0.724(**)	0.592(**)	-0.516(**)	-0.634(**)	0.554(**)	-0.541(**)
Silt	0.646(**)	-0.598(**)	0.755(**)	0.627(**)	-0.592(**)	0.622(**)
Clay	0.538(**)			0.422(*)		

CEC$_e$: effective cation exchange capacity, exch.: exchangeable. (**): significant at the $p = 0.01$ level, (*): significant at the $p = 0.001$ level.

The results show that organic matter correlates well, and better than any other soil characteristic, with almost all the model parameters (the chief exceptions concerned *b’* for Cu and Pb sorption). Nevertheless, some other soil characteristics (CEC_e, exchangeable K, exchangeable Al, and Al oxides contents) also correlate well with a number of parameters.

In order to estimate the influence of all of the well-correlated soil characteristics indicated above on the energy required for Cu and Pb (b') immobilization, sorption capacity (β_L) and the relative sorption and retention capacities at an equilibrium concentration of 1 μmol L^{-1} (K_F), equations of various kinds were fitted to relate the soil component quantity to the model equation parameters. Graphs of the fitted equations in a non-standardized form are shown in **Figures 2-6**, and the corresponding standardized equations are listed in **Tables 5 and 6**.

Table 5: Standardized equations fitted to the model parameters for Cu sorption and retention as a function of various soil characteristics

Soil property (x)	Parameter (y)	Sorption		Retention	
		R^2	Equation	R^2	Equation
Organic matter	β_L	0.94	$\ln y = \ln x^{0.97}$	0.91	$\ln y = \ln x^{0.95}$
	b'	0.93	$\ln y = \ln x^{-0.96}$	0.91	$\ln y = \ln x^{-0.96}$
	K_F	0.93	$\ln y = \ln x^{0.96}$	0.87	$\ln y = \ln x^{0.93}$
Al oxides	β_L	0.78	$\ln y = \ln x^{0.89}$	0.65	$\ln y = \ln x^{0.81}$
	b'	0.85	$y = -0.92 \ln x$	0.77	$y = -0.88 \ln x$
	K_F	0.87	$\ln y = \ln x^{0.94}$	0.73	$\ln y = \ln x^{0.85}$
CEC_e	β_L	0.68	$y = 0.83x$	0.74	$y = 0.86x$
	b'	0.68	$\ln y = e^{-0.76x}$	0.59	$\ln y = e^{-0.76x}$
Exchangeable Al	β_L	0.71	$y = 0.84x$	0.76	$y = 0.87x$
	b'	0.59	$\ln y = e^{-0.77x}$	0.61	$\ln y = e^{-0.78x}$
Exchangeable K	β_L	0.78	$y = 0.88x$	0.79	$y = 0.89x$
	b'	0.83	$\ln y = \ln x^{-0.91}$	0.77	$\ln y = \ln x^{-0.88}$
	K_F	0.64	$\ln y = \ln x^{0.8}$	0.64	$\ln y = \ln x^{0.8}$

CEC_e: effective cation exchange capacity.

Table 6: Standardized equations fitted to the model parameters for Pb sorption and retention as a function of various soil characteristics

Soil property (x)	Parameter (y)	Sorption		Retention	
		R^2	Equation	R^2	Equation
Organic matter	β_L	0.96	$\ln y = \ln x^{0.98}$	0.93	$\ln y = \ln x^{0.96}$
	b'	0.67	$\ln y = \ln x^{-0.82}$	0.95	$\ln y = \ln x^{-0.97}$
	K_F	0.92	$\ln y = \ln x^{0.96}$	0.93	$\ln y = \ln x^{0.98}$
Al oxides	β_L	0.76	$\ln y = \ln x^{0.87}$	0.63	$\ln y = \ln x^{0.79}$
	b'	<0.6		0.79	$y = -0.89 \ln x$
	K_F	0.66	$\ln y = \ln x^{0.82}$	0.66	$\ln y = \ln x^{0.81}$
CEC_e	β_L	0.72	$y = 0.85x$	0.76	$y = 0.87x$
	b'	<0.6		0.59	$\ln y = e^{-0.77x}$
	K_F	0.63	$y = 0.79x$	0.68	$y = 0.83x$
Exchangeable Al	β_L	0.73	$y = 0.86x$	0.93	$y = 0.88x$
	b'	<0.6		0.61	$\ln y = e^{-0.78x}$
	K_F	0.64	$y = 0.8x$	0.70	$y = 0.84x$
Exchangeable K	β_L	0.84	$y = 0.91x$	0.84	$y = 0.92x$
	b'	0.6	$\ln y = \ln x^{-0.77}$	0.82	$\ln y = \ln x^{-0.91}$
	K_F	0.73	$\ln y = \ln x^{0.85}$	0.84	$\ln y = \ln x^{0.92}$

CEC_e: effective cation exchange capacity.

As noted above, organic matter increases the capacity of soils to retain nutrients and pollutants, including metal ions. Therefore, knowledge of its concentration in the horizons of acid soils provides a reliable explanation (**Figure 2**) and prediction (**Tables 5 and 6**) of the dependent variables in all the horizons ($R^2 > 0.8$ in all cases except b' for Pb retention of Pb for which $R^2 = 0.68$). All the fitted equations are power laws, i.e. the capacity of each horizon to immobilize Cu and Pb increases much more rapidly than its organic matter content. This is mainly due to the energy required for the immobilization of a given amount of metal falling rapidly as organic matter content increases.

The Al oxide contents of the horizons of acid soils also significantly influence Cu and Pb sorption and retention capacity (**Figure 3**). At an acid and neutral pH, significant amounts of humic acids can be adsorbed on positively charged surfaces of soil minerals such as Al oxides and oxyhydroxides, inverting their charge (Davis and Bhatnagar 1995); and organomineral surface coatings strongly sorb heavy metal ions, hindering their progress towards underground waters (Murphy and Zachara 1995; Fein and Delea 1999). The equations explaining the β_L and K_F values as functions of Al oxides content are power laws and, as in the case of organic matter content, the horizons with the highest content are therefore those with the greatest Cu and Pb sorption and retention capacity. However, the accompanying decrease in required energy (**Figure 3**) is less pronounced than for organic matter.

The cation exchange capacity depends on the quantity and type of both its organic and mineral components. However, the fact that the coefficients of determination for the fitted equations are lower for CEC (**Figure 4**) than for organic matter (**Figure 2**) suggests, as does the corresponding comparison of the Pearson's correlation results (see above), that clay in these horizons has a poor sorption capacity or has little influence on Cu and Pb immobilization. Note how the equations for $ß_L$ and K_F vs. CEC are linear, i.e. a given increment in CEC induces the same increase in the sorption and retention capacities, regardless of the absolute CEC value.

In soils, heterovalent cation exchange reactions normally involve the exchange of monovalent and divalent cations, although cations of a higher valency, such as Al^{3+}, are also exchanged (Evangelou and Phillips 2005). In the present study, the likelihood of a significant exchange of Al^{3+} is suggested by both the low pH (since Al^{3+} requires a low pH to remain in solution or in an exchangeable form) and by Al^{3+} being one of the two exchangeable cations – the other is K^+ – that are reasonably well correlated with $ß_L$, K_F and b' (**Table 4**). Additionally the equations fitted to explain Cu and Pb sorption and retention as functions of Al^{3+} and K^+ (**Figures 5 and 6**) show how these are the cations responsible for the influence of CEC_e on Cu and Pb immobilization in the horizons of the acid soils studied. Furthermore, since the exchange complexes of the horizons studied are dominated by Al, generally with K as the second most abundant exchangeable cation (**Table 1**), it is likely that the sorption and desorption experiments involve the establishment of relations of a Cu^{2+}-Al^{3+}-K^+ and Pb^{2+}-Al^{3+}-K^+ type.

In this study, horizon UC.A had the highest organic matter content, the highest CEC_e, and one of the highest Al oxide contents (**Table 1**). All three characteristics will have significantly contributed to its higher capacity for Cu and Pb immobilization as shown by the sorption and desorption isotherms in **Figure 1**, and as summarized in fitted Langmuir, Freundlich and Temkin equation parameters (**Tables 2 and 3**). In contrast, horizon HU1.Bw has the lowest organic matter and Al oxide contents, and one of the lowest CEC_es (**Table 1**); therefore these characteristics contribute to its scant Cu and Pb immobilization capacity (**Figure 1**; **Tables 2 and 3**).

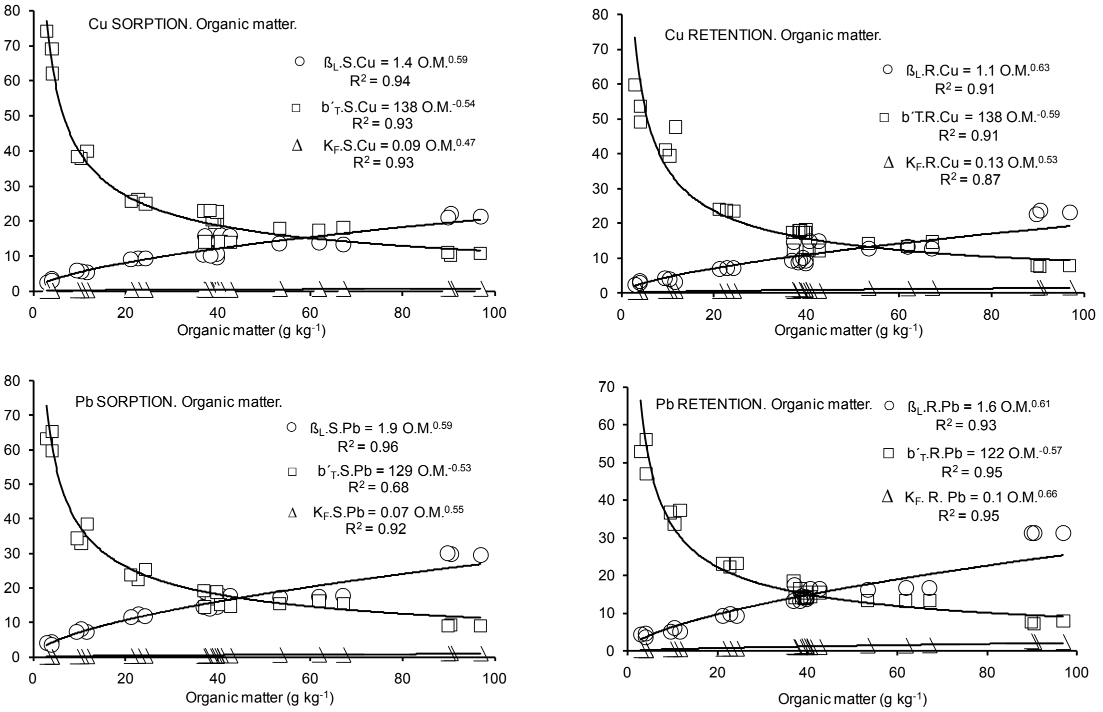

Figure 2. Fitted equations relating organic matter content to the model equation parameters.

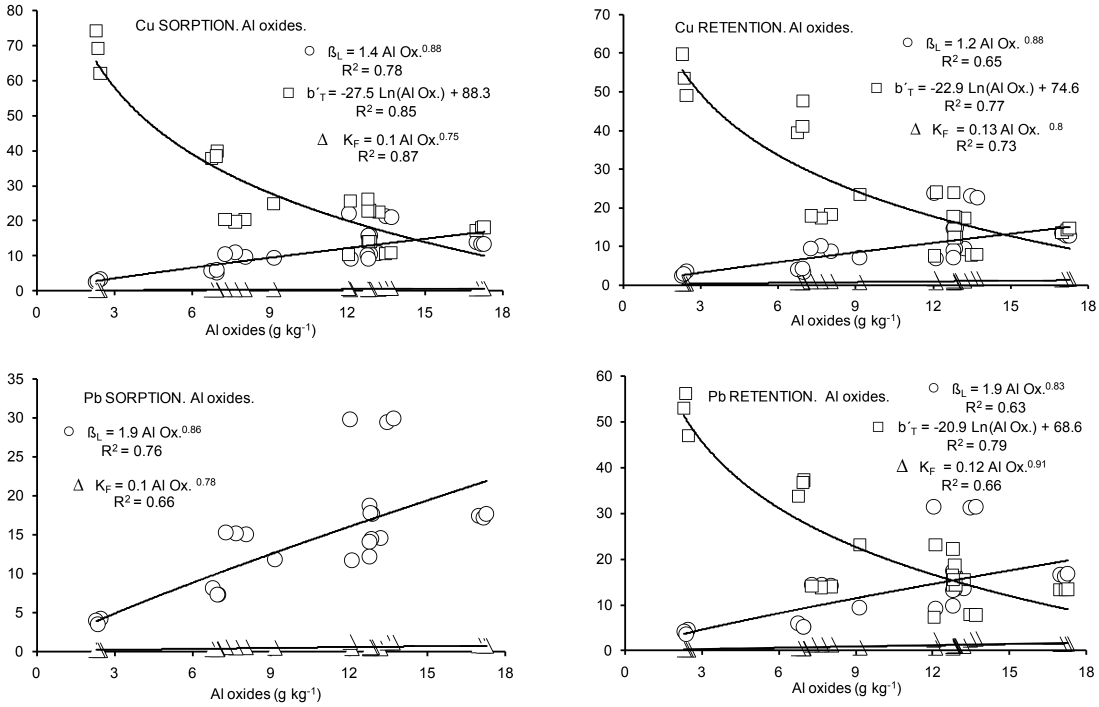

Figure 3. Fitted equations relating Al oxides content to the model equation parameters.

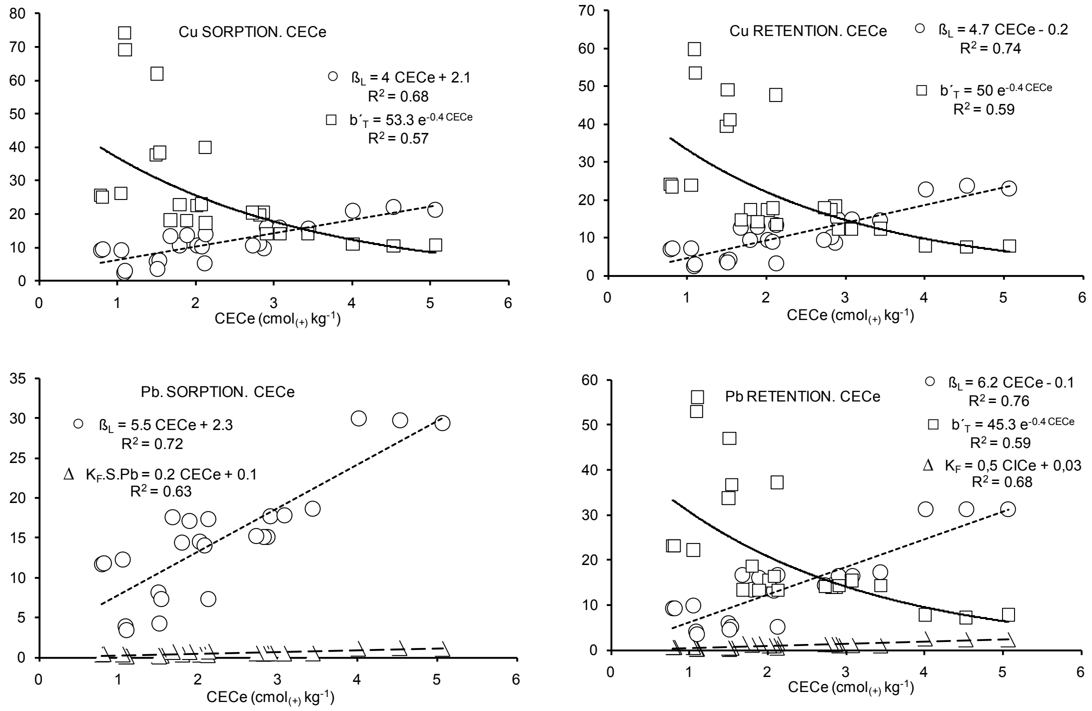

Figure 4. Fitted equations relating CEC_e to the model equation parameters.

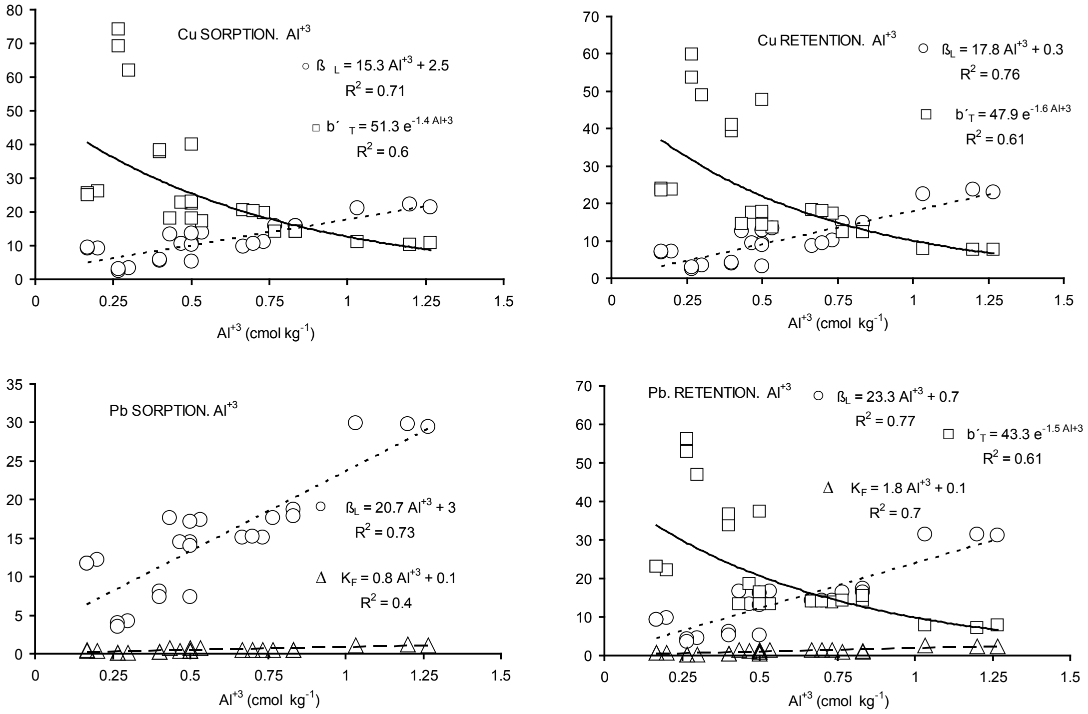

Figure 5. Fitted equations relating exchangeable Al contents to the model equation parameters.

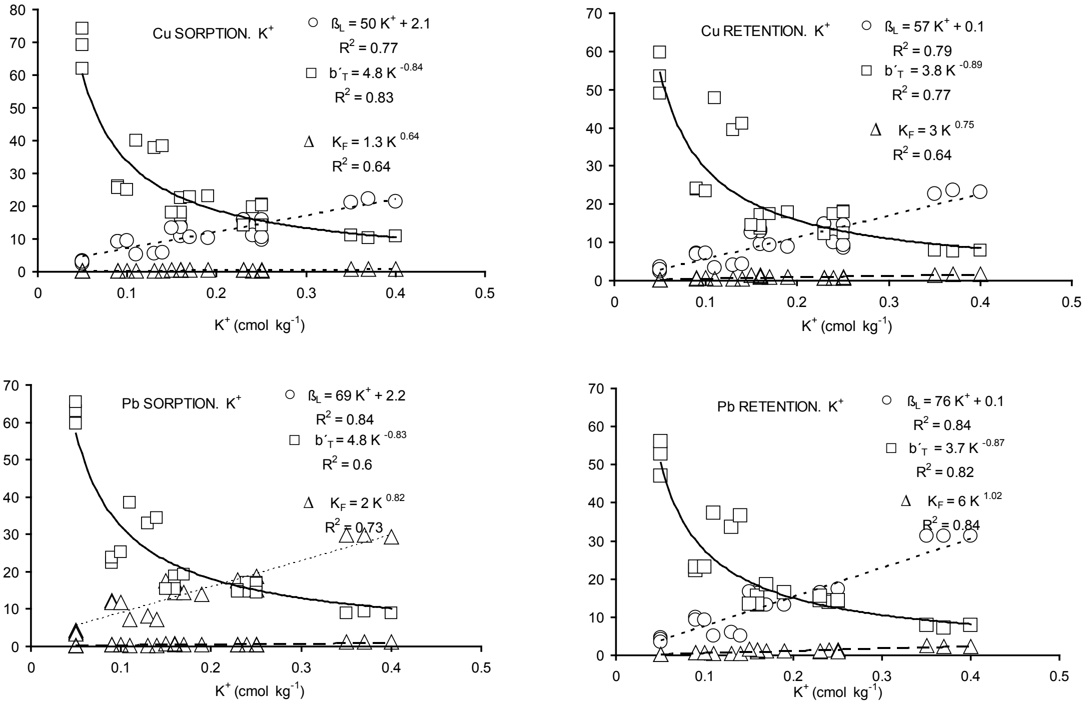

Figure 6. Fitted equations relating exchangeable K contents to the model equation parameters.

5. Conclusions

This study has verified the validity of the Langmuir, Freundlich and Temkin models to analyze Cu and Pb sorption and retention by acid soils. The parameters of the fitted models of these types coherently reflect maximum sorption and retention capacities in relation to the energy required for these processes. These parameters also make it possible to identity the soil characteristics that most influence Cu and Pb immobilization.

The soil component that most strongly determines the capacity of acid soils to immobilize Cu and Pb is organic matter content, followed by Al oxide content. High contents of these components, especially organic matter, contribute to a smaller energy requirement for the immobilization of metal cations, which corresponds to a greater capacity for sorption and retention of Cu and Pb by the soil.

In the horizons studied, the exchange complex is dominated by Al^{3+}, followed by K^+, and these cations are responsible for the linear relationship between CEC_e and the immobilization of Cu and Pb in the horizons of the acid soils studied.

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