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Pb and Cd Complexation with Soluble Organic Carbon and Speciation in Alkaline Soil Leachates

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Abstract

The total concentrations of metals and ligands including dissolved organic carbon were measured in alkaline soil leachates to determine the speciation of Pb and Cd in solution. The stabilities of the Cd and Pb complexes formed by soluble organic carbon were described in terms of pH-dependent stability constants, using the soil fulvic acid fraction as a surrogate, and potentiometric titration data as a function of pH in the absence and presence of metal cations. The species HA (where A stands for the organic ligand), CdA, PbA and PbOHA and their corresponding equilibrium constants were thus determined. To solve the total metallic concentrations of the leachates in the different chemical species, these reactions and their equilibrium constants were introduced in the equilibrium modelling program SOILCHEM, which was consequently slighly modified. The results show that organic complexation can be effective in alkaline leachates for both trace metals - up to 50% of total Pb and 15% of total Cd. Carbonate is the main inorganic ligand, particularly for Pb, for which the free species remain very low (<1%). On the contrary, Cd is still distributed between the free and carbonate species. In these systems, Ca appears as the main competing cation for the reactive sites of the organic matter. The findings are discussed in terms of validity of the input data and of the constants used in the data base.

Introduction

The presence of heavy metals in soils poses the problem of pollution for crops, waters and human health. This pollution is associated with heavy metal

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mobility and bioavailability, which in turn depend on many physicochemical conditions in soils. When a metal cation is introduced into a soil, it is distributed between the solid and liquid phases, depending on the affinity of the constituents. The soil solution is the compartment through which the heavy metals move, either to plants or to water reservoirs, and is where many reactions such as acid-base and complex formation occur (Mattigod *et al.*, 1981, Bruemmer *et al.*, 1986). A knowledge of the speciation of heavy metals in the soil solution is essential for the evaluation and prediction of risks. Unfortunately, this speciation is not easy to establish experimentally in natural soil solutions. The use of computer programs can be an interesting alternative approach, by calculating the concentrations of all metal species based on a knowledge of organic and inorganic ligands present in a soil solution (Nordstrom and Ball, 1984). These computer programs use thermodynamic constants to determine the distribution of a compound among its different chemical species, provided that all the constants are properly expressed and determined. They suffer, however, from the lack of characterization of important natural complexing agents such as fulvic acids, ie polyfunctional soluble organic matter. Consequently, the database for soluble organic carbon is often restrictive. For example, when using the computer program SOILCHEM (Sposito and Coves, 1988), metallic binding data for fulvate ligands are strictly valid only at pH 5, because they result from experiments performed at fixed pH by incremental
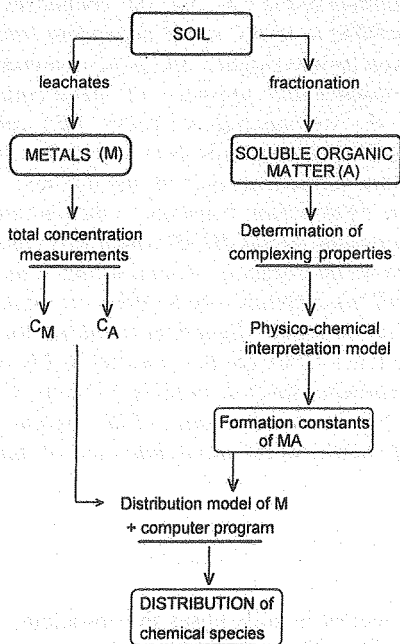

Figure 1 *Step diagram for determining the speciation of Cd and Pb in the soil leachates.*

additions of metal cations to a solution of fulvic acids (Sposito *et al.* 1981 and 1982).

The aim of this work was to determine the speciation of lead and cadmium cations in alkaline soil leachates recovered from a polluted soil. For this we adopted the approach shown in Figure 1. This included measurements of total concentrations of metals and ligands in the soil leachates, and the use of the program SOILCHEM in which the complexation data on soluble organic matter was adapted to our particular conditions. In the SOILCHEM database, the fulvate ligands are treated as in the classical Scatchard model (Sposito, 1986), ie they react only with metal ions, not protons. There is the possibility, however, of introducing another physicochemical interpretation model which includes reactions with protons. Hence, potentiometric measurements were used to determine the complexing properties of soluble organic carbon as a function of pH, using extracted fulvic acids as surrogates and a simple continuum affinity interpretation model of the data. The resulting parameters were introduced within the equilibrium speciation program.

Materials and Methods

Soil column and leachates

The soil originates from the North of France, in areas polluted by heavy metals from non-ferrous metallurgic activities. It is located in a damp zone, and contains significant amounts of carbonate (8 g kg^{-1}), clay (20%) and organic matter (18.3 g kg^{-1}); total Cd and Pb concentrations are 19.7 and 1180 mg kg^{-1}, respectively. A column (0.2 x 0.2 x 0.25 m^3) was cut up in the upper layer of this polluted soil, and was wrapped in a synthetic resin *in situ*. Then the column was put on sand bed in the laboratory, 200 mL aliquots of water with an admixture of very dilute sulphuric acid were slowly poured into the column from the surface, and all draining solutions - the leachates - were collected at the bottom. After filtration at 0.45 mm, the pH was recorded and the solutions kept at 4^oC for further analyses. Major and trace cations were analysed by flame or flameless atomic absorption spectrometry (Perkin Elmer HGA 700), and inorganic anions were analysed by ionic chromatography (Watters 410, ILC-2, Millipore). Organic and inorganic soluble carbon were measured with a Dorhmann DC 190 analyser (Rosemount Analytical, Inc. Santa Clara, California).

Extraction of fulvic acids

Most of the organic carbon measured in percolating solutions was viewed as due to the presence of fulvic acids. To measure the complexation parameters of this fraction, fulvic acids were obtained by extraction of the <2 mm fraction of the soil with 0.5 M NaOH, followed by precipitation of the humic fraction with HCl. After dialysis against deionized water, and concentration on a rotary evaporator at about 35^oC, the final product was treated with H^+ exchange resin (Amberlite IRN77). Stock solutions of fulvic acids, stored at 4^oC, had a pH of 3 and an organic carbon content of 176 mg L^{-1}.

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Potentiometric measurements

Potentiometric titrations were performed at a constant ionic strength of 0.1 M $NaClO_4$ under nitrogen. Solution temperatures were maintained at 25°C using a thermostated water cell. Aliquots of stock fulvic acids were titrated with 0.1 M NaOH in the presence of a known amount of $HClO_4$, and in the absence or presence of different concentrations of $Cd(ClO_4)_2$ or $Pb(ClO_4)_2$. The pH was monitored with a Metrohm model 60102100 glass electrode and a Tacussel model XR110 calomel reference electrode including a salt bridge filled with 0.1 M $NaClO_4$, connected to a Tacussel TT processor automatic titrator (Radiometer, Copenhagen). The electrodes were calibrated with freshly prepared standard buffer solutions, and by titration of a known concentration of strong acid with strong base in 0.1 M $NaClO_4$. It was thus possible to assess the results as pH = $-\log[H^+]$ where brackets denote concentrations. In the presence of metal cations, the concentration of free cadmium or lead in solution was determined using a cadmium-selective electrode (Tacussel XS300) or a lead-selective electrode (Tacussel XS310), which were calibrated with freshly prepared metallic buffers and with blank titrations without soluble organic matter at the same ionic strength.

Calculations

A physicochemical model was needed to interpret the potentiometric data. First, the acid-base characteristics of the fulvic acids were determined from the titration curves without metal cations. The ligand concentration was determined after linearization of the titration curves of the blank ($HClO_4$ alone) and of $HClO_4$ plus fulvic acids by using the Gran functions (Lamy *et al.*, 1988). The comparison of the two curves gives the beginning and end of reactive site titration, which allows a definition of the ligand concentration, C_A, in terms of total titratable reactive sites, assuming a continuum of monodentate sites. The total concentrations of proton C_H and ligand C_A can then be expressed at each point of the titration curves, taking into account the dilutions, by:

$$C_H = C_A - C_B + E = [HA] + h - oh \qquad (1)$$

$$C_A = [HA] + a \qquad (2)$$

where h and oh are the concentrations of free proton and hydroxyl known after the potentiometric measurements respectively, E is the concentration of strong acid initially added, C_B is the concentration of added strong base, a is the concentration of free ligand sites and [HA] is the concentration of protonated sites. From the previous equations, the dissociation of all sites can be described by one degree of dissociation, α_A, and the continuous variation of the conditional dissociation constant, K_A, can be calculated versus pH:

$$\alpha A = a / C_A = (C_B - E + h - oh) / C_A \qquad (3)$$

$$K_A = h.a/[HA] = \alpha_A.h /(1 - \alpha_A) \qquad (4)$$

For the interpretation of the titration curves in the presence of metal cation, M, it is possible to assume 1:1 complex formation, and to take the first hydrolysis of the cation into account, The following mass balance equations can be written:

$$C_H = C_A - C_B + E = [HA] + h - oh - [MOH] \qquad (5)$$

$$C_A = [HA] + a + [MA] \qquad (6)$$

$$C_M = m + [MA] + [MOH] \qquad (7)$$

where C_M is the total concentration of metallic cation, m is the concentration of free metallic cation, [MOH] is the concentration of hydrolysed cation and [MA] is the concentration of cation bound to the ligand.

If we assume the same dissociation of the fulvic acids in the absence or presence of M, ie that K_A is only dependent on pH, and taking the correction for the formation of MOH from the literature (Baes and Mesmer, 1986), it is possible to calculate [MA] from equations (4), (5) and (6). This can be compared with (C_M - m), ie the concentration of bound cation, by using equation (7) and the data obtained with the metal ion selective electrodes, which validates or invalidates the hypothesis. The results for Cd were reasonably described by this simple model and thus a unique stability constant for Cd-fulvate complexes was defined, whereas still depending on pH :

$$K_{MA} = [MA] / m . a \qquad (8)$$

The results for Pb led us to try several hypotheses for the formation of more general Pb-fulvate complexes M_nH_pA (n=1, 2; p = +/- 1) (Buffle, 1980; Sposito and Blaser, 1992). We finally supposed formation of the two complexes MA and MAOH. The mass balanced equations become:

$$C_H = C_A - C_B + E = [HA] + h - oh - [MOH] - [MAOH] \qquad (9)$$

$$C_A = [HA] + a + [MA] + [MAOH] \qquad (10)$$

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$$C_M = m + [MA] + [MOH] + [MAOH] \tag{11}$$

From all of the titration curves obtained with the glass and lead selective electrodes, it was possible to solve these equations with the unknowns a, [HA], [MA], and [MAOH]. Thus, binding of Pb by the fulvic acids could be represented by:

$$K_{MA} = [MA] / m \cdot a \tag{12}$$

$$K_{MAOH} = [MAOH] \cdot h / m \cdot a \tag{13}$$

where the two conditional constants were experimentally determined versus pH.

Speciation in the soil leachates

The chemical speciation of aqueous solutions by SOILCHEM can be obtained by inputting the total concentrations of eg calcium, cadmium, carbonate, sulphate etc and pH. Preliminary trials have shown that ionic strengths calculated by the program were always about 0.01 M, and that several compounds can be omitted, either because they are in low concentrations (eg Fe), or they have no significant effect on the speciation of other elements. All the stability constants contained in the SOILCHEM database for the inorganic complexes were not questioned, the main difficulty remaining being the interpretation of the presence of organic carbon and possible organic complexes. Hence, the previously determined values of acid-base and binding characteristics of the fulvic acids were introduced in the database. In fact , compounds that mimic the fulvic acids - FUL and complexes such as MFUL - are already in the database, but the complexes HFUL, CdFUL, PbFUL and PbOHFUL corresponding to our previously determined data were also introduced, together with their stability constants relevant to the pH and the ionic strength of the leachates. The total concentrations of the fulvate ligands to be input were also consistent with previous potentiometric determinations, taking into account the ratio of the concentrations of soluble organic carbon in the leachates and in the fulvic acid solutions .

Results

Lead and cadmium binding characteristics of the fulvic acid fraction

The dissociation coefficient of the functional reactive sites calculated according to equation (3) for the titration of the soil fulvic fraction in the absence of metal cations is shown in Figure 2. The total number of protons titrated between pH 3 and 11 is 2.08 mmol L^{-1}, ie 11.80 mmol per gramme of organic carbon. This value

is comparable, in the lower range, to the total acidity of soil fulvic acids generally encountered (Buffle, 1988a), assuming that the fulvic acid fraction is 50% organic carbon for comparison. Only one inflexion point at about pH 7 was detectable on the original (pH, V) titration curves, which allowed the total titratable sites to partition between about 30% of carboxyl-type groups (dissociation across pH 3-7), and 70% of phenolic-type groups (dissociation above pH 7), (Perdue, 1985). The absence of any clearly defined intermediate plateaus is typical of potentiometric titration results obtained with fulvic acids (Brady and Pagenkopf, 1978; Stevenson, 1982). This justifies not converting the inflexion point to the equivalence point for the titration of a particular functional group, and supports the idea that a continuum of reactive sites are titrated until pH 11. In the presence of metal cations, an apparent dissociation coefficient for the whole type of sites?, α_M, can be first calculated from the corresponding pH-metric data via equation (3), without making any assumptions concerning the complexed species (even hydroxylated ones):

$$\alpha_M = (C_B - E + h - oh) / C_A \tag{14}$$
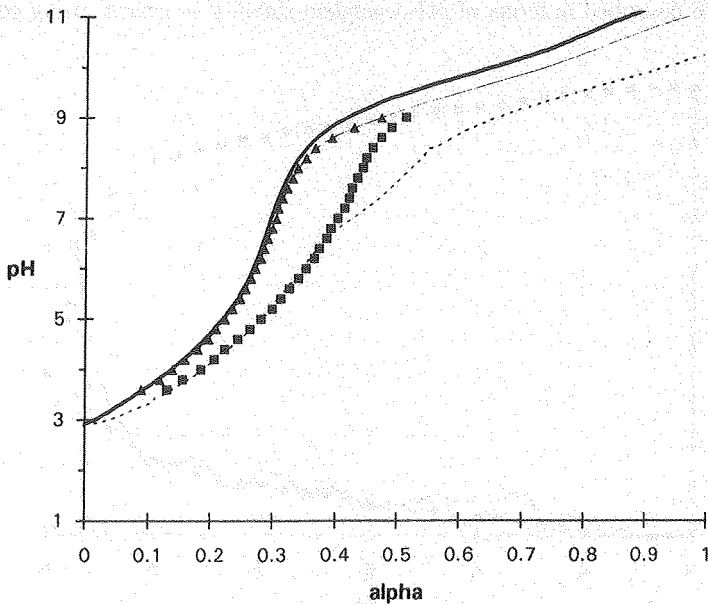
Figure 2 *Degree of dissociation α as a function of pH, for the fulvic acid fraction alone (━━) and in the presence of Cd (━) and Pb (- - -), calculated according to equations (3) or (14). The symbols ▲ (Cd) and ■ (Pb) are the values calculated using the model. Conditions are $C_{Cd} = 99.1$ μM, $CPb = 176$ μM ; and $C_M / C_A = 0.85$ for Cd and 2.0 for Pb (in mmol g^{-1} of organic carbon).*

The complexation of Pb or Cd is clearly seen in Figure 2 by the higher dissociation of the reactive sites at a given pH, indicating a competition between H^+ and the metal cation for the functional groups. In the case of Pb, however, the second inflexion point at above pH 7 must be related to the hydrolysis of lead, either free or bound to the organic ligand, and not to the further dissociation of sites. The curves in Figure 2 indicate appreciable formation of Cd-organic complexes, though less than with Pb, which is in agreement with general findings.

Several methods of calculating formation constants for metal-soluble organic carbon have been developed, all of which are biased (Fitch and Stevenson, 1984; Sposito, 1986; Turner *et al.*, 1986; Buffle *et al.*, 1990). In all of the approaches, however, metal-binding data vary with recovery ratio and, more generally, with pH (Giesy *et al.*, 1986; Buffle, 1988b). For practical considerations, a discrete holistic model of metal complexation was used in this study, to take advantage of the pH-titration curves of fulvic acids in the presence of metal cations. Because no discrimination between different type of sites can be made *a priori*, and in view of the complex nature of the operational defined fulvic acid fraction, the titration data were directly interpreted using the values deduced from the glass and ion-selective electrodes. The stabilities of the trace metal complexes formed with soluble organic carbon were described in terms of pH-dependent stability constants using equation
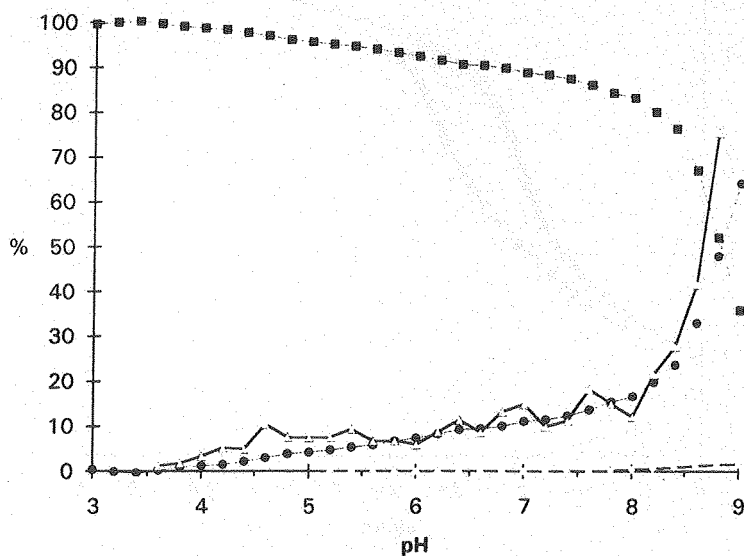

Figure 3 *Speciation diagram for the fulvic acid - Cd system: % of the different species as a function of pH. Closed symbols are for experimental values from the Cd specific electrode (▇ = free Cd in solution, ● = bound Cd = C_M - m); open symbols are for the calculated complex species: (▵ = CdA and ⬧ = CdOH).*

(8) for the Cd species (CdA) and equations (12) and (13) for the Pb species (PbA and PbOHA). These different complexes were sufficient to explain the experimental data and their concentrations as a function of pH are plotted in Figure 3 for Cd, and Figure 4 for Pb. The sums of the concentrations of these complexes correspond to the experimental values (C_M - m). This cannot be considered as a proof of their existence, but this method enables the elimination of other hypotheses that gave inconsistent results (eg negative concentrations if formation of MA_2 species is involved). It also allows binding parameters at high pH values to be introduced in the geochemical model program SOILCHEM. The parameters determined (Table 1) cannot be strictly compared with literature data, because the values are model-dependent. The formation constants of Pb-fulvate complexes increase much more significantly with pH, by a factor of more than one log unit per unit pH, than do those of Cd complexes (Buffle, 1988b; Bizri *et al.*, 1984; Baron *et al.*, 1990).

Composition of soil leachates
Six sets of values of parameters representing the evolution of the chemical composition of the leachates with time were selected (Table 2). Each set represents averages values over one month, except for the first two, when the evolution of the leachates was faster. Chemical analyses given in Table 2 indicate that an inorganic cation-anion balance was nearly achieved, despite the fact that only mean values for long periods were retained for calculations.
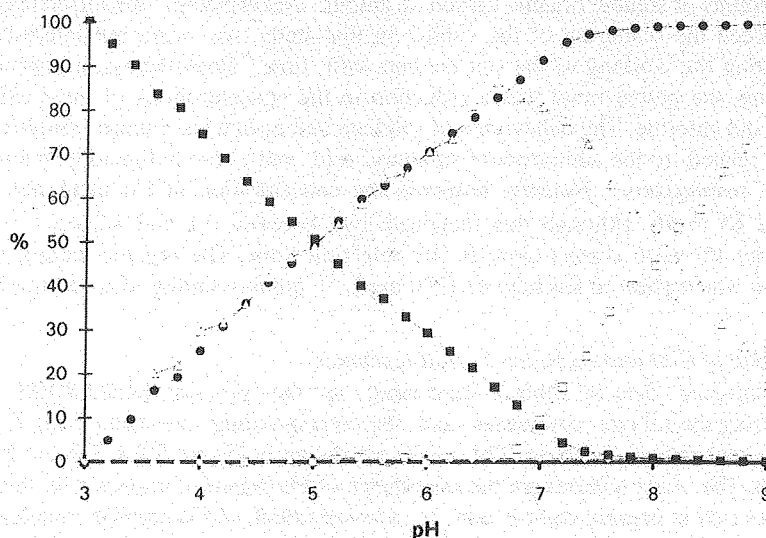

Figure 4 *Speciation diagram for the fulvic acid-Pb system: % of the different species as a function of pH. Closed symbols are for experimental values from the Pb-specific electrode (▨ , free Pb in solution, ●, bound Pb = C_M - m); open symbols are for the calculated complex species: (△, PbA; ▫, PbOHA; and ◇, PbOH).*
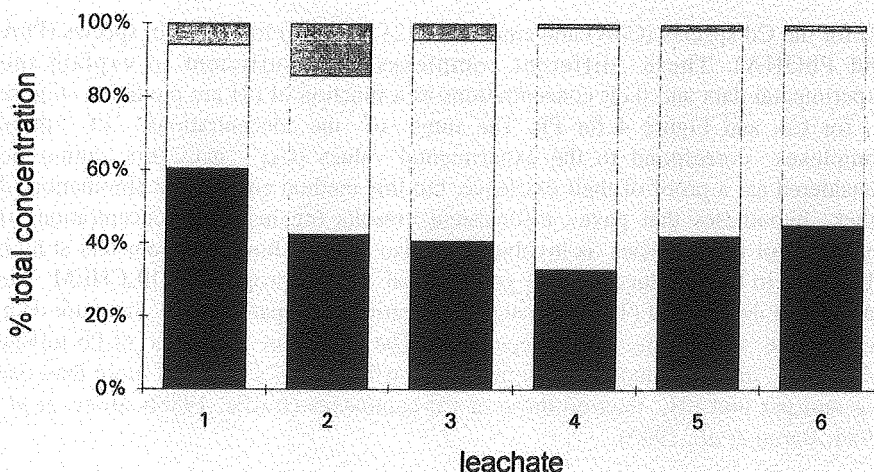
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Figure 5 *Calculated speciation of Cd in soil leachates: % of total Cd concentration. (Black = free cation; white = inorganic complexes; and grey = fulvate complexes.)*

For the first leachates, the differences can be accounted for by the presence of high amounts of soluble organic carbon, ie anions. Nevertheless, the differences do not exceed the scattering of the values. In this study, we were not interested in interpreting the working of the soil column with time. Nevertheless, except at the beginning, the global trend was a reduction in the concentrations of most cations, carbon and chloride. The behaviours of sulphate and nitrate were more complex, and can be related to the admixture of sulphuric acid and to the indigenous microbial activity, respectively. Notably, however, the concentration of Cd increased from leachate #3 to #6, although this remained low, between 0.1 and 1.2 μg L^{-1}. The values for Pb were always close to the detection limit. The organic carbon concentration was highest in leachate #2 (290 mg L^{-1}), quickly falling to *ca* 30 mg L^{-1} .

Speciation of lead and cadmium in soil leachates
The analytical data in Table 2 were input in the program SOILCHEM after introducing the fulvate complexes and the corresponding constants from Table 1 in the geochemical database. The results are shown in Figure 5 for Cd and Figure 6 for Pb. The main features are the importance of Pb-organic complexes in the first leachates rich in organic carbon and, to a lesser extent, of Cd-organic complexes in the same solutions. The main difference between the two trace elements, however, appeared in the ratio of free species:inorganic complexes, which is very low for Pb. The inorganic complexes are dominated by $PbCO_3$ or $CdCO_3$ and $CdHCO_3^+$. Calcium is always present as Ca^{2+}, but Ca-fulvate species are also important in leachates #1 to 3; up to 50% of total Ca is predicted to occur as fulvate
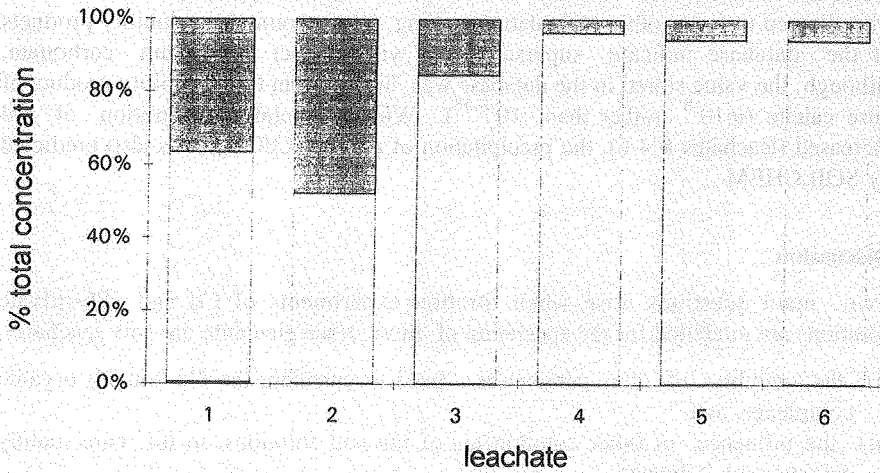
Figure 6 *Calculated speciation of Pb in soil leachates: % of total Pb concentration. (Black = free cation; white = inorganic complexes; and grey = fulvate complexes.)*

Table 1 *Values of the stability constants of the species CdA, pBA and PbOHA as a function of pH (A stands for the soluble organic C of the fulvic fraction of the soil), with the corresponding value of proton dissociation constant (pK_A).*

		Cd	Pb	
pH	pK_A	$log([MA]/m*a)$	$log([MA]/m*a)$	$log([MaOH]*h/m*a)$
5.0	5.56	2.20	3.69	–
5.5	5.90	2.25	3.86	–
6.0	6.45	2.35	4.02	–
6.5	6.85	2.42	4.25	–
7.0	7.38	2.50	4.57	−3.35
7.5	7.80	2.60	5.16	−2.70
8.0	8.30	2.65	5.33	−2.75
8.5	8.80	2.95	5.42	−2.85

complexes for leachate #2, while there is less than 7% in leachates #4 to 6. The other complexes occur with carbonate and sulphate, but are always under 10%.

It should be noted that the fulvate ligand seems to be mainly occupied by Ca and H; the free ligand represents only 9-12% of its total concentration.

While these results were obtained in accordance with the hypothesis that no solid was allowed to form, other calculations taking into account the solubility products of the database indicate supersaturation with respect to calcium carbonate, although the value stored in the database was higher than the solubility product of pure calcite (ie 10^{-8} rather than $10^{-8.48}$). When the total concentration of Cd increased (leachates # 4-6), the precipitation of otavite ($CdCO_3$) was also predicted by SOILCHEM.

Discussion

Two main questions arise when titration experiments of Cd and Pb-fulvate solutions are modelled for the speciation of these trace elements in soil leachates,

(i) the validity of the parameters used to calculate the Cd and Pb organic complexes; and

(ii) the influence of other components of the soil solutions, in this case mainly calcium and carbonate.

(i) The main difference between the conventional use of SOILCHEM and the way that it was used in this study is that here the fulvate compounds were considered in terms of the usual MA complexes, and also as HA and PbOHA complexes, which means involving the proton. We chose the stability constants and the concentration of the fulvate ligands according to data was obtained by potentiometry, taking into account the conditions of the soil solutions: pH and content in organic carbon, which was similar in fulvic acid solutions and leachates. Thus, calculations with SOILCHEM give results that are consistent with the previous potentiometric experiments except for the large difference between the metal concentrations in leachates and in solutions previously studied. The detection limit of the ion-selective electrodes account for this difference in ranges. At constant pH, a reduction in the metal:ligand ratio generally increases the strength of organic complexes, because then, the strongest sites are supposed to be involved (Stevenson and Chen 1991). Thus, the results of our calculations could underestimate the importance of trace metal-organic complexes.

(ii) The speciation of Ca is important because it is the major cation competing with Cd or Pb for fulvate ligands. The percentage of Ca-organic complexes was calculated with the same concentration of fulvate ligand as for Cd and Pb, but with the constant stored in the SOILCHEM database, which was supposed to be valid only at pH 5. Few data are available on Ca complexation by the fulvate ligand at different pHs. But Dempsey and O'Melia (1983) did not find a dramatic increase in the formation of Ca-fulvate complexes versus pH. Indeed, they proposed smaller formation constants than those used in our calculations, with similar values for the concentrations of ligand sites. But they did not consider the competition between Ca and H, which is effective in our application since only about 10% of the ligand remained free.

Table 2 Evolution of leachate composition with time (average values for 1-month periods, except #1: 2 first days).

| | | | | | $\mu mol\ l^{-1}$ | | | | | $\mu mol\ l^{-1}$ | | $meq\ l^{-1}$ | |
	pH	Fulvate(*)	Carbotate+	Nitrate	Chloride	Sulphate	Ca	Mg	K	Cd	Pb	Anions	Cations(°)
1	7.72	1.52	4.66	1.24	0.60	0.51	3.44	0.30	0.41	0.0044	0.048	7.52	7.89
2	8.08	3.45	6.19	0.56	0.34	0.70	3.87	0.42	0.51	0.0013	0.039	8.48	9.10
3	8.35	1.02	5.83	0.00	0.21	0.33	3.44	0.31	0.54	0.0009	0.048	6.71	8.05
4	8.45	0.36	7.49	0.32	0.18	0.42	3.59	0.28	0.51	0.0044	0.034	8.83	8.25
5	8.40	0.32	5.24	1.25	0.21	0.65	2.99	0.23	0.64	0.0071	0.015	7.99	7.08
6	8.40	0.29	4.58	1.93	0.16	0.69	3.24	0.23	0.64	0.0107	0.024	8.04	7.58

* From total organic carbon, and titration experiments (see text)

+ From total inorganic carbon

° From respectively, $[HCO_3^-]+[NO_3^-]+[Cl^-]+2.[SO_4^{2-}]$, and $2.[Ca^{2+}]+2.[Mg^{2+}]+[K^+]$

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Instead of determining the Ca-fulvate concentrations, it is possible to determine the free Ca concentration since, in our calculations, total Ca is distributed mainly between free Ca and the Ca-fulvate species. In our application, a Ca-selective electrode was not used, but one way of estimating the free Ca concentration would be to consider the equilibrium with carbonates - remembering the apparent supersaturation of leachates that have been filtered at 0.45 μm. The validity of the solubility product and the data we introduced in the database should be considered in complex media such as soil solutions. Total inorganic carbon and pH values are particularly important in the calculations, since they determine the concentration of free carbonate. About 100 mL aliquots of the leachates were collected after being flushed through a column for several hours, during which time the solutions were in contact with air. Then the analytical determinations were obtained and introduced in the program as fixed values of pH and total concentrations of a closed system, though it is doubtful that this was at equilibrium.

The supersaturation of soil solutions with respect to calcite is a common observation that has been interpreted by Reddy *et al.* (1990) as due to an underestimation of Ca organic complexes, leading to an overestimation of Ca^{2+} activity. The ion activity product $(Ca^{2+})(CO_3^{2-})$ calculated for the first leachates - those richest in soluble organic carbon - was not much higher than the solubility product (10^{-8}) stored in the database. Leachates #4-6 with low concentrations of organic carbon were the most supersaturated, with up to 89% of total Ca predicted for. Suarez *et al.* (1992) supported the idea that soil solutions can be supersaturated with respect to calcite due to kinetic and surface processes, and reported solubility product ranging from 8.0 to 8.2 on a -log scale. In our case, it is likely that the leachates were saturated in calcium carbonate with a solubility product close to 10^{-8}, and further apparent supersaturation was due to estimation of the free concentration of CO_3^{2-}, which derived mainly from inorganic carbon and pH measurements. Consequently, the free Ca concentrations calculated in this study can be considered to be reasonably accurate. Therefore the stability of the Ca-fulvate complexes, which roughly account for the difference between total and free Ca, should also be well estimated by our calculations.

Carbonate is the main inorganic ligand for Cd and Pb. Despite the difficulties in estimating its free concentration, all calculations confirmed the importance of its role as a complexing agent in alkaline soil solutions, especially for Pb. The same conclusions as for calcite can be drawn for the apparent supersaturation with respect to otavite $(CdCO_3)$ for leachates #4-6. Particularly, if Cd^{2+} is displaced from cation exchange sites by the H^+ input, the ion activity product $(Cd^{2+})(CO_3^{2-})$ can surpass the solubility value for otavite because of slow precipitation kinetics (Sposito and Coves, 1988).

Conclusion

A step diagram was followed to determine the speciation of Pb and Cd in polluted soil leachates exhibiting alkaline pH values. This included the determination of total concentrations of metals and ligands in the leachates, and the determination of the complexing properties of the soluble organic carbon, taking the fulvic

fraction of the soil as a surrogate. A model was developed from the potentiometric studies of the fulvic acids, and was consequently introduced into a slightly modified version of the geochemical program SOILCHEM used later on to determine the speciation of the leachates. This model comprised the competition between the metallic cations and protons for the organic reactive sites, A, and allowed the determination of the stability of the complexes CdA, PbA and PbOHA as a function of pH. These parameters, together with the analytical data of the leachates, permitted the speciation to be done at the corresponding high pH values. Primarily, the results show that:

(i) Pb and Cd are effectively bound to the soluble organic matter, up to 50% of total concentration for Pb and 15% for Cd when soluble organic carbon is maximum (290 mg L^{-1});

(ii) free Pb concentrations are always very low (<1%), while Cd is distributed between free and inorganic species; and

(iii) the main inorganic ligand is always carbonate.

This latter point indicates the role of carbonate species as a complexing agent. Calcium appeared to be the main competing cation, and its speciation would have to be better understood in complex alkaline media, to better appreciate the precise distribution of trace elements with soluble organic carbon.

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