094906

Heavy Metals Desorption from Synthesized and Natural Iron and Manganese Oxyhydroxides: Effect of Reductive Conditions

Mélanie Davranche and Jean-Claude Bollinger[1]

Laboratory of Aquatic and Environmental Sciences, Faculty of Sciences, University of Limoges, 123 avenue Albert Thomas, 87060 Limoges Cedex, France

Reductive conditions in soils can lead to the dissolution of iron and manganese oxyhydroxides, releasing heavy metal pollutants (e.g., Pb and Cd) bound to them. The present study used hydroxylamine as a reducing agent. Laboratory batch experiments were conducted, varying pH and hydroxylamine concentrations, with artificially contaminated synthetic amorphous $Fe(OH)_{3s}$ and MnO_2 and with a polluted cultivated soil. Until conditions were reductive enough to dissolve solids, remobilization of metals depended on their surface complexation constant and readsorption of metal was possible. However, if conditions were sufficiently reductive, all solids were dissolved and metals were released into solution. A straightforward surface complexation model for cation desorption was carried out to support these results. © 2000 Academic Press

Key Words: reduction; iron and manganese oxyhydroxides; Pb; Cd; desorption; readsorption; modeling.

INTRODUCTION

Contamination of soils by metallic pollutants due to anthropogenic activities raises several questions. Are these pollutants potentially mobile? What can be done to decrease the mobility in order to lower the pollution level *in situ*? Is it possible to increase the mobility in order to decontaminate, for instance, soils contaminated by heavy metals?

In the environment, various situations can cause significant variations in redox conditions: flooding, a rising water table, excess organic matter, an increase in biological activity due to an increase in nutriments, deterioration of the soil's physical properties (compaction, deforestation, etc.) (1). All of these phenomena can provoke reductive dissolution of soil components (iron and manganese oxyhydroxides) (2–4), thereby releasing the heavy metals bound to them into the aqueous phase. Indeed, iron and manganese oxides and hydroxides are known to be strong adsorbents (5).

The effect of variations in redox potential on trace element mobility has been illustrated in rice fields (6, 7) and freshwater estuary soils (8). Chuan *et al.* (9) showed by monitoring pH and redox potential changes that heavy metal solubility increases under reductive conditions. In many cases metal release seems to be caused by changes in the bonds between the metal and the solid, induced by redox conditions.

The reactivity of solid surfaces in response to variations in redox conditions depends on their nature. Functional groups present at mineral surfaces can react with oxidizing or reducing agents to form outer- or inner-sphere complexes. The reductive dissolution of oxyhydroxides proceeds in three steps: (i) diffusion of the reducing agent to the surface, (ii) surface reactions, and (iii) release of reaction products and diffusion toward the bulk solution (3).

Each soil has its own natural redox buffering capacity, which enables it to resist redox changes. This capacity depends on the availability of reducing (electron donor) and oxidizing (electron acceptor) species. Oxidation and reduction capacities of a given soil can be quantified. They are important parameters for understanding the geochemical control and fate of micropollutants in the environment (1, 10, 11).

OXC: oxidation capacity

$$OXC = 4[O(0)] + 5[N(V)] + 2[Mn(IV)] + [Fe(III)] + 8[S(VI)] + 4[\text{oxidized C}] \qquad [1]$$

REC: reduction capacity

$$REC = 8[N(-III)] + 2[Mn(II)] + [Fe(II)] + 8[S(-II)] + 4[\text{reduced C}]. \qquad [2]$$

Soil redox capacity has to be taken into account in order to modify redox conditions.

The objective of this work was to evaluate the role of slightly reducing conditions on the remobilization of heavy metals (Pb and Cd) from polluted solids. This study tried to provide evidence of and explain release mechanisms for heavy metals under controlled reductive conditions. Batch experiments were carried out in the presence of a reducing agent (hydroxylamine) for model solids (simple solids) and a natural solid (cultivated soil) in order to induce metals release phenomena. Moreover, a simple desorption model was realized in order to interpret the results obtained in a reductive medium.

[1] To whom correspondence should be addressed. Fax: 33(0)555-457-459. E-mail: jcbollinger@unilim.fr.

531

MATERIALS AND METHODS

All chemicals used in this study were of reagent or analytical grade. All solutions were prepared with doubly deionized water (Milli-Q system, Millipore). All experiments were carried out in polyethylene containers that were cleaned according to the following protocol: washed with detergent, soaked in 10% HNO_3 for 48 h, and rinsed with Milli-Q water for 24 h.

Solids and Their Characterization

Synthetic amorphous iron hydroxide (HFO) was prepared in the laboratory according to Schwertmann and Cornell (12). First 1.5 M of NaOH was added slowly to 0.5 M of $Fe(NO_3)_3$. The solution was continuously bubbled with nitrogen during the synthesis to prevent carbonate formation. Pb and Cd were added to the solution of $Fe(NO_3)_3$ just before precipitation. The salts of heavy metal ions were all nitrates and were used as received. The

HFO precipitate was centrifuged and washed three times with Milli-Q water. The solid obtained was dried at 20°C, sieved for homogenization, and stored in a desiccator. Its amorphous structure was confirmed by X-ray diffraction (XRD) analyses realized with a SIEMENS D5000 diffractometer (Fig. 1a). Surface area (BET) was determined by three-points N_2 adsorption measurement. A specific surface area of 273 $m^2 \cdot g^{-1}$ was found. Total concentrations of heavy metals were evaluated by acidic digestion according to Ritter and Sung's protocol (13–15). Pb and Cd were analyzed by polarography (DPASV). Respectively 343 and 7 ppm were determined for Pb and Cd.

Manganese dioxide was precipitated by rapid addition of 10% HCl to a 0.5 M solution of $KMnO_4$ (16), in the presence of nitrate salts of Cd and Pb. The precipitate was heated for 24 h at 30°C in order to eliminate excess Cl^-, then it was filtered and washed three times with Milli-Q water. The solid obtained was dried at 38°C for 24 h, sieved, and stored in a desiccator. Its
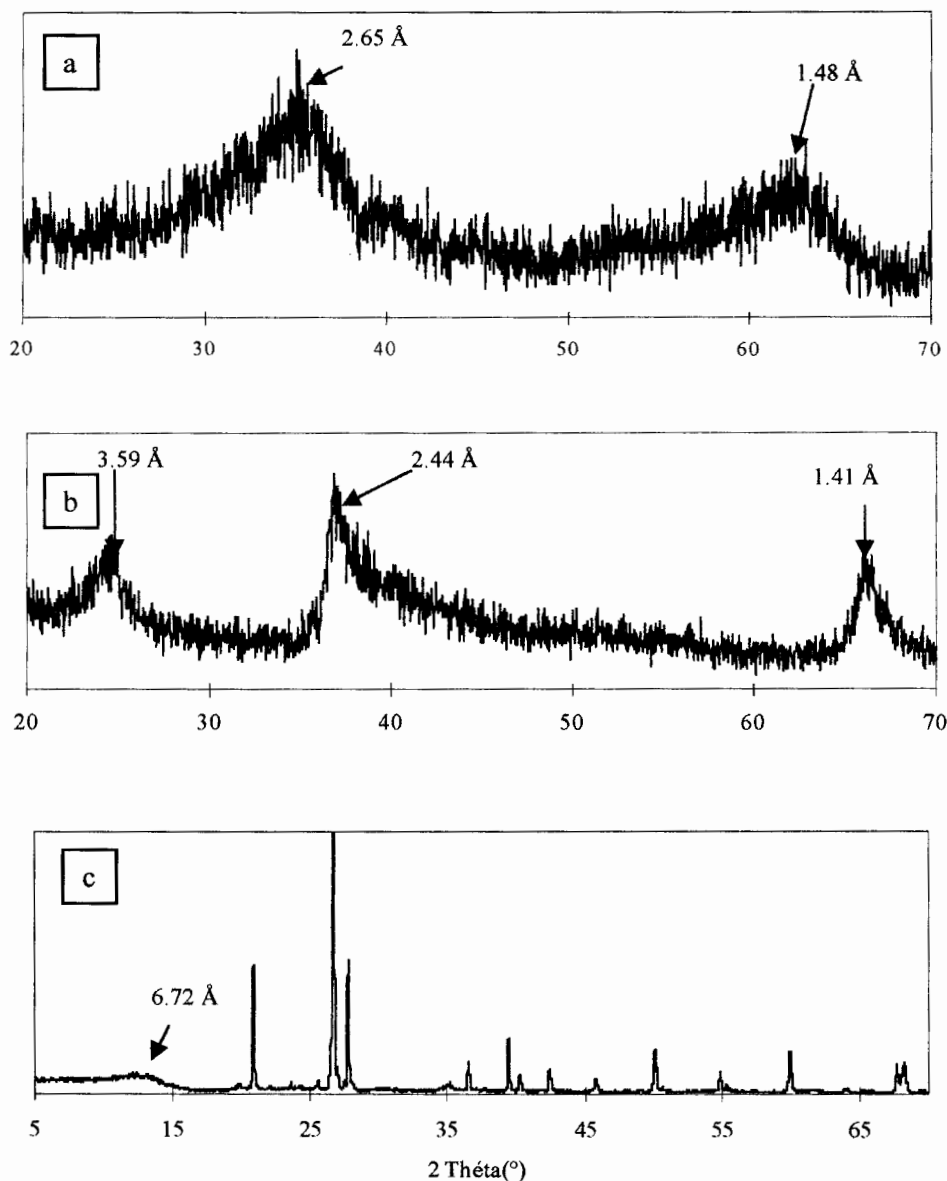

FIG. 1. X-ray diffraction patterns of HFO (a), MnO_2 (b), and soil (c).

TABLE 1
Geochemical Composition and Metal Concentrations in Soil Sample

Component	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	K$_2$O	MnO	TiO	Corg	CO$_3^{2-}$	Pb (ppm)	Cd (ppm)
Quantities in %	77.8	7.40	2.50	1.30	<1.00	2.10	0.05	0.67	1.85	0.8	250	9

amorphous structure was confirmed by XRD analyses (Fig. 1b). Total concentrations of heavy metals were evaluated by acidic digestion according to Ritter and Sung's protocol (13–15). Pb and Cd were analyzed by polarography (DPASV); 500 ppm of Pb and 7 ppm of Cd were determined.

A soil sample was collected (upper 30 cm) in northern France (Nord Pas de Calais region). The site was contaminated over several years through atmospheric transport from the nearby steel industry. This sample was air-dried and sieved at 2 mm.

Geochemical characterization was carried out at the French Geological Survey (BRGM, Orléans) (Table 1). The total concentrations of heavy metals (Table 1) were determined after acidic digestion (13–15). A grain size distribution study was carried out using the AFNOR protocol X 31-107 (17). The sand, silt, and clays contents expressed as the percentage of dry weight were 2, 78, and 20, respectively. X-ray diffraction analysis indicated the presence of quartz and feldspar, but no traces of crystallized iron. However, a convexity at 6.72 Å indicated a trace of amorphous material (Fig. 1c). Clays characterization was carried out by X-ray diffraction analysis on the <2-μm size fraction, extracted following the AFNOR protocol X 31-107 (17) (XRD pattern not shown). Illite and kaolinite were determined. Moreover, these clays are relatively stable at pH 3 to 9 (18). Thus, under our experimental conditions, clays dissolution should be slight in the major part of the pH range.

The soil was characterized by extraction with oxalate and pyrophosphate (19). Oxalate extraction provides an estimate of noncrystalline iron oxide and organically complexed Fe. Pyrophosphate extraction gives an estimate of Fe complexed by organic matter. Oxalate extractable Fe was measured by mixing 0.05 g of dried soil with 20 ml of 0.2 M acid ammonium oxalate (pH 3). The solution was shaken for 2 h in the dark at 20°C and then filtered. Pyrophosphate extractable Fe was measured by mixing 0.04 g of dried soil with 20 ml of 0.1 M sodium pyrophosphate solution at 20°C for 16 h. Iron in the oxalate and pyrophosphate extracts was analyzed by atomic absorption spectroscopy (Varian SpectrAA 220). The amorphous iron oxyhydroxide content in the soil was 17% of total Fe.

Soil carbonate content was evaluated according to the Rauret protocol (20). It was determined by back-titrating an excess of 0.1 M HCl added to 6 g of dry soil sample with 0.1 M NaOH under a continuous stream of pure N$_2$(g). The carbonate content in soil was 0.8% w/w. So, carbonate dissolution/precipitation should have a low effect on the metal mobility under our experimental conditions.

Moreover, the distribution of heavy metals was estimated using Tessier *et al.*'s protocol of sequential chemical extractions

(21) (Table 2). The major operationally defined forms for Pb were oxyhydroxide (40%) and carbonate (25%) and for Cd, exchangeable fraction (60%) and carbonate (20%) (Fig. 2). We can therefore predict that under reductive and acidic (pH 2 to 6) conditions, a large fraction of Cd and Pb will be released to the aqueous solution. Iron was mainly present in the residual fraction (75%). This metal could be part of the crystalline structure of aluminosilicate minerals (such as clay) and thus hardly solubilized. About 15% of the iron was present as oxyhydroxides which would provide adsorbing surfaces; this percentage was in concordance with oxalate–pyrophosphate extractable Fe. We can conclude that ca. 15% of Fe was in amorphous iron oxide form. About 40% of the manganese was distributed among the oxyhydroxides of Fe and Mn and 15% under carbonate forms. Under reductive conditions, one could therefore expect 15% of Fe and 40–55% of Mn to be solubilized. Results in Fig. 2 are only indicative: indeed, sequential selective chemical extractions cannot provide quantitative data related to the association of heavy metals with specific geochemical phases in soil.

Surface acidity constants of soil were determined from potentiometric titrations of 10 g · l^{-1} of soil with NaOH (0.1 M) and HNO$_3$ (0.1 M) in a 0.1 M NaNO$_3$ medium as the supporting electrolyte (22, 23). Titrations were carried out with a Metrohm 716 DMS Titrino apparatus equipped with a Metrohm 6.0233.100 combined (3 M KCl) glass electrode.

The cation exchange capacity (CEC) was determined by the cobalthexammine method (NF X 31-130) (17). Ions linked to the solid surface are exchanged with cobalthexammine ions, the CEC is the concentration of cobalthexammine ions eliminated from the solution. First, 50 g of soil was mixed with 50 ml of 0.017 M cobalthexammine solution for 3 h. The suspension was then centrifuged and the concentration of cobalthexammine ion remaining in the solution was measured at 470 nm with a Shimadzu-160A UV spectrophotometer.

TABLE 2
Chemical Extractions Protocol (21)

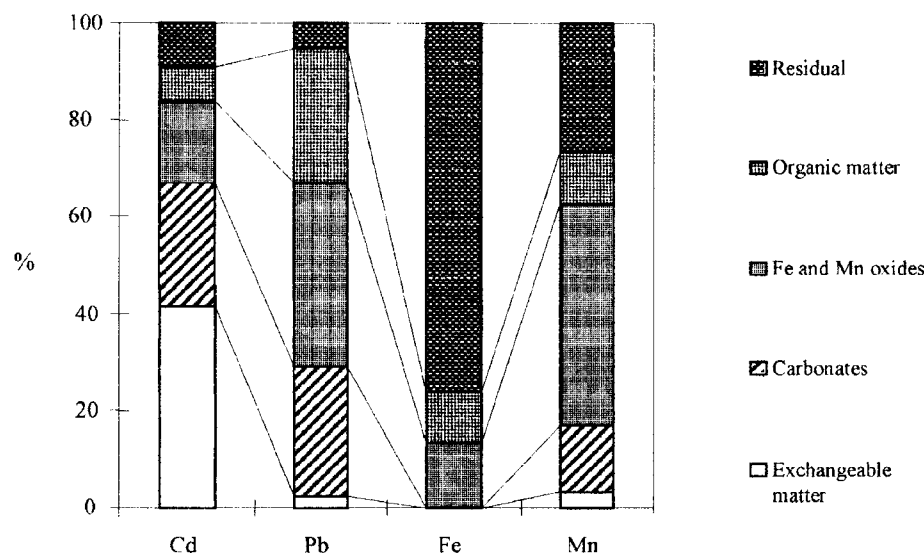| Chemical attacks	Phases denominations	Reagents
I	Exchangeable matter	MgCl$_2$ (1 M)
II	Carbonates	NaOAc (1 M)
III	Iron and manganese oxides	NH$_2$OH · HCl (0.04 M)
IV	Organic matter	HNO$_3$ (0.02 M), H$_2$O$_2$ (30%), NH$_4$OAc (3.2 M)
V	Residual	Acidic digestion, HNO$_3$/HClO$_4$

FIG. 2. Distribution of heavy metals among geochemical phases in the soil.

Dissolution Experiments

Experiments were conducted first with a solid concentration of 10 g · l^{-1}, in a 0.01 M $NaNO_3$ electrolyte solution without reducing agent. The pH was regulated with concentrated solutions of HNO_3 or NaOH. The equilibration time was 48 h, determined by previous studies as a function of time under the same conditions for a pH fixed at 4.

The same protocol was used in a second series of experiments but with 10^{-2} M hydroxylamine. The experiments were conducted at 96°C for 5 h equilibrium time as determined by Tessier et al. (21). This temperature was used to catalyze the reaction; however, under such conditions it was impossible to follow the redox potential of the suspension. The hydroxylamine concentration used was determined from an estimation of the soil oxidation capacity (Eq. [1]) calculated using only iron and manganese total concentrations in solids (10, 11).

Another series of experiments was carried out on HFO and $MnO_{2(s)}$ at various hydroxylamine concentrations in a 0.01 M $NaNO_3$ electrolyte solution.

At the end of these experiments, the solid suspension was filtered through a 0.2-μm cellulose nitrate filter (Sartorius). The filtrate was collected in a polypropylene tube to which 100 μl of 69% HNO_3 had been added to keep all metals in solution. Samples were stored at 4°C before analysis.

Analytical Techniques

The solutions of Cd and Pb were analyzed by voltammetry (DPASV) on a Metrohm VA 746 Trace Analyzer and with a VA 747 stand with a triple-electrode system: a calomel reference electrode (3 M KCl/1 M KNO_3), a graphite counter electrode, and a mercury drop electrode. Dissolved oxygen was removed from the sample by prepurging $N_2(g)$ through the solution for 600 s. The deposition step was carried out at −1.2 V for 60 s followed by metal stripping.

Fe and Mn concentrations were measured by atomic absorption, either FAAS (Varian SpectrAA 220) or GFAAS (Varian SpectrAA 800).

RESULTS

Dissolution Experiments for HFO and Manganese Oxide

Reducing conditions significantly increased the quantity of Cd remobilized but had no effect on Pb solubility (Fig. 3). The presence of hydroxylamine induced very little dissolution of the solid phase (only 1% of MnO_2 or HFO). The dissolution of hydroxides, therefore, occurred only at the surface. About 90% of the Cd adsorbed on the HFO surface was released into the solution. The low Pb release could be explain by two hypotheses:

—Pb was substituted from Fe(III) into the solid matrix and its solubilization depended on solid dissolution. Martinez and McBride (24) showed that iron oxyhydroxides may be an important sink for metal retention, especially for Pb, and that they still prove to be relatively ineffective in lowering activities of some metals such as Cd.

—Pb was effectively solubilized in the solution; however, as soon as it was released it was readsorbed on the solid surface not yet dissolved under these redox conditions. This hypothesis was supported by the comparison of Pb and Cd surface complexation constants log K_{FeOPb} = 4.65 ≫ log K_{FeOCd} = 0.47 (intrinsic constants) (25).

Dissolution as a Function of Reducing Agent Concentration for HFO and Manganese Oxide

A second series of experiments was carried out with synthesized oxyhydroxides for a concentration range of hydroxylamine more adapted to Mn and Fe total amounts.
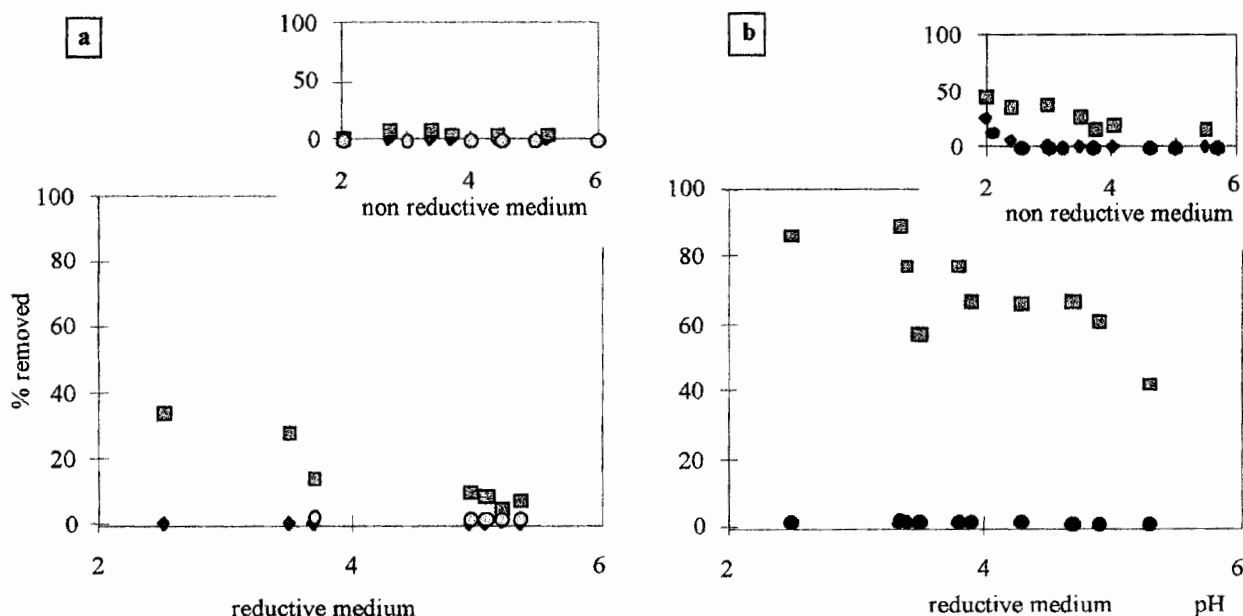
FIG. 3.   Heavy metals released from MnO_2 ($10 \cdot g \cdot l^{-1}$) (a) and HFO ($10 \cdot g \cdot l^{-1}$) (b) as a function of pH: ■, Cd; ◆, Pb; ○, Mn; ●, Fe.

For MnO_2, 80% of the solid was dissolved. About $90 \pm 10\%$ of every metal bound to this solid was released into the solution (Fig. 4a). The reducing agent dissolved almost all of the solid (80%) as soon as the ratio of solid/reducing agent concentration rose above 1.2. Below this value, dissolution was a function of the hydroxylamine concentration. In the first part of the curve, the Cd released was clearly linked to the quantity of solid surface dissolved. Pb was not released into the solution although 20% of the solid surface was destroyed. It seems that Pb was effectively readsorbed on the 40% of solid surface not dissolved under these redox conditions.

For $10 \cdot g \cdot l^{-1}$ of solid, the reductive dissolution of $Fe(OH)_{3s}$ was very low, so the quantity of solid hydroxide was decreased to $0.5 \cdot g \cdot l^{-1}$ (Fig. 4b). The fraction of Fe dissolved

reached a plateau (70%) for a hydroxylamine concentration of 0.05 M. The dissolution of iron hydroxide took place at a solid/reducing agent concentration ratio of 0.1. The value of this ratio showed the HFO redox buffer effect. In order to totally dissolve the solid matrix, this redox buffering capacity of HFO should be supplanted. Moreover, this ratio indicated that the redox buffering capacity of HFO is greater than that for MnO_2, so it should be easier to solubilize Mn than Fe under reductive conditions.

In this experiment (Fig. 4b), Cd was 100% released, as before. Pb solubilization was increased. Indeed, iron dissolution induced a remobilization of 50% of the Pb. The other 50% of the Pb should be readsorbed on the surface of HFO not destroyed or trapped on the solid matrix not yet dissolved.
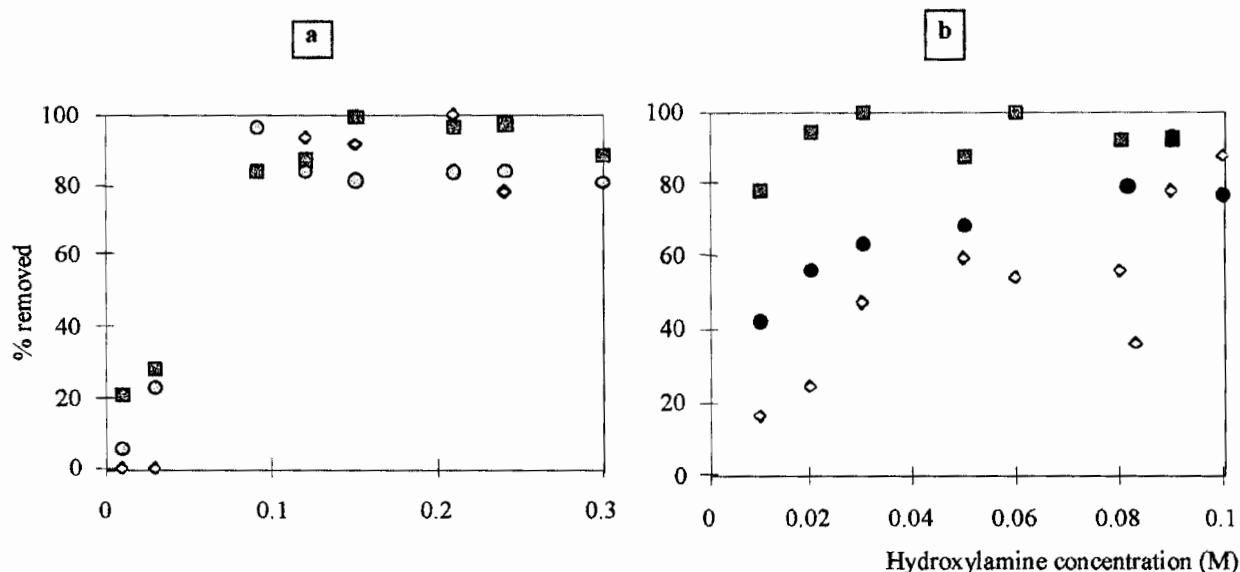

FIG. 4.   Heavy metals released from MnO_2 ($10 \cdot g \cdot l^{-1}$) (a) and HFO ($0.5 \cdot g \cdot l^{-1}$) (b) as a function of hydroxylamine concentration: ■, Cd; ◆, Pb; ○, Mn; ●, Fe; pH 4; equilibrium time, 5 h.
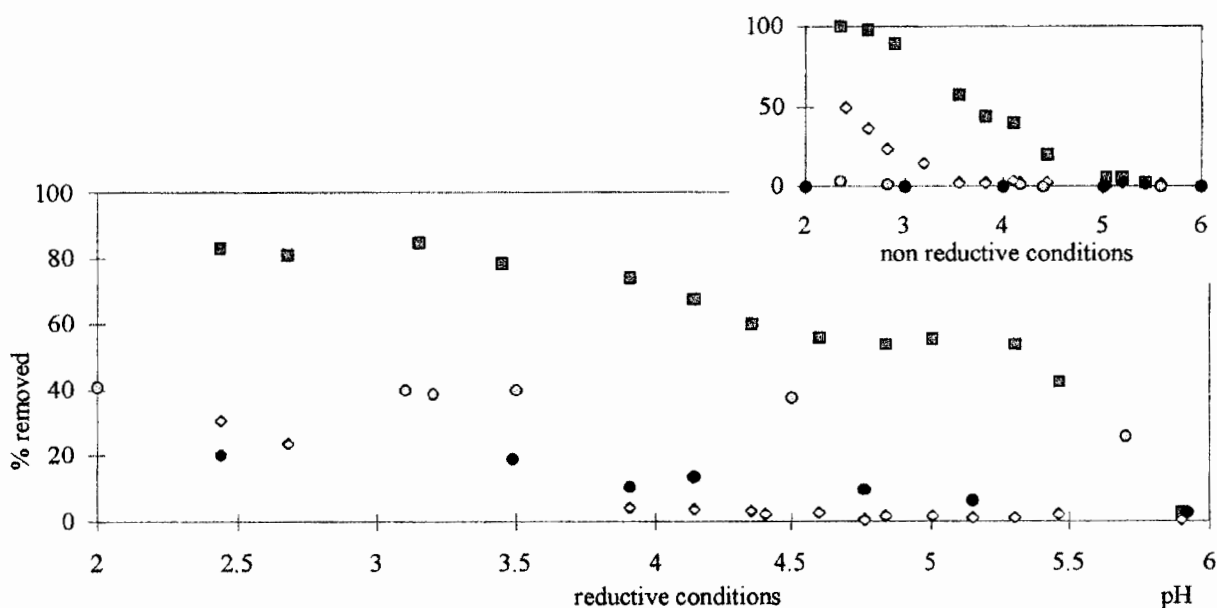
FIG. 5. Release of heavy metals from the soil sample ($10 \text{ g} \cdot \text{l}^{-1}$) as a function of pH: ■, Cd; ◆, Pb; ○, Mn; ●, Fe.

Dissolution Experiment for Soil Sample

Two series of experiments were conducted on the soil sample as a function of pH, one under mildly reductive conditions and one in the absence of a reducing agent (Fig. 5). This sample was a cultivated soil containing iron oxyhydroxides in the amorphous form, 78% of silt and 20% of clays.

In the absence of a reducing agent, the solubilization of heavy metals increased with decreasing pH. Under reductive conditions, remobilization of Pb and Cd increased, Cd being soluble as soon as pH dropped below 5.5 and Pb as soon as pH dropped below 3.

The fraction of Fe solubilized under acidic and reducing conditions ($\approx 20\%$) corresponds to the value of the amorphous iron oxide form. Hydroxylamine efficiently dissolved almost all of the Fe present in the amorphous oxide form in the soil sample. Around 40% of the Mn was remobilized. The solubilization level of Mn was constant in the whole pH range. The pH-independent solubilization of Mn under reducing conditions can be explained by the reduction of oxides.

A higher extent of Cd remobilization appeared at near neutral pH; and Cd solubilized should be readsorbed onto iron and manganese oxyhydroxides under oxidative conditions. Under reductive conditions, however, it would remain in solution since all of the oxyhydroxides of Mn and Fe are dissolved.

The dissolved Pb level increases under reductive conditions at low pH but the Pb concentration does not correspond to the amount that was estimated to be remobilizable by sequential extractions (20 versus 40–65%). Although the sequential extraction did not give quantitative data, this difference was sufficiently significant to be taken into account. Moreover, when the pH is near neutral, Pb release is very low although all of the manganese and iron oxides were dissolved. Ainsworth et al. (26) and Wang and Chen (27) have shown that, for natural solid surfaces, the pH adsorption edges of Pb and Cd are about 2 pH units apart, 50%

of Cd being adsorbed at around pH 6.5 and 50% of Pb at around pH 4.5. In our experiment, 40% of the Cd was removed at pH 5.5. If a similar rule is respected, 40% of the Pb should have been solubilized at pH 3.5 but, in fact, only 20% was present in the solution. As this rule was not evidenced for our dissolution experiments, Pb would most likely have been readsorbed onto clay minerals (not dissolved under reductive conditions), and its concentration in solution was therefore lower than expected. Moreover, this hypothesis is supported by the results obtained under nonreductive conditions where desorption of Pb and Cd differed by ca. 2 pH units.

Surface Complexation Model

A straightforward surface complexation model (SCM) for cation desorption as a function of pH was carried out to support these results. The aim of this model was to determine the pH desorption-edges of Pb and Cd on this type of soil.

Soils are considered as a whole of functional surface groups expressed as a generic binding site SOH (28, 29). This model is based on conventional reactions of surface hydroxyl groups formulated by analogy with reactions already known occurring in a simple amphoteric compound:

$$\text{SOH}_2^+ \rightleftharpoons \text{SOH} + \text{H}^+ \tag{3}$$

$$K_{a1} = [\text{SOH}][\text{H}^+]/[\text{SOH}_2^+] \tag{4}$$

$$\text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+ \tag{5}$$

$$K_{a2} = [\text{SO}^-][\text{H}^+]/[\text{SOH}]. \tag{6}$$

Van Benschoten et al. (30) have shown that neglecting electrostatic effects in their sorption model may be a reasonable assumption for strongly sorbing ions. This implies that free energy of adsorption dominates over coulombic effects. We have therefore not taken into account electrostatic effects in our model.

TABLE 3
Model Parameters

Pb_T	Cd_T	$CEC = S_T$	pK_{a1}	pK_{a2}	$pK_{SOPb}{}^a$	$pK_{SOCd}{}^a$
1.22×10^{-3} M	8×10^{-5} M	1.32×10^{-3} M	5.3	8.7	12.2	10.3

[a] Surface complex formation constants determined by model fitting.

The desorption of divalent cations Me^{2+} on the soil surface may be considered as the following surface complexation reactions,

$$SOH + Me^{2+} \rightleftharpoons SOMe^+ + H^+ \qquad [7]$$

$$SO^- + Me^{2+} \rightleftharpoons SOMe^+, \qquad [8]$$

where the dissolved surface complex constants are defined as

$$K_{SOMe} = [SOMe^+][H^+]/[SOH][Me^{2+}] \qquad [9]$$

$$K'_{SOMe} = [SOMe^+]/[SO^-][Me^{2+}]. \qquad [10]$$

These reactions assume that surface acid/base reactions and surface ion complexation were taken into account. In this model, only the monodentate surface complex was considered, because it was previously shown that this type of complex can describe a cation sorption edge reasonably well (30).

The total site concentration S_T was obtained according to

$$S_T = [SOH_2^+] + [SOH] + [SO^-] + \sum[SOMe^+]. \qquad [11]$$

TABLE 4
Complex Formation Constants

	Log β	
Complex species	Ionic strength $= 0^a$	Ionic strength $= 10^{-1}$ M^b
$Cd(OH)^+$	3.9	3.4
$Cd(OH)_2^0$	7.7	7.0
$Cd(OH)_3^-$	9.52	8.8
$Cd(OH)_4^{2-}$	8.78	8.3
$Cd_2(OH)^{3+}$	4.6	4.6
$Cd_4(OH)_4^{4+}$	23.3	22.7
$Cd(CO_3)^0$	6.6^c	5.6
$Cd(CO_3)_2^{2-}$	7.05	6.1
$Cd(HCO_3)^+$	2.4	1.9
$Pb(OH)^+$	6.3	5.8
$Pb(OH)_2^0$	10.9	10.2
$Pb(OH)_3^-$	13.9	13.2
$Pb_2(OH)_3^+$	7.6	7.6
$Pb_3(OH)_4^{2+}$	32.1	30.7
$Pb_4(OH)_4^{4+}$	36.1	35.6
$Pb_6(OH)_8^{4+}$	68.4	66.5
$Pb(CO_3)^0$	6.47	5.5
$Pb(HCO_3)^+$	2.9	2.4

[a] Ref. (31).
[b] Calculated according to the Davies equation.
[c] Ref. (32).

The metals species included in the model were free metal, hydroxide, carbonate, and hydrogenocarbonate complexes of metal. The total metal concentration was therefore

$$Me_T = [Me^{2+}] + [SOMe^+] + \sum[Me(OH)_x] + \sum[Me(CO_3)_y] + \sum[Me(HCO_3)_z]. \qquad [12]$$

With this equation, we could find the concentration of free metal in solution as a function of pH,

$$[Me^{2+}] = Me_T \Big/ \Big(1 + K_{SOMe}[SOH][H^+]^{-1} + \sum \beta_x^{OH}[OH^-]^x + \sum \beta_y^{CO_3}[CO_3^{2-}]^y + \sum \beta_z^{HCO_3}[HCO_3^-]^z \Big), \qquad [13]$$

where β_i^L is the formation constant for the MeL_i complex with the ligand L.

Me_T was measured, $[OH^-]$ was calculated from pH, and $[CO_3^{2-}]$ and $[HCO_3^-]$ were determined knowing the pH value and the total carbonate concentration in the sample. Literature thermodynamic constants (31, 32) were recalculated for an ionic strength of 10^{-2} M according to the Davies equation; they are listed in Table 4. S_T was assimilated to the CEC (Table 3). Metals included in the system were Pb and Cd simultaneously (Table 3). pK_a and CEC values determined for the present soil sample corresponded with those often met in the environment (pH_{zpc} of 7 and CEC around 1.3×10^{-4} mol $\cdot$ g^{-1}) (2). Thus, this model was constituted of three algebraic equations, Eq. [11] and Eq. [13] written for both Pb and Cd with three unknown concentrations, [SOH], [Pb^{2+}], and [Cd^{2+}], which varied as a function of pH. They were solved by successive iterations with the calcul program ProSolver version 1.0. The surface complexation constants K_{SOPb} and K_{SOCd} were determined by fitting. Stability constants determined by our SCM were in good concordance with other data determined for natural or simple solids (Table 5).

TABLE 5
Comparison of Pb and Cd Complexation Constants
with Different Surfaces

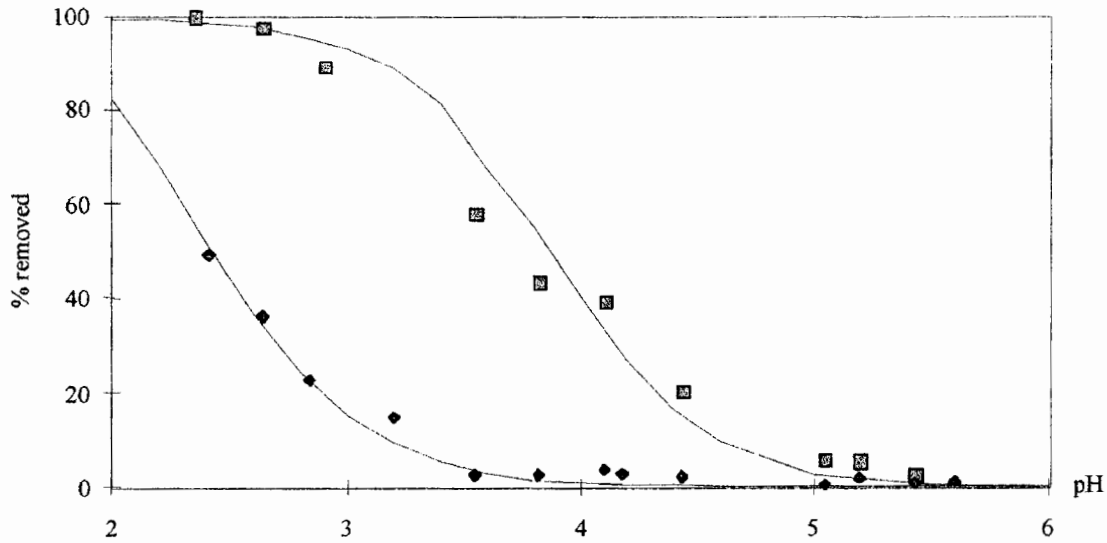| Solids	pK'_{SOPb} $SO^- + Pb^{2+} \rightleftharpoons SOPb^+$	pK'_{SOCd} $SO^- + Cd^{2+} \rightleftharpoons SOCd^+$	Ref.
Cultivated soil	3.55	1.6	This work
Surface sediments	1.3 to 3.5	−0.83 to 1.85	(27)
Surface sediments	4.26	−1.1	(33)
HFO	4.65	−0.47	(25)

FIG. 6. Comparison of Pb and Cd desorption model (lines) with experimental results (symbols) for the soil sample: ■, Cd; ◆, Pb.

Results of fitting this simple SCM to the experimental data obtained for Pb and Cd desorption as a function of pH appear in Fig. 6. The SCM could reasonably well reproduce experimental data. Total metal concentration, total surface sites, and ionic strength were sufficient to simulate metal desorption behavior. This modeling approach described adequately the soil desorption processes. Moreover, a model simulation including both mono- and bidentate complexes was carried out but the fitting of this metal desorption model with experimental data was no more accurate than the model presented in this paper.

This result indicates that our soil sample seems to show quite different desorption capacities for each metal, pH metal desorption edges for Pb and Cd being about 1.5 units apart. This confirms the Pb readsorption in a reductive medium as the gap between Pb and Cd pH desorption edges is modified in the presence of the reducing agent in the medium.

DISCUSSION

Metal cation solubility significantly increases under reductive conditions in the pH range of 2 to 5 (Fig. 7). Under reductive con-

ditions, metal solubilization takes place due to the dissolution of manganese and iron oxyhydroxides. The effective remobilization seems to be controlled by the metal surface complexation constant. Metals having a great affinity for iron and manganese oxides (e.g., Pb) seem to be readsorbed onto the solids that are not dissolved by the reducing agent. This result was confirmed by Patrick and Verloo (34) who have shown that Pb is weakly affected by pH and redox conditions. Nevertheless, metals having a low affinity to the solid are released into the solution and are not readsorbed on the unsolubilized surface (e.g., Cd).

In the case of the soil sample studied, the presence of a reducing agent enabled all of the iron oxyhydroxides to dissolve (quantity estimated to be reducible by the sequential selective chemical extractions). The metal bound to these solids was therefore remobilized in the solution by phenomena similar to those identified for iron and manganese oxyhydroxides. In a reductive system, the destruction of oxides seems to prevent the readsorption of metals although several metals such as Pb could be readsorbed onto the soil (heterogeneous medium) or other geochemical phases like clay or organic matter. For both nonreductive and mildly reducing conditions, pH is a master variable
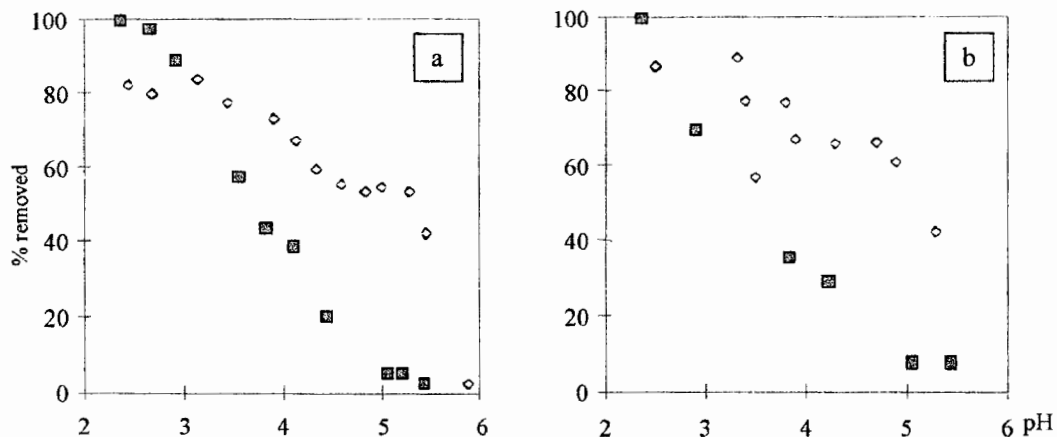

FIG. 7. Cd released under reductive (◆) and nonreductive conditions (■) for the soil sample (10 g · l^{-1}) (a) and HFO (10 g · l^{-1}) (b).

of the solubilization yield. Solubility is always high at low pH (pH 2–6) in the case of HFO in the presence of ascorbate (35).

SUMMARY

A risk of remobilization under reductive condition has been shown. Indeed, the use of hydroxylamine allows solubilization of soil iron and manganese oxides by a mechanism of reductive dissolution, inducing the release of heavy metals into the solution. The phenomena are due to both dissolution and desorption. However, if conditions are mildly reductive a small amount of the oxides is dissolved, and therefore only metals having a poor affinity to the surface are remobilized (e.g., Cd). Other metals are partly readsorbed (e.g., Pb).

In the environment, therefore, redox variations (modification of soil physical properties, flooding, etc.) could induce the release of heavy metals bound to solids, thus contaminating groundwater. Nevertheless, solubilization is easy only for partly adsorbed metals such as Cd, whereas manganese and iron oxyhydroxides must be totally dissolved for the total remobilization of all metals.

ACKNOWLEDGMENTS

REFERENCES

1. Bourg, A. C. M., and Loch, J. P. G., in "Biogeodynamics of Pollutants in Soils and Sediments: Risk Assessment of Delayed and Non-linear Responses" (W. Salomons and B. Stigliani, Eds.), p. 87, Springer Verlag, Berlin, 1996.
2. Stumm, W., and Morgan, J. J., "Aquatic Chemistry," 3rd ed., Wiley Interscience, New York, 1990.
3. Hering, J. G., and Stumm, W., in "Mineral–Water Interface Geochemistry" (M. F. Hochella and A. F. White, Eds.), p. 427, Mineralogical Society of America, Washington, DC, 1990.
4. Stumm, W., and Sulzberger, B., Geochim. Cosmochim. Acta 56, 3223 (1992).
5. Förstner, U., and Wittman, G. T. M., "Metal Pollution in the Aquatic Environment," 2nd ed., Springer Verlag, Berlin, 1979.
6. Assami. T., Pollution of soil by cadmium, in "Changing Metal Cycle and Human Health" (J. O. Nriagu, Ed.), p. 95, Springer Verlag, Berlin, 1984.
7. Reddy, K. J., and Patrick, W. H., Soil Sci. Soc. Am. J. 54, 67 (1977).
8. Van den Berg, G. A., Loch, J. P. G., and Winkels, H. J., Water Air Soil Pollut. 102, 377 (1998).
9. Chuan, M. C., Shiu, G. Y., and Liu, J. C., Water Air Soil Pollut. 90, 543 (1996).
10. Barcelona, J. M., and Holm, M. J., Environ. Sci. Technol. 25, 1565 (1991).
11. Heron, G., Crouzet, C., Bourg, A. C. M., and Christensen, T. H., Environ. Sci. Technol. 28, 1698 (1994).
12. Schwertmann, U., and Cornell, R. M., "Iron Oxides in the Laboratory, Preparation and Characterization," VCH Verlag, Weinheim, 1991.
13. Ritter, C. J., and Bergman, S. C., At. Absorption Newsl. 17, 70 (1978).
14. Sung, J. F. C., Nevissi, A. E., and Dervalle, F. B., J. Environ. Sci. Health A 19, 959 (1984).
15. Al Shukry, R., Serpaud, B., Matejka, G., and Caullet, C., Environ. Technol. 13, 129 (1992).
16. Meguellati, N., Mise au Point d'un Schéma d'Extraction Sélective des Polluants Métalliques associés aux Diverses Phases Constitutives des Sédiments. Doctoral thesis, Univ. Pau, France, 1982.
17. AFNOR, "Qualité des Sols," AFNOR, Paris, 1994.
18. Velde, B., "Introduction to Clay Minerals," Chapman and Hall, London, 1992.
19. Bigham, J. M., Schwertmann, U., and Pfag, G., Appl. Geochem. 11, 845 (1996).
20. Rauret, G., Rubio, R., Lopez-Sanchez, J. F., and Casassas, E., Wat. Res. 22, 449 (1988).
21. Tessier, A., Campbell, P. G. C., and Bisson, M., Anal. Chem. 51, 844 (1979).
22. Kummert, R., and Stumm, W., J. Colloid Interface Sci. 55, 1170 (1980).
23. Sigg, L., and Stumm, W., Colloids Surf. 2, 101 (1981).
24. Martinez, C. E., and McBride, M. B., Environ. Sci. Technol. 32, 743 (1998).
25. Dzombak, D. A., and Morel, F. M. M., "Surface Complexation Modeling, Hydrous Ferric Oxides," Wiley-Interscience, New York, 1990.
26. Ainsworth, C. C., Pilon, J. L., Gassman, P. L., and Van Der Sluys, W. G., Soil Sci. Soc. Am. J. 58, 1615 (1994).
27. Wang, F., and Chen, J., Environ. Sci. Technol. 31, 448 (1997).
28. Schindler, P. W., in "Surface Complexes at Oxides–Water Interfaces. Adsorption of Inorganics at Solid Liquid Interfaces" (M. N. Anderson and A. J. Rubin, Eds.), p. 12, Ann Arbor Science, Ann Arbor, MI, 1981.
29. Sigg, L., Goss, K., Haderlain, S., Harms, H., Hug, S. J., and Ludwig, C., Chimia 51, 893 (1997).
30. Van Benschoten, J. E., Young, W. H., Matsumoto, M. R., and Reed, B. E., J. Environ. Qual. 27, 24 (1998).
31. Smith, R. M., and Martell, A. E., "Critical Stability Constants," Vols. 2–6, Plenum, New York, 1975–1989.
32. Lacour, S., Deluchat, V., Serpaud, B., and Bollinger, J. C., Environ. Technol. 20, 249 (1999).
33. Kedziorek, M., Mobilité Naturelle et Provoquée de Polluants Métalliques dans les Sols et Sédiments. Doctoral thesis, Univ. Limoges, France, 1997.
34. Patrick, W. H., and Verloo, M., Wat. Sci. Technol. 37, 165 (1998).
35. Deng, Y., Langmuir 13, 1835 (1997).