Interactions between cadmium and lead with acidic soils: Experimental evidence of similar adsorption patterns for a wide range of metal concentrations and the implications of metal migration

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ABSTRACT

The importance of high- and low-affinity surface sites for cadmium and lead adsorption in typical European and Asian soils was investigated. Adsorption experiments on surface and deep horizons of acidic brown (Vosges, France) and red loess soils (Hunan, China) were performed at 25 °C as a function of the pH (3.5–8) and a large range of metal concentrations in solution (10^{-9}–10^{-4} mol l^{-1}). We studied the adsorption kinetics using a Cd^{2+}-selective electrode and desorption experiments as a function of the solid/solution ratio and pH. At a constant solution pH, all samples exhibited similar maximal adsorption capacities (4.0 ± 0.5 μmol/g Cd and 20 ± 2 μmol/g Pb). A constant slope of adsorbed–dissolved concentration dependence was valid over 5 orders of magnitude of metal concentrations. Universal Langmuir and Freundlich equations and the SCM formalism described the adsorption isotherms and the pH-dependent adsorption edge over very broad ranges of metal concentrations, indicating no high- or low-affinity sites for metal binding at the soil surface under these experimental conditions. At pH 5, Cd and Pb did not compete, in accordance with the SCM. The metal adsorption ability exceeded the value for soil protection by two orders of magnitude, but only critical load guarantees soil protection since metal toxicity depends on metal availability.

1. Introduction

Sorption onto soil particles is known to control the migration of metals through soils, plants and river systems and to determine metal availability and toxicity to the components of trophic chains, including animals and humans. Consequently, the adsorption of important pollutants such as cadmium and lead onto minerals [1–8] and organic matter [9–11] surfaces and the interactions between heavy metals and soil colloids [12–17] have been extensively studied with a particularly focus on the rigorous characterization of metal adsorption onto natural sorbents such as soils [18–34] and sediments [35]. At the beginning of studies of metal adsorption onto mineral substrates the typical approach was to investigate the pH-dependent adsorption edge at a constant concentration of the adsorbent and a rather high concentration of dissolved metals, in the order of mmol l^{-1}. Many investigators

proposed that there is more than one type of site on the surface of the substrate: depending on the metal to surface concentration ratio, a low abundance of sites with a high affinity for metals can be more important than an abundance of low-affinity sites [3,36]. As a result, the adsorption constant itself can depend on the metal concentration in solution. For example, the constant measured at a high (mmolar) metal concentration might not be applicable to natural settings of the nanomolar to micromolar concentration range. In contrast to the large efforts that have been undertaken to test this hypothesis for natural organic matter (OM) or mineral surfaces [37–40] for natural multicomponent adsorbents such as soils, this issue has rarely been addressed by rigorous experimental approaches under controlled laboratory conditions [41].

Most studies of metal adsorption on various mineral surfaces were restricted to measuring the adsorption edge in a very narrow range of metal concentrations and were aimed at predicting surface adsorption constants and the percentage of adsorbed metal as a function of pH under given conditions (i.e., [21,42–45]). However, these studies did not always allow quantification of the maximal number of available surface sites, a crucial parameter for the environmental modelling of metal migration. For this, experiments on

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both the pH-dependent adsorption edge and the "Langmuirian" adsorption at a constant pH should be conducted.

This study aimed to provide new insights into toxic metal interactions with soils by performing a thorough investigation of Cd and Pb adsorption onto various types of acidic soils in a very wide range of metal concentrations. Indeed, Cd and Pb are among the most common toxic metals in soils in the world and their soil transport and bioavailability strongly depend on soil parameters (pH and organic matter content, among others) (cf. [46,47]).

Acid soils are most vulnerable to heavy metal loads due to their rather low adsorption capacities at acidic or circumneutral soil solution pH levels. As part of a general quantitative assessment of acid soil interactions with metal toxicants all over the world, this study compared metal adsorption parameters in two representative European and Asian acid soils. The specific objectives of this work were: (1) to measure and compare the adsorption parameters of Cd and Pb on surface and deep soil horizons as a function of pH; and (2) to assess the adsorption yield in the widest possible experimental range of metal concentrations in solution (several orders of magnitude). The results should allow a better quantification of the Cd and Pb-adsorption capacity of these soils and should help to constrain the modelling of critical loads [46,47] in Europe and Asia (where increasing levels of metal deposition are being found) and, more generally, to improve our understanding of soil protection regarding acid and metal pollution around the world.

2. Materials and methods

2.1. Soil samples

The experiments were performed on soils that originated from France and China in order to represent a variety of acid soils from regions that receive a wide range of acidic atmospheric inputs [27,47–49]. A red acidic soil (labelled CS, Allitic Udic Ferrisols, FAO system, Changsha Region, North of Hunan Province, China) developed on Quaternary red clay and an acidic brown soil (labelled PP, Dystric Cambisol, FAO system) from the Strengbach catchment (Vosges, France), developed on granite, were considered. Samples from different depths were collected using a plastic shovel, sieved through a 2 mm mesh, dried at 105 °C and kept at ambient temperature in the dark. The chemical and physical compositions, specific surface areas and selected parameters of the soils studied are provided in Table 1. Two mineral horizons from each soil: the surface (CS1: 0–30 cm and PPAB: 5–30 cm) and bottom (CS4: 90–120 cm and PPC: ±180 cm), were selected for this study.

The PP soil had a sandy loam texture; the pH of the water extract varied from pH 4.1 on the surface to pH 4.6 at depth. The main minerals in the composition of this soil were quartz and mica with plagioclase and traces of apatite [50]. The OM content decreased from 2.6 to 0.1% from the surface to the deep horizon, respectively. Illite and smectite were the dominant clay minerals within this soil type. The specific surface areas (SSA) of the surface and deep horizons of this soil were 6.2 and 4.8 $m^2 g^{-1}$, respectively, as measured by the B.E.T. (Brunauer–Emmett–Teller) N_2 multi-point adsorption technique. The aluminium content (mainly as Al oxides) ranged between 15 and 20%. The CS soil had a clay texture (~60% of fine particles < 0.01 mm), with low aluminium content. The pH_{water} was around pH 5 and the OM content was close to that of the PP soil. The clay mineralogy of the soils was studied using small-angle X-ray diffraction of oriented samples prepared by depositing a clay suspension on a glass slide and subjecting it to conventional treatment (heating to 500 °C, ethyleneglycol expansion). The spectra were recorded using a diffractometer with a Cu Ka anti-cathode. The clay minerals illite and chlorite, and interlayered I–C, were the dominant constituents in the CS soil. The SSAs ranged from

14.8 $m^2 g^{-1}$ to 19.7 $m^2 g^{-1}$ from the surface to depth, respectively. The range of SSAs for soils < 2 mm in this study (5–20 $m^2 g^{-1}$) is in good agreement with data in the literature for different soils around the world [51].

2.2. Adsorption experiments

Batch adsorption experiments were performed in pre-cleaned 30 ml polypropylene vials at 25 ± 0.5 °C in 0.01 M $NaNO_3$ with a very wide range of metal concentrations, from 2–4 $nmol l^{-1}$ to 0.1–0.2 $mmol l^{-1}$. The concentrations of Cd and Pb ranged from 10^{-9} to 10^{-4} M. All adsorption experiments were performed at a constant soil/solution ratio equal to 8 $g l^{-1}$. Desorption experiments were performed with each type of soil in MilliQ water suspensions at concentrations of 4, 8, 20 and 40 $g l^{-1}$ and pH 5.0 ± 0.5. The exposure time varied from 1 to 2 weeks to ensure the equilibrium of metal distribution between the soil and the solutions, as evidenced from preliminary adsorption experiments which showed that 1–2 days was sufficient to achieve stable ($\pm 10\%$) metal concentrations in solution in contact with the soils. After the adsorption equilibrium was achieved the pH of the suspensions were measured and the samples were centrifuged for 15 min at $2000 \times g$ and filtered through a pre-washed 0.22 μm Nylon filter. The filtrate was acidified with bidistilled HNO_3 and stored at 4 °C before analysis. For all of the experiments described below, CO_2-free MilliQ water saturated with high-purity N_2 gas was used.

2.2.1. Adsorption of Cd and Pb at a constant pH

All of the experiments were performed at a constant soil/solution ratio equal to 8 $g l^{-1}$ in 0.01 M $NaNO_3$ as a background electrolyte solution. The initial Cd and Pb concentrations varied from 4 nM to 100 μM (Cd) and from 2.4 nM to 240 μM (Pb). The amount of metals added always exceeded the amount that could be potentially desorbed from the soil surface (see Section 2.4) by a minimum factor of 5. The necessary corrections for the desorbed metals were always made, especially at low concentrations. The samples were continuously shaken at 25 ± 0.5 °C in the dark for 1–2 weeks to ensure adsorption equilibrium was achieved. Such a long exposure time is also consistent with the rather long (days to weeks) residence time of interstitial soil solutions. Blank samples were prepared in MilliQ water or 0.01 M NaO_3 solution with the same metal concentrations but without the addition of soil in order to account for the adsorption of metals onto container walls under typical experimental conditions. Corrections for the blank adsorption ranged from 10% of the adsorbed amount of metal at a nMol concentration range to, typically, <1% at the μMol concentration range.

2.2.2. Effect of pH on adsorption

In order to study the effect of pH on adsorption equilibria, the soils were placed in contact with 0.01 M $NaNO_3$, with 8 g soil l^{-1} and an initial Cd or Pb concentration of 0.9 or 0.48 μM, respectively. The pH was varied by adding HNO_3 or NaOH to cover the range between pH 2 and 8. All adsorption experiments were performed in solutions undersaturated with respect to metal hydroxides and carbonates, as verified by MINTEQA2 calculations [53] of the initial solution compositions.

2.2.3. Adsorption competition between Cd and Pb

Competitive adsorption experiments were performed with each type of soil at pH ~ 5 in 0.01 M $NaNO_3$, with 8 g soil l^{-1} and three types of initial solutions: 0.44 μM Cd + 0.12 μM Pb, 0.22 μM Cd + 0.36 μM Pb, and 0.66 μM Cd + 0.06 μM Pb. After an exposure period of 48 h at 25 °C in the dark, the pH was measured and the solution was centrifuged (15 min, speed $2500 \times g$), filtered

Table 1
Properties of the tested soils.

Property		PPAB	PPC	CS S1	CS S4
Sampling site		Strengbach catchment – Vosges, France	Strengbach catchment – Vosges, France	Changsha, Hunan, China	Changsha Hunan, China
Soil type		Acid brown soil (Dystic Cambisol)	Acid brown soil (Dystric Cambisol)	Allitic Udic Ferrisols	Allitic Udic Ferrisols
Bedrock		Granite	Granite	Quaternary red clay	Quaternary red clay
Depth (cm)		5–30	±180	0–30	90–120
Density (g cm^{-3})		1.60	2.0	1.15	1.33
Specific surface area (m^2 g^{-1})		6.2	4.8	14.8	19.7
pH (H$_2$O)		4.10	4.60	5.0	5.2
pH (KCl)		3.20	3.90	4.0	4.1
CEC (cmol kg^{-1})		9.10	5.10	3.6	3.3
BS (%)		4.90	7.10	14.40	12.47
C org (g kg^{-1})		13.10	7.70	13.23	4.74
Organic matter (g kg^{-1})		22.5	13.2	22.8	8.2
Content of major metal iron (g kg^{-1})	Al$_2$O$_3$	15.60	18.20	2.25	2.14
	Fe$_2$O$_3$	2.10	2.20	3.44	3.63
Content of soil particles (mm, %)	2–0.20	60.70	62.10	7.07	10.18
	0.20–0.05	7.40	8.10	10.44	8.2
	0.05–0.02	1.60	7.40	6.27	8.16
	0.02–0.002	12.50	8.10	43.86	40.81
	<0.002	17.80	15.90	32.37	32.65
Main constituent minerals[a] (%)	Quartz	35–8	26–7	x	x
	Orthose	15–1	10–1	x	x
	Muscovite	14–0.4	33–2	x	x
	Plagioclase	5–3	11–4	x	x
	Apatite	0.06–0.05	0.21–0.09	x	x
	Kaolinite	1–3	1–3	x	x
	Illite	22–64	9–57	++	+++
	Vermiculite	–	–	–	–
	Chlorite	–	–	+++	+++
	Smectite	4–14	4–15	–	–
	Interlayered I–V	++	+	–	–
	Interlayered C–S	–	–	++	+
Total content of trace metals (mg kg^{-1})	Cd	0.03	0.03	0.18	0.10
	Cu	2.0	0.50	23.47	27.34
	Pb	56.6	9.9	24.1	22.17
	Zn	25.0	24.0	99.19	75.32
	Cr	9.0	19.0	124.71	128.12

[a] For the Vosges samples (PPAB and PPC): after Fichter et al. [50], the first value is based on weighted mineralogy, the second one on mineral surface area. Interlayered I–V: Interlayered clay Illite–Vermiculite; Interlayered C–S: Interlayered clay Chlorite–Smectite. +++: abundant; ++, medium abundant; + detected; –: not detected; x: not measured.

(0.22 μm acetate cellulose filter), acidified (ultrapure HNO$_3$) and stored at 4 °C before analysis.

2.3. Adsorption kinetics

The adsorption kinetics were studied in 0.01 M NaNO$_3$ with 8 g l^{-1} of solid concentration and an initial Cd concentration of 88 μM. In order to monitor Cd activity, a Cd^{2+}-selective electrode was used. Solid-contact Cd-sulphide electrodes (NIKO Analit®, Russia) coupled with an Ag/AgCl reference electrode in 3.5 M KCl connected with the solution via a 1 M NaNO$_3$ salt bridge were calibrated at 3 < pH < 9 and 4 < pH < 7 in standard Cd(NO$_3$)$_2$ solutions. Potentiometric measurements were performed at 25 ± 0.5 °C in a working concentration range of 10^{-6}–10^{-2} M with a detection limit of 10^{-7} M and an uncertainty of level 5%; a Nernstian slope of 29.1 ± 0.5 mV/pCd was obtained. Prior to and after the measurements the electrode was calibrated in a cell supernatant solution with the same concentration of background electrolytes as the experimental solution. Measurements were also performed in 10 mg l^{-1} Cd solution in 0.01 M NaNO$_3$ without added soil. The electrode potential was recorded every 10 s and converted to a free Cd^{2+} concentration using a standard calibration procedure. The typical response time of this electrode to variations in the Cd concentration was 2 s (see [52] for details). These experiments were typically run for 30 min, until a steady-state Cd^{2+}(aq) concentration was achieved.

Although the adsorption kinetics of Pb^{2+} were not studied, a comparison of the adsorption constant values derived for the Cd and Pb adsorption experiments on organic and mineral surfaces, performed at the same pH, showed that the adsorption kinetic constant of Pb was about 20–25 times higher than the corresponding value for Cd, a ratio that was almost the same as that between the rate constants of water loss from aqueous Pb and Cd ions (i.e., [52]). As such, the adsorption equilibrium of Pb^{2+} should be achieved significantly faster compared to that of Cd^{2+}.

2.4. Desorption

Metal desorption experiments were designed to measure the amount of metal released from the original soils as a result of mineral dissolution or surface desorption phenomena. Desorption experiments were performed with each type of soil, in suspensions of MilliQ water at a soil concentration of 4, 8, 20 and 40 g l^{-1} at pH = 5.0 ± 0.5. The reason why MilliQ water was used instead of an electrolyte solution was to simulate the interaction between soil and penetrating low-level mineralized rainwater, and to avoid the release of exchanged metal complexes. Another series of experiments was performed in a soil suspension of 20 g l^{-1}, 0.01 M NaCl and pH 4–8, as adjusted by the addition of HCl and NaOH. In all of the adsorption experiments described below the amount of desorbed Cd and Pb at each given pH was subtracted from the metal concentration measured.

2.5. Analyses

The pH was measured, with an accuracy of ± 0.01 pH units, using a combined Schott–Geräte electrode calibrated against N.I.S.T. (National Institute of Standards and Technology) buffer solutions (pH = 4.00 and 6.86 at 25 °C). Dissolved organic carbon (DOC) was analysed using a Total Organic Carbon Analyzer (Shimadzu TOC 5000, Paris, France, uncertainty better than 3% [47]). Cadmium and lead were measured by *Inductively Coupled Plasma Mass Spectrometry* (ICP-MS 7500 ce, Agilent Technologies Santa Clara, CA, USA, uncertainty of 2%, detection limits of 0.001 μg l^{-1}). Indium and rhenium were used as internal standards. The international geostandard SLRS-4 was used to check the validity and reproducibility of the analyses. The main soil properties were analysed at the Institut National de la Recherche Agronomique (INRA, Laboratory of Soil Science, Arras, France), following standard methods (http://www.arras.inra.fr/).

2.6. Adsorption models

The partition coefficient (K_d, l g^{-1}) is defined as the ratio of the concentration of metal in the soil and in the equilibrium solution, respectively:

$$K_d = \frac{[Me]_{soil}}{[Me]_{solution}} \tag{1}$$

The adsorption reaction on a solid surface, including the interaction of one ion on one surface site, can be written as:

$$>S^- + Me^{2+} = >S-Me^+ \tag{2}$$

where $>S^-$ is the surface site, Me^{2+} is Cd^{2+} or Pb^{2+} ions in solution and $>S-Me^+$ is the adsorbed complexes. The conventional stability constant of this reaction (K_L) is defined as:

$$K_L = \frac{\{>S-Me^+\}}{\{>S^-\} \cdot [Me^{2+}]} \tag{3}$$

where {} is the surface concentration and [] stands for the aqueous metal concentration. The concentration of adsorbed metal (Γ_{ads}) is represented by the Langmuir equation:

$$\Gamma_{ads} = \{>S-Me^+\} = \frac{K_L \cdot \Gamma_{max} \cdot [Me^{2+}]}{1 + K_L \cdot [Me^{2+}]} \tag{4}$$

where Γ_{max} is the maximal adsorbed concentration corresponding to the occupation of all surface sites available for a given metal at a given pH. Another way to describe the adsorption phenomenon is via the Freundlich equation:

$$>S^- + (n)Me^{2+} = >S-Me^+ \tag{5}$$

The stability constant is defined as:

$$K_F = \frac{\{>S-Me^+\}}{[Me^{2+}]^n} \tag{6}$$

and the adsorbed metal concentration can be calculated by the Freundlich equation (5):

$$\Gamma_{ads} = K_F \cdot [Me^{2+}]^n \tag{7}$$

where K_F is the Freundlich adsorption constant and n corresponds to the number of metal ions adsorbed onto one surface site. The values of n in Eq. (7) usually vary between 0.9 and 1.4. When $n = 1$, $K_F = \Gamma_{ads}/[Me^{2+}] = K_d$, the so-called distribution coefficient, which is the slope of the isotherm at the origin [43]. Eqs. (4) and (7) are only valid for a given pH and ionic strength. Nevertheless, the Langmuir and Freundlich models are the most extensively used for modelling solid (soil, sediments) sorption affinities. The use of both Langmuir and Freundlich equations was warranted
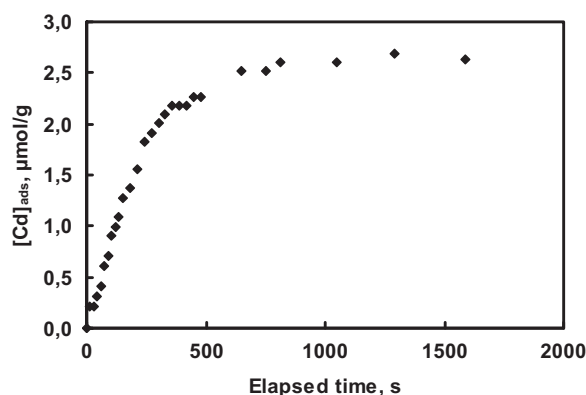

Fig. 1. Adsorbed Cd concentration as a function of time for the acid loess soil (CS-S1). Experimental conditions: 0.01 M NaNO$_3$, 8 g soil l^{-1}, [Cd]$_0$ = 10 mg l^{-1}, pH = 7.0 $\pm$ 0.2.

because: (1) most experiments in this study were performed at a constant pH and ionic strength; (2) both equations were widely used to describe soil adsorption phenomena, and (3) they covered the full range of the metal concentrations investigated and allowed a straightforward comparison of the adsorption capacity between the different soils. In contrast, a different set of K_L and K_F was necessary for each solution composition in case of pH variations in solution. These difficulties are overcome in surface complexation models (SCM), which account for chemical reactions that occur at the solid/solution interface in terms of real surface species, and predict the pH-dependence of adsorption in a wide range of solution compositions using a unique set of surface stability constants [36]. Typically, a rigorous SCM approach requires an explicit identification of proton/hydroxyl and metal-active surface sites (concentration and stoichiometry of surface binding groups such as $>Si-OH$, $>Al-OH$, $>FeOH$, $>R-COOH$, different exchangeable sites). The thorough characterization of these surface moieties implies a multidisciplinary approach comprising surface titration and electrophoresis supported by state-of-the-art spectroscopic techniques such as FT-IR (Fourier Transformed-InfraRed) and XPS (X-Ray Photoelectron Spectroscopy), for example (see [53] as an example of multisite surface characterization). Because of the complexity of mineral and organic surfaces in soils, we used a simplified SCM approach implying metal adsorption onto one surface site according to the reaction:

$$>S-H° + Me^{2+} = >S-Me^+ + H^+ \tag{8}$$

The intrinsic surface stability constant ($K_{ads}°$) is defined as:

$$K_{ads}° = \left[\frac{a_{H+} \cdot \{>S-Me^+\}}{a_{Me^{2+}} \cdot \{>S-H°\}} \right] \cdot \exp\left(\frac{-\Psi_0}{RT} \right) \tag{9}$$

where a_i is the activity of ith species in solution, $\{>S-i\}$ is the surface concentration of ith species, Ψ_0 is the electric potential at the surface, R is the gas constant and T is the temperature. The surface and solution equilibria were calculated using the MINTEQA2 program [54] within the concept of constant capacitance of the electric double layer.

3. Results

3.1. Kinetics

The adsorption kinetics were assessed in order to determine the minimal contact time necessary to achieve adsorption equilibrium, corresponding to the constant concentration of metal adsorbed during the following sorption/desorption experiments. The adsorbed Cd concentration is shown in Fig. 1 as a function of
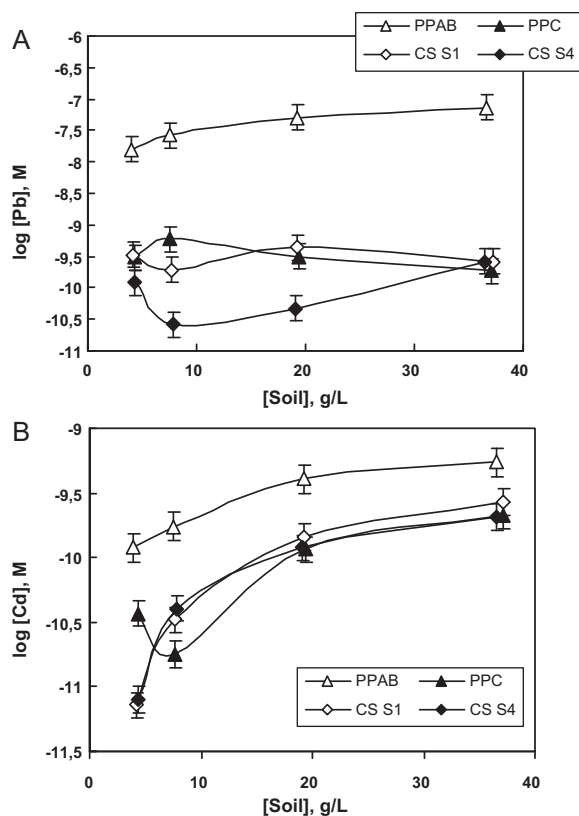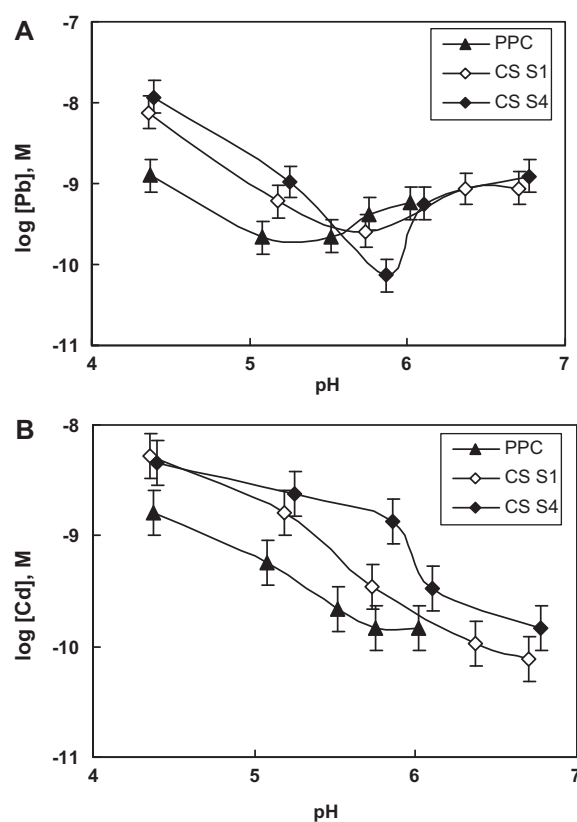
Fig. 2. Concentrations of lead (A) and cadmium (B) in a solution saturated with non-contaminated soils as a function of soil concentration in solution. Experimental conditions: pH = 4.43 ± 0.22 (PPAB), 5.48 ± 0.3 (PPC), 5.58 ± 0.23 (CS S1), 5.47 ± 0.18 (CS S4); 0.01 M NaCl, 1 week exposure at 25 °C. The symbols represent the measurements and the connecting lines are for guiding purposes.

time. Similar to most adsorption processes (i.e., [7] and references therein), the constant concentration of metal in solution in contact with the suspension was achieved within 10–20 min and did not change for at least 1 week (data not shown). As a result, a period of 24 h was accepted as being sufficient to achieve the adsorption equilibrium.

3.2. Metal desorption from non-contaminated soils

These experiments, which aimed to determine the amount of metal that can be released from soil due to (i) the dissolution of some mineral/organic phases bearing this metal and (ii) "desorption" from the surface of soil particles, were performed with various soil to solution mass ratios (Fig. 2). For the surface horizon of the PP soil with the highest Pb and Cd contents, the amount of desorbed metals increased with the mass of the solid. For the other samples, the release of Pb did not change with an increase in soil mass (Fig. 2A) whereas an increase in Cd release with soil mass (Fig. 2B) was found. These results enabled the lowest limits of the Cd and Pb concentrations that could be used for the adsorption experiments to be determined.

The effect of pH on metal desorption from soil is shown in Fig. 3A and B. The concentration of Cd and Pb in solution decreased with the pH, similar to the situation found for the adsorption equilibria (see below). The weak increase in the desorbed lead concentration at pH > 6 (Fig. 3A) can be partly explained by its mobilization by organic matter, which is more soluble at these pH levels [47]. Indeed, the concentration of DOC in the experiments with surface horizons in both soils increased from 2–3 mg l^{-1} at $4 \leq pH \leq 6$ to 8–10 mg l^{-1} at pH ~ 7 (data not shown). It was also previously

Fig. 3. Concentrations of desorbed lead (A) and cadmium (B) from non-contaminated soils as a function of pH. Experimental conditions: 0.01 M NaCl, 20 g soil l^{-1}, 1 week exposure at 25 °C. The symbols represent the measurements and the lines are for guiding purposes.

Table 2
Parameters of the Langmuir equation (4) for the four studied soil samples.

| Soil	K_L (l/mol)	Γ_{max} (μmol/g)
Cadmium		
PPAB	$(0.8 \pm 0.2) \times 10^5$	4.8 ± 0.3
PPC	$(0.6 \pm 0.1) \times 10^5$	4.0 ± 0.2
CS S1	$(2.2 \pm 0.1) \times 10^5$	5.8 ± 0.2
CS S4	$(1.0 \pm 0.1) \times 10^5$	4.2 ± 0.2
Lead		
PPAB	4000 ± 500	22 ± 2
PPC	6000 ± 100	14 ± 2
CS S1	4500 ± 500	25 ± 2
CS S4	8000 ± 500	14 ± 1

shown that the proportion of dissolved Pb present in the form of organic complexes in soil solutions strongly increases at a near-neutral pH compared to a low pH [55].

3.3. Effect of metal concentration in solution on adsorption at a constant pH

The aim of these experiments was to quantify the amount of adsorbed metal at a constant pH in order to allow a straightforward comparison of the adsorption capacity of different soils under otherwise identical environmental conditions. The concentration of adsorbed Cd is plotted as a function of its equilibrium concentration in solution (Fig. 4) and the parameters of Eq. (4) are shown in Table 2. Of the four types of soil samples studied, only the surface horizon of the Chinese red soil (CS S1 sample) exhibited a higher cadmium adsorption capacity and adsorption constant, by a factor of 2 to 3, whereas the deep horizons of the two soils demonstrated a lower adsorption capacity than the surface horizons. The
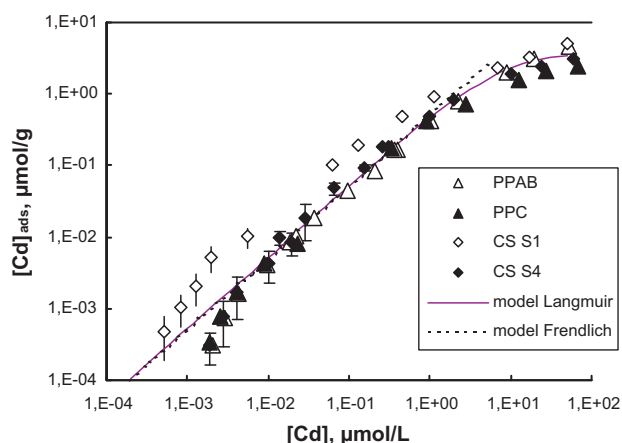
Fig. 4. Concentrations of adsorbed Cd as a function of the equilibrated Cd concentrations in solution for the four types of solid. Experimental conditions: 25 °C, 0.01 M NaNO₃, 1 week exposure under darkness. The pH values were pH 4.47 ± 0.09; 4.16 ± 0.30; 5.5 ± 0.2 and 5.4 ± 0.1 for the PPAB, PPC, CSS1 and CSS4 soils, respectively. When not visible, the experimental uncertainties are within the size of the symbols. The solid and dashed lines correspond to model calculations using the Langmuir and Freundlich equations, respectively. Parameters of the Langmuir equation: $\Gamma_{max} = 4.0 \pm 0.5$ μmol/g, $K_L = (1.3 \pm 0.3) \times 10^5$ l/mol. Parameters of the Freundlich equation: $K_F = 5 \times 10^5$; $n = 1$.
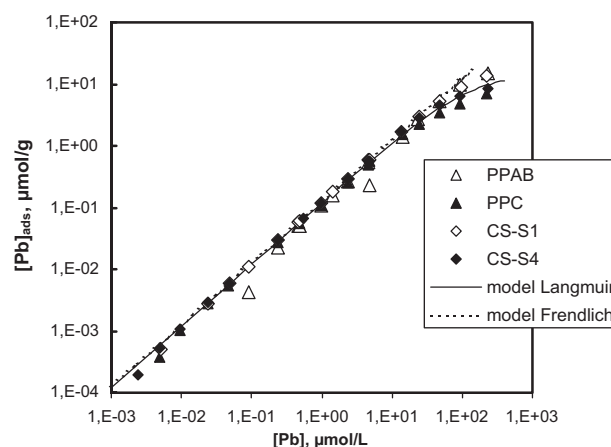

Fig. 5. Concentrations of adsorbed Pb as a function of the equilibrated Pb concentrations in solution for the four types of solid. Experimental conditions: 25 °C, 0.01 M NaNO₃, exposure 1 week in the darkness. The pH values were pH 4.4 ± 0.2; 5.0 ± 0.3; 5.3 ± 0.4 and 5.2 ± 0.3 for the PPAB, PPC, CS S1 and CS S4 soils, respectively. When not visible, the experimental uncertainties are within the size of the symbols. The solid and dashed lines correspond to the model calculations using the Langmuir and Freundlich equations, respectively. Parameters of the Langmuir equation: $\Gamma_{max} = 20 \pm 2$ μmol/g, $K_L = 6000$ l/mol. Parameters of the Freundlich equation: $K_F = 1.25 \times 10^5$; $n = 1$.

maximal adsorption capacity was estimated from fitting a Langmuir isotherm equation and ranged between 3 and 5 μmol/g or 0.2 and 0.8 μmol/m² for the different soils, which is comparable to the values of goethite, amorphous silica and clays [36]. We attempted to treat the data obtained for the whole concentration range (i.e., from 10^{-9} to 10^{-4} M) using Langmuir (Eq. (4)) and Freundlich (Eq. (7)) isotherms. We used a non-linear least squares fitting with 10% residual disagreement between the model and the experimental data. In contrast to the traditional linear fitting of adsorption equations, this simultaneously accounted for the wide range of high and low Cd and Pb concentrations used in this study. The semi-linear dependencies obtained on a log–log scale (Fig. 4) were valid over a large concentration range and could be successfully modelled using the same equations ((4) and (7)) parameters for all data collected from the four different soil samples: $\Gamma_{max} = 4.0 \pm 0.5$ μmol/g, $K_L = (1.3 \pm 0.3) \times 10^5$, $K_F = 5 \times 10^5$; $n = 1$.

The concentration of adsorbed Pb was plotted as a function of its equilibrium concentration in solution (Fig. 5), and the parameters of Eq. (4) are listed in Table 2. Similar to the results for cadmium, the surface horizon of Chinese red soil exhibited the highest adsorption capacity for lead, particularly for high cadmium concentrations. However, within the level of experimental uncertainty, the full set of data could be approximated using the same parameters of the Langmuir and Freundlich equations: $\Gamma_{max} = 20 \pm 2$ μmol/g, $K_L = 6000 \pm 500$; $K_F = 1.25 \times 10^5$; $n = 1$. The 1:1 slope between the adsorbed and aqueous Pb concentration was preserved over 5 orders of magnitude, suggesting the presence of only one type of surface site for all of the soil types, or that the different sites were not distinguishable within the resolution of our measurements.

### 3.4. Effect of pH on metal adsorption

The experiments on the pH-dependent adsorption edge allowed the effect of solution pH on the degree of metal adsorption to be assessed and thus an evaluation of the impact of amphoteric properties of soil surface sites on metal binding in a wide range of solution pH levels. The percentage of adsorbed Cd is plotted as a function of pH in Fig. 6. The level of adsorption increased with the pH level to achieve a maximum adsorption at pH ≥ 6 for each of the four samples. The adsorption edge was similar for both soils
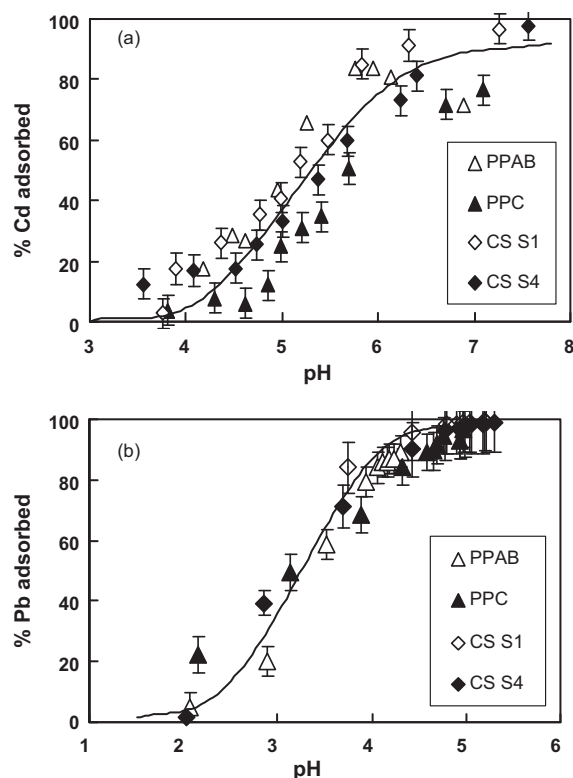
Fig. 6. Percentages of adsorbed Cd (a) and Pb (b) as a function of pH for the four types of soils. Experimental conditions: [Cd]₀ = 0.9 μM, 0.01 M NaNO₃, [Pb]₀ = 0.48 μM, 0.01 M NaNO₃, 8 g soil l⁻¹. The solid line represents the surface complexation modelling (SCM) results using a constant capacitance of the electric double layer equal to 1 F/m², surface sites density of 4 μmol/g (Cd, (a)) and 20 μmol/g (Pb, (b)) for soils with a specific surface area of 15 m² g⁻¹ and surface stability constants of reactions (10) and (11) equal to −4.0 and −0.1 ± 0.6 (Cd) and −4.0 and 0.7 ± 0.3 (Pb), respectively. The average uncertainty of the SCM prediction of adsorbed Cd was ±10%.

but the surface horizons exhibited a stronger affinity for metal as the adsorption began, and achieved a maximum at lower pH levels. The decrease in Cd adsorption at pH > 6.5 for the PPAB soil was most likely related to the increase in the DOC concentration and the release of metal in the form of organic complexes, as discussed earlier for the desorption experiments (Section 3.2).

We attempted to describe the pH-dependence of Cd adsorption in soils within the framework of the surface complexation model (SCM). The exact proportions of various mineral and organic composites of the studied soils and their metal and proton binding properties could not be determined. Therefore, we used the generalized composite approach, which assumes that the adsorptive reactivity of the surface can be described by surface complexation equilibria with the stoichiometry and formation constants determined by fitting the experimental data [56]. For simplicity, two surface reactions were postulated to control the metal adsorption on soils:

$$>SO–H^\circ = >SO^- + H^+, \quad \log K_a = -4.0 \quad (10)$$

$$>SO–H^\circ + Cd^{2+} = >SO–Cd^{2+} + H^+, \quad \log K_{Cd} = -0.1 \quad (11)$$
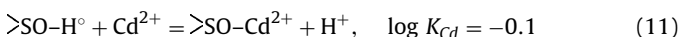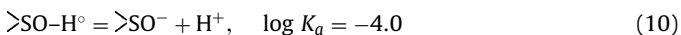
The first constant (K_a) was fixed within the range reported for acid–base parameters of Chinese loess soils [57] and soil clay minerals [1] and the second constant was allowed to vary in order to reproduce the experimental data using the MINTEQA2 code. The surface site density was fixed at 4 μmol/g (0.3–0.7 μmol/m^2), as measured in our experiments using the Langmuirian modelling approach (Fig. 4), and the constant capacitance of the electric double layer (EDL) was postulated as 1 F/m^2, which is the most common value used in surface complexation modelling. An example of a model calculation of the experimental data is shown in Fig. 6. We used a numerical approach to fit the percentage of adsorbed metal as a function of pH. A ≤10% difference between the measured and modelled percentages of adsorbed metal at each pH value was taken as a criterion of goodness of fit.

The uncertainty in experimental data does not allow K_a and K_{Cd} constants to be resolved with an accuracy greater than ±0.5 log units. Similar uncertainty levels can be attributed to $\log K_{Cd}$ variations between the surface and bottom horizons of various soil types. However, we would like to note the similarity of the pH-dependent adsorption edges for the four types of soil in the present study. This result agrees with the previous findings of Muller and Duffek [58], who found that the surface-normalized value of the adsorption constant for Cd on mineral oxides, sediments and suspended matter can be considered as a constant parameter within ±0.4 logarithmic units. This finding suggests, in accordance with the surface coordination theory [36], that the terminal oxygen sites >S–O$^-$ responsible for metal binding on solid surfaces are similar between various soil minerals and organic matter. As a result, one can use a universal surface adsorption constant to describe the interaction between metal pollutants and various soils.

The percentage of adsorbed Pb is plotted as a function of pH in Fig. 6b. Similar to cadmium, the adsorption increased with pH, achieving a maximum adsorption at pH ≥ 4 for the four types of soils. The adsorption edge was similar for the two soils. The results of the surface complexation modelling are presented as a solid line corresponding to the uncertainties attributed to the reaction (Eq. (8)) stability constant (Eq. (9)). For the Pb adsorption modelling the surface site density for all soils was fixed at 20 μmol/g (1–3 μmol/m^2), which was five times higher than for cadmium, as measured using the adsorption isotherms (Fig. 5). This difference between Cd and Pb in maximal surface adsorption densities is often reported for the adsorption of these metals on common inorganic and organic sorbents [31,52,59,60]. A recent study [61] showed that Pb retention on >FeOH soil sites occurred at a lower pH than Cd retention, suggesting that Pb adsorbs to surface hydroxyl groups at
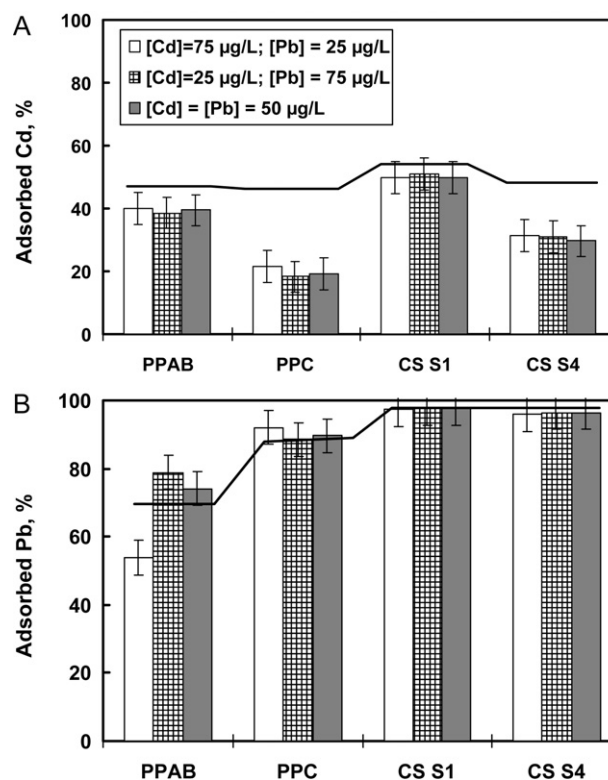

Fig. 7. Percentages of adsorbed Cd (A) and Pb (B) for four types of soil samples and different initial Cd/Pb ratios. Experimental conditions: [Pb]$_o$, [Cd]$_o$ = 25, 50 and 75 μg l^{-1} (0.06, 0.12 and 0.36 μM for Pb and 0.22, 0.44 and 0.66 μM for Cd), 0.01 M NaNO$_3$, 8 g soil l^{-1}. The pH values were pH 4.12, 4.61, 4.86 and 4.98 for PPAB, PPC, CSS1 and CSS4, respectively. See the comments written in Fig. 6.

pH values where Cd only interacts with exchange sites. In this study, consistent with the results for Cd, similar Pb adsorption edges, within ±10%, can be recognized in the four soil samples, in agreement with previous findings [11,58]. The disagreement between the measured and calculated adsorption yields at 4 ≤ pH ≤ 5 could be related to Pb complexation with dissolved organic matter, which would not have been taken into account by the model calculations.

3.5. Competition experiments

The metal adsorption competition experiments quantified the adsorption reactions under the most relevant environmental pollution conditions, i.e., when both metals were present in interstitial soil solutions. The results of simultaneous Cd and Pb adsorption onto four soil samples are reported as stack diagrams (Fig. 7A and B). Within experimental uncertainty, the percentage of each adsorbed metal did not depend on the presence of the second metal over the concentration range, which corresponded to realistic environmental pollution (0.1–1 μM). Indeed, within this concentration range at circumneutral pH, the surface sites were undersaturated by 100–1000 times with respect to the maximal amount of adsorbed metal. This was further supported by surface complexation modelling performed using the model parameters assessed for Cd and Pb in Section 3.4: the percentages of adsorbed lead and cadmium did not vary with the initial Cd/Pb ratio for each soil sample. Although high levels of experimental uncertainty associated with the reaction (Eq. (8)) stability constant do not allow the percentage of adsorbed metals at each given pH to be precisely reproduced, the general trend can be determined.

4. Discussion and conclusions

The first main result of this study is that over the very wide metal concentration range studied, from the nMol to the mMol scale in solution, the concentration of adsorbed Cd and Pb followed a similar pattern in a log–log scale for all four, rather contrasting, soil samples (Figs. 4 and 5). This indicates the similarity, within an order of magnitude, of the surface adsorption constants and the number of binding sites over the concentration range studied, from extremely polluted environments with mMol-level metal loads [49] to pristine interstitial soil solutions (nMol level [47,62]). This finding disagrees with the notion of having to consider low- and high-affinity sites in order to describe Cd or Pb adsorption in the soil samples studied. As such, it contradicts the common view of high surface heterogeneity of natural sorbents but greatly facilitates the predictive modelling of metal migration in both polluted and pristine soil settings.

The surface horizons of acidic brown soil (France) and red soils (China) exhibit great capacities for metal adsorption. Lead exhibits a higher adsorption affinity than Cd with respect to the soil surfaces studied, which is consistent with the different affinities of metals to clay [1] and soil organic matter [41]. It is known that anthropogenic lead migrates within the soil profile in the form of organic matter and Fe oxy(hydr)oxides [63]. The affinity of Pb to podzol soil is controlled by exchangeable clay fractions in the surface zone and by iron oxides throughout the whole profile [64]. However, a rigorous characterization of the chemical status of Pb, which can be associated both with organic and mineral components, would require *in situ* spectroscopic observations [65,66]; for example, the maximum surface adsorption capacities for these soils (i.e., 0.3–0.7 and 1–3 μmol/m^2 for Cd and Pb, respectively) are comparable with those of the most effective sorbents, such as iron oxides, clays and algal biomass [5,6,58]. The Γ_{max} values obtained are within the range reported for major Indian soils (0.3–0.6 μmol/g for Pb, 0.5–0.9 μmol/g for Cd [18]) but they are much lower than the range reported for humic acid soils (~770 μmol/g) [15] and organic-rich topsoils (3–10 μmol/g) [31]. Apparently, the presence of soil organic matter in the form of humus is likely to increase the adsorption of metals at pH ~ 5 [19,32]: the formation of ternary surface complexes between metal ions, oxide surface centres and organic ligands [67] can be evoked. Moreover, a humic-acid coating on montmorillonite might significantly enhance the sorption of cadmium and lead [4,68], and the presence of soluble organic matter amplifies the interaction of copper and zinc with amorphous allophanes [69].

The adsorption results indicate that the soil samples studied were not strongly polluted. Compared to the amount of metals that can be retained in the solid phase (i.e., ~450 mg kg^{-1} for Cd and ~3000 mg kg^{-1} for Pb, Figs. 4 and 5), the actual metal concentrations were low (0.03–0.2 mg kg^{-1} for Cd and 10–60 mg kg^{-1} for Pb). This is also supported by results of the simultaneous adsorption of Cd and Pb at environmentally relevant concentration levels: no competition was observed between these two metals (Fig. 7) as the surface sites remained far from being saturated. These soils are thus capable of adsorbing 100–1000 times more metals than levels authorized by the Environmental Policy. The actual metal concentrations did not exceed the maximum acceptable limit of 2 mg kg^{-1} for Cd or 70 mg kg^{-1} for Pb, as reported by [70] for soil organism protection. However, the maximal adsorption capacities were very different from the critical limits for soil damage. Although the soil samples studied had very high total metal adsorption capacities, the toxicity of metals to soil organisms is mainly related to metal availability and speciation in soils [47,48,71]. Therefore, increasing knowledge about the metal sorption capacity of soils is of great importance for understanding accumulated anthropogenic inputs because these constitute a future challenge for ecosystem protection based on the critical load concept [72].

Acknowledgements

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