Modelling lead(II) sorption to ferrihydrite and soil organic matter

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Environmental context. Lead(II) is a toxic metal pollutant with many anthropogenic sources. We show that lead(II) is bound more strongly to soil surfaces than previously understood. This knowledge may lead to better models for lead(II) dissolution from the soils, which will improve risk assessments for this metal.

Abstract. Lead(II) adsorption to soil organic matter and iron (hydr)oxides is strong, and may control the geochemical behaviour of this metal. Here, we report the adsorption of Pb^{2+} (i) to 2-line ferrihydrite, and (ii) to a mor layer. The results showed that ferrihydrite has heterogeneous Pb^{2+} binding. Use of a surface complexation model indicated that $\sim 1\%$ of the surface sites adsorbed Pb^{2+} more strongly than the remaining 99%. Although only one surface complexation reaction was used (a bidentate complex of the composition $(\equiv FeOH)_2Pb^+$), three classes of sites with different affinity for Pb^{2+} were needed to simulate Pb^{2+} binding correctly over all Pb/Fe ratios analysed. For the mor layer, Pb^{2+} sorption was much stronger than current models for organic complexation suggest. The results could be described by the Stockholm Humic Model when the binding heterogeneity was increased, and when it was assumed that 0.2% of the binding sites were specific for Pb. Use of revised model parameters for nine Vietnamese soils suggest that lead(II) binding was more correctly simulated than before. Thus, underestimation of lead(II) sorption to both (hydr)oxide surfaces and organic matter may explain the failure of previous geochemical modelling attempts for lead(II).

Introduction

Lead is a common soil pollutant and it often occurs in elevated levels in, for example, shooting ranges and in roadside soils. The ionic form of lead, Pb^{2+}, forms very stable complexes with several oxygen-containing ligands, for example carboxylate groups of organic matter and singly coordinated OH groups of (hydr)oxides. Because many soils contain appreciable amounts of organic matter and (hydr)oxides, the mobility and plant availability of Pb^{2+} is usually low. Nevertheless for environmental risk assessments of lead-polluted environments, it is of interest to understand and to model the process by which Pb^{2+} may be rendered soluble and potentially toxic.

In recent years, several efforts have been made to describe Pb^{2+} solubility and speciation in soils with process-oriented geochemical models such as WHAM with Model VI,[1] Ecosat/ NICA–Donnan[2] and Visual MINTEQ with SHM.[3,4] When applying the models, it has been assumed either that soil organic matter (SOM) is the dominant sorbent of Pb^{2+},[5–8] or that Pb^{2+} sorption is determined by reactions with both SOM, Fe/Al (hydr)oxides, and phyllosilicate clay minerals.[9–12]

Although it has been found that the solution speciation of Pb^{2+} is satisfactorily described with these models,[9,12] it has nearly always been observed that the lead dissolution from the solid phase is overestimated when generic parameters for Pb^{2+} binding to the different soil adsorbents are used. Weng et al.[9] observed that their multisurface geochemical model predicted total dissolved lead(II) concentrations that were between 0.5 and 2.1 log units larger than measured; these authors used the NICA–Donnan model for organic complexation in combination with the CD-MUSIC[13] and Diffuse Layer Models[14] for goethite and ferrihydrite respectively. Application of WHAM with Model VI to 116 surface horizons from British soils showed that total dissolved lead(II) was overestimated by a factor of 8.9, on average.[5] MacDonald and Hendershot[8] compared the NICA–Donnan and SHM (Stockholm Humic Model) organic complexation models for a range of smelter-affected Canadian soils, and they found that the dissolution of lead(II) was overestimated with 0.42 and 0.62 log units for the NICA–Donnan and SHM models respectively. In agreement with this, other researchers[6,7,15] had to

Table 1.   Properties of the Risbergshöjden Oe mor layer

Soil	Moisture (%)	Organic C (%) (dry weight)	BaCl$_2$ extraction (m mol kg^{-1}) (dry weight)		HNO$_3$ extraction (m mol kg^{-1}) (dry weight)		
			Ca	Mg	Al	Fe	Pb
Risbergshöjden Oe	69.5	41.7	80.3	13.8	15.7	1.3	0.18

adjust the Pb^{2+} binding affinity upwards in their models to match the observations.

Different hypotheses have been put forward to explain the systematic deviation between the models and the observations for lead(II). For example, it has been argued that the solutions used to extract lead(II) from the soil (usually weak acid or ethylenediaminetetraacetic acid (EDTA) solutions) may release not only geochemically active lead(II), but also other lead(II) forms, leading to an overestimation of the analytically determined pool of adsorbed lead(II).[9,15] Iron (hydr)oxides may be more efficient lead(II) scavengers than previously believed.[10] Other hypotheses have concerned the existence of other important soil adsorbents that are currently not accounted for in the models. For example, it has been pointed out that the presence of Mn oxide could lead to strong lead(II) sorption.[12,16]

Furthermore, it has been suggested that soil organic matter may bind Pb more strongly than isolated humic and fulvic acids (HA and FA) used to calibrate models for organic complexation.[10] This might be explained by the presence of different non-humic biomaterials that are known to bind lead(II) strongly. For example, very strong complexation of Pb^{2+} to alginic and pectic acids have been noted, even at very low pH.[17,18] These and similar acids are common constituents of plant biomaterials and microbes and they may be common in soils. Similarly, Conrad and Hansen[19] observed very strong Pb^{2+} complexation to coir, with practically 100% sorbed at pH 2.5 and higher. The mechanism of this interaction is not precisely known, although it most likely involves carboxylate groups.[18]

Concerning lead(II) binding to iron (hydr)oxides, spectroscopic studies have revealed that lead(II) is bound to iron (hydr)oxides such as goethite and ferrihydrite as an inner-sphere, edge-sharing, bidentate surface complex,[20–22] and possibly also as a corner-sharing bidentate complex under certain conditions.[20,23] In the case of ferrihydrite, some results indicate that the adsorption of lead(II) displays strong site heterogeneity, meaning that a small fraction of the surface sites seem to adsorb lead(II) much more strongly than other sites. This was first documented by Benjamin and Leckie[24,25] and later supported by results of Swedlund et al.[26]

The reason for the often observed site heterogeneity remains unknown although several efforts have been made to link it to various structural facets and integrate them into a surface complexation model.[27] A more empirical approach was taken by Dzombak and Morel,[14] who suggested the subdivision of the surface sites into high-affinity and low-affinity sites, accounting for 2.5 and 97.5% of the total number of sites respectively.

The purpose of this study was to address the reason for the unsuccessful modelling of the solid-solution partitioning of lead(II) by more closely investigating the lead(II) binding properties of ferrihydrite and organic matter, two phases that are believed to be of central importance for lead(II) binding. We tested whether soil organic matter is a strong lead(II) adsorbent by adding lead(II) to suspensions of a well-characterised Oe horizon from a Spodosol, which was low in other soil adsorbent phases. Furthermore, lead(II) adsorption to ferrihydrite was studied also at the very low Pb/Fe ratios typical of soil environments to investigate whether the heterogeneous lead(II) binding affinity to this sorbent is correctly described by current geochemical models.

Experimental

Ferrihydrite synthesis

A suspension of 2-line ferrihydrite was prepared using a method adapted from Swedlund and Webster[28] and Schwertmann and Cornell,[29] described in detail by Gustafsson.[30] Briefly, a solution containing 36 mM Fe(NO$_3$)$_3$ and 12 mM NaNO$_3$ was brought to pH 8.0 through drop-wise addition of 4 M NaOH. The resulting suspension was aged for 18–22 h at 20 °C. The iron (hydr)oxide particles in this suspension was examined by EXAFS spectroscopy[31] and found to be 2-line ferrihydrite. Shortly before use, the ferrihydrite suspension was back-titrated to pH 4.6 to avoid contamination with carbonate.

Soil properties

The mor layer sample used in this investigation, Risbergshöjden Oe, has been used in several previous works.[6,31,32] Some key properties of this soil are shown in Table 1.

Laboratory methods

To determine lead(II) adsorption to ferrihydrite, batch experiment suspensions were prepared by mixing an amount of ferrihydrite suspension with stock solutions of NaNO$_3$ and the appropriate concentration of Pb(NO$_3$)$_2$ to produce a range of concentrations of Pb and ferrihydrite. Various amounts of acid (as HNO$_3$) or base (as NaOH) were added to produce a range of pH values. The samples were equilibrated in 40-mL polypropylene centrifuge tubes.

The suspensions were shaken gently in an end-over-end shaker for 24 h at room temperature (21 °C), after which they were centrifuged for 30 min at ~5000 *g* at 21 °C, and filtered using 0.2-μm single-use filters (Acrodisc PF, Pall Corp., Port Washington, NY). The pH was measured on the unfiltered sample, using a Radiometer combination electrode (Radiometer Analytical SAS, Lyon, France). Part of the filtered suspension was acidified (1% HNO$_3$) and analysed for Pb and Fe with mass spectrometry using a Perkin-Elmer ELAN 6100 instrument (Perkin-Elmer Inc., Waltham, MA).

To check for possible artefacts owing to Pb^{2+} adsorption to container walls and to the filters, some solutions were equilibrated with 2.82 μM Pb^{2+} but without the ferrihydrite suspension. These results showed 0% Pb^{2+} adsorption at pH 4.1, 26% at pH 5.5, and 49% at pH 9.3; this indicated a negligible role of Pb^{2+} adsorption to container walls under most conditions of the experiment. However, based on these results it was concluded that a slight contribution of container wall sorption

Table 2. Surface complexation reactions used in the CD-MUSIC model for ferrihydrite

Δz_0, Δz_1 and Δz_2 are the change of charge in the o-, b- and d-planes respectively. For log K data two or three numbers indicate binding to sites with different affinity, the percentages of which are within parentheses (c.f. text)

Reaction	$(\Delta z_0, \Delta z_1, \Delta z_2)$	log K	Data source(s)
$FeOH^{1/2-} + H^+ \leftrightarrow FeOH_2^{1/2+}$	(1,0,0)	8.1	[14]
$FeOH^{1/2-} + Na^+ \leftrightarrow FeOHNa^{1/2+}$	(0,1,0)	−0.6	[34]
$FeOH^{1/2-} + H^+ + NO_3^- \leftrightarrow FeOH_2NO_3^{1/2-}$	(1,−1,0)	7.42	[34]
$2FeOH^{1/2-} + Pb^{2+} \leftrightarrow (FeOH)_2Pb^+$	(1.2,0.8,0)	9.45 (99 %)	This study
		12.18 (0.9 %)	
		14.15 (0.1 %)	

might have affected the results in high-pH samples at the highest Pb/Fe ratio used (results were not corrected for this effect). Similarly, the Fe concentrations in the filtrate were analysed to check for possible dissolution of ferrihydrite, or penetration of ferrihydrite through the filter. Some dissolution of ferrihydrite was noted at low pH, with at most 10 % of the ferrihydrite dissolved at pH 3.0, which fell to <1 % at pH 3.5 for suspension concentrations of 0.3 mM Fe as ferrihydrite. When the suspension concentrations were 3 mM Fe (as they were in most experiments), the corresponding errors were ten times lower. At pH 4 and above, the concentration of filterable Fe always accounted for less than 0.3 % of total Fe, and commonly less than 0.05 %. This indicates that the potential errors associated with assuming insignificant dissolution and penetration of ferrihydrite through the filters are not likely to have caused significant errors in the modelling calculations.

Concerning the soil experiments, the protocol has been described in detail earlier.[31,32] The sample was sieved through a 4-mm sieve immediately after collection, homogenised, and divided into two samples, one part that was air-dried at 40 °C and the other part was kept in its field-moist state at 5 °C. Organic C was determined using a LECO CHN analyser (LECO Corp., St Joseph, MI) on air-dried samples. The mor layer sample was extracted with 0.1 M $BaCl_2$ for 2 h to quantify initially bound Ca, Mg, Na and K. Initially bound, geochemically active, Al and Fe^{III} were estimated from extraction with 0.1 M HNO_3 for 16 h at a liquid to solid (L/S) ratio of 10. This acid extraction is expected to dissolve organically complexed Al and Fe^{III} as well as reactive inorganic phases; however, previous results showed that the contribution of inorganic phases in this mor layer is likely to be small (Gustafsson et al.[31]). Extracted Ca, Mg, Na, K, Al and Fe were determined with ICP-OES using a Jobin-Yvon JY24 ICP instrument (Instruments SA, Longjumeau, France)

Briefly, the batch experiments involved the mixing of 2 g of field-moist soil with 30 mL of solution for 7 days on an end-over-end shaker at 10 °C. The solution consisted of 0.01 M $NaNO_3$ to which different additions of lead(II) (as $Pb(NO_3)_2$), and acid (as HNO_3) or base (as NaOH) had been made. To some samples, iron(III) (as $Fe(NO_3)_3$) and aluminium (as $Al(NO_3)_3$) had been added as well. Procedures for centrifugation and filtration were the same as for the ferrihydrite samples except that the pH measurement was carried out at 10 °C.

Surface complexation modelling, ferrihydrite

In this work we used the 3-plane CD-MUSIC model[13] using the surface charging parameters of Gustafsson et al.[33] In the model approach, singly coordinated ≡FeOH groups are assumed to determine proton charging. The site density is set to 6.3 sites nm^{-2} using a molecular weight of ferrihydrite of 89 g mol^{-1} and a specific surface area of 750 m^2 g^{-1}. The inner- and outer-layer

capacitances are set to 1 and 0.74 C m^{-2}. Recently, Hiemstra and van Riemsdijk[34] presented a related but slightly more complex model for ferrihydrite in which they also considered proton-active triply coordinated ≡Fe₃O groups, present at a site density of 1.2 sites nm^{-2} (17 % of the total). However, in the light of recent structural determinations of ferrihydrite,[35,36] which suggest a small or insignificant role of the ≡Fe₃O groups, we believe that our model, in which the ≡Fe₃O groups are neglected, is reasonable.

The implementation of the CD-MUSIC model for uranium(VI)[33] considered the possible existence of surface site heterogeneity by dividing the sites into high- and low-affinity sites with 99 and 1 % of the number of sites respectively. This approach is similar to the one Dzombak and Morel[14] used for the Diffuse Layer Model. In the present study it was observed (see below) that a third site, present at a very low concentration but having a very strong affinity for Pb^{2+}, was needed to adequately describe Pb^{2+} adsorption at very low Pb/Fe ratios. Hence every surface complexation reaction was defined for three different sites that amounted to 99, 0.9 and 0.1 % of the total number of sites respectively.

The surface complexation reactions were constrained from spectroscopic evidence showing that Pb^{2+} forms a bidentate complex with iron (hydr)oxides.[20–22] Therefore in the modelled reaction, one Pb^{2+} ion was reacted with two ≡FeOH groups (Table 2). For the Pb^{2+} surface complexes the CD (charge distribution) values that describe the change in o-plane and b-plane charge were fitted.

In the model optimisation process, surface complexation constants and CD values for a given reaction were optimised with Brent's method to minimise the RMSE (root-mean square error) in the adsorbed fraction. This was done by using specially developed software, which used Visual MINTEQ[37] as its calculation engine. When CD values were being fitted, the procedure was repeated until an optimal set of CD values (that led to the lowest RMSE values) was found.

Some other datasets with Pb^{2+} adsorption data to ferrihydrite[24–26] were also analysed to investigate whether they were consistent or not with our own laboratory data. The datasets were scanned in from the original publications using Engauge Digitizer. It soon became apparent that the data of Swedlund et al.[26] were consistent with our own; when the two datasets were optimised separately very similar surface complexation constants for Pb^{2+} were obtained (data not shown). It was therefore decided to merge these datasets into one single dataset with 65 data points collected at 8 different combinations of Pb^{2+} and ferrihydrite concentrations.

Complexation of Pb to mor layer material

The SHM[3] was used to simulate the binding of Pb and major cations (Ca, Mg, Na, K, Al and Fe) to soil organic matter.

Table 3. Parameter values for cation complexation to soil organic matter in the Stockholm Humic Model (SHM)

Constants for Ca^{2+} and Mg^{2+} are from Gustafsson et al.,[31] those for Fe^{3+} are from Sjöstedt et al.,[41] and those for Al^{3+} were optimised using the same methods as for Pb^{2+}[38]

Cation	Humic acid and fulvic acid				
	$\log K_{Mm}$	$\log K_{Mb}$	$\log K_{Mt}$	$\log K_{MtOH}$	ΔLK_2
Al^{3+}	–	−4.06	−9.45	–	1.06
Ca^{2+}	−2.2	–	–	–	0.3
Fe^{3+}	–	−1.68	−4.6	–	1.7
Mg^{2+}	−2.5	–	–	–	0.3
Pb^{2+}	−0.40	−5.92	–	–	0.98/1.55[A]

	High-affinity ligand	
	$\log K_{Mm}$	Site concentration (mmol kg^{-1} dry soil)
Pb^{2+}	3.0	3.52 (0.2 % of total number of sites)

[A]The ΔLK_2 value for the $\log K_{Mm}$ constant of solid-phase organic matter was set to 1.55; for the $\log K_{Mb}$ constant of solid-phase organic matter, and for the constants for dissolved organic matter, $\Delta LK_2 = 0.98$.

The SHM is a discrete-site/electrostatic model in which the HA or FA is assumed to have eight proton-binding sites with different acid-base characteristics. Metals are allowed to bind to HA or FA by forming monodentate and bidentate complexes, or by electrostatic attractions. The use of the model for soil suspensions has been detailed in other publications.[4,31] We used the same proton-binding parameters as in earlier publications.[4] Generic Pb-binding parameters for the SHM were calculated using datasets given by Milne et al.[38] Equilibrium constants for the complexation of lead(II) and major cations are given in Table 3.

To describe lead(II) binding to the Risbergshöjden Oe horizon, it was found that addition of a high-affinity site, to which Al and Fe^{III} did not bind, was necessary to correctly reproduce the data (c.f. Results section).

Several assumptions had to be made to set up the model. For the Oe horizon, we assumed that 75 % of the 'active' solid-phase organic matter consisted of HA, whereas 25 % was FA.[31] The fraction of the solid-phase organic matter that was 'active' was estimated in the manner described by Gustafsson and van Schaik.[32] Furthermore, we assumed that 100 % of the dissolved organic matter in these suspensions was FA. The suspension concentrations of Pb and major cations that were used as input in the model were determined from extractions.[31]

Modelling Pb sorption to Vietnamese soils

Khai et al.[11] reported batch experiment results for desorption of lead(II) and other metals from the surface horizon of nine Vietnamese soils, and applied a multisurface model involving SHM and DLM (Diffuse Layer Model) to investigate the model fit (which was rather poor in the case of lead(II)). In our study, the results from the modelling attempts with ferrihydrite and mor layer material were combined to see whether the fits of Khai et al.[11] for lead(II) could be improved.

Methods for data collection and modelling were described in detail by Khai et al.,[11] and we followed the same procedures here, for consistency. In summary, the concentration of ferrihydrite (or HFO) in the model was calculated from ascorbate extraction, taking into account the contribution of crystalline Fe (hydr)oxides and Al hydroxide as extracted by dithionite-citrate and oxalate.[39] The concentration of solid-phase HA and FA was constrained from NaOH extraction, the cation exchange capacity of the clay was set to 0.1 eq kg^{-1}, and the concentration

of geochemically active (adsorbed + dissolved) metals and exchangeable cations were provided by EDTA and NH_4NO_3 extractions respectively.

Results and discussion

Lead sorption to ferrihydrite in single-sorbate systems

The adsorption data collected at four different Pb/Fe ratios varying from 9.3×10^{-5} to 9.3×10^{-2} showed that the adsorption edge was displaced to lower pH values when the Pb/Fe ratios were lowered (Fig. 1). The results agreed with those of Swedlund et al.[26] and indicated substantial surface site heterogeneity.

To describe these data in the surface complexation model, we tested a model that did not lead to a release of H^+ in the reaction (Table 2), according to the model for Pb^{2+} adsorption to goethite that was suggested by Hiemstra and van Riemsdijk.[40] However, three sites with different affinity for Pb^{2+} were needed to describe all the datasets adequately. The resulting model was able to fit all data from both this study and from the study of Swedlund et al.[26] (Fig. 2) almost perfectly ($rmse = 0.025$), but only when the CD values for the o-plane and b-plane were set to 1.2 and 0.8 respectively, which indicates an unusually asymmetric Pb-O bonding environment for the $(\equiv FeOH)_2Pb^+$ surface complex. This means that the fraction of the Pb^{2+} charge attributed to the surface (f) would be high (i.e. 0.6). This result is identical to the one of Hiemstra and van Riemsdijk[40] for Pb^{2+} adsorption to goethite. It should be pointed out, however, that an equally good fit to our data can be obtained with an alternative model in which Pb^{2+} is able to displace one H^+ from the surface. On the basis of the present data it is not possible to deduce which model is the more likely one – we will return to this subject in a later paper.

Note that the modelling exercise precludes a substantial role of a hydrolysed $(\equiv FeOH)_2PbOH^0$ complex, as the f value for this complex would be unrealistically low ($f = 0.05$) to explain Pb^{2+} binding in the pH region of the adsorption edge. This is consistent with the asymmetry of the bound Pb^{2+} ion, which would make it less prone to hydrolyse. However, a $(\equiv FeOH)_2PbOH^0$ complex could possibly be of some importance at high pH, several pH units above the adsorption edge.[40]

The results can be also compared to those of some earlier studies, most importantly perhaps those of Benjamin and Leckie,[24,25] whose results formed the basis of the Pb^{2+} surface complexation constants for the DLM as suggested by Dzombak
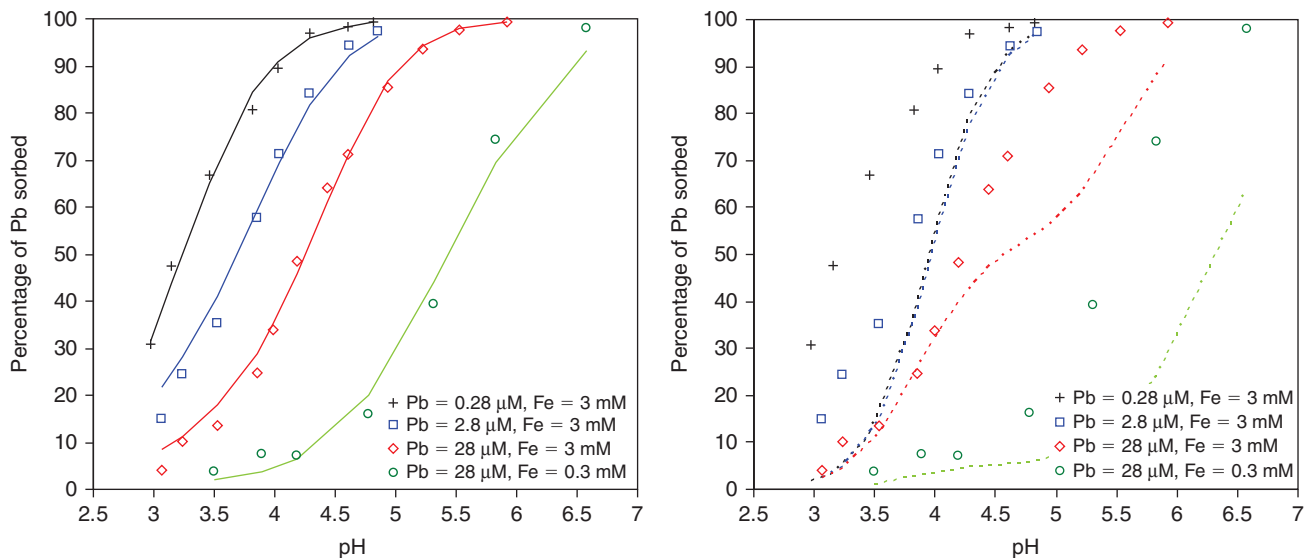
Fig. 1. Percentage adsorption of lead on ferrihydrite as a function of pH in 0.01 M NaNO₃. The points are measurements; legends show total concentrations of Fe and Pb in the suspensions. Left panel: Lines are fits with the optimised surface complexation parameters shown in Table 1. Right panel: Lines are fits with parameters and constants of Dzombak and Morel.[14]
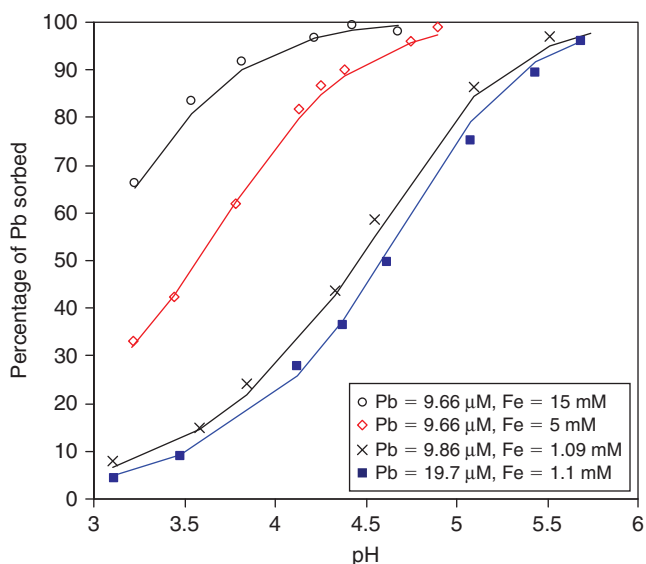

Fig. 2. Percentage adsorption of lead on ferrihydrite as a function of pH in 0.1 M NaNO₃, data from Swedlund et al.[26] The points are measurements; legends show total concentrations of Fe and Pb in the suspensions. Lines are fits with the optimised surface complexation parameters shown in Table 1.

and Morel.[14] As Fig. 1 shows, this model underestimates Pb^{2+} binding in our systems, particularly at low Pb/Fe ratios, which would be more realistic for field conditions. Possible reasons include (i) a relatively short equilibration time (4 h), and (ii) insufficient solid-solution separation conditions (the samples were not filtered) in the study of Benjamin and Leckie[24,25]; these factors might have contributed to the lower observed Pb^{2+} binding affinity[26]. This suggests that many previous multisurface modelling attempts, in which Dzombak and Morel's model parameterisation was employed, are likely to have underestimated the extent of Pb^{2+} adsorption to ferrihydrite.

Mechanism of lead adsorption to ferrihydrite

The finding that lead(II) has a heterogeneous binding affinity over a wide concentration range is in accordance with several earlier batch experiment studies on lead binding to ferrihydrite. Apart from Swedlund et al.,[26] whose results are accounted for in the model, similar results were obtained also by Benjamin and Leckie,[24,25] although the latter study did not include results at very low Pb/Fe ratios.

For modelling purposes we employed the empirical approach of Dzombak and Morel[14] to divide the ferrihydrite surface into different site classes with similar acid-base properties but with different Pb^{2+} surface complexation constants. The type of distribution that provided the best model fits was one in which the sites with lowest affinity accounted for a relatively large part of the total number of sites (i.e. 99%). Because the site heterogeneity for Pb^{2+} manifests itself only at small Pb/Fe ratios, models that address Pb^{2+} binding heterogeneity in a more process-oriented way (e.g. by considering various complexes bound to different major sites)[27] are difficult to constrain as this requires confirmation of the assumed surface structures by means of EXAFS spectroscopy at very low lead(II) concentrations (which are difficult to get with today's generation of synchrotrons). It is interesting to note, however, that the Pb^{2+} sorption data, despite the three different site classes, can be described well using just one type of surface complexation reaction. This indicates that the Pb^{2+} sorption mechanism may not differ in a significant way as a function of the Pb/Fe ratio, and that the extremely strong Pb^{2+} binding at very small Pb/Fe ratios could be owing to, for example, favourable steric arrangements for a small number of Pb^{2+} surface complexes, rather than to a fundamental difference in surface structures.

Lead adsorption to mor layer material

Because Pb^{2+} adsorption to organic matter is very strong in the natural pH range, correct solid-solution separation and analytical speciation become issues that are not easily overcome without the use of a reliable analytical speciation method. To avoid this we carried out equilibrations with the mor layer sample at a very low pH value (2.5). Despite these extreme conditions, the Risbergshöjden Oe horizon was able to remove >95% of the added Pb^{2+} from solution over a wide range of Pb^{2+} additions (Fig. 3).
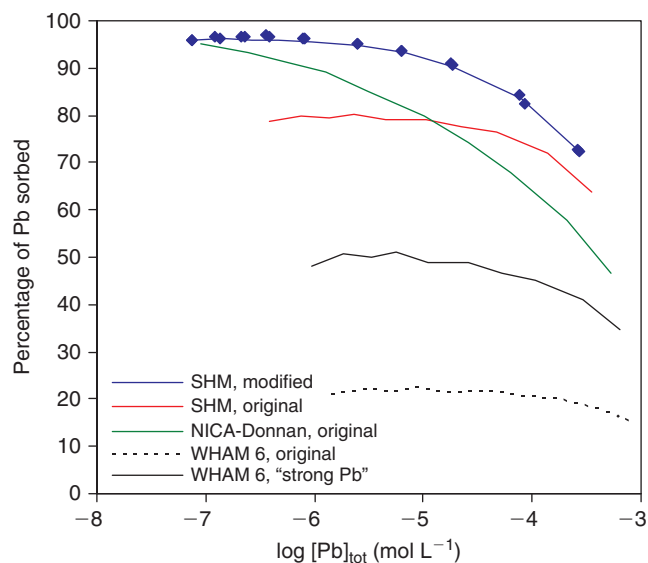
Fig. 3. The percentage Pb sorbed to the Risbergshöjden Oe sample at pH 2.5, as a function of the logarithm of the total dissolved Pb concentration, log $[Pb]_{tot}$. Points are measurements, whereas the lines are model fits using different model versions (c.f. text).

Fig. 4. Total dissolved Pb against pH for Risbergshöjden Oe. Titrations of soil samples with HNO_3 or $NaOH$, with and without the addition of $1500\,\mu M$ $Fe(NO_3)_3$ or $1500\,\mu M$ $Al(NO_3)_3$. The points are observed values. The lines are SHM fits with the parameters described in Table 3.

In the next step, we investigated the ability of today's organic complexation models to properly describe the observed patterns when complexation constants for dissolved humic and fulvic acid were assumed to properly represent Pb^{2+} binding also to solid-phase humic and fulvic acid. The model WHAM 6.0, with constants given by Tipping[1] behaved poorly for this particular system, and underestimated Pb^{2+} adsorption considerably. Revised Pb complexation constants were suggested by Tipping et al.[15]; this improved the simulation somewhat but Pb^{2+} adsorption was still underestimated. We also employed the NICA–Donnan model[2] with generic Pb^{2+} complexation constants for humic and fulvic acid.[38] Although this model still underestimated lead(II) binding, it behaved far better particularly at very low Pb^{2+} concentrations. At higher Pb^{2+} concentrations the NICA–Donnan model behaved less satisfactorily. Lastly we performed the same kind of simulation using the Stockholm Humic Model with generic parameters for humic and fulvic acid. Again Pb^{2+} adsorption was underestimated considerably, suggesting that the generic complexation constants, developed for dissolved humic and fulvic acid, were not appropriate for solid-phase organic matter.

Three measures were taken to improve the fit in the SHM: (1) using the approach of Gustafsson and Kleja,[4] we accounted for the stronger contribution of electrostatic effects to the overall sorption of Pb to solid-phase humic and fulvic acid; (2) the heterogeneity parameter ΔLK_2 was increased from 0.98 to 1.55 for both solid-phase humic and fulvic acid; and (3) inclusion of a high-affinity site in the model that was specific for Pb^{2+}, the concentration of which amounted to 0.2 % of the total number of sites on humic and fulvic acid combined (see Table 3). The resulting model was able not only to fit the Pb binding isotherm at pH 2.5 (Fig. 3), but it also provided a good fit to a series of batch experiment data for the same soil, at different pH and in the absence or presence of added Al and Fe^{III} (Fig. 4).

Mechanism of lead adsorption to organic soil materials

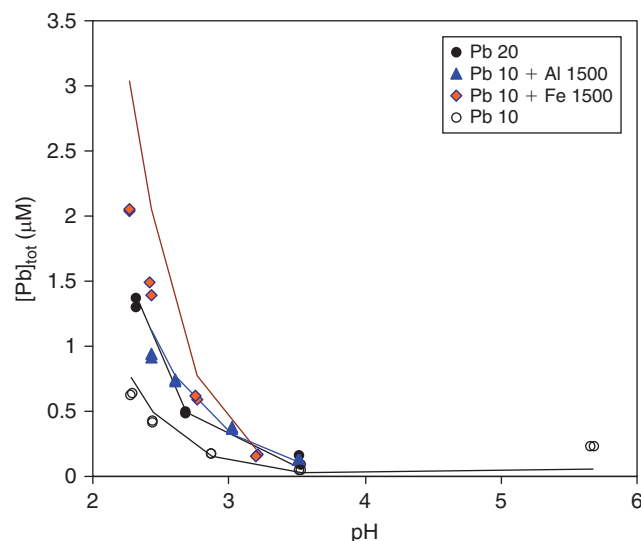From the above it seems clear that the mor layer material binds Pb^{2+} more strongly than the models suggest, when these models assume humic and fulvic acid to be the active components. Because the Risbergshöjden Oe horizon is very low in inorganic components,[31] the most likely explanation for the poor behaviour of the original SHM seems to be connected to the Pb binding affinity of soil organic matter. The modelling exercise indicated that some unknown organic component, probably non-humic, was in part responsible for the strong Pb^{2+} retention at low pH. More detailed studies employing a range of advanced spectroscopic and other techniques will be required to cast light on the exact mechanism, however.

Lead adsorption to Vietnamese soils

At first we investigated the model performance when (i) metal binding to solid-phase HA and FA was calculated using the assumption that generic parameters for dissolved HA and FA could be used and when (ii) lead(II) binding to Fe (hydr)oxides was calculated using the Dzombak and Morel model.[14] The result is seen in Fig. 5 on the left; as expected, the model predicted much higher dissolved lead(II) concentrations than observed. When metal binding to solid-phase HA and FA was instead described with the revised model for Risbergshöjden Oe, and when the three-site CD-MUSIC model as parameterised above was used for lead(II) adsorption to Fe (hydr)oxides, a much improved fit was obtained (although certainly not perfect), with simulated concentrations of dissolved lead(II) being of the correct magnitude (Fig. 5). The root-mean square error of the logarithm of the lead(II) concentration was found to be 0.35, compared to 0.76 when the original model was used. A closer look at the modelling results with the revised model reveals that organic lead(II) complexation is predicted to predominate at pH < 6, whereas lead(II) adsorption to (hydr)oxides is dominant at higher pH (Fig. 6).

Implications

Our results indicate, first of all, that there may be different factors that explain the poor Pb fits of earlier multisurface modelling attempts. Our lead(II) binding results for ferrihydrite and mor layer material show that lead(II) binding to these soil components may have been previously underestimated. In the
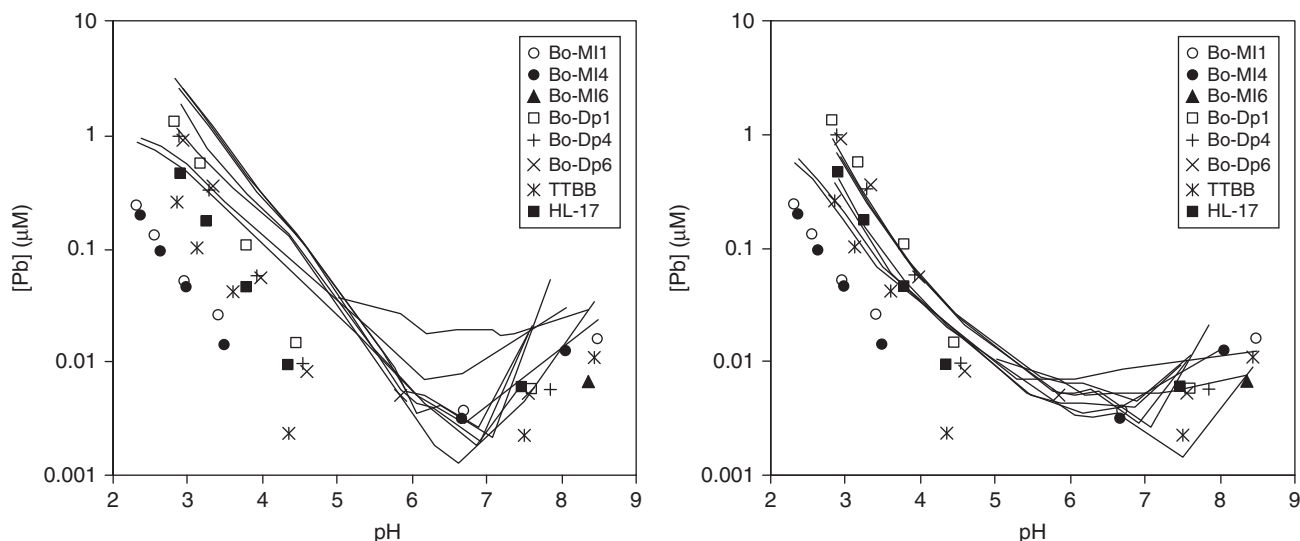
Fig. 5. Total dissolved Pb against pH for nine Vietnamese soils.[11] Titrations of soil samples with HNO$_3$ or NaOH. The points are observed values. Left panel: Lines are fits with generic parameters for SHM in combination with the DLM for oxide adsorption according to Dzombak and Morel.[14] Right panel: Lines are fits with revised parameters for the SHM and CD-MUSIC models as suggested in this paper.
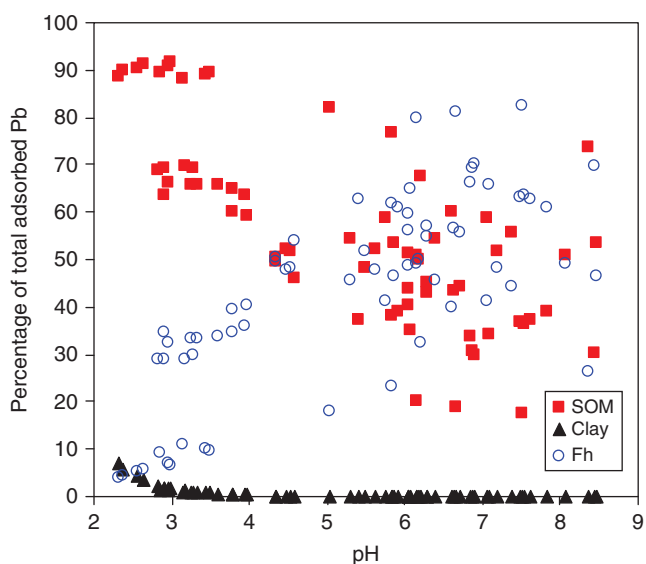

Fig. 6. Modelled composition of adsorbed Pb as a function of pH for nine Vietnamese soils. SOM, Pb bound to soil organic matter; Clay, Pb ion-exchanged to clay; Fh, Pb bound to Fe and Al (hydr)oxides.

case of ferrihydrite, the heterogeneity of Pb^{2+} adsorption may extend to even lower Pb/Fe ratios than previously realised, which could explain part of the model deviation. For soil organic matter, there seems to be an unknown component that binds lead(II) very strongly at low equilibrium Pb^{2+} concentrations, a component that does not exist in isolated humic or fulvic acid. It may be hypothesised that this component may be related either to plant matter or to microorganisms such as bacteria, and that it may be an important scavenger for lead(II) in the surface horizon of soils.

The much improved model fit for Vietnamese soils obtained after revised parameterisation of the SHM and CD-MUSIC models indicates that it may be possible to consider the stronger Pb binding in current multisurface models without too much difficulty.

Conclusions

The binding of lead(II) to both ferrihydrite and soil organic matter was stronger than is currently accounted for in most geochemical models. This study confirms earlier research that 2-line ferrihydrite has a heterogeneous Pb^{2+} binding-site affinity. Application of the CD-MUSIC surface complexation model to the observations indicates that ∼1 % of the surface sites bind Pb^{2+} more strongly than the remaining 99 %. Although three different classes of sites were needed to simulate Pb^{2+} binding correctly over the whole range of Pb/Fe ratios, only one type of surface complexation reaction was required.

Concerning lead(II) binding to a mor layer, more than 95 % of applied lead(II) was bound at a very low pH (2.5) and at low equilibrium lead(II) concentrations. The results could be described only when substantial changes were made to the Pb^{2+} binding parameters of solid-phase HA and FA of the Stockholm Humic Model, indicating stronger binding, particularly at low lead(II) concentrations. It is suggested that the strongly Pb-binding organic component is non-humic in nature.

When combining the revised models and applying them for a set of Vietnamese soils that were previously studied, it was found that much improved fits for lead(II) were obtained. This shows that it may be possible to revise current geochemical models to consider the stronger binding of lead(II) to the studied soil components.

Acknowledgements

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