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

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18
19 **Environmental context.** Lead(II) is a well-known metal pollutant with many
20 anthropogenic sources. Here we show that lead(II) is bound more strongly to soil surfaces
21 (iron (hydr)oxide, organic matter) than previously understood. This knowledge may lead
22 to better models for lead(II) dissolution from the soils, which will improve risk
23 assessments for this metal.

1 **Abstract.** Lead(II) adsorption to soil organic matter and iron (hydr)oxides is strong, and
2 may control the geochemical behavior of this metal. Here, we report the adsorption of
3 Pb^{2+} (i) to 2-line ferrihydrite, and (ii) to a mor layer. The results showed that ferrihydrite
4 has heterogeneous Pb^{2+} binding. Use of a surface complexation model indicated that
5 about 1 % of the surface sites adsorbed Pb^{2+} more strongly than the remaining 99 %.
6 Although only one surface complexation reaction was used (a bidentate complex of the
7 composition $(\equiv FeOH)_2 Pb^+$), three classes of sites with different affinity for Pb^{2+} were
8 needed to simulate Pb^{2+} binding correctly over all Pb/Fe ratios analysed. For the mor
9 layer, Pb^{2+} sorption was much stronger than current models for organic complexation
10 suggest. The results could be described by the Stockholm Humic Model when the binding
11 heterogeneity was increased, and when it was assumed that 0.2 % of the binding sites
12 were specific for Pb. Use of revised model parameters for nine Vietnamese soils suggest
13 that lead(II) binding was more correctly simulated than before. Thus, underestimation of
14 lead(II) sorption to both (hydr)oxide surfaces and organic matter may explain the failure
15 of previous geochemical modelling attempts for lead(II).

16

17 **Introduction**

18 Lead is a common soil pollutant and it often occurs in elevated levels in, for example,
19 shooting ranges and in roadside soils. The ionic form of lead, Pb^{2+} , forms very stable
20 complexes with a number of oxygen-containing ligands, for example carboxylate groups
21 of organic matter and singly coordinated OH groups of (hydr)oxides. Because many soils
22 contain appreciable amounts of organic matter and (hydr)oxides the mobility and plant
23 availability of Pb^{2+} is usually low. Nevertheless for environmental risk assessments of

1 lead-polluted environments it is of interest to understand and to model the process by
2 which Pb^{2+} may be rendered soluble and potentially toxic.

3

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

10

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

1 researchers^[6,7,15] had to adjust the Pb^{2+} binding affinity upwards in their models to match
2 the observations.
3
4 Different hypotheses have been put forward to explain the systematic deviation between
5 the models and the observations for lead(II). For example, it has been argued that the
6 solutions used to extract lead(II) from the soil (usually weak acid or EDTA solutions)
7 may release not only geochemically active lead(II), but also other lead(II) forms, leading
8 to an overestimation of the analytically determined pool of adsorbed lead(II)^[9,15]. Iron
9 (hydr)oxides may be more efficient lead(II) scavengers than previously believed^[10]. Other
10 hypotheses have centered around the existence of other important soil adsorbents that are
11 currently not accounted for in the models. For example, it has been pointed out that the
12 presence of Mn oxide could lead to strong lead(II) sorption.^[12,16]
13
14 Furthermore, it has been suggested that soil organic matter may bind Pb more strongly
15 than isolated humic and fulvic acids (HA and FA) used to calibrate models for organic
16 complexation.^[10] This might be explained by the presence of different non-humic
17 biomaterials that are known to bind lead(II) strongly. For example, very strong
18 complexation of Pb^{2+} to alginic and pectic acids have been noted, even at very low
19 pH.^[17,18] These and similar acids are common constituents of plant biomaterials and
20 microbes and they may be common in soils. Similarly, Conrad and Hansen^[19] observed
21 very strong Pb^{2+} complexation to coir, with practically 100 % sorbed at pH 2.5 and
22 higher. The mechanism of this interaction is not precisely known, although it most likely
23 involves carboxylate groups.^[18]

1

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

10

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

16

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

1 to investigate whether the heterogeneous lead(II) binding affinity to this sorbent is
2 correctly described by current geochemical models.

3

4 **Experimental**

5 *Ferrihydrite synthesis*

6 A suspension of 2-line ferrihydrite was prepared using a method adapted from Swedlund
7 and Webster^[28] and Schwertmann and Cornell^[29], described in detail by Gustafsson.^[30]
8 Briefly, a solution containing 36 mM Fe(NO₃)₃ and 12 mM NaNO₃ was brought to pH
9 8.0 through drop-wise addition of 4 M NaOH. The resulting suspension was aged for 18-
10 22 h at 20°C. The iron (hydr)oxide particles in this suspension was examined by EXAFS
11 spectroscopy^[31] and found to be 2-line ferrihydrite. Shortly before use, the ferrihydrite
12 suspension was back-titrated to pH 4.6 to avoid contamination with carbonate.

13

14 *Soil properties*

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

17

18 **Table 1. Properties of the Risbergshöjden Oe mor layer**

Soil	moisture	Organic C	BaCl ₂ extraction		HNO ₃ extraction		
	%	%	mmol kg ⁻¹		mmol kg ⁻¹		
		(dry weight)	(dry weight)		(dry weight)		
			Ca	Mg	Al	Fe	Pb
Risbergshöjden Oe	69.5	41.7	80.3	13.8	15.7	1.3	0.18

19

1

2 *Laboratory methods*

3 To determine lead(II) adsorption to ferrihydrite, batch experiment suspensions were
4 prepared by mixing an amount of ferrihydrite suspension with stock solutions of NaNO_3
5 and the appropriate concentration of $\text{Pb}(\text{NO}_3)_2$ to produce a range of concentrations of Pb
6 and ferrihydrite. Various amounts of acid (as HNO_3) or base (as NaOH) were added to
7 produce a range of pH values. The samples were equilibrated in 40 ml polypropylene
8 centrifuge tubes.

9

10 The suspensions were shaken gently in an end-over-end shaker for 24 h at room
11 temperature (21°C), after which they were centrifuged for 30 min at about 5000g, and
12 filtered using 0.2- μm single-use filters (Acrodisc PF). The pH was measured on the
13 unfiltered sample, using a Radiometer combination electrode. Part of the filtered
14 suspension was acidified (1 % HNO_3) and analyzed for Pb and Fe with mass
15 spectrometry using a Perkin-Elmer ELAN 6100 instrument.

16

17 To check for possible artifacts because of Pb^{2+} adsorption to container walls and to the
18 filters, some solutions were equilibrated with 2.82 μM Pb^{2+} but without the ferrihydrite
19 suspension. These results showed 0 % Pb^{2+} adsorption at pH 4.1, 26 % at pH 5.5, and 49
20 % at pH 9.3; this indicated a negligible role of Pb^{2+} adsorption to container walls under
21 most conditions of the experiment. However, based on these results it was concluded that
22 a slight contribution of container wall sorption might have affected the results in high-pH
23 samples at the highest Pb/Fe ratio used (results were not corrected for this effect).

1 Similarly, the Fe concentrations in the filtrate were analyzed to check for possible
2 dissolution of ferrihydrite, or penetration of ferrihydrite through the filter. Some
3 dissolution of ferrihydrite was noted at low pH, with at most 10 % of the ferrihydrite
4 dissolved at pH 3.0, which fell to < 1 % at pH 3.5 for suspension concentrations of 0.3
5 mM Fe as ferrihydrite. When the suspension concentrations were 3 mM Fe (as they were
6 in most experiments) the corresponding errors were ten times lower. At pH 4 and above,
7 the concentration of filterable Fe always accounted for less than 0.3 % of total Fe, and
8 commonly less than 0.05 %. This indicates that the potential errors associated with
9 assuming insignificant dissolution and penetration of ferrihydrite through the filters are
10 not likely to have caused significant errors in the modelling calculations.

11

12 Concerning the soil experiments, the protocol has been described in detail earlier.^[31,32]
13 The sample was sieved through a 4 mm sieve immediately after collection, homogenized,
14 and divided into two samples, one part that was air-dried at 40°C and the other part was
15 kept in its field-moist state at 5°C. Organic C was determined using a LECO CHN
16 analyzer on air-dried samples. The mor layer sample was extracted with 0.1 M BaCl₂ for
17 2 hours to quantify initially bound Ca, Mg, Na and K. Initially bound, geochemically
18 active, Al and Fe(III) were estimated from extraction with 0.1 M HNO₃ for 16 h at a
19 liquid to solid (L/S) ratio of 10. This acid extraction is expected to dissolve organically
20 complexed Al and Fe(III) as well as reactive inorganic phases; however, previous results
21 showed that the contribution of inorganic phases in this mor layer is likely to be small
22 (Gustafsson et al., 2007).. Extracted Ca, Mg, Na, K, Al and Fe were determined with
23 ICP-OES using a Jobin-Yvon JY24 instrument.

1

2 Briefly, the batch experiments involved the mixing of 2 g field-moist soil with 30 cm³
3 solution for 7 d on an end-over-end shaker at 10°C. The solution consisted of 0.01 M
4 NaNO₃ to which different additions of lead(II) (as Pb(NO₃)₂), and acid (as HNO₃) or base
5 (as NaOH) had been made. To some samples, iron(III) (as Fe(NO₃)₃) and aluminium (as
6 Al(NO₃)₃) had been added as well. Procedures for centrifugation and filtration were the
7 same as for the ferrihydrite samples except that pH measurement was carried out at 10°C.

8

9 *Surface complexation modelling, ferrihydrite*

10 In this work we used the 3-plane CD-MUSIC model^[13] using the surface charging
11 parameters of Gustafsson et al.^[33] In the model approach, singly coordinated ≡FeOH
12 groups are assumed to determine proton charging. The site density is set to 6.3 sites nm⁻²
13 using a molecular weight of ferrihydrite of 89 g/mol and a specific surface area of 750
14 m²/g. The inner- and outer-layer capacitances are set to 1 and 0.74 C m⁻², respectively.
15 Recently, Hiemstra and van Riemsdijk^[34] presented a related but slightly more complex
16 model for ferrihydrite in which they also considered proton-active triply coordinated
17 ≡Fe₃O groups, present at a site density of 1.2 sites nm⁻² (17 % of the total). However, in
18 the light of recent structural determinations of ferrihydrite^[35,36], which suggest a small or
19 insignificant role of the ≡Fe₃O groups, we believe that our model, in which the ≡Fe₃O
20 groups are neglected, is reasonable.

21

22 The implementation of the CD-MUSIC model for uranium(VI)^[33] considered the
23 possible existence of surface site heterogeneity by dividing the sites into high- and low-

1 affinity sites with 99 % and 1 % of the number of sites, respectively. This approach is
 2 similar to the one Dzombak and Morel^[14] used for the Diffuse Layer Model. In the
 3 present study it was observed (see below) that a third site, present at a very low
 4 concentration but having a very strong affinity for Pb²⁺, was needed to adequately
 5 describe Pb²⁺ adsorption at very low Pb/Fe ratios. Hence every surface complexation
 6 reaction was defined for three different sites that amounted to 99, 0.9 and 0.1 % of the
 7 total number of sites, respectively.

8
 9 The surface complexation reactions were constrained from spectroscopic evidence
 10 showing that Pb²⁺ forms a bidentate complex with iron (hydr)oxides.^[20-22] Therefore in
 11 the modelled reaction, one Pb²⁺ ion was reacted with two ≡FeOH groups (Table 2). For
 12 the Pb²⁺ surface complexes the CD (charge distribution) values that describe the change
 13 in *o*-plane and *b*-plane charge were fitted.

14

15 **Table 2. Surface complexation reactions used in the CD-MUSIC model for**
 16 **ferrihydrate**

Reaction	($\Delta z_0, \Delta z_1, \Delta z_2$) ^A	log K^B	Data source(s)
$\text{FeOH}^{1/2-} + \text{H}^+ \leftrightarrow \text{FeOH}_2^{1/2+}$	(1,0,0)	8.1	[14]
$\text{FeOH}^{1/2-} + \text{Na}^+ \leftrightarrow \text{FeOHNa}^{1/2+}$	(0,1,0)	-0.6	[34]
$\text{FeOH}^{1/2-} + \text{H}^+ + \text{NO}_3^- \leftrightarrow \text{FeOH}_2\text{NO}_3^{1/2-}$	(1,-1,0)	7.42	[34]
$2\text{FeOH}^{1/2-} + \text{Pb}^{2+} \leftrightarrow (\text{FeOH})_2\text{Pb}^+$	(1.2,0.8,0)	9.45 (99 %)	This study
		12.18 (0.9 %)	
		14.15 (0.1 %)	

17 ^AThe change of charge in the *o*-, *b*- and *d*-planes respectively.

1 ^BTwo or three numbers indicate binding to sites with different affinity, the percentages of which are within
2 brackets (c.f. text).

3

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

10

11 Some other data sets with Pb²⁺ adsorption data to ferrihydrite^[24-26] were also analyzed
12 to investigate whether they were consistent or not with our own laboratory data. The data
13 sets were scanned in from the original publications using Engauge Digitizer. It soon
14 became apparent that the data of Swedlund et al.^[26] were consistent with our own; when
15 the two data sets were optimized separately very similar surface complexation constants
16 for Pb²⁺ were obtained (data not shown). It was therefore decided to merge these data sets
17 into one single data set with 65 data points collected at 8 different combinations of Pb²⁺
18 and ferrihydrite concentrations.

19

20 *Complexation of Pb to mor layer material*

21 The SHM (Stockholm Humic Model)^[3] was used to simulate the binding of Pb and major
22 cations (Ca, Mg, Na, K, Al and Fe) to soil organic matter. The SHM is a discrete-site /
23 electrostatic model in which the HA or FA is assumed to have eight proton-binding sites
24 with different acid-base characteristics. Metals are allowed to bind to HA or FA by

1 forming monodentate and bidentate complexes, or by electrostatic attraction. The use of
 2 the model for soil suspensions has been detailed in other publications.^[4,31] We used the
 3 same proton-binding parameters as in earlier publications.^[4] Generic Pb-binding
 4 parameters for the SHM were calculated using data sets given by Milne et al.^[38]
 5 Equilibrium constants for the complexation of lead(II) and major cations are given in
 6 Table 3.

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

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 ^B
	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)			

10 ^AConstants for Ca²⁺ and Mg²⁺ are from [31], those for Fe³⁺ are from [41], and those for Al³⁺ were optimized
 11 using the same methods as for Pb²⁺.^[38]

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

14

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

4

5 A number of assumptions had to be made to set up the model. For the Oe horizon, we
6 assumed that 75 % of the ‘active’ solid-phase organic matter consisted of HA, whereas 25
7 % was FA.^[31] The fraction of the solid-phase organic matter that was ‘active’ was
8 estimated in the manner described by Gustafsson and van Schaik.^[32] Furthermore, we
9 assumed that 100 % of the dissolved organic matter in these suspensions was FA. The
10 suspension concentrations of Pb and major cations that were used as input in the model
11 were determined from extractions.^[31]

12

13 *Modelling Pb sorption to Vietnamese soils*

14 Khai et al.^[11] reported batch experiment results for desorption of lead(II) and other metals
15 from the surface horizon of nine Vietnamese soils, and applied a multisurface model
16 involving the SHM and DLM models to investigate the model fit (which was rather poor
17 in the case of lead(II)). In our study, the results from the modelling attempts with
18 ferrihydrite and mor layer material were combined to see whether the fits of Khai et al.
19 ^[11] for lead(II) could be improved.

20

21 Methods for data collection and modelling were described in detail by Khai et al. ^[11], and
22 we followed the same procedures here, for consistency. In summary, the concentration of
23 ferrihydrite (or HFO) in the model was calculated from ascorbate extraction, taking into

1 account the contribution of crystalline Fe (hydr)oxides and Al hydroxide as extracted by
2 dithionite-citrate and oxalate.^[39] The concentration of solid-phase HA and FA was
3 constrained from NaOH extraction, the cation exchange capacity of the clay was set to
4 0.1 eq kg⁻¹, and the concentration of geochemically active (adsorbed+dissolved) metals
5 and exchangeable cations were provided by EDTA and NH₄NO₃ extractions,
6 respectively.

7

8

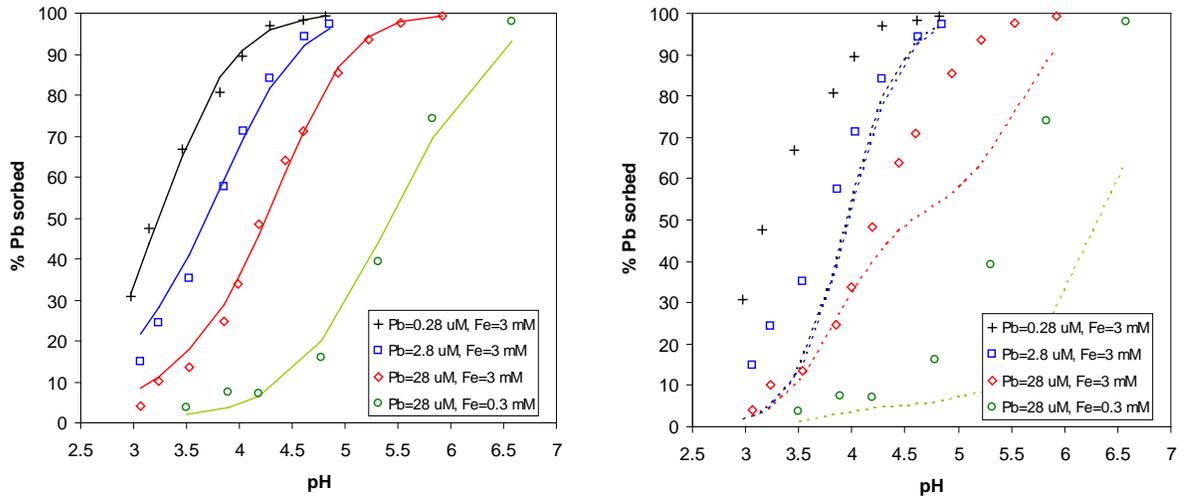
9 **Results and discussion**

10

11 *Lead sorption to ferrihydrite in single-sorbate systems*

12 The adsorption data collected at four different Pb/Fe ratios varying from 9.3×10^{-5} to
13 9.3×10^{-2} showed that the adsorption edge was displaced to lower pH values when the
14 Pb/Fe ratios were lowered (Fig. 1). The results agreed with those of Swedlund et al.^[26]
15 and indicated substantial surface site heterogeneity.

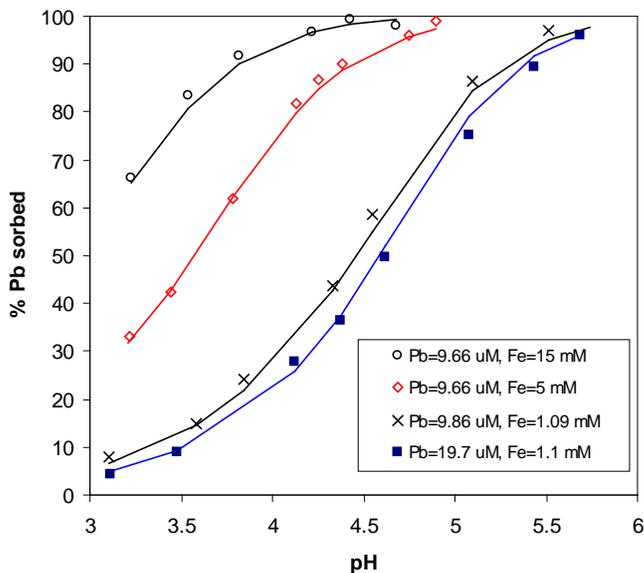
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Fig. 1. Percent adsorption of lead on ferrihydrite as a function of pH in 0.01 M NaNO₃.

The points are measurements; legends show total concentrations of Fe and Pb in the suspensions. Left panel: Lines are fits with the optimized surface complexation parameters shown in Table 1. Right panel: Lines are fits with parameters and constants of Dzombak and Morel. ^[14]



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

6
 7 To describe these data in the surface complexation model, we tested a model that did
 8 not lead to a release of H⁺ in the reaction (Table 2), according to the model for Pb²⁺
 9 adsorption to goethite that was suggested by Hiemstra and van Riemsdijk.^[40] However,
 10 three sites with different affinity for Pb²⁺ were needed to describe all the data sets
 11 adequately. The resulting model was able to fit all data from both this study and from the
 12 study of Swedlund et al.^[26] (Fig. 2) almost perfectly (*rmse* = 0.025), but only when the
 13 CD values for the *o*-plane and *b*-plane were set to 1.2 and 0.8, respectively, which
 14 indicates an unusually asymmetric Pb-O bonding environment for the (≡FeOH)₂Pb⁺
 15 surface complex. This means that the fraction of the Pb²⁺ charge attributed to the surface

1 (f) would be high, i.e. 0.6. This result is identical to the one of Hiemstra and van
2 Riemsdijk^[40] for Pb²⁺ adsorption to goethite. It should be pointed out, however, that an
3 equally good fit to our data can be obtained with an alternative model in which Pb²⁺ is
4 able to displace one H⁺ from the surface. On the basis of the present data it is not possible
5 to deduce which model is the more likely one – we will return to this subject in a later
6 paper.

7
8 Note that the modelling exercise precludes a substantial role of a hydrolyzed
9 ($\equiv\text{FeOH}$)₂PbOH⁰ complex, as the *f* value for this complex would be unrealistically low (*f*
10 = 0.05) to explain Pb²⁺ binding in the pH region of the adsorption edge. This is consistent
11 with the asymmetry of the bound Pb²⁺ ion, which would make it less prone to hydrolyze.
12 However, a ($\equiv\text{FeOH}$)₂PbOH⁰ complex could possibly be of some importance at high pH,
13 several pH units above the adsorption edge.^[40]

14
15 The results can be also compared to those of some earlier studies, most importantly
16 perhaps those of Benjamin and Leckie^[24,25] whose results formed the basis of the Pb²⁺
17 surface complexation constants for the DLM (Diffuse Layer Model) as suggested by
18 Dzombak and Morel.^[14] As Fig. 1 shows, this model underestimates Pb²⁺ binding in our
19 systems, particularly at low Pb/Fe ratios, which would be more realistic for field
20 conditions. Possible reasons include (i) a relatively short equilibration time (4 h), and (ii)
21 insufficient solid-solution separation conditions (the samples were not filtered) in the
22 study of Benjamin and Leckie^[24,25]; these factors might have contributed to the lower
23 observed Pb²⁺ binding affinity^[26]. This suggests that many previous multisurface

1 modelling attempts, in which Dzombak and Morel's model parameterization was
2 employed, are likely to have underestimated the extent of Pb^{2+} adsorption to ferrihydrite.

3

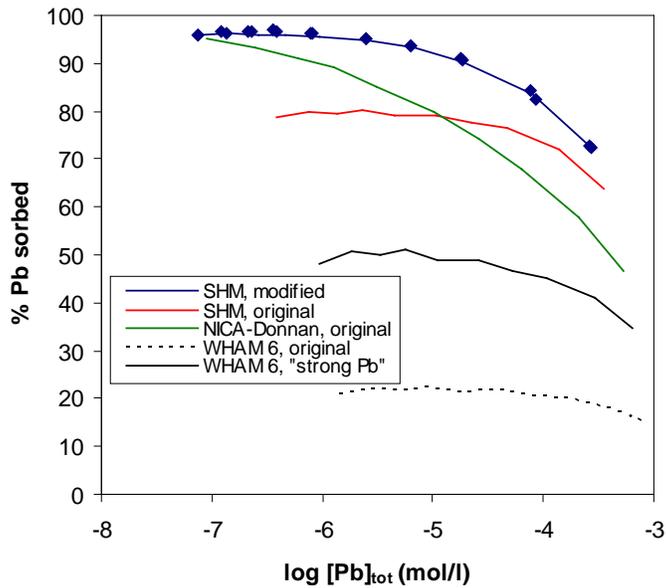
4 *Mechanism of lead adsorption to ferrihydrite*

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

10

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

1 differ in a significant way as a function of the Pb/Fe ratio, and that the extremely strong
2 Pb^{2+} binding at very small Pb/Fe ratios could be due to, *e.g.*, favorable steric
3 arrangements for a small number of Pb^{2+} surface complexes, rather than to a fundamental
4 difference in surface structures.
5



6
7
8 **Fig. 3.** The percentage Pb sorbed to the Risbergshöjden Oe sample at pH 2.5, as a
9 function of the logarithm of the total dissolved Pb concentration, $\log [\text{Pb}]_{\text{tot}}$. Points are
10 measurements, whereas the lines are model fits using different model versions (c.f. text).

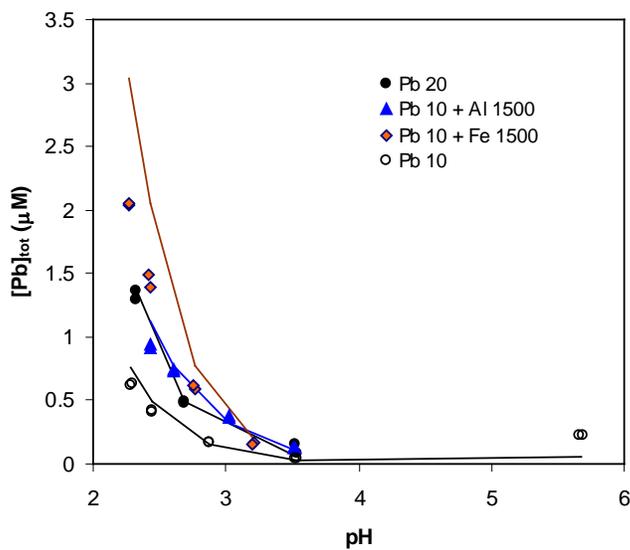
11

12 *Lead adsorption to mor layer material*

13 Because Pb^{2+} adsorption to organic matter is very strong in the natural pH range, correct
14 solid-solution separation and analytical speciation become issues that are not easily
15 overcome without the use of a reliable analytical speciation method. To avoid this we
16 carried out equilibrations with the mor layer sample at a very low pH value (2.5). Despite

1 these extreme conditions, the Risbergshöjden Oe horizon was able to remove > 95 % of
2 the added Pb^{2+} from solution over a wide range of Pb^{2+} additions (Fig. 3).
3
4 In the next step, we investigated the ability of today's organic complexation models to
5 properly describe the observed patterns when complexation constants for dissolved humic
6 and fulvic acid were assumed to properly represent Pb^{2+} binding also to solid-phase
7 humic and fulvic acid. The model WHAM 6.0, with constants given by Tipping^[11]
8 behaved poorly for this particular system, and underestimated Pb^{2+} adsorption
9 considerably. Revised Pb complexation constants were suggested by Tipping et al.^[15];
10 this improved the simulation somewhat but Pb^{2+} adsorption was still underestimated. We
11 also employed the NICA-Donnan model^[21] with generic Pb^{2+} complexation constants for
12 humic and fulvic acid.^[38] Although this model still underestimated lead(II) binding, this
13 model behaved far better particularly at very low Pb^{2+} concentrations. At higher Pb^{2+}
14 concentrations the NICA-Donnan model behaved less satisfactorily. Lastly we performed
15 the same kind of simulation using the Stockholm Humic Model (SHM) with generic
16 parameters for humic and fulvic acid. Again Pb^{2+} adsorption was underestimated
17 considerably, suggesting that the generic complexation constants, developed for dissolved
18 humic and fulvic acid, were not appropriate for solid-phase organic matter.
19
20 Three measures were taken to improve the fit in the SHM: 1) Using the approach of
21 Gustafsson and Kleja^[4], we accounted for the stronger contribution of electrostatic effects
22 to the overall sorption of Pb to solid-phase humic and fulvic acid; 2) The heterogeneity
23 parameter ΔLK_2 was increased from 0.98 to 1.55 for both solid-phase humic and fulvic

1 acid, and 3) Inclusion of a high-affinity site in the model that was specific for Pb^{2+} , the
 2 concentration of which amounted to 0.2 % of the total number of sites on humic and
 3 fulvic acid combined (see Table 3). The resulting model was able not only to fit the Pb
 4 binding isotherm at pH 2.5 (Fig. 3) but it also provided a good fit to a series of batch
 5 experiment data for the same soil, at different pH and in the absence or presence of added
 6 Al and Fe(III) (Fig. 4).



7
 8 **Fig. 4.** Total dissolved Pb against pH for Risbergshöjden Oe. Titrations of soil samples
 9 with HNO_3 or NaOH , with and without the addition of $1500 \mu\text{M Fe}(\text{NO}_3)_3$ or $1500 \mu\text{M}$
 10 $\text{Al}(\text{NO}_3)_3$. The points are observed values. The lines are SHM fits with the parameters
 11 described in Table 3.

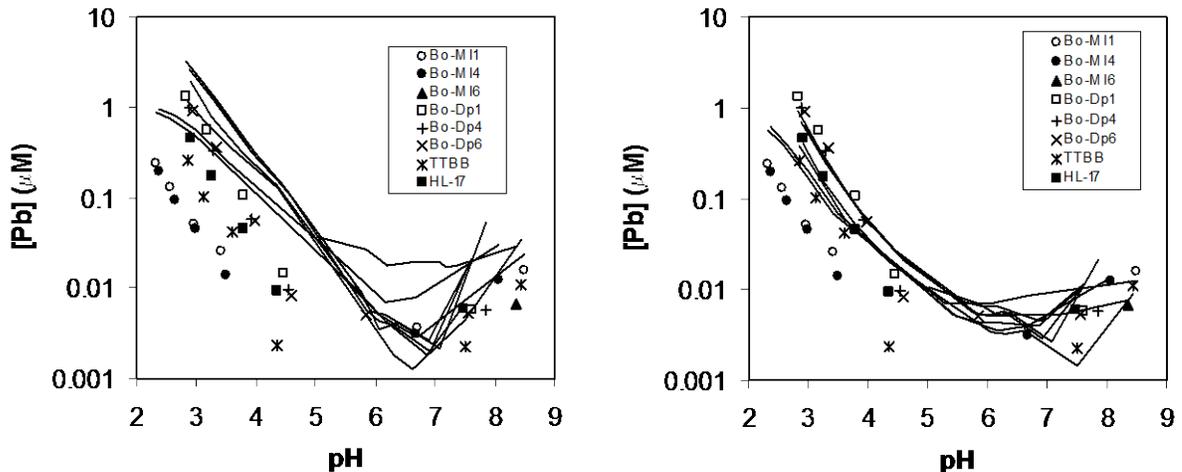
12

13 *Mechanism of lead adsorption to organic soil materials*

14 From the above it seems clear that the mor layer material binds Pb^{2+} more strongly than
 15 the models suggest, when these models assume humic and fulvic acid to be the active

1 components. Because the Risbergshöjden Oe horizon is very low in inorganic
 2 components^[31] the most likely explanation for the poor behaviour of the original SHM
 3 model seems to be connected to the Pb binding affinity of soil organic matter. The
 4 modelling exercise indicated that some unknown organic component, probably non-
 5 humic, was in part responsible for the strong Pb²⁺ retention at low pH. More detailed
 6 studies employing a range of advanced spectroscopic and other techniques will be
 7 required to cast light on the exact mechanism, however.

8



9

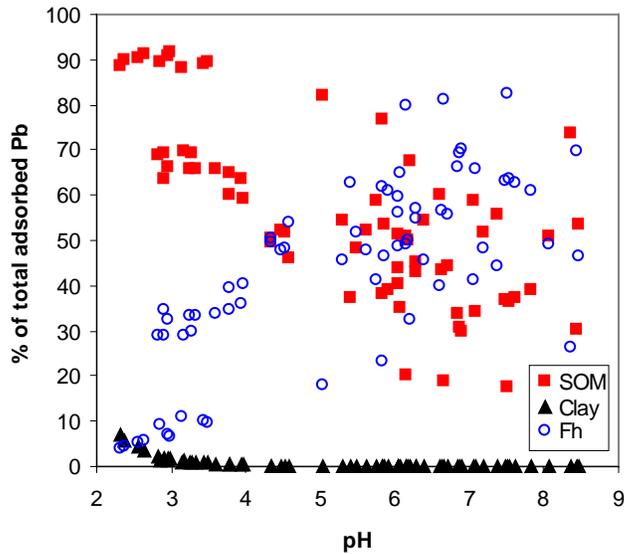
10 **Fig. 5.** Total dissolved Pb against pH for nine Vietnamese soils.^[11] Titrations of soil
 11 samples with HNO₃ or NaOH. The points are observed values. Left panel: Lines are fits
 12 with generic parameters for SHM in combination with the DLM for oxide adsorption
 13 according to Dzombak and Morel.^[14] Right panel: Lines are fits with revised parameters
 14 for the SHM and CD-MUSIC models as suggested in this paper.

15

16

1 *Lead adsorption to Vietnamese soils*

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



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

4

5 *Implications*

6 Our results indicate, first of all, that there may be different factors that explain the poor
 7 Pb fits of earlier multisurface modelling attempts. Our lead(II) binding results for
 8 ferrihydrite and mor layer material show that lead(II) binding to these soil components
 9 may have been previously underestimated. In the case of ferrihydrite, the heterogeneity of
 10 Pb^{2+} adsorption may extend to even lower Pb/Fe ratios than previously realized, which
 11 could explain part of the model deviation. For soil organic matter, there seems to be an
 12 unknown component that binds lead(II) very strongly at low equilibrium Pb^{2+}
 13 concentrations, a component that does not exist in isolated humic or fulvic acid. It may be
 14 hypothesized that this component may be related either to plant matter or to

1 microorganisms such as bacteria, and that it may be an important scavenger for lead(II) in
2 the surface horizon of soils.

3
4 The much improved model fit for Vietnamese soils obtained after revised
5 parameterization of the SHM and CD-MUSIC models indicates that it may be possible to
6 consider the stronger Pb binding in current multisurface models without too much
7 difficulty.

8

9 **Conclusions**

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

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

23

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

5

6

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13

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