Environ. Chem. **2013**, *10*, 465-474
doi:10.1071/EN13153_AC

Supplementary material

Predicting Pb^{II} adsorption on soils: the roles of soil organic matter, cation competition and iron (hydr)oxides

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Description of the SHM and CD-MUSIC models

The SHM is a discrete-site/electrostatic model which was described in details in previous studies.[1–3] It is assumed that the HA or FA has eight proton-binding sites and metals can bind to HA or FA by forming monodentate and bidentate complexes, or by electrostatic attractions. The following reactions describe the formation of monodentate and bidentate metal complexes (using Pb^{2+} as an example):

$$\mathrm{ROH} + \mathrm{Pb}^{2+} = \mathrm{ROPb}^{+} + \mathrm{H}^{+} \quad K_{Mm} \text{ (S1)}$$

$$2\mathrm{ROH} + \mathrm{Pb}^{2+} = (\mathrm{RO})_2\mathrm{Pb} + 2\mathrm{H}^{+} \quad K_{Mb} \text{ (S2)}$$

The heterogeneity of site affinity for metal complexation for both monodentate and bidentate sites can be accounted for by introducing the parameter ΔLK_2:

$$\log K_{Mm,x} = \log K_{Mm} + x \cdot \Delta LK_2 \text{ (S3)}$$

$$\log K_{Mb,x} = \log K_{Mb} + 2x \cdot \Delta LK_2 \text{ (S4)}$$

where $x = 0, 1, 2, 3$.

Furthermore, a high-affinity site that was specific for Pb^{2+} and to which Al and Fe^{III} did not bind was added in the model.[3] The concentration of the high-affinity site amounted to 0.2 % of the total number of sites on humic and fulvic acid combined. The equilibrium constants for cation complexation in the SHM are presented in Table S1.

Table S1. Equilibrium constants for cation complexation in the SHM (from Gustafsson et al.[3])

Cation	log K_{Mm}	log K_{Mb}	ΔLK_2
		HA and FA	
Al^{3+}	–	–4.06	1.06
Ca^{2+}	–2.2	–11.3	0.3
Fe^{3+}	–	–1.68	1.7
Mg^{2+}	–2.5	–	0.3
Pb^{2+}	–0.40	–5.92	1.55
		High-affinity site	
Pb^{2+}	3.0	–	–

The 3-plane CD-MUSIC model, which was described in details by Gustafsson et al.,[3] was used to describe Pb^{2+} complexation with amorphous Fe (hydr)oxides, input as ferrihydrite. For ferrihydrite, the site density is 6.3 sites nm^{-2} and the specific surface area is 750 m^2 g^{-1}. The inner- and outer-layer capacitances are set to 1 and 0.74 F m^{-2}. The surface complexation reaction of Pb^{2+} with ferrihydrite can be described with following equation:

$$2FeOH^{1/2-} + Pb^{2+} = (FeOH)_2Pb^{+} \quad K \text{ (S5)}$$

In this equation one Pb^{2+} ion was reacted with two $FeOH^{1/2-}$ groups. To account for the surface site heterogeneity, there are three different sites that amounted to 99, 0.9 and 0.1 % of the total number of sites with log *K* values of 9.45, 12.18, and 14.15. The changes of charge in the *o*- and *b*- planes are 1.2 and 0.8. The surface complexation reactions used in CD-MUSIC model for ferrihydrite are summarised in Table S2.

Table S2 Surface complexation reactions used in CD-MUSIC model for ferrihydrite (from Gustafsson et al.[3])

Reaction	log *K*
$FeOH^{1/2-} + H^{+} = FeOH_2^{1/2+}$	8.1
$FeOH^{1/2-} + Na^{+} = FeOHNa^{1/2+}$	–0.6
$FeOH^{1/2-} + H^{+} + NO_3^{-} = FeOH_2NO_3^{1/2-}$	7.42
$2FeOH^{1/2-} + Pb^{2+} = (FeOH)_2Pb^{+}$	9.45 (99%); 12.18 (0.9%); 14.15 (0.1%)

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Additional modelling results

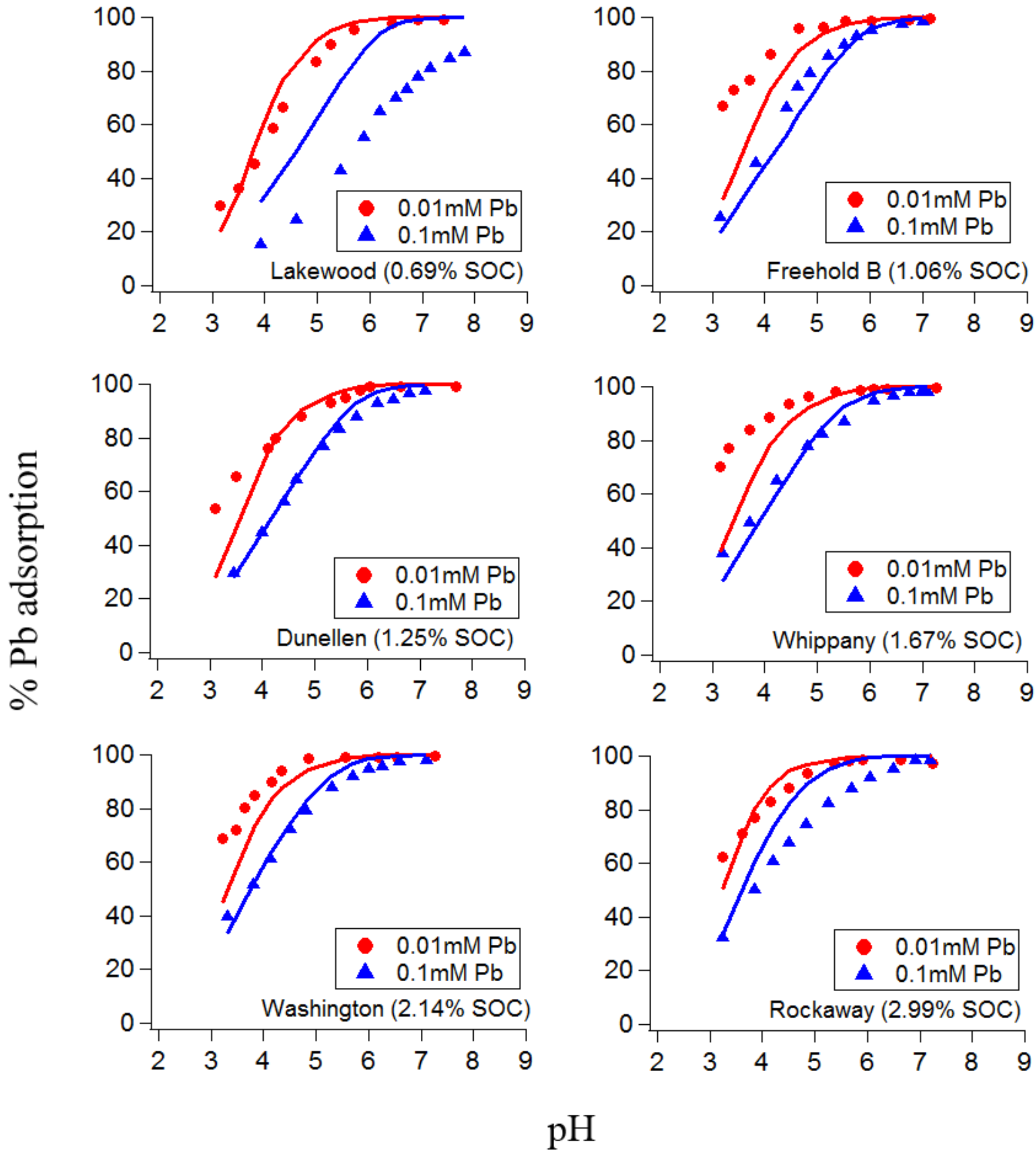

Fig. S1. Predicting adsorption edges for Pb adsorption on six soils at two initial Pb concentrations. Symbols are experimental data and solid lines are model predictions. The soil names, soil organic carbon (SOC) concentrations, and initial Pb concentrations are indicated in the figure.

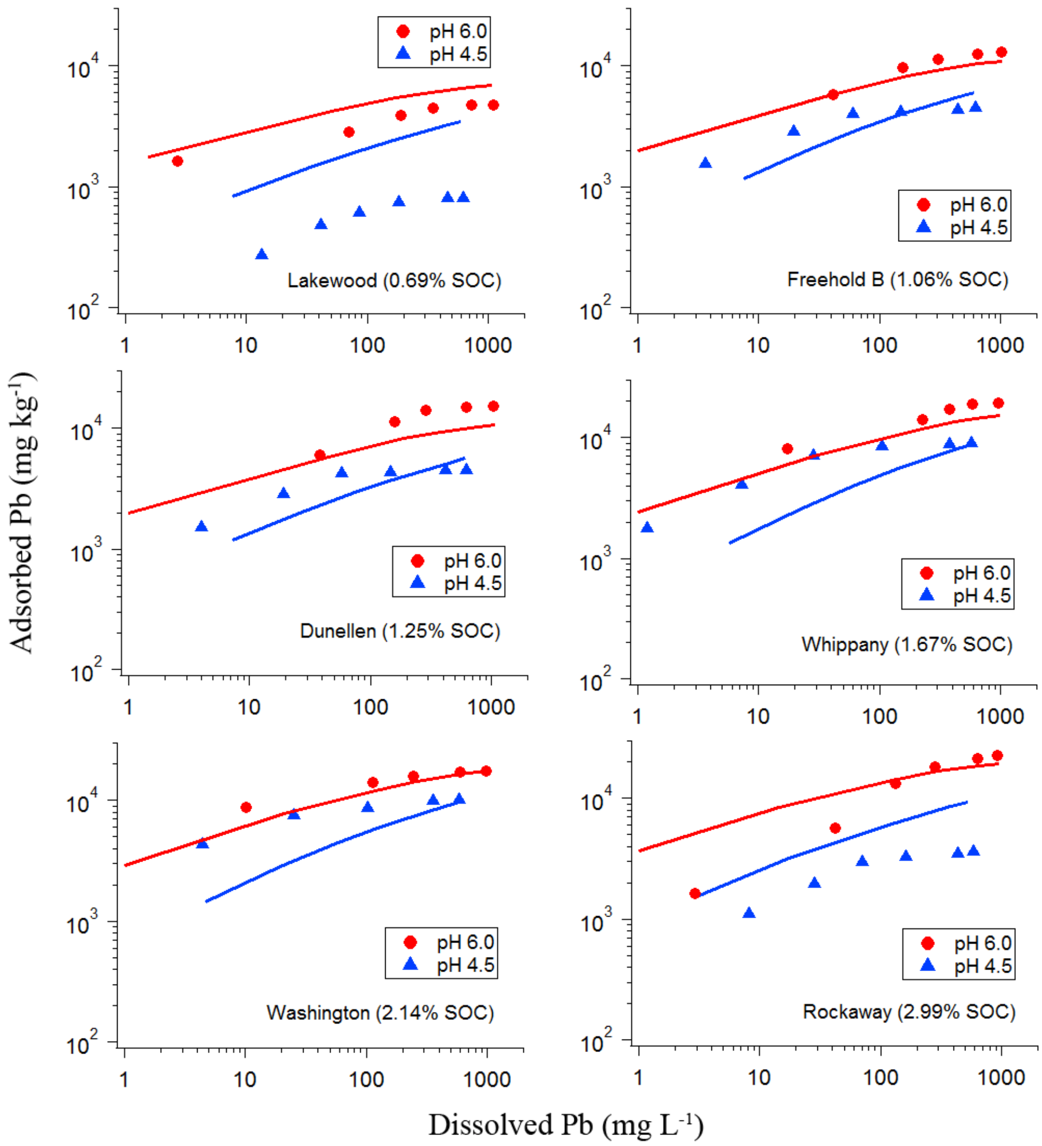

Fig. S2. Predicting isotherms of Pb adsorption on six soils at two pHs. Symbols are experimental data and solid lines are model predictions. The soil names, soil organic carbon (SOC) concentrations, and reaction pH are indicated in the figure.

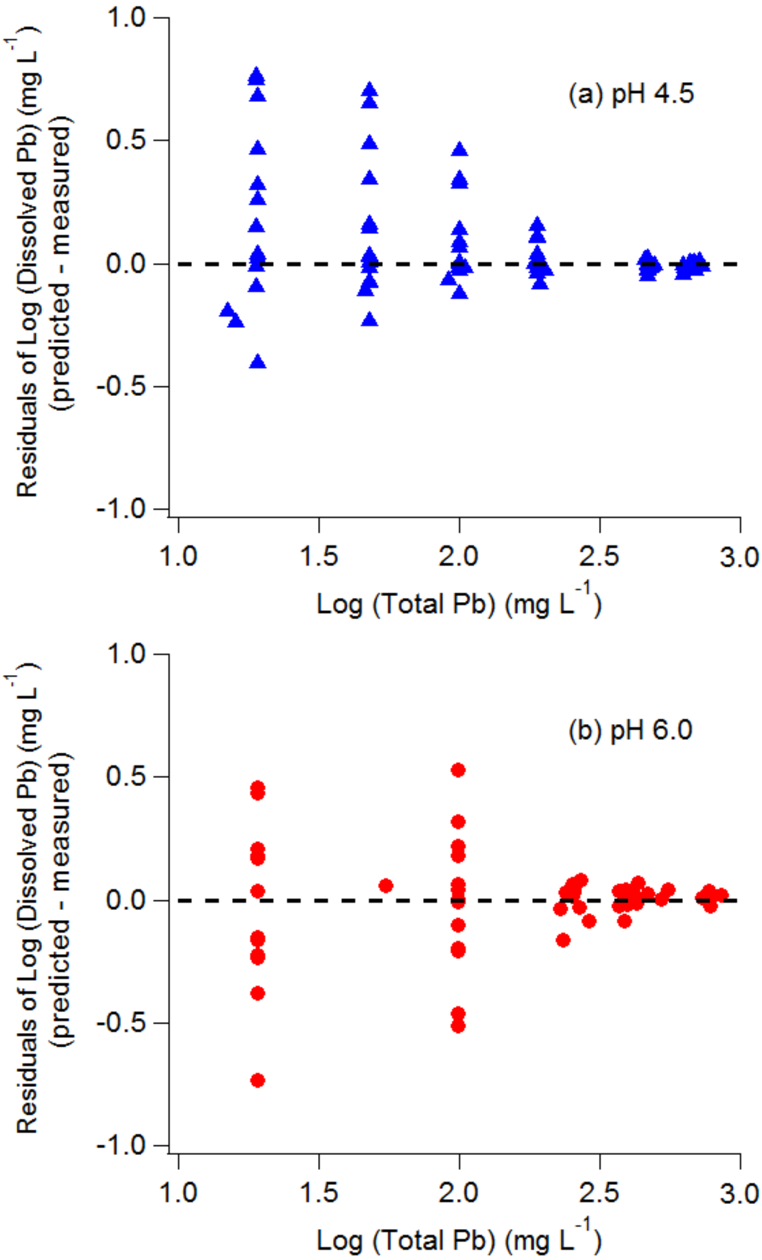

Fig. S3. Residual plot for dissolved Pb concentrations (log unit) at (a) pH 4.5 and (b) pH 6.0.

Table S3. Speciation of dissolved Pb for the adsorption isotherm experiment at pH 6.0 with the Boonton Bergen County soil

Total dissolve inorganic Pb (M)	4.4E–07	3.9E–05	4.0E–04	1.0E–03	2.8E–03	4.5E–03
Free Pb^{2+} ion (M)	4.0E–07	3.5E–05	3.5E–04	8.8E–04	2.4E–03	3.8E–03
Pb^{2+} complexed with NO_3^- (M)	4.0E–08	3.7E–06	4.0E–05	1.1E–04	3.5E–04	6.4E–04
Pb^{2+} complexed with OH^- (M)	7.3E–09	6.4E–07	6.4E–06	1.6E–05	4.3E–05	6.8E–05
Pb^{2+} complexed with CO_3^{2-} /HCO_3^- (M)	1.6E–09	1.4E–07	1.3E–06	3.3E–06	8.5E–06	1.3E–05

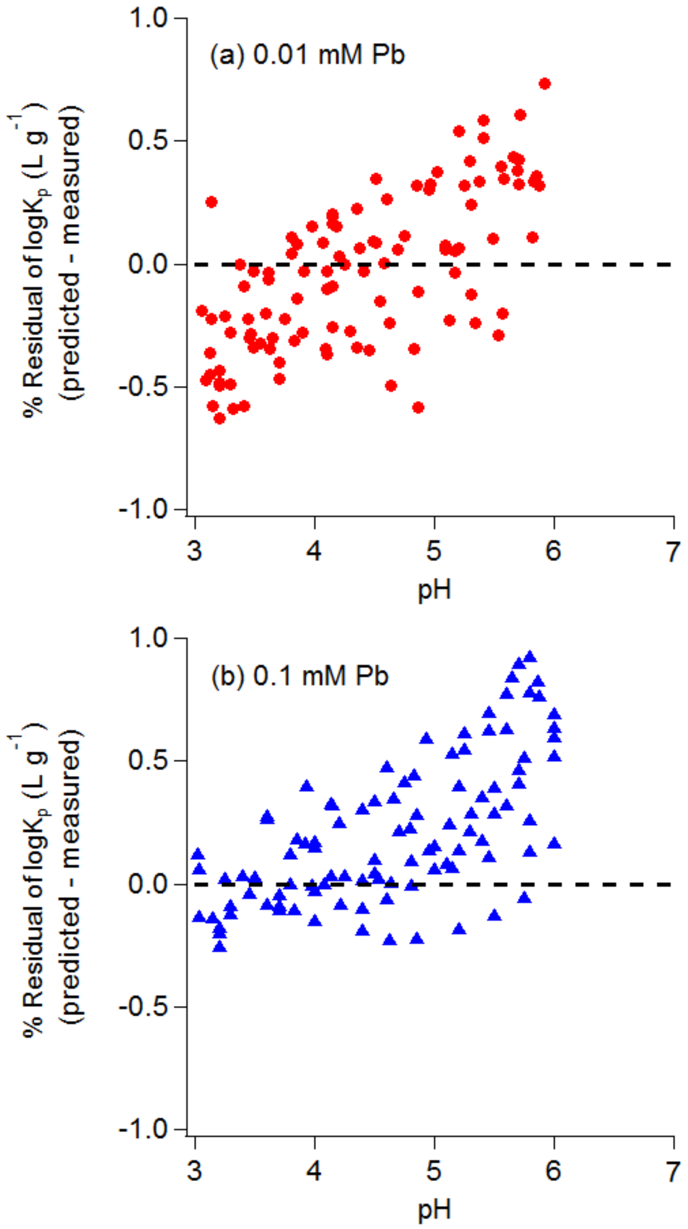

Fig S4. Residual plot for logK_p obtained in adsorption edge experiment between pH 3.0 and 6.0: (a) 0.01 mM total Pb and (b) 0.1 mM total Pb.

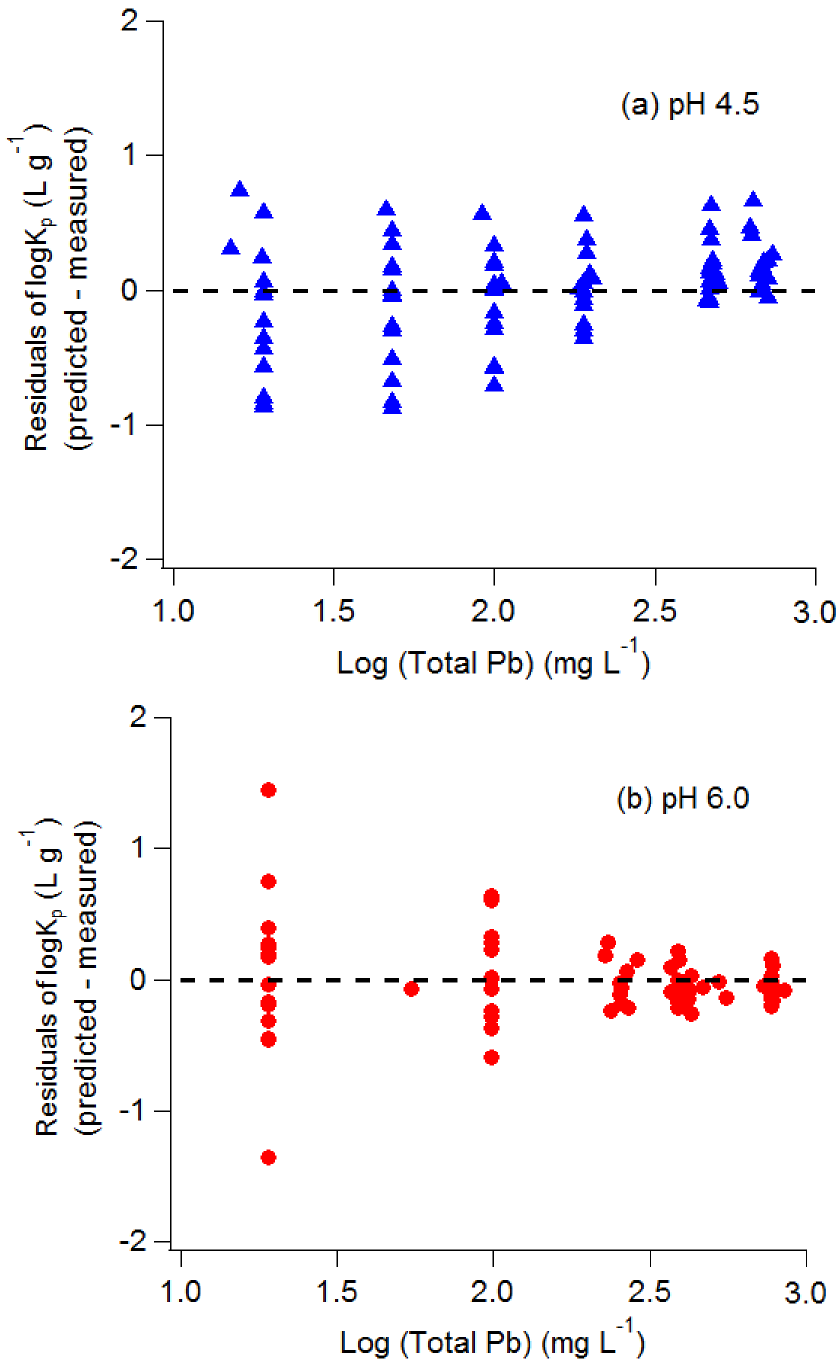

Fig. S5. Residual plot for logK_p obtained in adsorption isotherm experiment: (a) pH 4.5 and (b) pH 6.0.

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