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Improved geochemical modeling of lead solubility in contaminated soils by considering colloidal fractions and solid phase EXAFS speciation

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ABSTRACT

Lead (Pb) is a common contaminant in soils at e.g. mining, shooting range, and glassworks sites. In order to make reliable risk assessments and appropriate decisions on various “gentle remediation options”, such as applying phosphate, compost, or zero-valent iron to soils, the binding mechanism of Pb and its speciation needs to be known. Multi-surface geochemical equilibrium models are useful tools for estimating trace metal solubility and speciation, but for Pb the predictions are often poor. This study evaluates the recent parameterization for Pb in the Visual MINTEQ code for its ability to predict the solubility of Pb at different pH values in four historically contaminated Swedish soils. As an independent validation of the model performance, the modeled solid-phase speciation was compared to measured Pb speciation retrieved using extended X-ray absorption fine structure (EXAFS) spectroscopy. Furthermore, potential artefacts by the presence of Pb colloids were investigated by filtering solutions through both 0.45 μm and 10 kDa filters. The model accuracy for predicting Pb solubility was improved compared with previous studies producing log root mean square error (RMSE) values below 0.42 in three out of four soils, just by using generic assumptions. The use of ultrafiltered (< 10 kDa) instead of the 0.45 μm-filtered Pb concentrations lowered the RMSE with ~0.4 log units in two soils, giving a more accurate evaluation of the model performance. EXAFS proved to be a useful tool for validating and constraining the model, since the solid phase speciation did not exactly agree with the modeled results using default assumptions. However, a sample-specific optimization of the amount of “active” solid organic matter and Al + Fe hydroxides resulted in improved prediction of Pb solubility as well as better agreement with the EXAFS measurements. Solubility of Pb in the fourth, As-rich soil was probably controlled by $Pb_5(AsO_4)_3Cl$ (mimetite) with a solubility product constant of $10^{-83.53}$.

1. Introduction

Lead (Pb) is a highly toxic and wide-spread contaminant in soils around the world. However, the environmental chemistry of Pb in contaminated soils is very complex due to its tendency to interact strongly with multiple mineral and organic phases dependent on pH, redox conditions, and other soil properties. Lead(II) can adsorb onto organic matter and (hydr)oxides of iron, aluminum, and manganese (Morin et al., 1999; Scheckel and Ryan, 2004; Hashimoto et al., 2011; Ahmad et al., 2016; Ren et al., 2017) or precipitate as secondary minerals, e.g., PbS, $PbSO_4$, $PbSiO_3$, $PbCO_3$, hydrocerussite, pyromorphites, and PbO (Manceau et al., 1996; Scheckel and Ryan, 2004; Hashimoto et al., 2011; Debela et al., 2013). Chloropyromorphite, $Pb_5(PO_4)_3Cl$, is commonly considered to be the most stable Pb(II) mineral under ambient soil conditions (Scheckel and Ryan, 2002).

To estimate speciation and solubility of metal(loid)s in complex systems, such as soils, multi-surface process-based geochemical models are valuable tools (Bonten et al., 2008; Groenenberg and Lofts, 2014). Besides giving a thorough, mechanistic understanding of solubility mechanisms, they can be a help in risk assessments of contaminant transport and in the process of designing efficient remediation actions. Examples of the latter, are remediation measures involving various amendments (e.g., phosphate, compost, zero-valent iron, lime) in order to reduce metal solubility (e.g., Tiberg et al., 2016). In most cases, submodels are being used to describe binding to different surfaces, such as humic substances (e.g., Model VI (Tipping, 1998), NICA-Donnan (Kinniburgh et al., 1999), SHM (Gustafsson, 2001)), iron, aluminum, and manganese hydroxides (e.g., CD-MUSIC (Hiemstra and van Riemsdijk, 1996), 2-pK Diffuse Layer Model (Dzombak and Morel, 1990)), and clay minerals (e.g., the Gaines-Thomas equation).

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However, compared to other divalent trace metal ions, such as Cu^{2+} and Cd^{2+}, the solubility of Pb^{2+} has proved difficult to model accurately in soils using multi-surface models (Weng et al., 2001; Schröder et al., 2005; Linde et al., 2007; Bonten et al., 2008; Khai et al., 2008; Dijkstra et al., 2009; Groenenberg et al., 2012, 2017). Usually the solubility is overestimated by the models, except at high pH values where underestimation can also occur (Dijkstra et al. (2009); Groenenberg et al. (2012); Gustafsson et al. (2011) (remodeling the results of Khai et al., 2008); Shi et al. (2013)). Several possible explanations for the tendency of models to overestimate Pb solubility have been proposed. Bonten et al. (2008) found that the optimized fraction of "active" solid organic matter (the fraction that is actively sorbing metals and protons) for Pb^{2+} (90%) was higher than for Cu^{2+}, Zn^{2+} and Cd^{2+}(between 39% and 54%) using the Nica-Donnan model, suggesting the existence of high affinity sites for Pb^{2+} (Table S1 in Supporting Information). This is consistent with the study by Gustafsson et al. (2011), who calibrated the SHM model for Pb^{2+} sorption by mor layers, where stronger electrostatic effects, higher site heterogeneity and specific sites with very strong bonding were needed in order to fit the solubility data. Furthermore, these sites do not appear to be present in isolated humic substances normally used for model calibration, which indicates the Pb-sorption capacity of natural organic matter may commonly be underestimated. Gustafsson et al. (2011) estimated the Pb-specific high affinity sites to be 0.2% of the total amount of active sites on solid-phase humic and fulvic acids.

Gustafsson et al. (2011) also calibrated the CD-MUSIC model for Pb^{2+} adsorption to ferrihydrite, by including high affinity sites for Pb^{2+}, posing another possible explanation for previous poor solubility predictions. The CD-MUSIC model was recently updated with a ternary surface complex involving phosphate, which favored the adsorption of Pb^{2+} (Tiberg et al., 2013). Such a complex on goethite has previously been suggested as one possible explanation for poor model fits (Schröder et al., 2005). In some soils, sorption to manganese (hydr) oxides can contribute considerably to Pb binding (Morin et al., 1999; Ren et al., 2017) and this fraction may either not be included or be underestimated in models (Cances et al., 2003; Ren et al., 2017).

Additionally, even if the solubility is well depicted by a model, it does not necessarily mean that the mechanisms are correctly described. To date, there are very few studies where modeled solid-phase speciation of trace elements have been compared with the results from non-destructive, *in-situ* speciation methods like X-ray absorption spectroscopy (XAS) (Cances et al., 2003; Tiberg et al., 2016). Such comparisons give an independent evaluation of the model performance, which is particularly important for Pb that binds strongly to (hydr)oxides of Al, Fe and Mn (Bargar et al., 1997; Matocha et al., 2001; Tonkin et al., 2004; Fan et al., 2005; Xu et al., 2006; Gustafsson et al., 2011), as well as to natural organic matter (Gustafsson et al., 2011). X-ray absorption spectroscopy is an ideal method in this respect because it requires no pre-treatment (e.g., extractions) that can alter the speciation (Manceau et al., 1996; Morin et al., 1999; Scheckel and Ryan, 2004; Lewis et al., 2010; Hashimoto et al., 2011; Debela et al., 2013).

In addition to incomplete process libraries and representations in models, the experimental design can contribute to model uncertainty for solubility data obtained in batch titrations. Often the equilibrium leachates are filtered through 0.2 μm filters or larger to separate the dissolved phase from the colloidal and particulate phases (e.g., Almås et al., 2007; Khai et al., 2008; Linde et al., 2007; Dijkstra et al., 2009; Groenenberg et al., 2012; Shi et al., 2013). However, small colloidal particles of iron and aluminum oxides may pass through such filters (Almås et al., 2007) potentially leading to erroneously assigning strongly adsorbed metal ions, such as Pb^{2+}, to the truly dissolved rather than the colloidal fraction. This could be a potential explanation for the underestimation of Pb solubility at high pH values found in some studies (Dijkstra et al., 2009; Groenenberg et al., 2012; Gustafsson et al., 2011 (remodeling the results of Khai et al., 2008); Shi et al., 2013). Ultrafiltration (Wang and Benoit, 1996; Pédrot et al., 2008) should effectively prevent this bias, but this approach has rarely been used in solubility studies of Pb in soils involving geochemical modeling. Further, ultrafiltration will give a better indicator of the speciation of Al and Fe, which has been an uncertainty in previous modeling studies (Almås et al., 2007; Shi et al., 2013).

The aim of this study was to evaluate the recent parameterization for Pb of the generic multi-surface geochemical equilibrium model incorporated in the Visual MINTEQ code (Gustafsson et al., 2011; Tiberg et al., 2013), including the SHM and CD-MUSIC models, for its ability to predict the solubility of Pb at different pH values in four historically contaminated Swedish soils. To obtain an independent validation of the model performance, the modeled solid-phase speciation was compared to measured Pb speciation using EXAFS spectroscopy. Furthermore, potential artefacts by the presence of Pb colloids were investigated by filtering solutions through both 0.45 μm and 10 kDa filters.

2. Material and methods

2.1. Sites and sampling

Four historically contaminated sites in Sweden were selected to represent different contamination sources and soil properties: Gyttorp,

Table 1
Texture and chemical properties of the four soils.

	Unit	Gyttorp		Vinterviken		Pukeberg		Åsbro	
Contamination source		Shooting range		Industry		Glassworks		Wood impregnation	
Depth below soil surface	cm	2–16	16–30	0–14	14–29	0–14	14–28	4–17	17–29
Soil texture		Silty loam		Sandy loam		Sand		Loamy sand/sandy loam	
Clay (< 0.002 mm)	%	3.9	3.9	12.0	10.1	3.7	3	4.6	4.7
Silt (0.002–0.06 mm)	%	51.5	53.3	26.0	25.2	10.1	7	20.2	31.8
Sand (0.06–2 mm)	%	44.7	42.7	62.0	64.7	86.2	90	75.3	63.5
pH (10 mM $NaNO_3$)		5.2	5.7	5.4	5.5	8.1	8.2	6.1	6.7
Org-C	weight %	2.25	1.47	5.37	3.81	1.05	0.92	4.06	5.39
Fe (oxalate extractable)	mg/kg DW	5200	5700	3300	3100	2000	1400	3000	3500
Al (oxalate extractable)	mg/kg DW	1800	1800	1900	1900	1800	1600	930	890
Mn (geochemically active)	mg/kg DW	24	32	180	160	200	150	1000	660
Pb (total)	mg/kg DW	2600	1200	810	970	600	270	720	2700
Pb (geochemically active)	mg/kg DW	2500	1200	620	780	510	330[a]	790[a]	510
As (total)	mg/kg DW	15	10	6	7	61	28	3100	2900
Ba (total)	mg/kg DW	12	14	140	150	380	200	140	150
Cr (total)	mg/kg DW	4	4	16	14	7	5	1250	1200
Cu (total)	mg/kg DW	18	11	56	42	19	11	240	530
Zn (total)	mg/kg DW	21	17	150	110	370	190	3000	2200

[a] Due to analytical uncertainties the geochemically active fraction was slightly higher than the total concentration.