



Surface complexation modeling of Pb(II) adsorption on mixtures of hydrous ferric oxide, quartz and kaolinite

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ARTICLE INFO

Article history:

Received 21 January 2010

Received in revised form 20 May 2010

Accepted 21 May 2010

Editor: J. Fein

Keywords:

Surface complexation model

Double layer model

Ionic strength

Component additivity

ABSTRACT

Pb adsorption is measured on hydrous ferric oxide (HFO), kaolinite and quartz as a function of pH (~2–10), ionic strength (0.001 to 0.1 M NaNO₃) and sorbate concentration (1 to 100 μM Pb on 2 g/L solid). The data are used to parameterize diffuse layer surface complexation models (DLMs) for each solid. Pb adsorption edges on HFO show little dependence on ionic strength and are described well by a DLM with Pb forming a monodentate complex on strong and weak surface sites. In contrast, Pb adsorption edges on quartz are strongly dependent on ionic strength and sorbate/sorbent ratios. A single-site DLM with a monodentate Pb complex describes Pb adsorption on quartz well over relatively restricted solution conditions, but cannot reproduce the observed dependence on ionic strength and Pb loading. As for quartz, Pb adsorption on kaolinite depends strongly on ionic strength and Pb loading. Several model approaches are tested, but none produces a good fit to the data over the full range of measured conditions. The best of the tested DLMs for kaolinite assumes Pb binding to a permanent charge (face) site and formation of a monodentate complex on a variable-charge (edge) site. A simple component additivity approach, assuming no mineral–mineral interactions and using models developed for the three pure sorbents generally produces good predictions of Pb adsorption for mixed solid systems. With the possible exception of the HFO and kaolinite system, mineral–mineral interactions between quartz, kaolinite and HFO appear to be smaller than the uncertainties associated with the pure sorbent models.

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1. Introduction

Surface water and sediment contamination from anthropogenically-introduced metals, such as lead, is a serious problem in the U.S. and elsewhere (Landsdown and Yule, 1986; Castellino et al., 1995). Children are particularly susceptible to health effects associated with exposure to lead; high blood levels of lead can cause serious damage to the brain and nervous systems, resulting in behavioral problems, learning disabilities, slowed growth rates and other medical issues (Landsdown and Yule, 1986; Castellino et al., 1995). Major sources of lead in soils include metal smelting and processing, secondary metals production, lead battery manufacturing, pigment and chemical manufacturing, and leaded gasoline (Landsdown and Yule, 1986; Castellino et al., 1995). The risk to living people and other organisms associated with lead and other heavy metal contaminants is primarily determined by metal speciation, rather than total metal concentration

(Allen et al., 1980). This provides a significant impetus toward the development of accurate models of metal speciation that can be readily applied to environmental systems.

Thermodynamically-based surface complexation models (SCMs) have been developed to describe adsorption of metals to a range of sorbents (see review in: Koretsky, 2000). While empirical or semi-empirical adsorption models, such as Langmuir isotherms or distribution coefficients, are strictly valid only for the specific solution conditions for which they are calibrated, SCMs should be capable of correctly predicting metal speciation in the presence of competing solutes, and as a function of pH, ionic strength and electrolyte composition (Bethke and Brady, 2000; Koretsky, 2000). A variety of different SCMs have been developed, differing mostly with respect to their treatment of electrical charge at the sorbent surface. For some, such as the constant capacitance model (CCM), treatment of the electrical double layer properties is relatively simple, resulting in ionic-strength dependent stability constants. Other models, such as the triple layer model (TLM) or charge distribution multisite model (CD-MUSIC), offer more sophisticated, and more intellectually satisfying treatments of sorbent surface properties (e.g., Hiemstra and Van Riemsdijk, 1996). However, developing these models requires either a large number of fit parameters or a wealth of targeted spectroscopic data. The double layer model (DLM) permits an intermediate approach, with relatively few fit parameters resulting

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in stability constants that are generally assumed to be ionic strength and electrolyte independent. Furthermore, a large, internally-consistent database of DLM parameters describing metal adsorption on hydrous ferric oxide (HFO) has been developed and incorporated into many commercially-available speciation codes (Dzombak and Morel, 1990; Van der Lee and de Windt, 2000; Bethke and Yeakel, 2009).

In theory, once parameterized, SCMs should be useful over broad variations in solution conditions. However, in many instances, SCMs have been calibrated using very limited data, for example based on experiments conducted at a single ionic strength or for a single sorbate/sorbent concentration. This is problematic, because recent work suggests that even diffuse layer model (DLM) parameters, which are generally assumed to be ionic strength and electrolyte independent, may actually depend strongly on ionic strength (Sverjensky and Sahai, 1996; Landry et al., 2009; Schaller et al., 2009). Other hurdles to the application of SCMs in environmental systems include a lack of internally-consistent data, i.e., parameterized using the same modeling framework, for many important sediment and soil constituents, together with a lack of information regarding adsorption processes in systems with mixed mineralogy.

Davis et al. (1998) suggested two possible approaches for modeling metal adsorption in mixed mineral systems, the generalized composite (GC) approach, and the component additivity (CA) approach. In the GC approach, site-specific SCMs are developed to describe metal adsorption on complex sediments or soils. This method has been used successfully to describe Pb adsorption on soils (e.g. Serrano et al., 2009). However, this approach does not allow ready extrapolation of the SCM to other systems, nor does it take advantage of previously published SCMs for simpler, single sorbent systems. In the CA approach, SCM parameters derived for single sorbents are applied to more complex, but well-characterized sediments and soils, based on their constituent mineralogy. This approach has also been useful for describing Pb adsorption on some soils and sediments (e.g., Pagnanelli et al., 2004, 2006; Hanna et al., 2009). Nonetheless, very little work has been done to assess mineral–mineral interactions and to determine whether they should be explicitly considered when using the CA approach.

The specific goals of this study are first, to determine whether the DLM can correctly describe Pb adsorption on HFO, kaolinite and quartz over a wide range of ionic strength conditions (set with 0.001 to 0.1 M NaNO₃) and at multiple sorbate/sorbent ratios. Next, a simple component additivity approach is tested by comparing predictions of Pb adsorption as a function of pH in systems containing mixtures of the three solids with measured data.

2. Materials and methods

2.1. Materials

HFO was synthesized by slowly titrating ferric chloride with 1 M NaOH in a glass beaker to a pH of 6.5 to 7.5 (Schwertmann and Cornell, 2000). The resulting precipitate was transferred to a plastic centrifuge tube, repeatedly (5–6 times) centrifuged and washed with DDI, and then freeze-dried. KGa-1b, a natural kaolinite from Washington County, GA, USA, was purchased from the Clay Minerals Society, Clay Minerals Repository. KGa-1b contains 45.2% SiO₂, 39.1% Al₂O₃, 1.64% TiO₂ and trace amounts of Fe₂O₃, MgO, CaO, Na₂O and K₂O (Pruett and Webb, 1993), and has a cation exchange capacity (CEC) of 3.0 meq/100 g (Bordon and Giese, 2001). Min-U-Sil 5, a natural crystalline quartz ground to produce a fine powder with an average grain size of 1.7 μm was purchased from U.S. Silica (Berkeley Springs, WV). According to U.S. Silica, Min-U-Sil 5 is comprised of 98.3% quartz with minor impurities of Fe, Al and other trace metals. Except where noted (see below), the quartz was baked at 500 °C, acid refluxed four times in 4 M HNO₃, rinsed with DDI water 8 times, centrifuged, and dried for 48 h at 37 °C. This procedure should remove some oxide

phases and amorphous silica and oxidize residual organic materials (Coston et al., 1995). Surface areas measured by 11-point N₂-BET for the same HFO, KGa-1b, and quartz (Table 1) are taken from Lund et al. (2008) and Landry et al. (2009).

2.2. Experimental methods

Batch experiments were completed under atmospheric conditions to measure adsorption of Pb as a function of pH, ionic strength (set with 0.001 to 0.1 M NaNO₃) and solid to Pb concentration ratio. Note that Swedlund et al. (2003) report no change in Pb adsorption on ferrihydrite under N₂ compared to open atmosphere conditions. All batch experiments were completed using methods similar to those described by Landry et al. (2009). Ionic strengths reported below and used in all models were calculated for each individual experiment from the concentration of the background electrolyte (NaNO₃), together with the initial quantity of Pb and nitric acid added to each batch reactor to achieve the starting pH for a given experiment. Pb solution and background electrolyte were added to a 500 mL polyethylene beaker with a stir bar under atmospheric conditions. A 10 mL aliquot was removed from the well-stirred mixture and kept as a control to analyze the initial concentration of Pb. Next, the solid was added to the batch reactor and the slurry was preequilibrated with constant stirring under atmospheric conditions and at room temperature for 24 h. After this preequilibration period, if necessary, the pH of the mixture was adjusted downwards using trace metal grade nitric acid and allowed to equilibrate for a few minutes. The adsorption edge was then measured by titrating the mixture upwards by increments of ~0.25 pH with small volumes of trace metal grade sodium hydroxide. The total addition of sodium hydroxide did not significantly change the initial ionic strength, except in the case of experiments with Pb adsorption on pure HFO with a starting concentration of 0.001 M NaNO₃. In these experiments, the ionic strength increased by up to 0.005 M over the course of the base titration. Following a short equilibration period (~2–10 min) after each addition of base, a 10 mL aliquot of the slurry was removed, and further equilibrated for 24 h at room temperature on a rotating shaker. After the 24 h, the pH of the slurry was remeasured and the aliquots centrifuged and syringe-filtered (0.2 μm nylon membrane) to remove the supernatant. The supernatant was acidified with trace metal grade nitric acid, spiked with an internal standard (100 or 1000 ppb Ho, Bi, In, Y or Sc) and analyzed for lead via ICP-MS (ThermoElectron) or ICP-OES (Perkin Elmer Optima 2100DV). Adsorbed lead was calculated by the difference between the metal concentration in the initial control aliquot and the concentration in the supernatant solution.

2.3. Modeling approach

The adsorption edge data were modeled using a diffuse double layer surface complexation model (Dzombak and Morel, 1990). Each individual edge was modeled by optimizing stability constants for a given reaction stoichiometry using FITEQL4.0 (Herbelin and Westall,

Table 1
Surface areas, surface site types and site densities used in DLM calculations.

Solid	Surface area (m ² /g)	Site types	Site density (μmol/m ²)
HFO (2-site model)	600 ^a	> Fe _(s) OH > Fe _(w) OH	0.094 ^c 3.74 ^c
Quartz	9.4 ^b	> SiOH	16.6 ^d
Kaolinite (KGa-1b)	13.6 ^b	> SOH X	16.6 ^d 2.2 ^e

a. The measured N₂-BET surface area for HFO was 220 m²/g, consistent with prior studies (Lund et al., 2008). However, for modeling purposes, the value 600 m²/g is adopted, consistent with recommendation of Dzombak and Morel (1990). b. Lund et al. (2008). c. Dzombak and Morel (1990). d. Sverjensky and Sahai (1996). e. From CEC (3.0 meq/100 g) measured by Bordon and Giese (2001) for kaolinite KGa-1b.

1999). Davies equation activity corrections were included for the aqueous species. In addition to the surface reactions, stability constants for formation of $\text{Pb}(\text{OH})^+_{(\text{aq})}$, $\text{Pb}(\text{OH})_{2(\text{aq})}$, $\text{Pb}(\text{OH})_{3-}^{-}(\text{aq})$, $\text{Pb}_2(\text{OH})^{+3}_{(\text{aq})}$, $\text{Pb}_3(\text{OH})^{+2}_{(\text{aq})}$, $\text{Pb}_4(\text{OH})^{+4}_{(\text{aq})}$, $\text{Pb}_6(\text{OH})^{+4}_{(\text{aq})}$, and $\text{PbNO}_3^+_{(\text{aq})}$ taken from the JCHESS default database (Table S1) were included in the calculations. For a given reaction stoichiometry, the median stability constant from the collection of edges spanning a range of ionic strength and sorbate/sorbent ratios was input into the software JCHESS (Van der Lee and de Windt, 2000). With JCHESS, edges were calculated using an extended Debye–Huckel activity correction and including stability constants for the formation of $\text{PbCO}_{3(\text{aq})}$, $\text{Pb}(\text{CO}_3)_2^{-2}_{(\text{aq})}$, $\text{NaOH}_{(\text{aq})}$, $\text{HNO}_{3(\text{aq})}$, $\text{NaHCO}_{3(\text{aq})}$ and $\text{NaCO}_{3(\text{aq})}$ (Table S1). The concentration of $\text{CO}_{2(\text{aq})}$ was set assuming equilibrium with an atmospheric concentration of 380 ppm. Addition of CO_2 species changed calculated edges by $\ll 1\%$. JCHESS was also used to calculate the saturation indices of cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), litharge (PbO), massicot (PbO) and $\text{PbCO}_3 \cdot \text{PbO}$ (Table S1). The default thermodynamic database, which is based on the published EQ3 database, was used for all calculations.

The goodness-of-fit of the calculated edges to the measured data was assessed using the equation given by Heinrich et al. (2008),

$$V(Y) = \frac{\sum_{PQ} \left(\frac{Y}{s_Y} \right)^2}{n_P \times n_Q - n_R} \quad (1)$$

where $V(Y)$ is the goodness-of-fit, Y is the difference between the calculated and measured concentration of metal remaining in solution for each data point, P ; s_Y is the standard deviation; n_P is the number of data points; n_Q is the number of components, Q , for which the concentration, C , and the total concentration, t , are known ($n_Q = 1$ for all edges in this study); and n_R is the number of parameters being optimized. The standard deviation, s_Y , was assumed to be equal to 5% of the Pb concentration used in each experiment with a lower limit of 25 ppb (based on ICP OES detection limits). $V(Y)$ is generally considered to be reasonable if it is between 1 and 10 or 20. Much larger values indicate either a poor model or unrealistically small estimates of s_Y , and much smaller values suggest that the model is overparameterized or the estimated s_Y values are too large (Herbelin and Westall, 1999). Goodness-of-fit confidence intervals were calculated from:

$$\frac{(n_Q \times n_P - n_R) \cdot V(Y)}{\chi^2_{1-\alpha/2}}, \frac{(n_Q \times n_P - n_R) \cdot V(Y)}{\chi^2_{\alpha/2}} \quad (2)$$

where χ^2_p is the quantile of the chi-square distribution with $(n_Q \times n_P - n_R)$ degrees of freedom with exceedence probability, p , and $\alpha = .05$ (95% confidence interval; Heinrich et al., 2008) using only data with

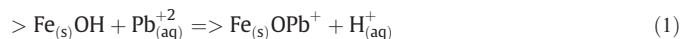
percentage of lead adsorbed $> 2\%$ and $< 98\%$. Goodness-of-fit values for the full range of data collected for each solid were used to choose the best and simplest model from a range of tested reaction stoichiometries. A model was considered to be statistically superior if the goodness-of-fit value was lower, with no overlap at the 95% confidence interval, compared to an alternative model. Goodness-of-fit values were also used to compare model fits calibrated to the individual minerals to those obtained by predicting sorption on mixtures of minerals from these models.

3. Results and discussion

3.1. Pb adsorption on hydrous ferric oxide

Lead adsorption was measured on HFO as a function of ionic strength (0.003 to 0.1 M) and sorbate concentration (1 to 100 μM) on 2 g/L HFO (Fig. 1). The edges show relatively little dependence on ionic strength, but the pH_{50} (pH with 50% of Pb adsorbed) shifts from ~ 2.6 – 3.1 in experiments with 1 μM Pb to ~ 3.3 – 3.5 in experiments with 100 μM Pb. JCHESS calculations indicate that in homogeneous solutions containing 100 μM Pb, hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) becomes supersaturated at $\text{pH} > 6.6$, which is well above the measured edges; likewise, litharge (PbO) is supersaturated only at $\text{pH} > 9.9$. A blank titration conducted in the absence of sorbent, with 100 μM Pb and 0.001 M NaNO_3 indicated removal of Pb from solution at $\text{pH} > 6.2$, in agreement with predictions from JCHESS.

Several surface complexation models have been proposed to describe Pb adsorption on HFO (Dzombak and Morel, 1990; Dyer et al., 2003; Swedlund et al., 2003). Dzombak and Morel (1990) developed a 2-site DLM with strong and weak variable-charge hydroxyl sites. They modeled lead adsorption data assuming complexes bind only to the strong site, according to:



where $> \text{Fe}_{(\text{s})}\text{OH}$ is a strong hydroxyl site. However, their model, which was calibrated on four adsorption edges all measured in 0.1 M NaNO_3 , significantly underestimates Pb adsorption data from this study, particularly at low Pb concentrations (Figure S1; Table S2; $V(Y) = 45.6$). Likewise, Swedlund et al. (2003) found that the Dzombak and Morel (1990) model consistently underestimated Pb adsorption compared to their data. They parameterized a new DLM to describe Pb adsorption on HFO, based on the approach of Dzombak and Morel (1990), using both isotherm and edge data. They found that the isotherm data, in particular, could only be satisfactorily described using a three-site model. Their DLM uses reaction (1), together with

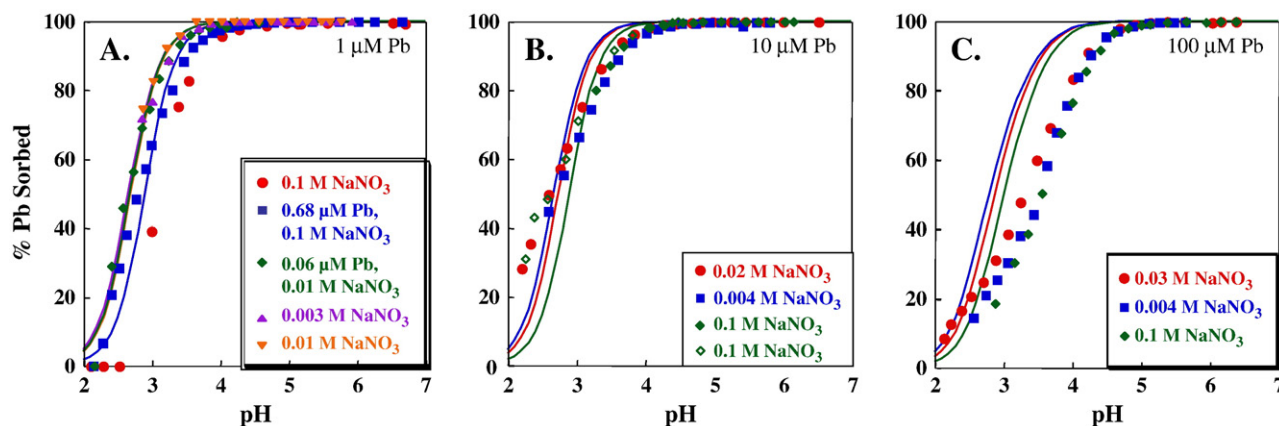
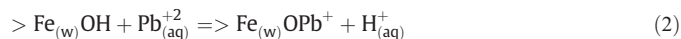
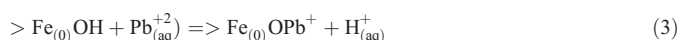


Fig. 1. Pb adsorption on 2 g/L HFO with (A) 1 μM Pb, (B) 10 μM Pb and (C) 100 μM Pb. Lines indicate model fits using DLM parameters shown in Tables 1 and 2.

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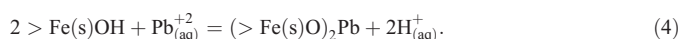


where $>\text{Fe}_{(\text{w})}\text{OH}$ is a weak hydroxyl site and $>\text{Fe}_{(\text{o})}\text{OH}$ is a third hydroxyl site, not present in the original Dzombak and Morel (1990) HFO model. Although the Swedlund et al. (2003) model produces an improved fit to our data (Table S2; $V(Y)=12.3$), their model consistently overpredicts Pb adsorption compared to edges measured in this study (Figure S2). To test the component additivity model, it is important that the endmember models describe the adsorption data well. Therefore, the edges measured in this study were used to calibrate a new DLM for Pb adsorption on HFO.

Using the 2-site DLM developed by Dzombak and Morel (1990), the stability constant for Pb adsorption on the strong site (Eq. (1)) was optimized for each edge with the parameters shown in Tables 1 and S1. The median stability constant of 6.11 produces a good fit to the full suite of data measured in this study ($V(Y)=9.6$), although it is not superior to the model of Swedlund et al. (2003) at the 95% confidence interval. It is, however, a simpler model with only one fitted stability constant compared to the three required for the Swedlund et al. (2003) model. A 2-site model was also tested, but attempts to simultaneously optimize stability constants for both reaction (1) and (2) failed to converge. Therefore, the stability constant for reaction (2), adsorption of Pb on the weak site, was optimized while holding the strong site stability constant for reaction (1) constant and equal to 6.11, the value obtained from the 1-site model optimization. The median value for reaction (2) from the full set of edges of 4.58 produces a poor fit to the data ($V(Y)=20.9$), presumably due to coupling between strong and weak site stability constant values. Using a stability constant of 2.49 for reaction (2), which is obtained from a 2-site model of the edge which produced the median value of 6.11 for the 1-site optimization, yields a much better fit to the full set of data ($V(Y)=9.4$; Table 2; Fig. 1). However, this $V(Y)$ value is not distinct from either the reoptimized 1-site or the Swedlund et al. (2003) model fits at the 95% confidence interval.

Several XAS studies of Pb adsorption on HFO suggest that Pb binds via innersphere, bidentate adsorption (Manceau et al., 1992; Scheinost et al., 2001; Trivedi et al., 2003; Xu et al., 2006). Therefore,

a bidentate stoichiometry was also tested to describe Pb adsorption on the strong HFO site according to,



This stoichiometry produces a poorer fit to the measured edges (Table S2; $V(Y)=14.3$). This may reflect the greater sorbate/sorbent ratio commonly used in XAS studies (Manceau et al., 1992; Scheinost et al., 2001; Xu et al., 2006), although Trivedi et al. (2003) did use Pb loadings comparable to those in this study for some of their experiments (10 to 1000 μM Pb per g HFO).

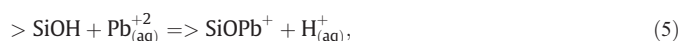
The statistically equivalent models optimized in this study with Pb adsorption on only the strong site, or with Pb adsorption on both the strong and weak sites, were applied to adsorption edges from three prior studies (Swedlund et al., 2003; Trivedi et al., 2003; Kulczycki et al., 2005). The model with Pb adsorption on both the strong and weak sites produces significantly better fits to data from these studies (Table S3), particularly for edges with higher sorbate/sorbent ratios then used in this study. This is because the model with Pb adsorption on only the strong site does not have a sufficiently high site density to account for all of the Pb adsorbed. Therefore, the model with Pb adsorption on both the strong and weak sites is adopted in this study (Fig. 1, Tables 1 and 2), in spite of the fact that the simpler model with adsorption on only the strong sites could produce statistically equivalent fits to the edges measured in this study.

3.2. Pb adsorption on quartz

Lead adsorption was measured on 2 g/L quartz as a function of ionic strength (set with 0.001 to 0.1 M NaNO_3) and sorbate concentration (1 to 100 μM). In contrast to Pb adsorption on HFO, there is a strong dependence on ionic strength, as well as on sorbate/sorbent ratio (Fig. 2). The pH_{50} values range from 4.3 to 6.8. Experiments conducted with 100 μM Pb have sharp edges initiating at $\text{pH} \sim 6.3$, very similar to observations made in the absence of sorbent (Figure S3), and suggesting that precipitation of hydrocerussite occurs in these experiments. Therefore, only 1 and 10 μM experiments were used to derive DLM stability constants. Several adsorption experiments were also conducted using unwashed quartz (Figure S4). Although the resulting edges are generally similar to those for the washed quartz, adsorption of Pb is somewhat enhanced, particularly at low ionic strengths.

Elzinga and Sparks (2002) used XAS to probe Pb surface complexes on amorphous silica at two electrolyte concentrations (0.005 and 0.1 NaClO_4) and as a function of pH. At $\text{pH} < 4.5$, the XAS spectra were consistent with formation of mononuclear, innersphere Pb complexes, while at higher pH, innersphere Pb dimers were indicated. Chen et al. (2006) also used XAS to characterize Pb sorption on quartz and concluded that innersphere complexes formed at $\text{pH} 6.5$ in 0.1 or 0.01 M NaCl . Elzinga and Sparks (2002) used a high surface area (280 m^2/g) amorphous silica with a much higher loading of Pb than in this study, while Chen et al. (2006) used much greater sorbent concentrations (100 g/L), so neither set of XAS results are directly applicable to the experiments reported here. However, the consistent observation of monodentate complexes, even at high loadings of Pb, suggests that Pb will form monodentate complexes at the lower loadings of Pb used in this study.

A 1-site DLM was calibrated for Pb adsorption on quartz using the site density and protonation and deprotonation stability constants from Sverjensky and Sahai (1996), given in Tables 1 and 2. Pb was assumed to form a monodentate complex, according to:



and consistent with the reported XAS observations. Although optimization of the stability constant for this reaction can produce a

Table 2

Reaction stoichiometries and stability constants used in DLM calculations. Average goodness-of-fit parameters ($V(Y)$) and 95% confidence intervals of $V(Y)$ are for the fit of each model to all of the Pb on HFO ($n_p=108$), kaolinite ($n_p=90$) and quartz ($n_p=82$) adsorption edge data.

Reaction	Log stability constant	$V(Y)$ ($V(Y)_{\text{min}}$, $V(Y)_{\text{max}}$)
HFO model		
$> \text{Fe}_{(\text{s})}\text{OH} + \text{H}_{(\text{aq})}^{+} = > \text{Fe}_{(\text{s})}\text{OH}_2^{+}$	7.29 ^a	
$> \text{Fe}_{(\text{w})}\text{OH} + \text{H}_{(\text{aq})}^{+} = > \text{Fe}_{(\text{w})}\text{OH}_2^{+}$	7.29 ^a	
$> \text{Fe}_{(\text{s})}\text{OH} = > \text{Fe}_{(\text{s})}\text{O}^{-} + \text{H}_{(\text{aq})}^{+}$	−8.93 ^a	
$> \text{Fe}_{(\text{w})}\text{OH} = > \text{Fe}_{(\text{w})}\text{O}^{-} + \text{H}_{(\text{aq})}^{+}$	−8.93 ^a	
$> \text{Fe}_{(\text{s})}\text{OH} + \text{Pb}_{(\text{aq})}^{+2} = > \text{Fe}_{(\text{s})}\text{OPb}^{+} + \text{H}_{(\text{aq})}^{+}$	6.11 (this study)	9.4
$> \text{Fe}_{(\text{w})}\text{OH} + \text{Pb}_{(\text{aq})}^{+2} = > \text{Fe}_{(\text{w})}\text{OPb}^{+} + \text{H}_{(\text{aq})}^{+}$	2.49 (this study)	(7.3, 12.5)
Quartz model		
$> \text{SiOH} + \text{H}_{(\text{aq})}^{+} = > \text{SiOH}_2^{+}$	−1.1 ^b	
$> \text{SiOH} = > \text{SiO}^{-} + \text{H}_{(\text{aq})}^{+}$	−8.1 ^b	11.6
$> \text{SiOH} + \text{Pb}_{(\text{aq})}^{+2} = > \text{SiOPb}^{+} + \text{H}_{(\text{aq})}^{+}$	−1.74 (this study)	(8.7, 16.2)
Kaolinite model		
$> \text{KaoliniteOH} + \text{H}_{(\text{aq})}^{+} = > \text{KaoliniteOH}_2^{+}$	2.1 ^b	
$> \text{KaoliniteOH} = > \text{KaoliniteO}^{-} + \text{H}_{(\text{aq})}^{+}$	−8.1 ^b	
$> \text{KaoliniteOH} + \text{Pb}_{(\text{aq})}^{+2} = > \text{KaoliniteOPb}^{+} + \text{H}_{(\text{aq})}^{+}$	−1.91 (this study)	
$\text{X}(\text{Na}) + \text{H}_{(\text{aq})}^{+} = \text{X}(\text{H}) + \text{Na}_{(\text{aq})}^{+}$	2.5 ^c	17.3
$2\text{X}(\text{Na}) + \text{Pb}_{(\text{aq})}^{+2} = \text{X}_2(\text{Pb}) + 2\text{Na}_{(\text{aq})}^{+}$	5.50 (this study)	(13.2, 23.8)

a. Dzombak and Morel (1990). b. Sverjensky and Sahai (1996). c. Landry et al. (2009).

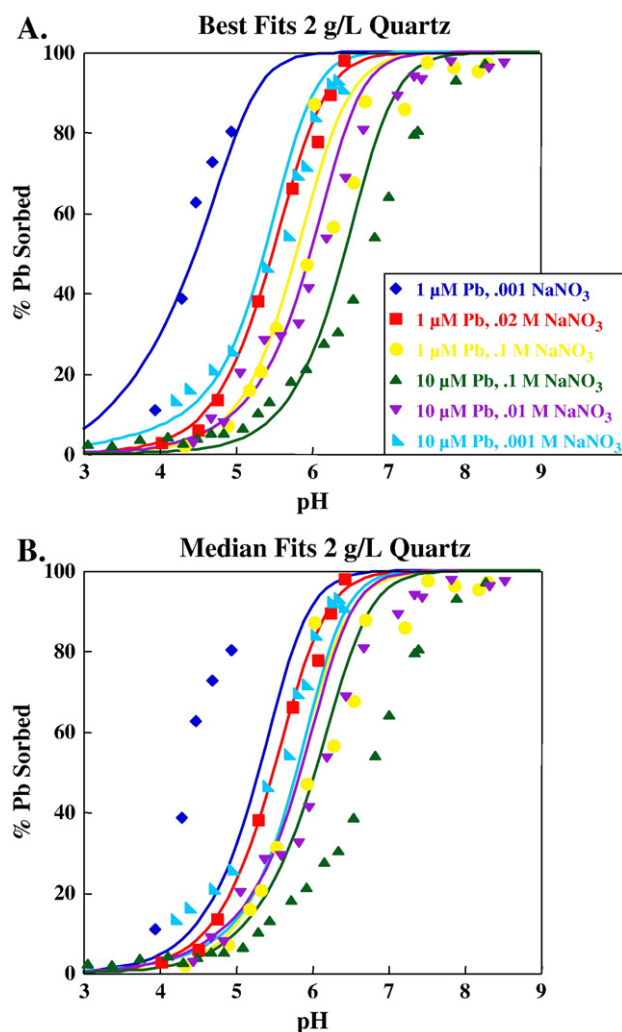
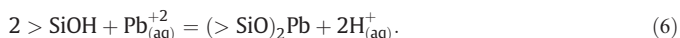


Fig. 2. Pb adsorption on 2 g/L washed quartz with 1 or 10 μM Pb and 0.001 to 0.1 M NaNO_3 . Lines indicate model fits using (A) optimized stability constants for formation of a monodentate $>\text{SiOPb}^+$ for each edge from FITEQL or (B) the median value of -1.74 for the monodentate $>\text{SiOPb}^+$ from all six experiments. Other model parameters are given in Tables 1 and 2.

reasonable fit to any single edge (Fig. 2A), the median stability constant derived from the full suite of data does not adequately describe the observed ionic strength or sorbate/sorbent ratio dependence of Pb sorption (Fig. 2B). A bidentate complex was also tested, according to:

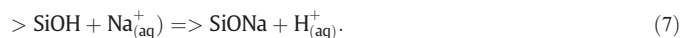


The resulting fits are statistically poorer at the 95% confidence interval compared to those obtained using the monodentate stoichiometry, and the bidentate model produces edges that demonstrate a greater sensitivity of Pb adsorption to changes in pH than is observed (Tables 2, S4; Figure S5).

Both the monodentate and bidentate DLMs do a poor job of replicating the strong ionic strength dependence observed in this study. Elzinga and Sparks (2002) also observed a significant increase in Pb adsorption with decreasing ionic strength. As might be expected, predicted edges using the monodentate model from this study for the experimental conditions used by Elzinga and Sparks (2002) underestimate the reported ionic strength dependence of their Pb adsorption edges (Figure S6A). In contrast, Chen et al. (2006) studied Pb adsorption on Min-U-Sil 5 as a function of pH, ionic strength and background electrolyte and report little change in the adsorption

edges for 0.1 compared to 0.01 M NaNO_3 , NaCl or NaClO_4 , although at higher ionic strengths (0.5 or 1 M NaCl), they did observe decreased Pb adsorption. The lack of ionic strength dependence at lower electrolyte concentrations might be due to the very high sorbent concentration used in their study (100 g/L quartz). Calculations using the monodentate model developed here for the experimental conditions reported by Chen et al. (2006) consistently result in overpredictions of their measured Pb adsorption at all ionic strengths (Figure S6B; Table S5).

XAS spectra rule out ternary complex formation with NaClO_4^- or Cl^- as a cause for the strong ionic strength dependence (Elzinga and Sparks, 2002; Chen et al., 2006); ternary formation with the NO_3^- used in this study is also unlikely to occur. Na is a weak sorbate, unlikely to compete effectively with Pb. Nonetheless, a model with explicit competition between a monodentate or bidentate Pb complex and a Na surface complex was tested, according to:



Although individually optimized edges could reproduce the measured data, median stability constants from this modeling approach do not correctly describe the ionic strength and sorbate/sorbent dependence of the data (Table S4; Figure S7).

In summary, although a single-site DLM can provide reasonable fits to Pb adsorption data over relatively restricted conditions (i.e., a single ionic strength or sorbate/sorbent ratio), it cannot adequately describe adsorption data over the breadth of conditions measured in this study. Thus, it is not surprising that it also cannot correctly predict Pb adsorption under the various conditions of previously published experiments. The poor predictions suggest that a more sophisticated treatment of the electrical double layer, or a multisite model, will be required to produce a model that can accurately describe Pb adsorption on quartz over a broad range of solution conditions. However, it is worth noting that attempts to model Co adsorption on silica using a TLM also failed to adequately reproduce the ionic strength dependence of the adsorption (Chen et al., 2006). For component additivity modeling completed in this study (below), we assume that Pb binds to quartz to form a monodentate complex (reaction (5)) and use the median stability constant of -1.74 from optimization of the edges measured in this study (Table 2).

3.3. Pb adsorption on kaolinite

Pb adsorption was measured on 2 g/L kaolinite as a function of pH, ionic strength (set with 0.001 to 0.1 M NaNO_3) and Pb concentration (1 to 100 μM Pb). The resulting edges are strongly dependent on both ionic strength and sorbate/sorbent ratio, with pH_{50} values ranging from ~ 4.4 to 6.6 (Fig. 3). Edges measured with 100 μM Pb did not reach 100% adsorption below the pH at which hydrocerrusite is predicted to be supersaturated, and therefore were not used to derive DLM parameters (Figure S8).

A variety of surface complexation models have been developed to describe metal adsorption on kaolinite, mostly relying on one of two approaches to describe the metal binding. In one set of studies, adsorption is modeled using two variable-charge sites, generally assumed to be silanol and aluminol sites (e.g., Benyahya and Garnier, 1999; Hizal and Apak, 2006). For example, Hizal and Apak (2006) developed a 2-site, 2-pK model to describe Pb adsorption on three varieties of kaolinite. They conducted all of their experiments at relatively high ionic strength (0.1 M NaClO_4) to eliminate any contribution to adsorption from permanent charge sites. In other studies, metal adsorption on kaolinite has been described using a combination of variable-charge (edge) and permanent charge (face) sites (e.g. Schindler et al., 1987; Angove et al., 1997, 1998, 1999; Ikhsan et al., 1999; Srivastava et al., 2005; Heidmann et al., 2005; Gu and Evans, 2008; Lund et al., 2008; Landry et al., 2009; Schaller et al.,

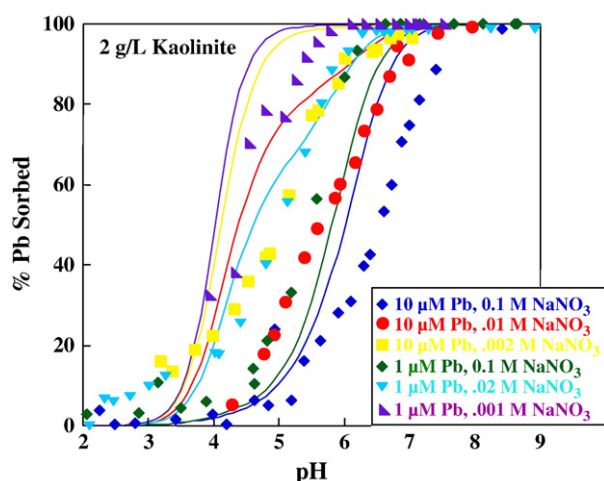


Fig. 3. Pb adsorption on 2 g/L kaolinite with 1 or 10 μM Pb and 0.001 to 0.1 M NaNO_3 . Lines indicate model fits using model parameters given in Tables 1 and 2.

2009). Pb adsorption on kaolinite has mostly been parameterized with these two types of sites using a constant capacitance model (CCM) framework. The CCM has been successfully used to describe Pb adsorption on kaolinite over a range of ionic strength (Schindler et al., 1987; 0.01 to 1 M NaClO_4 ; Gu and Evans, 2008; 0.001 to 0.1 M NaNO_3) and over a range of pH and Pb loadings at a single ionic strength (e.g., Srivastava et al., 2005; 0.005 M KNO_3). Heidmann et al. (2005) developed an extended CCM to describe Pb adsorption on kaolinite over a range of ionic strength (0.01 to 0.1 M NaNO_3) and over a wide range of Pb loadings. They found that combination of a Stern model to describe Pb adsorption on variable-charge edge sites with a Gaines–Thomas cation exchange model to describe Pb adsorption on permanent charge sites could not adequately capture the full ionic strength and sorbate/sorbent dependence of Pb adsorption. Of the models tested by Heidmann et al. (2005) only a combination of Stern models to describe Pb adsorption on a variable-charge edge site and on a permanent negative charge face site, with formation of a ternary X–Pb NO_3 complex, resulted in good fits to their full suite of data.

None of the previously published models for Pb adsorption on kaolinite have used a DLM, and therefore, none can be easily combined with the widely used DLM model for HFO or the model developed here for Pb adsorption on quartz to test the component additivity approach. Furthermore, with the exception of the model developed by Heidmann et al. (2005), most previously published models have been developed for limited ranges of ionic strength and use ionic-strength dependent stability constants.

Therefore, a DLM is developed here to describe Pb adsorption on kaolinite. Ideally, spectroscopic data should guide the parameterization of surface complexation models. However, there is relatively little spectroscopic data available describing Pb adsorption on kaolinite. Although Grafe et al. (2007) used XAS to examine the structure of Pb adsorbed on kaolinite, they used high Pb loadings (667 μM Pb on 6.67 g/L kaolinite). At these conditions Pb(OH) $_2$ is slightly over-saturated, although no evidence for Pb(OH) $_2$ precipitation was found in their study. Instead, the XAS spectra suggested that Pb polynuclear complexes formed on the kaolinite surface. However, these findings are not necessarily applicable at the much lower loadings of Pb used in this study. Therefore, as for previously published SCMs describing Pb adsorption on kaolinite, only mononuclear complexes are used to develop models in this study.

As discussed above, most previous studies have described Pb adsorption on kaolinite using both a variable-charge and a permanent charge site. However, as pointed out by Srivastava et al. (2005), Pb hydrolyzes readily, and is therefore expected to adsorb on variable-

charge surface hydroxyl sites even at relatively low pH. Thus, it is possible that permanent charge sites would not play a strong role in Pb adsorption. For this reason, a very simple Pb adsorption model was tested, using only a single variable-charge site, with protonation and deprotonation stability constants and the site density taken from Sverjensky and Sahai (1996). Pb was assumed to form either a mononuclear, monodentate complex according to:



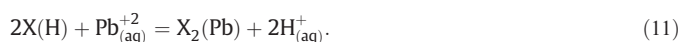
or a mononuclear, bidentate complex according to:



Mean stability constants for reactions (8) or (9) calculated based on fits to the individual edges shown in Fig. 3, produce very poor fits to the measured data (Figure S9A, B; Table S6). The models do not reproduce the significant adsorption observed at low pH under low ionic strength conditions and do not correctly describe the strong ionic strength and sorbate/sorbent ratio dependence of the measured edges. Therefore, reactions (9) or (10) were combined with ion exchange reactions describing Na^+ , H^+ and Pb^{+2} adsorption on a permanent charge site according to:



and



Median stability constants derived for reactions (8), (10) and (11) or (9), (10), and (11) from individual fits of the full suite of edges also fail to adequately reproduce the ionic strength and sorbate/sorbent ratio dependence of the data (Figure S9C, D; Table S6). Median stability constants derived by fitting for (8) and (11) or (9) and (11) while setting the log K for reaction (10) equal to 2.5 (Landry et al., 2009) produced better fits to the data (Figs. 3, S9E; Tables 2, S6) compared to fits with all three parameters optimized. The improved fits are likely due to the interdependence of the three stability constants derived for any given edge; taking the median value of all three values thus produces poor fits to most of the edges.

Because the ion exchange and variable-charge site model does not produce a satisfactory fit to Pb adsorption under the range of conditions considered in this study, a two variable-charge site model was also tested. This model is based on the DLM of Benyahya and Garnier (1999), which they developed to describe Cd, Zn, Co and Mn adsorption on kaolinite as a function of pH in 0.05 M NaNO_3 . Using their site densities, and protonation and deprotonation stability constants for the aluminol and silanol sites (Table S7), stability constants were optimized for Pb adsorption on the aluminol and silanol sites according to:



and



The resulting model does not adequately reproduce the ionic strength or sorbate/sorbent dependence of Pb adsorption (Figure S9F). As for quartz, none of the tested models can produce a good fit to the measured data over the full range of ionic strength and sorbate/sorbent conditions, although nearly any of the models can produce a good fit to data measured over limited solution conditions.

For the purposes of testing the component additivity model, the 2-site model, Pb uptake on a permanent charge site, and formation of a monodentate Pb complex on a variable site, is used. This model was also applied to previously reported Pb adsorption edges (Table S8),

and does a reasonable job of approximating data reported by Hizal and Apak (2006) for three different types of kaolinite with $V(Y) = 11.4$ (Figure S10A). However, in contrast to the data reported in this study for 0.1 M NaNO_3 , the edges are somewhat overestimated. This could be due to the difference in electrolyte (NaClO_4) or clays used by Hizal and Apak (2006). The Pb adsorption edge of Ikhsan et al. (1999) for 0.005 M KNO_3 is significantly overestimated by the model developed in this study ($V(Y) = 56.3$; Figure S10B). Predictions compared to edges from Gu and Evans (2008) are very similar to those for data reported in this study (Figure S10C); Pb adsorption is somewhat overpredicted for 0.001 and 0.01 M NaNO_3 , with an overall $V(Y)$ of 11.7. Similarly, Pb adsorption is overestimated compared to edges from Srivastava et al. (2005) for 0.01 M NaNO_3 , with a $V(Y)$ of 21.8 (Figure S10D).

In summary, the DLM cannot reproduce Pb adsorption edges correctly for the full range of ionic strength and Pb loadings used in this study. The lowest goodness-of-fit values are obtained for the 2-site model with a permanent charge site and monodentate or bidentate Pb complex on a variable-charge site. This model has the advantage of internal consistency with prior models published for Cu, Cd and Co adsorption on kaolinite (Lund et al., 2008; Landry et al., 2009; Schaller et al., 2009). Nonetheless, as for quartz, a more sophisticated approach, such as that of Heidmann et al. (2005) seems to be required to accurately characterize Pb adsorption on kaolinite over wide ranges of solution composition.

3.4. Pb adsorption on mixtures of HFO, kaolinite and quartz

Pb adsorption was measured on binary and ternary mixtures of HFO, quartz and kaolinite as a function of pH, using varying ratios of the sorbents. Based on the DLMs calibrated for the pure endmember systems, predictions were made for Pb adsorption on the mixtures with a component additivity approach, assuming no interactions among the sorbents and no ternary complex formation. Previous studies have shown that this approach typically yields predictions for Cd, Cu and Co adsorption on these substrates that are as good as the model predictions for the endmember solids (Lund et al., 2008; Landry et al., 2009; Schaller et al., 2009).

Pb adsorption was measured on mixtures of quartz and HFO for 6 sorbent ratios, spanning a range of quartz:HFO from 1:1 to 500:1 with 10 μM Pb and 0.01 M NaNO_3 (Fig. 4). Predicted Pb adsorption edges for these conditions were made using the 2-site HFO model, with $>\text{Fe}_{(\text{w})}\text{OPb}^+$ and $>\text{Fe}_{(\text{s})}\text{OPb}^+$, and the 1-site quartz DLM, with

formation of monodentate $>\text{SiOPb}^+$, calibrated using the pure endmember sorbents (Tables 1 and 2). The predicted edges are in very good agreement with the measurements with $V(Y) = 6.8$, compared to $V(Y) = 9.4$ and $V(Y) = 11.6$ for the pure HFO and quartz systems, respectively. The comparatively excellent fit for the binary system likely reflects, at least in part, the fact that the edges were measured at only a single ionic strength and sorbate concentration. For the pure HFO and pure quartz systems, the $V(Y)$ values drop to 2.6 and 2.7, respectively if only 0.01–0.02 M experiments are considered, which is somewhat lower than the $V(Y)$ observed the mixed system. At higher concentrations of HFO, the predictions somewhat overestimate Pb adsorption compared to the measured values, which is similar to fits for pure HFO at the same conditions (Fig. 1). The reasonable predictions across a range of sorbent ratios suggest that sorbent–sorbent interactions in this system are smaller than the uncertainty of the model fits in the pure sorbent systems.

As noted above, an optimized single-site HFO model with Pb adsorption only on the strong site produced fits that were not statistically distinguishable from those of the optimized 2-site HFO model (Tables 2 and S2). However, the 1-site HFO model does not provide sufficient sites for Pb adsorption in the binary mixtures with low concentrations of HFO. Thus, use of the 1-site HFO model produces poorer predictions of Pb adsorption on the binary system under these conditions (Figure S11). This highlights the importance of deriving surface complexation models that are robust over broad ranges of conditions (sorbate/sorbent ratio and ionic strength) if they are to be applied to, and produce accurate predictions of, metal adsorption in natural sediments and soils.

Pb adsorption was measured on mixtures of HFO and kaolinite with 10^{-5} M Pb, 0.02 M NaNO_3 and 2 g/L total sorbent for kaolinite: HFO ratios from 1:1 to 500:1 (Fig. 5). The predicted trends in adsorption as a function of kaolinite:HFO using model parameters from Tables 1 and 2 are generally reasonable, resulting in a $V(Y)$ of 14 (Table 3) for the set of kaolinite and HFO data, which is in the range of the fits for the full range of the pure HFO ($V(Y) = 9.4$) and kaolinite ($V(Y) = 17$) systems, and for the pure systems including only 0.01–0.02 M experiments (HFO: 2.6; kaolinite: 19.9). In the 1:1 to 1:10 mixtures, i.e. the systems with relatively greater concentrations of HFO, Pb adsorption is overpredicted, much as it is in the binary HFO and quartz and pure HFO systems (Figs. 1, 4). However, in mixtures with more kaolinite, Pb adsorption is underestimated. This is somewhat surprising, given that Pb adsorption is significantly overpredicted in the pure kaolinite system for similar conditions (Fig. 3). A

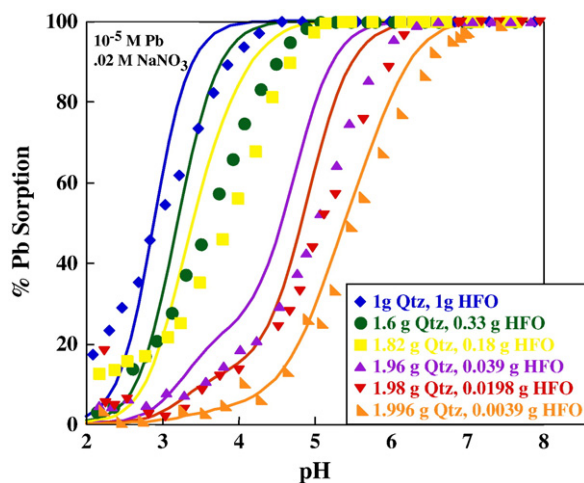


Fig. 4. Pb adsorption on binary mixtures of quartz and HFO with 10 μM Pb and 0.02 M NaNO_3 . Lines indicate model fits using optimized stability constants for the 2-site HFO model and 1-site quartz model developed for the pure sorbent systems. Model parameters are given in Tables 1 and 2.

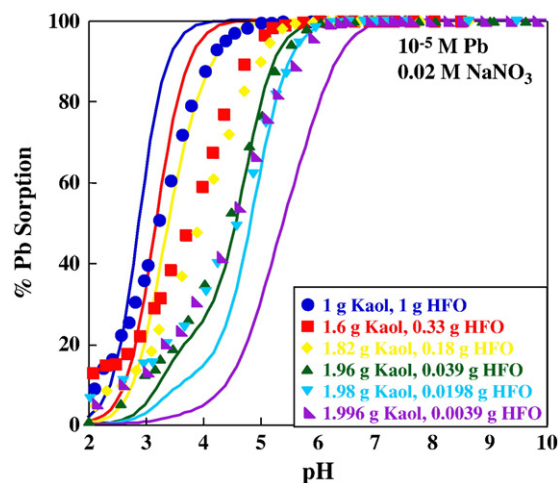


Fig. 5. Pb adsorption on binary mixtures of kaolinite and HFO with 10 μM Pb and 0.02 M NaNO_3 . Lines indicate model fits using optimized stability constants for the 2-site HFO model and 2-site kaolinite model developed for the pure sorbent systems. Model parameters are given in Tables 1 and 2.

Table 3

Average goodness-of-fit parameters ($V(Y)$) and 95% confidence intervals of $V(Y)$ for Pb adsorption edge data for mixed solid systems.

Solid mixture	$V(Y)$ ($V_{\min}(Y)$, $V_{\max}(Y)$)	n_p
HFO/quartz	6.8 (5.2, 9.2)	95
HFO/kaolinite	14 (10, 19)	83
Kaolinite/quartz	8.4 (6.4, 11)	71
HFO/kaolinite/quartz	5.8 (3.6, 11)	28

similar underprediction has been reported for Cd adsorption on binary systems of kaolinite and HFO containing high quantities of kaolinite (Schaller et al., 2009).

Pb adsorption was measured on four mixtures of kaolinite and quartz with 10^{-5} M Pb in 0.01 M NaNO_3 (Fig. 6). Predicted edges using models calibrated for the endmember sorbents (Tables 1 and 2), produce remarkably good fits to the measured data, especially for systems with equal or greater quantities of quartz compared to kaolinite. The $V(Y)$ value of 8.4 (Table 3) is better than the values for the pure quartz (11.6) or kaolinite (17.3) systems, which probably reflects the limited range of ionic strength and sorbate concentration used in the binary mixtures, as it is intermediate between the $V(Y)$ values for 0.01–0.02 M experiments in the pure systems (quartz: 2.6, kaolinite: 19.9). In contrast to the binary HFO and kaolinite systems, Pb adsorption is overpredicted for systems with greater quantities of kaolinite, which is in agreement with the overpredictions for the pure kaolinite system at similar conditions. The good agreement between the component additivity predictions and the measured data suggests that any kaolinite–quartz interactions are significantly smaller than the uncertainties of the model fits for the pure endmember sorbents.

Pb adsorption was measured on two ternary systems of HFO, quartz and kaolinite, with 10^{-5} M Pb in 0.02 M NaNO_3 (Fig. 7). Both systems contained 2 g/L total sorbent, but in one system equal quantities of the three sorbents were used by mass (Fig. 7A; 0.67 g/L of each), whereas in the other system, equal quantities of the three sorbents were used according to surface areas (Fig. 7B; 0.81 g/L kaolinite, 0.018 g/L HFO and 1.17 g/L quartz). The component additivity predictions are in remarkably good agreement with the measured data ($V(Y)=5.8$; Table 3), correctly describing the two distinct Pb adsorption edges. In the experiment with equal mass of each sorbent, the strong site on HFO accounts for nearly all of the

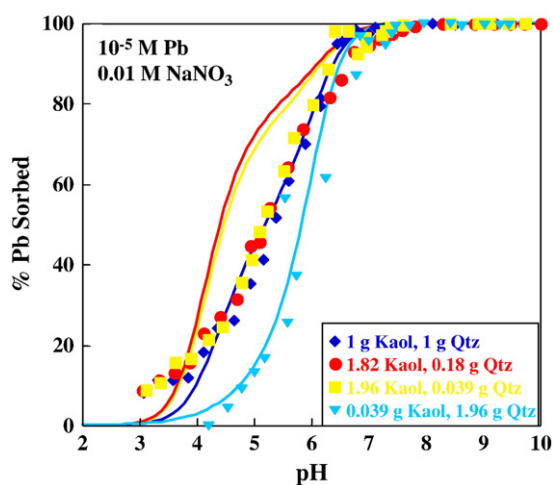


Fig. 6. Pb adsorption on binary mixtures of quartz and kaolinite with $10 \mu\text{M}$ Pb and 0.01 M NaNO_3 . Lines indicate model fits using optimized stability constants for the 2-site HFO model and 1-site quartz model developed for the pure sorbent systems. Model parameters are given in Tables 1 and 2.

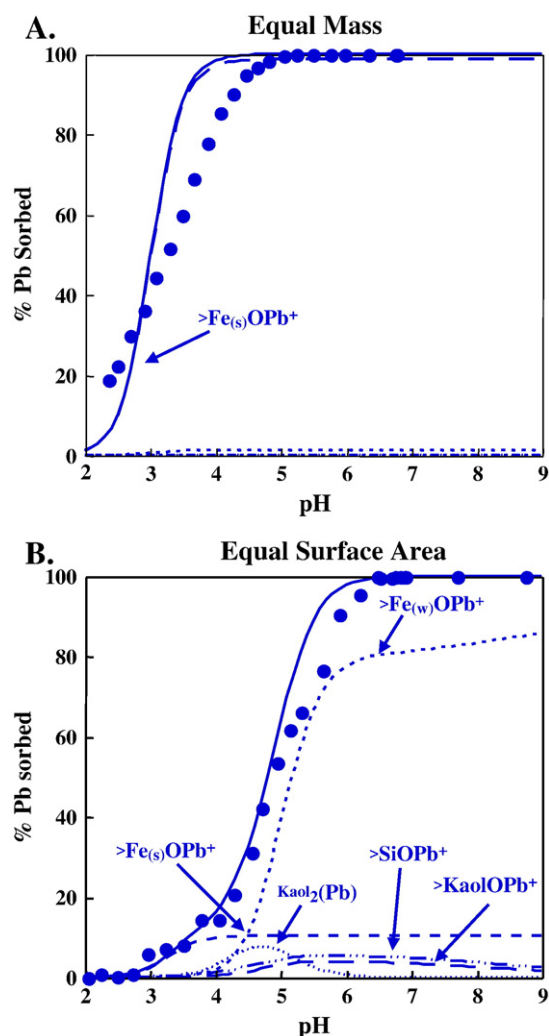


Fig. 7. Pb adsorption on ternary mixtures of quartz, kaolinite and HFO with $10 \mu\text{M}$ Pb, 2 g/L total solid and 0.02 M NaNO_3 with (A) an equal quantity of each sorbent by either mass or (B) surface area. Solid lines indicate predicted total Pb adsorbed from a component additivity approach using the optimized stability constants for the 2-site HFO model, 2-site kaolinite and 1-site quartz model developed for the pure sorbent systems. Model parameters are given in Tables 1 and 2.

adsorbed Pb. At $\text{pH} > 3$, the predicted edge overestimates the quantity of Pb adsorbed and is slightly too steep, as observed for the pure HFO system under similar conditions (Fig. 1B). In the experiment with equal surface areas of the three sorbents, Pb is predicted to adsorb significantly on all three solids. The weak site of the HFO dominates at $\text{pH} > 5$, accounting for up to 87% of the adsorbed Pb at $\text{pH} 9$, whereas the strong site on HFO accounts for $\sim 10\%$ of the adsorbed Pb between $\text{pH} 4$ and 9 . Quartz is predicted to adsorb at most 5.4% of the Pb, at $\sim \text{pH} 5.7$. The permanent charge site of kaolinite is most important at low pH, taking up 7% of the Pb at 5.0, whereas the variable-charge site on kaolinite is predicted to adsorb $\sim 4\%$ of the Pb between $\text{pH} 5$ and 6 . It would be interesting to test these predictions of metal distribution in the equal mass compared to the equal surface area ternary experiments using spectroscopic methods, such as XAS. In many natural sediments, quartz dominates by mass, however, HFO may be more important by surface area, particularly if it forms coatings on other minerals. The component additivity predictions suggest that in such systems, a quantitative understanding of metal adsorption on each individual sorbent, and potential interactions between HFO and clay minerals, may be required to produce accurate predictions of total Pb sorbed.

4. Conclusions

Pb adsorption on HFO shows little dependence on ionic strength. A 2-site DLM assuming Pb adsorption on strong and weak sites produces a good fit to Pb adsorption data collected over a range of ionic strength (0.003 to 0.1 M) and sorbate/sorbent ratios (1 to 100 μM Pb on 2 g/L HFO). In contrast, Pb adsorption on both quartz and kaolinite shows a strong dependence on both ionic strength and Pb loading. Previous studies have calibrated DLMs to accurately represent data measured over limited ranges of solution conditions. However, only by collecting data over a wide range of pH, ionic strength and Pb concentration, as in this study, does it become apparent that such models do a poor job of reproducing data collected over a broad range of solution conditions. This is a significant limitation of the DLM approach, because robust models producing accurate predictions of metal speciation over a broad range of conditions are necessary, if they are to be applied successfully in field settings. More sophisticated treatments of the electrostatics, such as a triple layer model, charge distribution MUSIC model or an extended-constant capacitance model, or possibly a multi-site modeling approach, will likely be required to correctly describe the strong dependence on ionic strength and Pb concentration. More spectroscopic data, collected over a range of solution conditions, would be particularly useful for the development of such models, because it would greatly reduce the required number of fit parameters.

Predictions of Pb adsorption in systems with two or more solids, based on the DLMs developed for the pure sorbent systems, are very encouraging. In spite of the difficulty associated with development of robust models for the single sorbent systems over broad ranges in solution conditions, the best DLMs for the single solid systems produce reasonable predictions of adsorption for systems with multiple sorbents. Mineral–mineral interactions generally appear to be absent, or less significant than uncertainties for the pure solid systems, although there is some indication that HFO–kaolinite interactions could be significant under some conditions. This observation deserves further study; spectroscopic data would be particularly useful for examining potential HFO–clay mineral interactions, as well as for testing the predicted speciation of Pb in the multisorbent systems.

Acknowledgement

This study was supported by a grant from the National Science Foundation CAREER program (NSF-EAR 0348435).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2010.05.017](https://doi.org/10.1016/j.chemgeo.2010.05.017).

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