

A WHAM—based Kinetics Model for Zn Adsorption and Desorption to Soils

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A novel model has been developed to describe the kinetics of Zn adsorption and desorption to soils. The model incorporates the mechanistic-based equilibrium model WHAM (Windermere humic aqueous model) to account for the chemical variation during the reaction (e.g., pH and Zn²⁺ concentration), the heterogeneity of binding sites of soil organic matter (SOM), and the nonlinear binding of Zn to SOM. To test the model, kinetic experiments were conducted using a stirred-flow method. Six soils, with low clay fractions and covering a wide range in SOM concentrations, and various Zn concentrations and pHs were studied. Under these experimental conditions, SOM is found to be the major adsorbent for Zn binding. The fast and slow Zn reactions with soils were associated, respectively, with the monodentate and bidentate binding sites of humic substances in WHAM. The model has only three fitting parameters, the two desorption rate coefficients for the fast (monodentate) and slow (bidentate) reaction sites which are constant and independent of soil type, and the reactive organic matter fraction of the total SOM in each soil. All other parameters are derived from WHAM. The model is able to predict Zn release from spiked soils including the effects of Ca competition.

Introduction

Knowledge of the rates of reactions between soils and dissolved trace metals is important for predicting trace metal behavior since an equilibrium assumption may not be appropriate under many conditions (1). Trace metal adsorption and desorption reactions with soils do not achieve equilibrium instantaneously (2–4). Compared with the extensively used equilibrium models for soil systems (5–7), less progress has been made in developing kinetics models. A quantitative understanding of the rates of trace metal adsorption and desorption with different soils at varying solution chemistry would be quite useful for accurately predicting metal fate and transport in the environment.

The kinetics of Zn adsorption/desorption have been modeled previously using linear adsorption isotherms (4, 8), where the adsorption and desorption rate coefficients remain constant at constant pH and are constrained by the equilibrium partition coefficient. This approach is successful for some conditions, e.g., within a narrow range of Zn concentrations. However, a nonlinear adsorption isotherm is often observed over wide range of Zn concentrations, and the adsorption rate may vary significantly with the Zn loading in soils. Moreover, Zn reactions with soils are controlled by both soil composition, such as soil organic matter (SOM) content, and solution chemistry, e.g., pH and Zn concentration. The kinetics model needs to account for all these variables.

The nonlinearity of adsorption reactions in soils has been described by using either the Langmuir or Freundlich equation in kinetics models (9, 10). However the applicability of the model parameters is limited. Recently, some mechanistic-based equilibrium models, such as the Windermere humic aqueous model (WHAM) (7, 11), have been developed and successfully used to describe trace metal partitioning between soils and solutions. WHAM is capable of calculating the equilibrium chemical speciation in waters, sediments, and soils (11), especially when the chemical speciation is dominated by humic substances.

In this paper, a Zn kinetics model incorporating WHAM is presented, which is able to account for the nonlinear Zn binding to SOM and variations in the solution chemistry and SOM concentration. The model is tested employing Zn adsorption and desorption kinetics experiments, over a wide range of SOM and Zn concentrations at various solution pH. The model focuses on short-term adsorption/desorption kinetics over a time scale of hours.

Materials and Methods

Soil Samples. Six uncontaminated soils were sampled from the U.S. and European countries. All soil samples were obtained from the 0–20 cm layer, air-dried, and then sieved using a 2 mm screen. These soils have low background Zn concentrations ranging from 16 to 127 mg kg⁻¹. The soils were selected to cover a wide range of soil organic carbon (SOC) concentrations (0.76–12.90%) and contain low clay fractions (9–24%). Selected soil properties are presented in Table 1.

Stirred-Flow Experiments. The stirred-flow reaction chamber used in the kinetic experiment is described in detail elsewhere (4). The soil sample (0.3 g for most experiments) and a Teflon-coated magnetic stir bar were placed into the reaction cell (volume = 6.4 cm³), which was then filled with the background electrolyte. A 25 mm diameter filter membrane with a 0.45 μm pore size was used in the reaction chamber to retain the soil in the reaction cell. After sealing the chamber, the suspension in the cell was mixed with the stir bar for 30 min without flow to hydrate the sample. Then the background electrolyte was passed through the cell for another 30 min to remove most of the soluble organic matter and cations released from the soils during hydration. Preliminary experiments showed that the release of Zn and organic matter from these uncontaminated soils was negligible. The background electrolyte was 3 mM Ca(NO₃)₂ and the pH (5.5–6.5) was kept at the desired value using 3 mM MES ([2-(*N*-morpholino) ethane sulfonic acid]) which does not complex Zn ions (12). The Zn(NO₃)₂ stock solution was added to the background electrolyte to prepare different concentrations of Zn solutions (0.83–3.62 mg L⁻¹).

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TABLE 1. Selected Soil Properties

soil	soil location	pH ^a	particle size composition (%)				exchangeable cations (cmol _c kg ⁻¹)		
			sand	silt	clay	total C ^b (%)	K	Mg	Ca
Boonton Bergen County Loam	New Jersey	4.9	60	27	13	3.43	0.02	0.6	2.6
Boonton Union Loam	New Jersey	4.9	49	35	16	7.15	0.2	0.4	1.6
Matapeake Silt Loam	Delaware	6.4	13	63	24	2.32	1.0	1.3	1.7
Montpellier Loamy Sand	France	6.4	87	4	9	0.76	0.0	0.2	1.6
Nottingham Sandy Loam	United Kingdom	4.2	64	23	13	5.20	0.2	0.3	1.7
Rhydtalog Loamy Sand	United Kingdom	4.7	51	36	13	12.90	0.1	0.7	7.8

^a DI H₂O. ^b Measured with a Variomax CN analyzer.

To initiate the adsorption experiment, the Zn solution was pumped through the chamber. The influent Zn concentration was constant during each experiment. After 3 h of adsorption, desorption was initiated by passing the background electrolyte through the chamber. The desorption continued for another 4 h. Effluents were collected with a fraction collector using 5 min time intervals for each sample, and then Zn was analyzed by ICP-MS. A blank experiment (without soil in the chamber) verified that the adsorption of Zn by the chamber and tubing was negligible. The flow rate for all experiments was 0.9 mL min⁻¹. For most of our experiments, the soil particle concentration was kept constant (46.9 g L⁻¹) but a 2-fold increase in particle concentration (93.8 g L⁻¹) was also tested for two soils with high and low SOC concentrations, respectively.

Model Development.

Two-Site Model Formulation. The basic formulation of the two-site adsorption and desorption kinetics model has been described previously (4). The Zn adsorption/desorption reaction is controlled by two groups of sites, one fast, labeled 1, and another slow, labeled 2. The kinetic equations for Zn adsorption/desorption on the two sites are

$$\frac{dC_{p1}}{dt} = -k_{d1}C_{p1} + k_{a1}C_{ion} \quad (1)$$

and

$$\frac{dC_{p2}}{dt} = -k_{d2}C_{p2} + k_{a2}C_{ion} \quad (2)$$

where $k_{a1,2}$ (L (g min)⁻¹), $k_{d1,2}$ (min⁻¹), and $C_{p1,2}$ (μg Zn g⁻¹) are the adsorption and the desorption rate coefficient and particulate Zn concentration for sites 1 and 2 respectively, and C_{ion} (μg Zn L⁻¹) is the solution concentration of the ionic Zn. As shown in our previous study (4), the Zn associated with dissolved organic matter (DOM) in the solution is negligible. The equation for ionic Zn concentration follows from a mass balance for the reactor volume

$$\frac{dC_{ion}}{dt} = -k_a m C_{ion} - k_a m C_{ion} + k_{d1} m C_{p1} + k_{d2} m C_{p2} - \frac{Q(C_{ion} - C_{ion,0})}{V} \quad (3)$$

where m (g L⁻¹) is the soil particle concentration, Q (L min⁻¹) is the flow rate, and V (L) is the reaction volume of the reactor. All concentration terms refer to concentrations in the reactor. Subscript 0 denotes the influent Zn concentration. All Zn species concentrations are expressed as the amount of Zn element per gram of soil (C_{p1} , C_{p2}) or per liter of solution (C_{ion} , $C_{ion,0}$).

In our previous study (4), we used an approach based on a linear adsorption isotherm, in which adsorption rate coefficients remained constant at constant pH, irrespective of Zn loadings in soils. This linear-adsorption-isotherm based model is successful when the change of particulate Zn

concentration is small (4) but has limitations which restrict its application. For example, it is not clear how to model the effect of competing cations. This suggested that using a mechanistic-based model for Zn adsorption on soils would generalize the model. It would be possible to calculate the change of the adsorption rates during the nonlinear binding process under different reaction chemistry conditions rather than using constant adsorption rates.

Model Equations. The modeling approach presented in this paper incorporates equilibrium sorption model WHAM. The derivations for the equations for fast and slow sites are similar. For the fast site, assuming there are n different reaction sites with different adsorption rate constants k_i and free site concentrations m_i , the overall adsorption reactions rate can be formulated as

$$k_1 m_1 C_{ion} + k_2 m_2 C_{ion} + \dots + k_n m_n C_{ion} = \left(\sum_{i=1}^n k_i m_i \right) C_{ion} = k_{a1} m C_{ion} \quad (4)$$

where k_{a1} is the overall adsorption rate coefficient based on the soil particle concentration m , $k_{a1} m = \sum_{i=1}^n k_i m_i$. The basic model assumption is that the Zn concentration in the particulate phase C_{p1} , which determines the free site concentrations, also determines the corresponding adsorption rate constant for Zn adsorption to these free sites. At a specific particulate Zn concentration C_{p1} and solution conditions, it is possible to compute concentration of ionic Zn in solution, C_{ion} , that is in equilibrium with this particulate Zn concentration based on the adsorption isotherm. The corresponding partition coefficient is $K_{p1}(C_{p1}) = C_{p1}/C_{ion}$, where the notation of $K_{p1}(C_{p1})$ is used to emphasize the fact that K_{p1} is a function of C_{p1} . The adsorption rate coefficient at equilibrium is found from eq 1 with $dC_{p1}/dt = 0$,

$$k_{a1} m C_{ion} = k_{d1} m C_{p1} \quad (5)$$

so that

$$k_{a1} = k_{d1} C_{p1} / C_{ion} = k_{d1} K_{p1}(C_{p1}) \quad (6)$$

It is assumed that this equation determines the adsorption rate coefficient at each time during the reaction. That is, the reaction is tending toward the equilibrium dictated by the local conditions at each time along the reaction path. Using eq 6 in eq 1 yields

$$\frac{dC_{p1}}{dt} = -k_{d1} C_{p1} + k_{a1} C_{ion} = -k_{d1} C_{p1} + k_{d1} K_{p1}(C_{p1}) C_{ion} \quad (7)$$

A similar equation applies for the slow site:

$$k_{a2} = k_{d2} C_{p2} / C_{ion} = k_{d2} K_{p2}(C_{p2}) \quad (8)$$

where the $K_{p2}(C_{p2})$ is the partition coefficient for the slow site at the specific particulate Zn concentration C_{p2} .

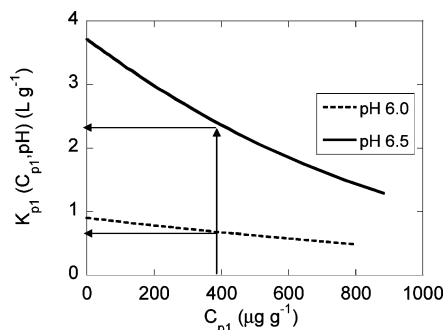


FIGURE 1. Obtaining the equilibrium partition coefficient in the nonlinear adsorption process based on the particulate Zn concentration in soils.

In both this and our previous model (4), desorption proceeds with constant desorption rate coefficients k_{d1} and k_{d2} irrespective of solution chemistry. The effect of solution chemistry is incorporated in the adsorption reaction. In order to obtain the partition coefficients K_{p1} and K_{p2} (thus k_{a1} and k_{a2} from eqs 6 and 8) at various reaction conditions, the equilibrium model WHAM is used.

Incorporation of WHAM into the Kinetics Model. WHAM is used to calculate the equilibrium partition coefficients at various reaction conditions. In recent studies (5–7), the equilibrium model calculations indicated that SOM is the major adsorbent to control Zn partition equilibrium between soils and solutions for soils with low clay fraction. Since the soils used in this study have low clay fractions, SOM was considered as the sole adsorbent for Zn binding to the tested soils (5–7).

In WHAM V (11), Zn can bind to either monodentate or bidentate sites of SOM, and also form outer-sphere complexes in the electrical double layer (DL) via electrostatic interactions. For the desorption reaction the bidentate complex involves breaking two metal-surface bonds. It is likely that these reactions have slower rates compared with desorption from monodentate complexes (13). Therefore, we assume that fast desorption reactions are from the monodentate sites and the slow desorption reactions are from the bidentate sites. The partition coefficients to the monodentate $K_{p1}(C_{p1})$ and bidentate $K_{p2}(C_{p2})$ sites can be independently calculated using WHAM at various reaction conditions. The formation of outer-sphere complexes is minimal in our experimental conditions.

A detailed description of WHAM V can be found in Tipping (11), and the input parameters are discussed in the Supporting Information. A version of WHAM V that was used for calculations is able to output the quantities of Zn binding to various sites. For the soil, only a fraction of SOC, called the reactive organic carbon (ROC), is assumed to bind Zn. This accounts for the fact that SOM contains a variety of components, including humic substances and some other subcomponents such as plant debris and microorganisms (5–7). A Zn adsorption/desorption isotherm database describing Zn binding to monodentate and bidentate sites at various reaction conditions was generated using WHAM V (e.g., different pHs and ROC concentrations). The isotherm database was expanded to include other reaction conditions as needed, such as varying concentrations of competitive cations (e.g., Ca). At the specific particulate Zn concentrations in mono- or bidentate sites during the adsorption/desorption process, $K_{p1}(C_{p1})$ or $K_{p2}(C_{p2})$ can be calculated by searching the isotherm database for each soil at the specific pH and ROC concentration. Figure 1 presents an example of obtaining $K_{p1}(C_{p1})$ for the monodentate sites as a function of C_{p1} at two pH values. This method is faster than performing a WHAM V calculation at each time step during numerical calculations. Note that there is no need to independently specify the site

densities of the fast and slow sites since they are associated with the monodentate and bidentate sites that are determined by WHAM V.

The adsorption rate coefficients for both fast and slow sites at different reaction chemistry conditions can be determined using eqs 6 and 8. The model parameters that remain to be specified are the desorption rate coefficients for the fast (k_{d1}) and slow (k_{d2}) sites, which remain constant, and ROC for each soil. Since WHAM has been calibrated over a wide range of reaction conditions, there is no need to add empirical fitting parameters to account for the variations in reaction chemistry, as used in our previous model (4).

Model Calculations. An implicit finite difference numerical method was used to solve the model equations (eqs 1–3) (4). All experimental data sets for the various soils and experimental conditions were tabulated in a Microsoft Excel 2000 spreadsheet. For each observation time, the square of the difference between measured and model calculated dissolved Zn concentrations were calculated. The sum of the squares for each data set was summed to obtain the total squared error. The SOLVER program in EXCEL was used to minimize the total squared error by varying the model fitting parameters. The resulting root-mean-square error (RMSE) was calculated for each experiment.

Results and Discussion

The effects of pH and influent Zn concentration were systematically tested with the Matapeake soil. At various influent Zn concentrations and pH values, the model fits were consistent with experimental data (Figures 2a–2c). Figures 2d–2f present the results of kinetics of Zn adsorption/desorption to different soils with various SOC concentrations. The RMSE ($\mu\text{g L}^{-1}$) for each curve fitting is presented. It appears that this kinetics model incorporating WHAM V can account for the variations in solution pH and influent Zn concentrations and for various soils with different SOC concentrations.

The role of monodentate (fast) and bidentate (slow) sites in controlling Zn adsorption/desorption kinetics can vary significantly depending on the reaction conditions and time as shown in Figure 3. At pH 5.5, the binding of Zn to monodentate sites dominates the overall adsorption/desorption reactions at the time scale of the stirred-flow experiment (Figure 3a). With an increase in pH to 6.0, the amount of Zn bound to the bidentate sites increases during the adsorption process and the Zn in SOM is slower to desorb (Figures 3b). At pH 6.5, more Zn is bound to bidentate sites than to monodentate sites after the adsorption phase and, as shown in Figure 3c, Zn continues to bind to the bidentate sites during the desorption phase, which accounts for the relatively small amount of Zn initially desorbed.

The model parameters are summarized in Table 2. The amount of ROC increased with an increase in the SOC concentration. However, since the ROC values presented in this study are estimated using the adsorption and desorption kinetic data, they are fitted parameters. Some researchers have used base extractable soil organic matter as a measure of the reactive organic matter (14), while others calculated reactive organic matter either based on the cation exchange capacity measurement of soils and the generic humic substance (5) or soil pH calculations using WHAM (7). The ROC/SOC ratios may vary depending on the different methods to characterize ROC.

Using the fitted model parameters, we applied the model to additional experimental data with a 2-fold increase in soil particle concentrations for a high and a low SOC soil (Figure 4). The model predictions were consistent with the experimental data. Increase or decrease of 10% ROC (dash lines) did not significantly affect the model predictions.

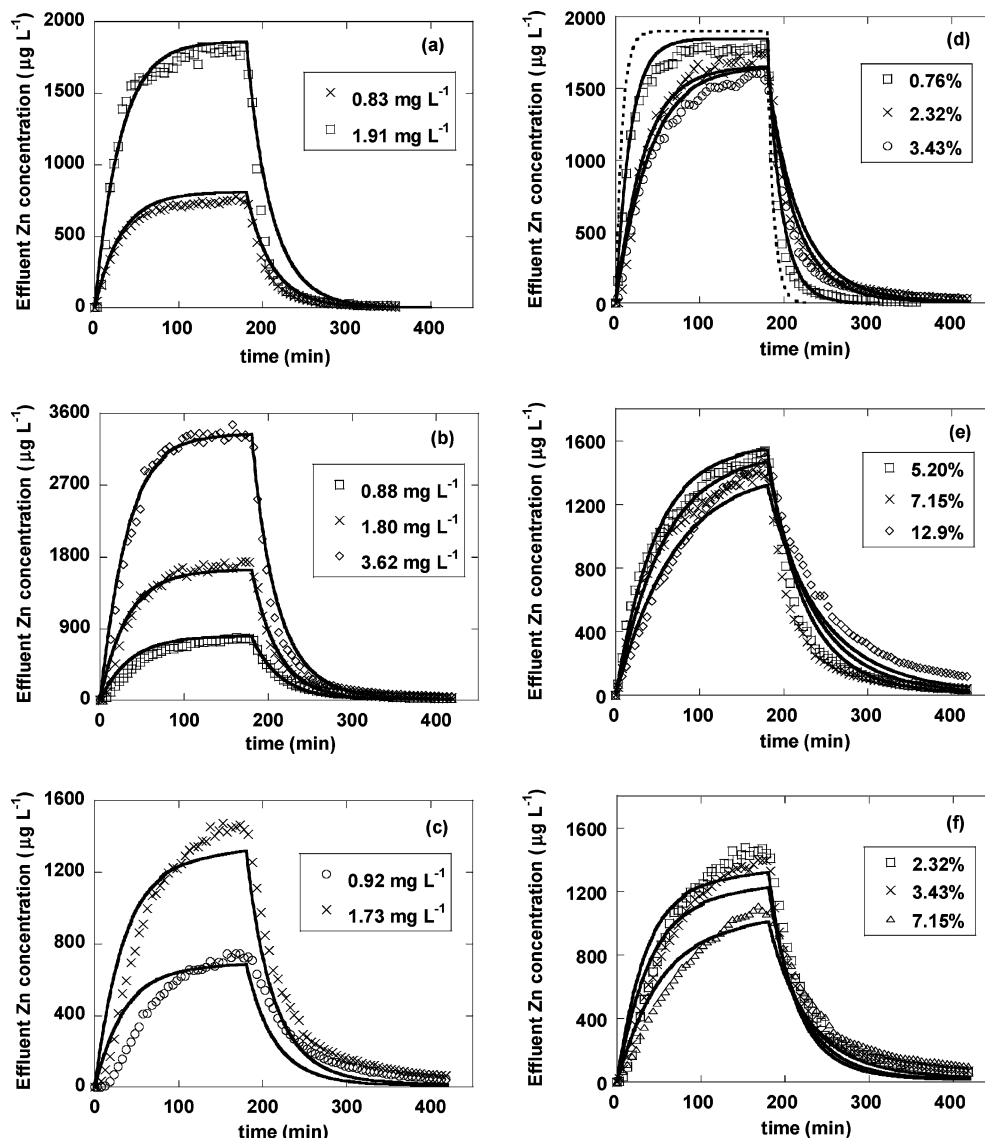


FIGURE 2. Kinetics of Zn adsorption and desorption on soils at different reaction conditions. Matapeake soil (2.32% SOC): (a) pH 5.5 (RMSE 48.8, 141.6); (b) pH 6.0 (RMSE 60.5, 66.8, 122.4); (c) pH 6.5 (RMSE 112.2, 134.5) (Influent [Zn] is presented in the figures). Other soils (SOC concentrations are presented in the figures): (d) pH 6.0 for low SOC soils (RMSE 82.4, 65.8, 99.4), (e) pH 6.0 for high SOC soils (RMSE 73.4, 127.7, 87.7); and (f) pH 6.5 (RMSE 134.5, 108.4, 94.6) (influent [Zn] = 1.60–1.90 mg L⁻¹). RMSE are presented from low to high influent [Zn] (plots a–c) or SOC concentrations (plots d–f). The dash line in plot d corresponds to dilution curve for the blank experiment without soil particles with influent [Zn] = 1.90 mg L⁻¹ for the adsorption. Solid lines are model calculations. Particle concentration $m = 46.9$ g L⁻¹. RMSE in $\mu\text{g L}^{-1}$.

We also applied the model to predict kinetics of Zn desorption from soils which were spiked with Zn solutions and then air-dried before desorption experiment (4). Besides the results presented in our previous study (4), we conducted similar experiments at various Ca concentrations (detailed experimental information can be found elsewhere (4)). In the previous model (4), the initial concentrations of Zn on the fast or slow sites after Zn spiking were fitted parameters. In this model, they can be obtained from WHAM V (Figure S1 and Table S1, Supporting Information). Generally, the model is able to account for the Zn release from the spiked soil with varying Ca competition (Figure 5) (other results are presented in Supporting Information Figures S2 and S3). WHAM does all necessary computations without any additional parameters.

In this model, two desorption rate coefficients account for the Zn desorption from SOM, and each of them may be an average value for a group of sites. This is consistent with the results by Selkaly et al. (15) and Fafous et al. (16), who have shown that the kinetics of Zn dissociation from DOM

can be approximated by two or three groups of sites. The desorption rate coefficients in our model are $k_{d2} = 5.1 \times 10^{-6}$ s⁻¹ and $k_{d1} = 3.0 \times 10^{-2}$ s⁻¹ for the slow and fast sites, respectively. Reported Zn desorption rate constants range from 1.1×10^{-3} s⁻¹ to 7.7×10^{-6} s⁻¹ (3), or higher than 1.7×10^{-5} s⁻¹ (17). The larger and smaller values are close to the desorption rate coefficients of our fast and slow sites.

It is encouraging to see that the desorption rate coefficients of the bidentate sites obtained in this study were close to what was reported in the natural environment (18, 19), e.g., $0.15 \text{ d}^{-1} = 1.74 \times 10^{-6} \text{ s}^{-1}$ (18). It is expected that, for high pH and low trace metal concentrations, most of the trace metal will be bound by the strong sites bidentate sites and even tridentate sites, and their release from organic matter particles to waters would be a slow process.

This model predicts that an interesting phenomenon takes place during the reactions. Due to the different reaction rates, Zn can be redistributed from monodentate to bidentate sites during the desorption process of the stirred-flow experiments (Figure 3c). We further investigated this redistribution using

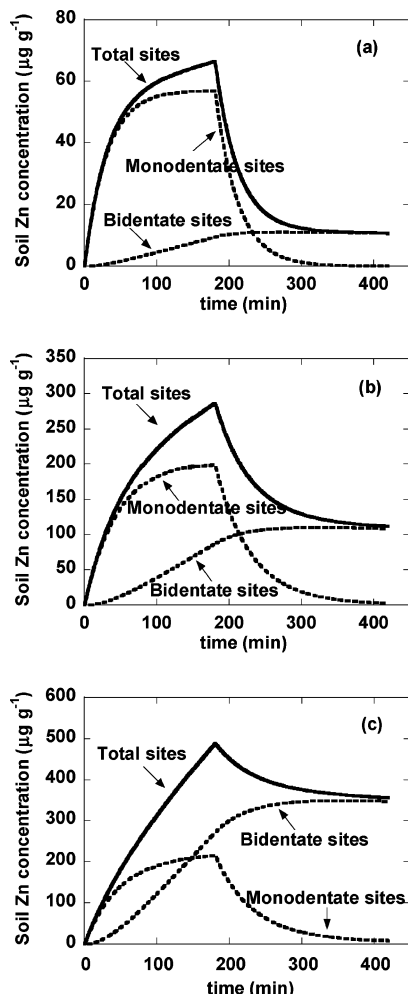


FIGURE 3. Kinetics of Zn adsorption/desorption on monodentate, bidentate sites, and total sites with the model calculations: (a) pH 5.5, 2.32% SOC and [Zn] 0.83 mg L⁻¹; (b) pH 6.0, 5.20% SOC and [Zn] 1.78 mg L⁻¹; (c) pH 6.5, 7.15% SOC and [Zn] 1.70 mg L⁻¹.

TABLE 2. Model Parameters Used for WHAM and Kinetics Model Calculations^a

ROC of each soil for WHAM calculations						
SOC (%)	0.76	2.32	3.43	5.20	7.15	12.90
ROC (%)	0.73	2.04	2.54	3.12	3.92	4.94
desorption rate coefficients for mono- and bidentate sites						
$k_{d1}(s^{-1})$						3.0×10^{-2}
$k_{d2}(s^{-1})$						5.1×10^{-6}

^a Detailed WHAM input parameters at different conditions are discussed in the Supporting Information.

model simulations for the Zn adsorption process in a batch reactor without flow (Figure 6). During the adsorption process, solution Zn decreased quickly within a few minutes (Figure 6a), which is due to the fast adsorption to the monodentate sites (Figure 6b). As the reaction time increases, the solution Zn concentration changed little (Figure 6a). However Zn was redistributed from monodentate sites to bidentate sites (Figure 6b). In the natural environment, due to the frequent change of reaction conditions, this redistribution could significantly affect the rate of subsequent Zn desorption.

Model Applicability. The kinetics model presented above incorporates the equilibrium model WHAM into a two-site

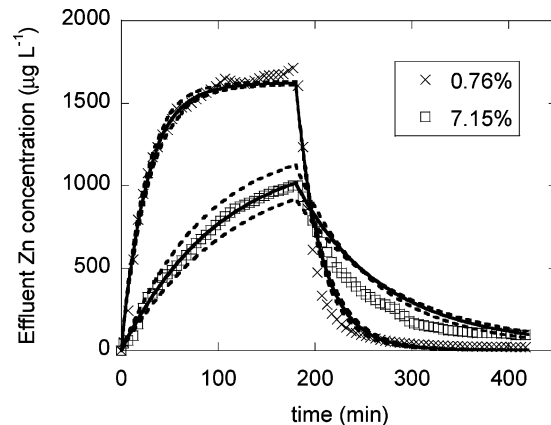


FIGURE 4. Kinetics of Zn adsorption/desorption with a 2-fold increase of soil particle concentrations (pH 6.0 and $m = 93.8 \text{ g L}^{-1}$). SOC concentrations are presented in the figure. Lines are model predictions and dashed lines are model predictions with 10% increase/decrease of ROC.

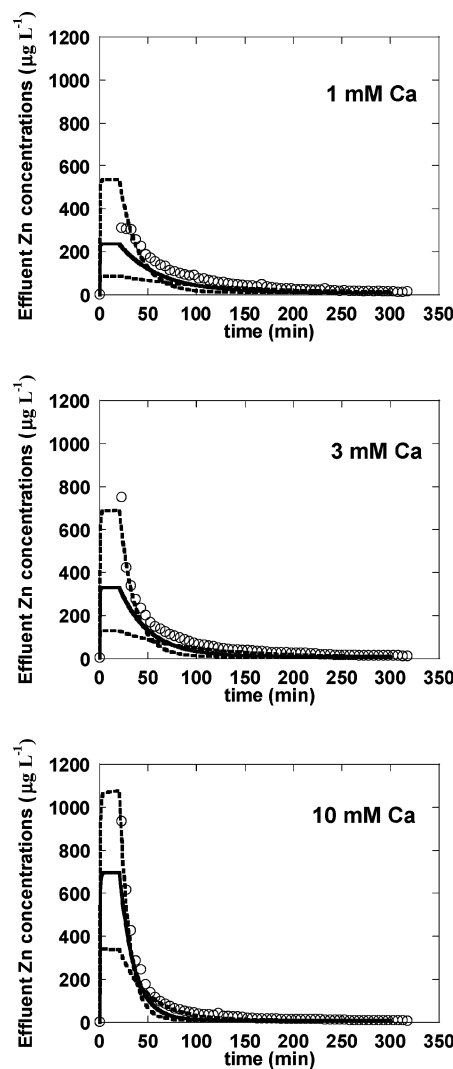


FIGURE 5. Predicting the effect of Ca concentration (values are annotated in the figure) on the kinetics of Zn release from the spiked Matapeake soil at pH 5.5 (4). Lines are model predictions and symbols are experimental data. Dash lines indicate the model predictions with K_{p1} and K_{p2} varying a factor of 3.

kinetics model. Therefore, in principle, it is able to account for the variations in reaction rates due to changes in soil

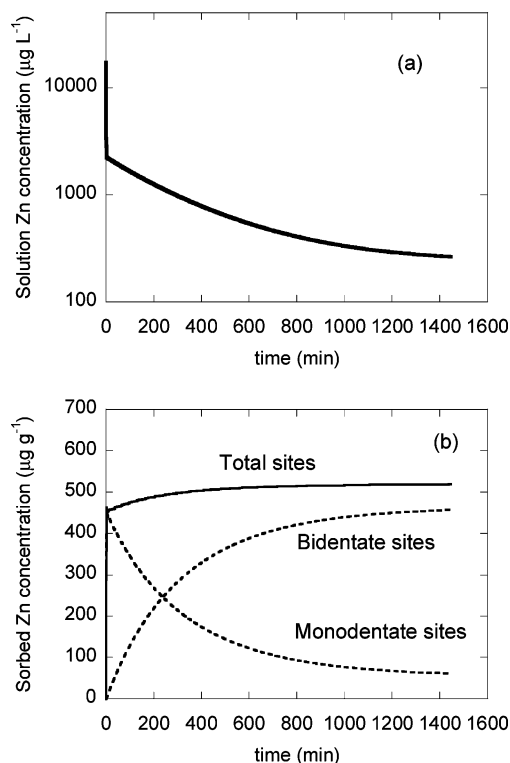


FIGURE 6. Model simulations of Zn adsorption in a batch reactor and the redistribution of Zn among mono- and bidentate sites. Simulations are calculated for the Rhydtalog Loamy Sandy soil with the initial Zn concentration of 17.2 mg L^{-1} in the batch reactor without flow. Model parameters are listed in Table 2. (a) Solution Zn concentration vs reaction time; (b) Sorbed Zn concentration in different sites vs reaction time.

properties and solution chemistry. However, this capability needs to be demonstrated in more realistic soil systems with varying solution chemistry and soil properties. Also a method for an independent determination of ROC is required for a truly predictive model.

This kinetics model is based on WHAM so the performance of WHAM will affect the accuracy of the kinetics model. Although WHAM was developed with mechanistic-based approaches, it contains some empirical parameters (11). For current widely used equilibrium models including WHAM, there are some uncertainties in model parameters, and different assumptions have been made on the composition of natural organic matter (20).

Currently this kinetics model is most suitable for describing the short-term adsorption/desorption kinetics when humic substance is the dominant adsorbent. In natural soil systems, the presence of high concentrations of DOM may affect Zn adsorption/desorption reactions since DOM forms complexes with Zn ions in the solutions. For soils with low SOM concentration, clay minerals could be significant for Zn sorption. Further work is needed to quantitatively incorporate the contributions of mineral phases and DOM in this model. Although WHAM presumably accounts for the Zn-DOM equilibrium, the kinetics of this reaction may be important. In addition, the short-term Zn adsorption and desorption reactions are different from the long-term reactions with aged soils, in which other processes such as diffusion may control the slow reactions (21). For the field contaminated soils with long aging time, the metal speciation could differ significantly from those in laboratory short-term adsorption experiments (22), and the kinetics model would need to be modified. Furthermore, it is desired that the Zn speciation and distribution among mono- and bidentate sites

calculated by WHAM can be further confirmed by advanced spectroscopic techniques.

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Supporting Information Available

(1) WHAM calculations in the kinetics model and (2) calculations of Zn release from spiked soils. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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