

Modeling Zn Adsorption and Desorption to Soils

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1. INTRODUCTION

The rate of reaction of trace metals between soils and solutions is important in predicting trace metal behavior as equilibrium may not be attained. Although chemical equilibrium models are commonly used for soil systems, there has been less progress in developing predictive kinetic models.

Kinetics of Zn adsorption/desorption have been modeled based on the linear adsorption isotherm assumption (1, 2), where adsorption and desorption rate coefficients remain constant at constant pH and are constrained by the equilibrium partition coefficient. This approach is in agreement with Zn adsorption/desorption behavior only within a narrow range of Zn concentrations. However, a nonlinear adsorption isotherm is often observed over wide range of Zn concentrations, indicating that a general kinetics model needs to account for the nonlinearity of Zn binding to soils. In the nonlinear adsorption process, the adsorption rate could vary with the Zn loading in soils. Moreover, Zn adsorption and desorption reactions with soil particles are controlled by both soil composition, such as soil organic matter (SOM) content, and solution chemistry, e.g. pH and Zn concentration.

2. MATERIALS AND METHODS

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. Soil organic carbon (SOC) concentrations were 0.76% to 12.90%.

The stirred-flow reaction chamber has a reaction volume of 6.4 cm³ and contained 0.3 g soil for most experiments. Zn concentrations were 0.83 to 3.62 mg L⁻¹ in 3 mM Ca(NO₃)₂ background electrolyte. The pH (5.5 – 6.5) was controlled using 3 mM MES, which does not complex Zn ions. After 4-h adsorption at a 0.9 mL min⁻¹ flow, Zn-free electrolyte was pumped through the flow chamber. Samples were analyzed by ICP-MS.

The basic formulation for the change in the concentration of sorbed zinc is a two-site adsorption and desorption kinetics model has been described previously (1). The Zn adsorption/desorption reaction is controlled by two groups of sites, one fast and another slow. The kinetic equations for Zn adsorption /desorption on the two sites are $\frac{dC_{p1}}{dt} = -k_{d1}C_{p1} + k_{a1}C_{ion}$ and $\frac{dC_{p2}}{dt} = -k_{d2}C_{p2} + k_{a2}C_{ion}$ where $k_{a1,2}$ ($L (g \text{ min})^{-1}$), $k_{d1,2}$ (min^{-1}), and $C_{p1,2}$ ($\mu\text{g Zn g}^{-1}$) are the adsorption and the desorption rate coefficient and particulate Zn concentration for sites 1 and 2 respectively, and C_{ion} ($\mu\text{g Zn L}^{-1}$) is the solution concentration of ionic Zn. The equation for ionic Zn concentration follows from a mass balance for the reactor volume.

In our previous study (1), we used a linear adsorption isotherm, in which adsorption rate coefficients remained constant at constant pH, irrespective of Zn loadings in soils. Using a mechanistic 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.

The basic model assumption is that the Zn concentration in the particulate phase, which determines the free sites concentrations, determines the corresponding individual adsorption rate constants for Zn adsorption to these free sites as follows. 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 and the corresponding partition coefficient $K_{p1}(C_{p1})$ based on the adsorption isotherm. Thus, with desorption rate coefficient k_{d1} , the adsorption rate at equilibrium is found from eq 1 with $\frac{dC_{p1}}{dt} = 0$. Then, $k_{a1} = k_{d1}C_{p1} / C_w = k_{d1}K_{p1}(C_{p1})$ where the $K_{p1}(C_{p1})$ is the partition coefficient for the fast site at the specific particulate Zn concentration C_{p1} . This equation determines the adsorption rate coefficient at each time during the reaction. A similar equation applies for the slow site. SOM was considered as the sole adsorbent for Zn binding to the tested soils (1).

The mechanistic model WHAM was used to obtain K_{p1} and K_{p2} at various reaction conditions. In WHAM V calculations (3), Zn can bind to either monodentate or bidentate sites, and can also form outer-sphere complexes in the electrical double layer (DL) via electrostatic interactions. We associate the fast adsorption reactions to both Zn binding to monodentate sites and formation of outer-sphere complexes in the DL. The slow adsorption reactions are assumed to be Zn binding to bidentate sites in SOM. Thus the

partition coefficients $K_{p1}(C_{p1})$ and $K_{p2}(C_{p2})$ can be calculated using WHAM at various reaction conditions.

3. RESULTS AND DISCUSSION

Three parameters must be fit for the model, desorption rate constants for the two sites and the fraction of the organic matter that is active in the partitioning. The partitioning coefficients are defined by WHAM. The data for all soils and all conditions tested were globally fit to obtain the best value for the desorption rate constants. These are 3.0×10^{-2} and $5.1 \times 10^{-6} \text{ sec}^{-1}$ for the fast and slow sites respectively. This result is very similar to that of Gee et al. (4) who found the desorption rate constant for zinc from particulate matter in South San Francisco Bay was $1.74 \times 10^{-6} \text{ sec}$.

As shown in Figure 1, the model fits are consistent with the experimental data. The kinetics model incorporating WHAM can account for the variations in Zn loading, solution pH and concentrations of SOC.

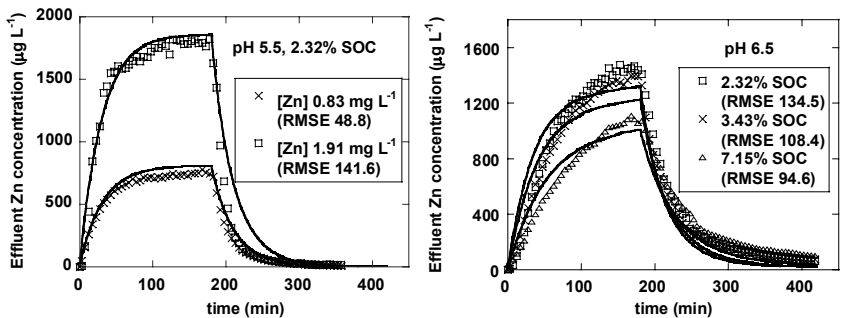


Figure 1. Kinetics of Zn adsorption and desorption on soils.

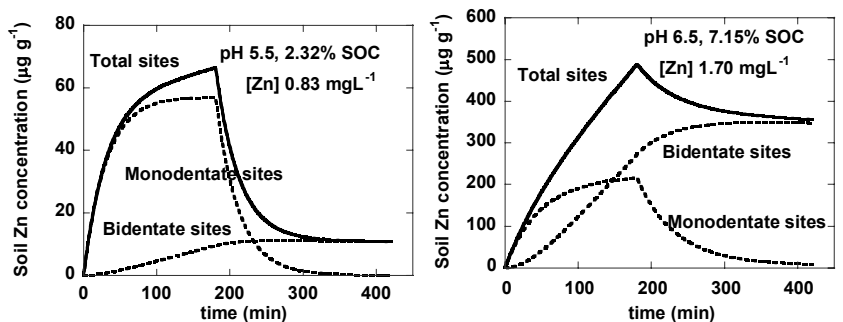


Figure 2. Kinetics of Zn adsorption/desorption on monodentate and bidentate sites.

The role of monodentate (fast) and bidentate (slow) sites on controlling Zn adsorption /desorption kinetics depends on reaction conditions and reaction time (Figure 2). At pH 5.5, binding of Zn to monodentate sites dominated the overall adsorption/desorption reactions. With an increase in pH to 6.5, more Zn was bound to bidentate sites than to monodentate sites after adsorption. During 4 h desorption experiments, the overall Zn release was mainly controlled by the monodentate sites. The amount of Zn adsorbed in bidentate sites continued to increase even during the desorption process, indicating a re-distribution of Zn from monodentate sites to bidentate sites.

4. CONCLUSIONS

Differences in the measured net desorption rate under various solution chemistries result from changes in the readsorption rate, not the desorption rate as has been claimed. Changes in solution speciation, for example by the addition of strong chelating agents, affect the rate of readsorption, not that of the desorption. The initial sorption to monodentate sites is followed by a slow transition to bidentate sites. Desorption of metal from the monodentate sites is rapid, but desorption from the bidentate sites is slow.

Desorption of Zn from soil is a slow process with many days required for a new equilibrium state to be attained. This is likely to have important effects on Zn bioavailability and Zn flux from soil in the field. Because laboratory studies of metal sorption desorption have usually been run for relatively short times relative to the reaction rates, the experimental soil – soil solution distribution will depend on the experimental conditions. Comparison of the results of different investigators and extrapolation to new conditions is difficult.

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