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Kinetics of Ni Sorption in Soils: Roles of Soil Organic Matter and Ni Precipitation

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S *Supporting Information*

ABSTRACT: The kinetics of Ni sorption to two Delaware agricultural soils were studied to quantitatively assess the relative importance of Ni adsorption on soil organic matter (SOM) and the formation of Ni layered double hydroxide (Ni-LDH) precipitates using both experimental studies and kinetic modeling. Batch sorption kinetic experiments were conducted with both soils at pH 6.0, 7.0, and 7.5 from 24 h up to 1 month. Time-resolved Ni speciation in soils was determined by X-ray absorption spectroscopy (XAS) during the kinetic experiments. A kinetics model was developed to describe Ni kinetic reactions under various reaction conditions and time scales, which integrated Ni adsorption on SOM with Ni-LDH precipitation in soils. The soil Ni speciation (adsorbed phases and Ni-LDH) calculated using the kinetics model was consistent with that obtained through XAS analysis during the sorption processes. Under our experimental conditions, both modeling and XAS results demonstrated that Ni adsorption on SOM was dominant in the short term and the formation of Ni-LDH precipitates accounted for the long-term Ni sequestration in soils, and, more interestingly, that the adsorbed Ni may slowly transfer to Ni-LDH phases with longer reaction times.
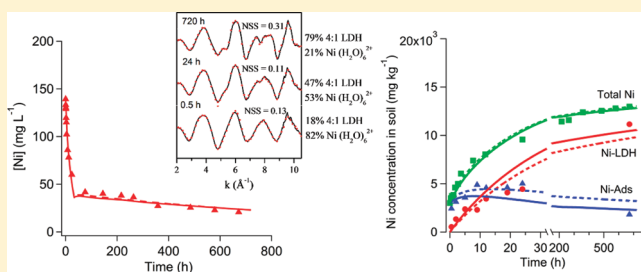
INTRODUCTION

The kinetics of Ni sorption in soils may be controlled by different reaction mechanisms at various time scales, such as adsorption/desorption reactions occurring at short-term scales (minutes to hours) and precipitation reactions lasting for days to years.[1−4] These soil reactions are affected by both solution chemistry (pH, Ni concentration, etc.) and soil composition (e.g., soil organic matter (SOM) and mineral phases). For most acidic soils, SOM has been assumed as the dominant adsorbent because of the high affinity of metal ions for humic substances.[5−8] At neutral to basic pH conditions, Ni may also form layered double hydroxides (LDH) on soil mineral phases.[4] These phases are thermodynamically preferred to pure metal hydroxides, and may be an important path for Ni sequestration in soils.[9] The mechanisms of Ni-LDH formation have been investigated in multiple studies with pure minerals,[4,10−13] minerals with organic coating,[14] and, more recently, with whole soils.[15−17] There is, however, a lack of a quantitative understanding of the kinetics of Ni-LDH precipitation, and the significance of Ni adsorption on SOM and Ni-LDH formation, especially as applied to whole soils.

To predict the kinetics of Ni sorption in soils, it is essential to develop models that account for variations in reaction chemistry, soil composition, and Ni speciation in soils at different time scales. In contrast to existing empirical kinetics models (summarized by Sparks),[3] we have recently developed a

more mechanistic-based kinetic modeling approach for heavy metal adsorption/desorption kinetic reactions in soils.[18,19] This kinetics model incorporates the mechanistic-based equilibrium model Windermere Humic Aqueous Model (WHAM),[6,20] which is able to account for the effects of solution chemistry and SOM concentration on metal adsorption/desorption reactions in soils. Previous versions of this kinetics model, however, did not consider metal precipitation reactions and focused on adsorption/desorption kinetics over short time scales (a few hours). On the basis of the mechanistic description of Ni adsorption reactions with SOM, it is possible to expand this kinetics model by independently quantifying the Ni precipitation kinetics, which is able to evaluate the individual contributions of Ni adsorption and Ni precipitation to overall Ni sorption in soils.

In this study, the effects of solution pH and SOM concentration on Ni speciation and Ni sorption kinetics in two Delaware soils were studied using batch kinetic experiments and X-ray absorption spectroscopy (XAS). A quick-scanning XAS data collection method (QEXAFS)[21] was used to obtain direct information on Ni speciation in the solid phase

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dx.doi.org/10.1021/es202376c | *Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

Table 1. Selected Soil Properties

soil	pH	sand (%)	silt	clay	clay mineralogy[a]	organic carbon (%)	ECEC[b] (meq (100 g)$^{-1}$)	soil Ni (mg kg^{-1})
Matapeake	5.7	30	58	12	K, V	1.41	5.3	10.5
Berryland	4.5	65	16	19	K, V	3.55	4.1	4.2

[a]K = kaolinite, V = chloritized vermiculite. [b]Effective cation exchange capacity.
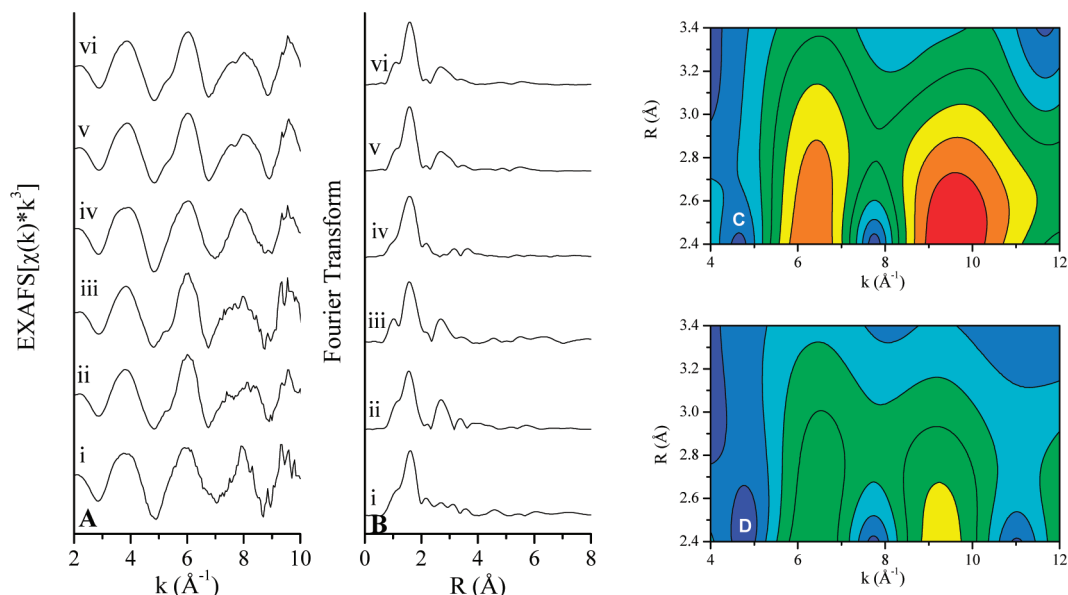

Figure 1. Ni EXAFS data for soil samples 24 h after Ni addition: (A) χ-extracted EXAFS spectra for (i-iii) Matapeake soil at pH 6.0, 7.0 and 7.5, respectively, and (iv-vi) Berryland soil at pH 6.0, 7.0 and 7.5, respectively, (B) Fourier-transformed spectra of the same samples, (C) and (D) Wavelet plots of ~2.7 Å FT peak for soils (iii) and (vi), respectively. Data for pH 6.0 samples were taken from Peltier et al.[15].

during the first 24 h after Ni addition. The Ni speciation information obtained from XAS analysis is essential for developing the full reaction kinetics model at various pHs. Based on experimental results, we developed a kinetics model that integrates Ni adsorption/desorption with Ni precipitation kinetics to simultaneously compute both Ni reactions with SOM and clay minerals and Ni precipitation from short-term (e.g., a few hours) to long-term (e.g., a few weeks) time scales. The significance of Ni adsorption and Ni precipitation in soils at various reaction times was quantitatively assessed with model calculations and compared with XAS results.

■ MATERIALS AND METHODS

Soil Samples. Two Delaware agricultural soils, a Matapeake silt loam and a Berryland loamy sand, were used in this study. Previous studies have shown that Ni-LDH precipitate phases can form in both soils at pH > 6.5 and conditions similar to this experiment.[10,15] Selected soil properties are presented in Table 1. Both soils contain a mixture of kaolinite and chloritized vermiculite clay minerals. The Matapeake has a higher vermiculite content, which accounts for its higher CEC despite the larger SOM fraction in the Berryland soil. The <2 mm fraction of the two soils was isolated for use in all experiments.

Batch Sorption Kinetic Experiments. A full description of the batch kinetic experiments performed with these soils is available elsewhere.[15] The experimental conditions were selected to allow for direct comparison to previous studies on Ni–Al hydroxide formation.[10,13] Briefly, for each sorption experiment a 0.1 M Ni(NO$_3$)$_2$ stock solution was added to a continuously stirred soil suspension (12 g L^{-1}) with 0.1 M NaNO$_3$ as the background electrolyte at various pHs (6.0, 7.0,

and 7.5). The Ni stock solution was added at a rate of 1 mL min^{-1} to reach a desired concentration of approximately 3 mM Ni within 20 min. The pH was maintained to within ±0.1 units by automated addition of 0.1 M NaOH for 24 h at pH 6.0 and 7.0, and 72 h at pH 7.5. All experiments were conducted under an N$_2$ atmosphere using N$_2$-purged reagents to minimize the potential for NiCO$_3$ formation. The pH 6.0 and 7.5 soil suspensions were then stored in sealed vessels in a constant temperature chamber at 25 °C and continuously shaken at low speed for the remainder of the experiment. The length of sorption experiments varied from 24 h (pH 7.0) up to one month (pH 7.5). Dissolved Ni was sampled and analyzed by flame atomic absorption spectroscopy at specific times throughout the reaction period. Soil samples were collected from the soils at 24 h after Ni addition, filtered, rinsed with deionized water, and then flash-frozen and stored at −20 °C for later XAS analysis of Ni speciation. Soil samples were also collected from the pH 7.5 experiments one month after Ni addition for XAS analysis.

XAS Experiments. X-ray absorption spectroscopy (XAS) studies were conducted at the Advanced Photon Source (APS) at Argonne National Laboratory (Argonne, IL) to determine the kinetics of surface precipitate formation in the Berryland soil in the first 24 h after Ni sorption at pH 7.0 and 7.5. In two separate experiments conducted entirely at the APS, a 12 g L^{-1} suspension of the Berryland soil was spiked with Ni solution. The reaction was performed identically to the batch experiments described above, except that the solutions were continuously bubbled with N$_2$ gas during the experiment, as a controlled-atmosphere chamber was not available, and pH was maintained using an organic buffer (40 mM of either MES (at
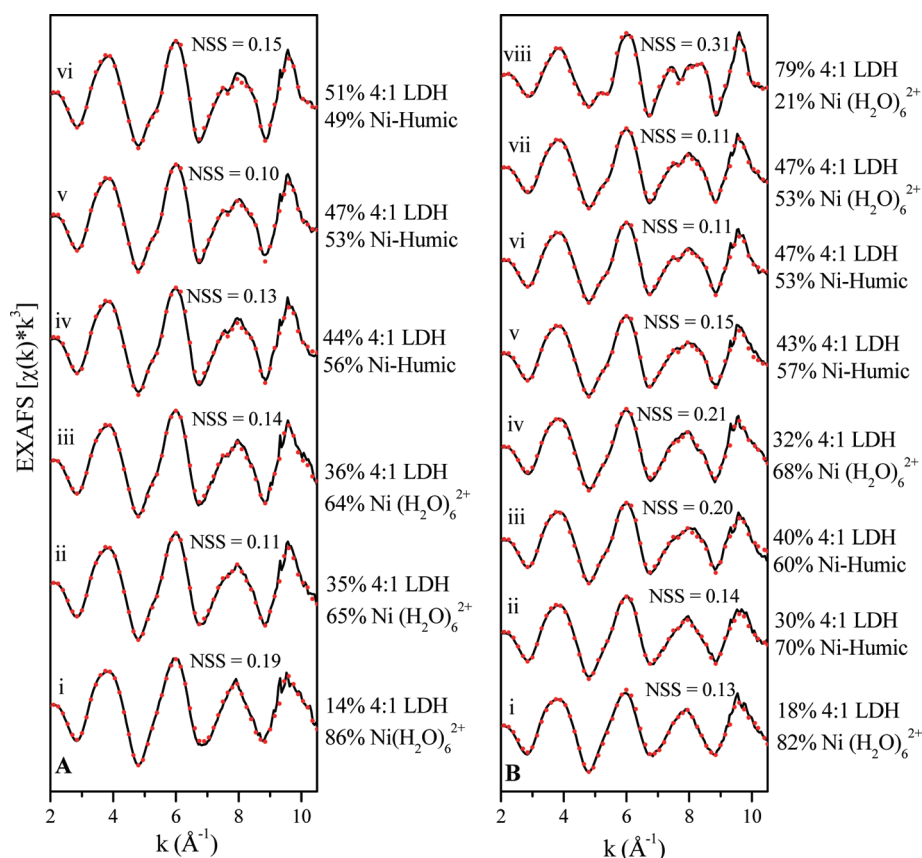
Figure 2. EXAFS spectra for Berryland soils from kinetic studies showing EXAFS data (—) and best fit lines (●) from linear-least-squares fitting: (A) Soils spiked at pH 7.0 after (i) 30 min, (ii) 4 h, (iii) 8 h, (iv) 12 h, (v) 18 h, and (vi) 24 h; (B) Soils spiked at pH 7.5 after (i) 30 min, (ii) 2 h, (iii) 5 h, (iv) 9 h, (v) 12 h, (vi) 19 h, (vii) 24 h, and (viii) 720 h. Data for the 720 h sample were taken from Peltier et al.[15] NSS, or normalized sum of squares, is a quality of fit parameter, with NSS = 0 indicating a perfect fit.

pH 7.0) or MOPS (pH 7.5)). These buffers are noncomplexing with Ni in the aqueous phase[22] and comparative studies showed less than 5% difference in rates of Ni loss from solution when the buffers were used in place of NaOH addition. Samples of the spiked soil were periodically collected, filtered and rinsed to remove entrained Ni, and immediately analyzed using XAS to determine Ni speciation.

A continuous-scanning quick-XAS data collection mode was used to rapidly obtain spectra at the Ni K-edge for each sample. After sample collection and processing, the Sixpack linear fitting module[23] was used to estimate the percentage of Ni present as surface precipitates in the soil samples. Detailed information on EXAFS data collection and processing and the linear fitting method are presented in the Supporting Information (section S1).

Model Descriptions. Adsorption kinetics were computed based on the modeling method developed previously,[18,19] in which the equilibrium model WHAM VI was integrated into the kinetics model to account for the effects of SOM concentrations and solution chemistry on Ni adsorption kinetics. In addition, Ni binding to clay minerals was computed by an electrostatic model built in WHAM VI for cation exchange on clay minerals. Ni precipitation kinetics were formulated based on a model Ni-LDH phase identified by XAS measurements using our experimental conditions. Detailed descriptions of the model development are presented in the results section.

■ RESULTS AND DISCUSSION

Ni Speciation in Soils during Kinetic Experiments. The XAS spectra at pH 6.0 after 24 h reaction showed no significant contributions from second-neighbor metal atoms (Figure 1A and B). This type of spectrum is consistent with Ni either weakly bound in outer-shell surface complexes or complexed with organic ligands, both of which exhibit no significant structure beyond the first neighboring atom (Supporting Information Figure S1). These results fit with previous studies showing no precipitate formation in either soil below pH 6.5, even after long times.[15] At 24 h, the EXAFS spectra of both soils at pH 7.0 and 7.5 clearly showed that a Ni precipitate has already begun to form, based on the dampening that occurs in the χ-transformed data at 7−8 Å^{-1} and the second shell Ni−Ni interactions present in the Fourier-transformed data (Figure 1A and B). Wavelet analysis of the second Fourier-transformed peaks (Figure 1C and D) showed the presence of both lighter and heavier atoms in this region, consistent with the substitution of Al or Si atoms into a Ni hydroxide structure.[15,24]

A goodness-of-fit analysis using the r-factor value provided by the Sixpack fitting routine (which provides the sum of squares of the fitting residuals divided by the sum of squares of the data points) found that the spectra from the Berryland soil kinetic experiments could be best fit using a combination of only two reference standards. Additional analysis indicated that, in all samples where precipitate formation was indicated, a Ni-LDH phase provided a significantly better fit than either Ni(OH)$_2$ or Ni-phyllosilicate. Two Ni-LDH spectra were used in the linear

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dx.doi.org/10.1021/es202376c | *Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

fitting, with a 2:1 and 4:1 Ni/Al ratio, respectively. For spectra collected within 12 h of Ni addition at both pHs, either LDH phase fit the data equally well. However, the 4:1 LDH phase provided significantly better fits at times ≥18 h. Therefore, the 4:1 LDH phase was used in the final fitting results for all spectra. These results suggest that Al availability may play a role in limiting the growth of the precipitate phase, as the 4:1 LDH phase has a low extent of Al substitution (∼ 23%) compared to most LDH structures.

Linear fitting results for the time-resolved samples from the Berryland soil sorption experiment are shown in Figure 2. From 2 to 4 h after Ni addition, a significant Ni-LDH component was observed in all samples at both pH 7.0 and 7.5, reaching 40% of total sorbed Ni by 12 h after Ni addition. From 12 to 24 h, the Ni-LDH fraction increased more slowly, to 51% and 47% of total Ni at 24 h in the pH 7.0 and 7.5 samples, respectively. The second component in the best fit spectrum consisted of either an aqueous Ni standard ($Ni(H_2O)_6^{2+}$), or Ni complexed with humic acids. In sorbed samples, the aqueous Ni reference spectrum primarily represents Ni atoms with no significant second-shell interactions, which could include both outer-sphere surface complexes and some Ni-SOM complexes. In the pH 7.0 spectra, the aqueous spectrum was a better fit up until 9 h, while the Ni−humic acid spectrum was an equal or better fit at 12−18 h. However, no similar pattern was observed in the pH 7.5 spectra. For all samples, fitting with aqueous Ni versus the Ni-humic acid reference spectrum resulted in only small changes (≤5%) to the total Ni-LDH fraction, which suggests that the two nonprecipitate standards were roughly equal at fitting the nonprecipitated Ni fraction over the data set as a whole. In cases where the Ni-humic acid and aqueous Ni sample produced statistically indistinguishable fits, the Ni-humic acid was used in the best fit, as it represents a better proxy for Ni-SOM complex formation.

In the earliest samples, collected 30 min after Ni addition, the best fit spectrum shows a small contribution (<20%) of Ni-LDH. However, these two spectra could also be fit using a combination of the aqueous Ni standard and a standard consisting of Ni adsorbed onto vermiculite clay at pH 6.0 (where no precipitate formation occurs). At these short times, therefore, it is likely that no significant precipitate formation has yet occurred, but that there is a contribution from inner-sphere Ni complexes with some second shell interactions. At pH 7.0 and 7.5, the 24-h samples of the Matapeake soil from the batch kinetics experiment also showed Ni distributed between adsorbed and precipitate phases (Figure S4, Supporting Information), although the percentages of Ni-LDH were somewhat higher than the Berryland samples, at 58% and 64% of total Ni, respectively.

(1). Modeling Kinetics of Ni Sorption. *Model Development.* This work extends our previous modeling approach[18,19] by integrating Ni precipitation kinetics into the adsorption kinetics model. Briefly, the kinetics model for Ni adsorption on SOM can be formulated as

$$\frac{dC_{p,SOM}}{dt} = -k_d C_{p,SOM} + k_a C_w \tag{1}$$

where k_a (L (g min)$^{-1}$) and k_d (min^{-1}) are the adsorption and desorption rate coefficients, respectively, $C_{p,SOM}$ (μg Ni g^{-1}) is the adsorbed Ni concentration in SOM, and C_w (μg Ni L^{-1}) is the solution Ni concentration.

The equilibrium model WHAM VI was integrated into the kinetics model to account for the effects of solution chemistry (e.g., pH and Ni concentration) and nonlinear Ni adsorption on SOM on Ni adsorption kinetics, as described previously.[19] The effect of solution chemistry is incorporated into the adsorption reaction, while the desorption rate coefficient k_d is assumed to be constant irrespective of the reaction conditions.[18,19] The adsorption rate coefficient at specific reaction times and reaction conditions can be calculated based on the equilibrium partition coefficient, $K_{p,SOM}$ (L g^{-1}), predicted by WHAM VI

$$k_a = k_d K_{p,SOM} \tag{2}$$

The reaction chemistry and the nonlinear binding behavior are accounted for by eq 2, or, more specifically, by the WHAM VI predicted equilibrium partition coefficients. As discussed by Shi et al.,[19] the performance of WHAM will affect the accuracy of the adsorption kinetics model. It has been reported that WHAM VI default Ni binding constants underestimated Ni binding to organic matter.[26] Thus we presented modeling results with both WHAM VI predicted $K_{p,SOM}$ and the $K_{p,SOM}$ increasing by a factor of 3 for adsorption kinetics model calculations at all reaction conditions, an approach we used in a previous modeling study.[19] Additional discussion is presented in the Supporting Information.

The Ni binding to clay minerals was computed by an electrostatic model for cation exchange on clays.[27] The Ni sorption on the clay minerals separated from the Matapeake soil was rapid at pH 6.0 based on a previous sorption study.[10] Since these two soils have similar clay mineral compositions, Ni binding to clay minerals was considered as instantaneous equilibrium to simplify this model

$$C_{p,clay} = K_{p,clay} C_w \tag{3}$$

where $C_{p,clay}$ (μg Ni g^{-1}) is the Ni concentration in clay minerals and $K_{p,clay}$ (L g^{-1}) is the partition coefficient predicted by the electrostatic model. The exchange capacity of clay minerals was calibrated based on the previous Ni sorption study with the Matapeake clay minerals under the same experimental conditions (see details in Supporting Information).[10]

The Ni-LDH precipitates can be formulated as $Ni_{(1-x)}Al_x(OH)_2[A^{n-}]_{(x/n)}*mH_2O$ (where $[A^{n-}]$ represents the interlayer anion concentration in the Ni-LDH precipitate, in this case NO_3^-),[9] and the precipitation reactions of Ni-LDH phases are described as

$$(1 - x)Ni^{2+} + xAl^{3+} + (x/n)A^{n-} + (2 + m)H_2O$$
$$\Leftrightarrow Ni_{(1-x)}Al_x(OH)_2[A^{n-}]_{(x/n)} \times mH_2O + 2H^+ \tag{4}$$
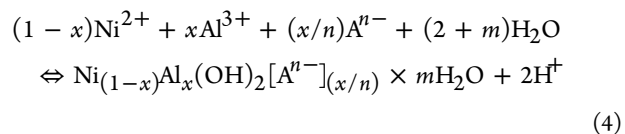
The rate of Ni-LDH precipitation can be formulated as

$$R_p = k\left(\frac{Q}{K_{eq}} - 1\right) \tag{5}$$

where R_p (mol Ni L^{-1} min^{-1}) is the precipitation rate, k is the precipitation rate constant, Q is the ion activity product, and K_{eq} is the precipitation equilibrium constant.

In the sorption experiments, Ni precipitation was far from equilibrium which means $(Q)/(K_{eq}) \gg 1$. As the pH and nitrate concentration were kept constant, Al release from soils is an important process affecting the formation of Ni-LDH

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phases.[13] The concentrations of Al in the solution were low during the sorption experiments,[15] precluding good estimations of the Al^{3+} activity (Figure S5, Supporting Information). In this model, soil Ni-LDH precipitates were represented by a model phase with formula $Ni_{0.77}Al_{0.23}(OH)_2(NO_3)_{0.23}*0.655H_2O$. This phase is similar to the Ni-LDH phase used in the linear fittings of the XAS spectra. The precipitation rate was simplified from eq 5

$$R_p = -k'[Ni]^n \quad (6)$$

where $[Ni]$ (mol Ni L^{-1}) is the molar concentration of Ni in the solution and n is the reaction order, which was set as 0.77.

The rate of Ni-LDH formation can be calculated as

$$\frac{dC_{p,LDH}}{dt} = k_f C_w^{0.77}/m \quad (7)$$

where $C_{p,LDH}$ (μg Ni g^{-1}) is the Ni concentration in the soils present as the Ni-LDH phase, k_f ((μg Ni $L^{-1})^{0.23}$ min^{-1}) is the precipitation rate coefficient, and m (g L^{-1}) is the soil particle concentration. For consistency with the adsorption/desorption kinetics model, the mass concentrations of Ni were used. Note that all Ni concentrations were based on elemental Ni, so the molar and mass concentrations can be converted with the atomic weight of elemental Ni. Based on mass balance, the solution Ni concentration is governed by the following equation in the batch system

$$\frac{dC_w}{dt} = -m\frac{dC_p}{dt} = -m\frac{d(C_{p,SOM} + C_{p,LDH} + C_{p,clay})}{t} \quad (8)$$

For the precipitation process at pH 7.5, two precipitation reactions were used to separately model the fast short-term precipitation and the slow longer-term precipitate formation. This is consistent with the fact that the Al release from two soils was rapid in the beginning of the sorption experiments, which favored the rapid formation of Ni-LDH precipitates, and then remained low at longer reaction times at pH 7.5.[15]

Equations 1, 7, and 8 were solved together to calculate total Ni sorption rates (including adsorption/desorption and precipitation while at pH 6.0 precipitation rate equals zero). The time zero for kinetic model calculations was set at the end of the Ni addition process. The WHAM VI input parameters and the initial conditions for kinetic model calculations are presented in the Supporting Information (section S2). For each soil, all sorption data (pH 6.0, 7.0 and 7.5) were globally fit to obtain model parameters, k_d and k_f, while k_d remained constant and k_f varied according to the reaction pH. An explicit finite difference numerical method was used to solve model equations. At each observation time, the square of the difference between measured and model-calculated dissolved Ni concentrations was calculated. These squares of difference for each data set were summed to obtain the total squared error. The SOLVER program in MS Excel 2010 was used to minimize the total squared error by varying the model fitting parameters.

(2). Modeling Results and Discussions. At pH 6.0, Ni adsorption on both soils showed typical biphasic adsorption kinetics, with fast Ni adsorption within the first 24 h, followed by steady concentrations after several days (Figure 3A). This fast adsorption kinetics, mainly accounted for by the Ni complexation reaction with SOM in the adsorption kinetics model, corresponds with a rapid decrease in partition
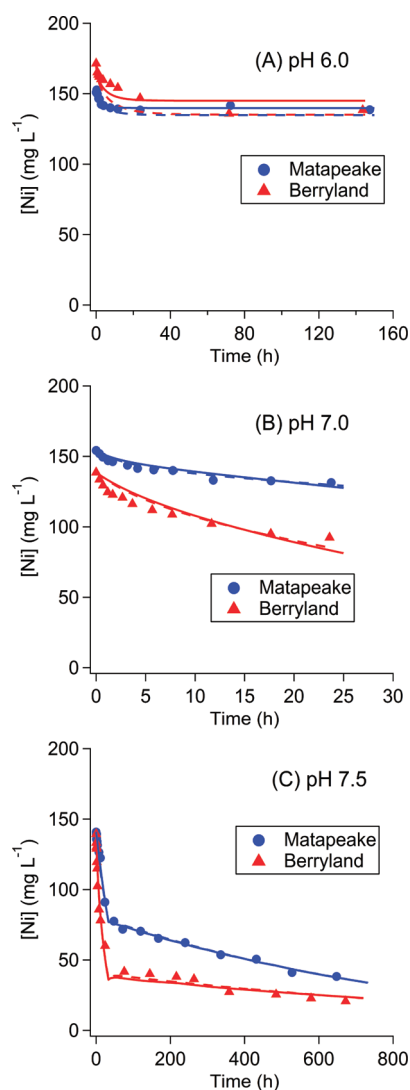

Figure 3. Kinetics of Ni sorption at (A) pH 6.0, (B) pH 7.0, and (C) pH 7.5 for both Matapeake and Berryland soils. Symbols are experimental data. Solid and dashed lines are model calculations using WHAM default $K_{p,SOM}$ and the $K_{p,SOM}$ increased by a factor of 3, respectively. Note that the time scales are different for the three plots.

coefficients as Ni concentrations increase in both soils (Figure S6, Supporting Information). At pH 7.0 and 7.5, Ni sorption from solution was significantly higher (Figures 3B and C), because of both more Ni adsorption on SOM and Ni precipitation. Ni sorption significantly slowed down after a few days for both soils at pH 7.5 (Figure 3C), presumably because of less dissolved Al available for the formation of Ni-LDH precipitates in the soils.[15] At pH 7.5, Ni adsorption on SOM suggested a kinetic controlled process even at long time scales, as demonstrated by both the partition coefficients and adsorbed Ni in SOM (Figures S6 and S7, Supporting Information), mainly due to the Ni transfer from adsorbed phases to Ni precipitates as discussed in detail later. At all pHs, Ni binding to clay minerals was relatively small compared with Ni adsorption on SOM (Figure S7, Supporting Information). Even for the Matapeake soil at pH 6.0 (lowest Ni adsorption on SOM), the amount of Ni bound to clay minerals is about 27% of total sorbed Ni in the soil after 24 h. This is consistent with previous observations that Ni binding capacity of the clay

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minerals separated from the Matapeake soil was relatively low at pH 6.0.[10]

Overall, there is little difference for model fits with WHAM predicted $K_{p,SOM}$ and the $K_{p,SOM}$ increasing by a factor of 3 at pH 7.0 and 7.5, while at pH 6.0, higher partition coefficients resulted in more Ni adsorption on SOM at equilibrium, which suggested the importance of analyzing soil Ni speciation change with time to evaluate the model.

The modeling results for Ni speciation between adsorbed phases (Ni-Ads), defined as total Ni bound to both SOM and clay minerals, and Ni-LDH phases were compared to the linear fitting results for the XAS spectra of the Berryland soil (Figure 4). At pH 7.0, following the Ni sorption process, the increase in
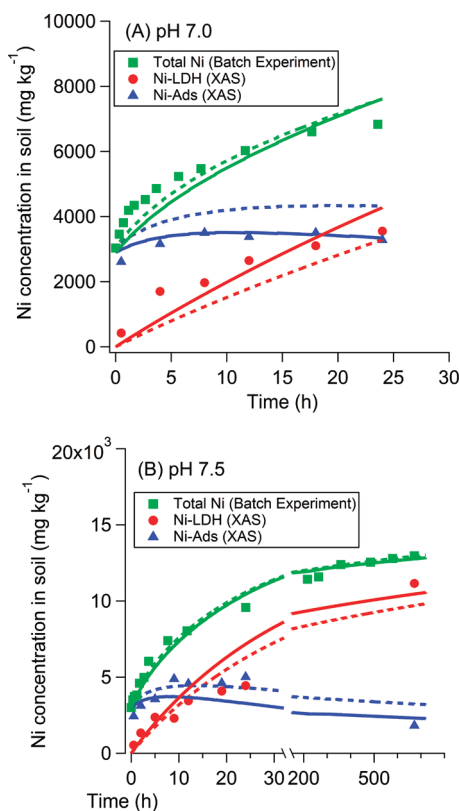

Figure 4. Ni speciation in Berryland soil at (A) pH 7.0 and (B) pH 7.5 during the sorption experiments. Symbols are results calculated from batch sorption experiments (for total Ni) and from linear-least-squares fitting of XAS results (for Ni-Ads and Ni-LDH). Solid and dash lines are model calculations using WHAM default $K_{p,SOM}$ and the $K_{p,SOM}$ increased by a factor of 3, respectively.

the adsorbed phases was small compared with the steady increase in Ni-LDH phases in the soil (Figure 4A). Generally, the model calculations with the WHAM default $K_{p,SOM}$ showed consistent results with the linear fitting results of the XAS spectra, while modeling results with the $K_{p,SOM}$ increasing by a factor of 3 overpredicted the adsorbed phases and, as a result, under-predicted the formation of Ni-LDH phases compared with XAS results.

At pH 7.5, both the modeling and XAS results showed consistent increase in Ni-LDH phases in the soil within the first 12 h, and then the model predicted more formation of Ni-LDH from 12 to 24 h compared with XAS results. Different from that at pH 7.0, model calculations with the WHAM default $K_{p,SOM}$ under-predicted Ni adsorption compared with XAS results. At

times greater than 24 h, both the modeling and XAS results showed a slow decrease in Ni-Ads concentrations while the Ni-LDH phase continued to increase (Figure 4B), and XAS results showed a more dramatic Ni speciation change over longer sorption time compared with the model calculations. While linear fitting results for the Matapeake soil are only available for the 24-h samples, both kinetics model and XAS showed consistent results for soil Ni speciation at both pH 7.0 and 7.5 (Figure S8, Supporting Information).

Overall the differences in Ni distribution between the adsorbed and LDH phases between the XAS-derived and model-calculated results are less than 17% in these soils. The uncertainty of the linear fitting process is estimated at approximately 10% for each component based on a previous similar fitting approach.[28] Given the uncertainties arising from both the XAS fit and the parameters of both the kinetics and WHAM models,[19] the close agreement of these two methods supports the validity of this modeling approach.

The slow Ni phase transfer in the soil suggests that, although SOM may quickly adsorb a significant amount of Ni due to the fast reaction kinetics, the formation of Ni-LDH phases controlled long-term Ni sequestration in the soils under our experimental conditions. The soil Ni phase transfer or transformation with longer reaction time, which contributes to the continuous Ni-LDH growth or increase in Ni-LDH stability in soils or soil minerals, has been studied based on XAS investigations.[11,15,24] From the modeling aspect, the soil Ni phase transfer or redistribution of soil Ni between adsorbed and precipitated phases, which can be explained by different kinetic rates of adsorption and precipitation reactions, is favorable at longer reaction times. This corresponds to results from our previous modeling study that suggested a redistribution of soil Zn between fast and slow reaction sites.[19]

(3). Model Evaluation. The kinetics of Ni adsorption on SOM computed by the model is decided by the desorption rate coefficients and WHAM predicted partition coefficients at specific reaction conditions. The Ni desorption rate coefficients obtained from this study (Table 2) are close to the values

Table 2. Kinetic Model Parameters (Obtained with WHAM Default $K_{p,SOM}$)

		k_f ($(\mu g\ Ni\ L^{-1})^{0.23}\ min^{-1}$)		
	k_d (min^{-1})	pH 7.0	pH 7.5 (fast)	pH 7.5 (slow)
Matapeake soil	1.7×10^{-3}	1.5×10^{-3}	4.8×10^{-3}	2.8×10^{-4}
Berryland soil	8.4×10^{-4}	4.9×10^{-3}	9.8×10^{-3}	1.9×10^{-4}

reported by other researchers.[1,2] For the partition coefficients, variations have been reported between WHAM VI-predicted $K_{p,SOM}$ values and $K_{p,SOM}$ obtained from equilibrium experiments.[25] With the recognition of the uncertainties of WHAM VI model parameters, our current approach of varying WHAM-predicted partition coefficients by a factor of 3 at various pHs showed consistency of Ni speciation between the model calculations and the XAS results. It should be noted that it is not our intention to calibrate WHAM VI for Ni adsorption on soils in this study, which should be done with more extensive equilibrium studies.[25,26]

The simplified Ni precipitation kinetics was required by the lack of solution Al activity data over the length of the sorption studies. There are no reported kinetic rate coefficients for Ni-LDH precipitation in the literature available for comparison to

the values obtained here. The wide range in the solubility product of Ni-LDH[9] suggested that the precipitation kinetics of Ni-LDH phases may vary significantly according to specific reaction conditions, such as the type of interlayer anions and available Al in soils. More detailed kinetic studies on Ni speciation in soils are needed to improve the current modeling approach. In addition, over long reaction times Ni-LDH phases may transform to a precursor metal phyllosilicate phase through the silication of the LDH interlayer space, which has not been addressed in the current model.[24] Nevertheless, our results suggest a promising start for quantitatively predicting Ni-LDH formation in competition with SOM complexation. The modeling approach, coupled with molecular investigations using advanced spectroscopic techniques at various time scales, also shows promise for developing kinetics models to predict the fate of other heavy metals in dynamic soil systems, while accounting for multiple sorbents and reaction mechanisms, and addressing soil metal speciation changes across various time scales.

Implications. The long-term transfer of soil Ni from adsorbed phases to a Ni-LDH phase at high reaction pHs, demonstrated by both modeling and XAS analysis, highlighted the dynamic properties of soil Ni speciation. The slow reactions can continue to sequestrate metals in thermodynamically stable surface precipitate phases for longer times even though there is little change of Ni concentrations in the solutions. This slow phase transfer of metals in soils, usually from kinetically fast sorption sites to slow sorption sites or even sites involving slow diffusion process, may help to explain the so-called aging effect in the field. Our results suggested that the adsorption on SOM may only play an important role in a short time scale at high Ni concentrations and pHs, which may be significant in many contaminated soils. For more acidic (pH < 6.5) or less contaminated soils, the formation of Ni-LDH is likely minimal due to low pH or much lower Ni concentrations. In these cases, SOM is still one of the most significant soil adsorbents controlling Ni speciation and bioavailability.

ASSOCIATED CONTENT

Ⓢ Supporting Information

EXAFS details and additional information on modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

REFERENCES

(1) Ernstberger, H.; Davison, W.; Zhang, H.; Tye, A.; Young, S. Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS. *Environ. Sci. Technol.* **2002**, *36*, 349−354.

(2) Ernstberger, H.; Zhang, H.; Tye, A.; Young, S.; Davison, W. Desorption kinetics of Cd, Zn, and Ni measured in soils by DGT. *Environ. Sci. Technol.* **2005**, *39*, 1591−1597.

(3) Sparks, D. L. *Kinetics of Soil Chemical Processes*; Academic Press: San Diego, CA, 1989.

(4) Scheidegger, A. M.; Sparks, D. L. Kinetics of the formation and the dissolution of nickel surface precipitates on pyrophyllite. *Chem. Geol.* **1996**, *132*, 157−164.

(5) Gustafsson, J. P.; Pechova, P.; Berggren, D. Modeling metal binding to soils: the role of natural organic matter. *Environ. Sci. Technol.* **2003**, *37*, 2767−2774.

(6) Tipping, E.; Rieuwerts, J.; Pan, G.; Ashmore, M. R.; Lofts, S.; Hill, M. T. R.; Farago, M. E.; Thornton, I. The solid-solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environ. Pollut.* **2003**, *125*, 213−225.

(7) Weng, L. P.; Temminghoff, E. J. M.; van Riemsdijk, W. H. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. *Environ. Sci. Technol.* **2001**, *35*, 4436−4443.

(8) Weng, L. P.; Wolthoorn, A.; Lexmond, T. M.; Temminghoff, E. J. M.; van Riemsdijk, W. H. Understanding the effects of soil characteristics on phytotoxicity and bioavailability of nickel using speciation models. *Environ. Sci. Technol.* **2004**, *38*, 156−162.

(9) Peltier, E.; Allada, R.; Navrotsky, A.; Sparks, D. L. Nickel solubility and precipitation in soils: A thermodynamic study. *Clays Clay Miner.* **2006**, *54*, 153−164.

(10) Roberts, D. R.; Scheidegger, A. M.; Sparks, D. L. Kinetics of mixed Ni-Al precipitate formation on a soil clay fraction. *Environ. Sci. Technol.* **1999**, *33*, 3749−3754.

(11) Scheckel, K. G.; Scheinost, A. C.; Ford, R. G.; Sparks, D. L. Stability of layered Ni hydroxide surface precipitatess—A dissolution kinetics study. *Geochim. Cosmochim. Acta* **2000**, 2727−2735.

(12) Scheckel, K. G.; Sparks, D. L. Dissolution kinetics of nickel surface precipitates on clay mineral and oxide surface. *Soil Sci. Soc. Am. J.* **2001**, 685−694.

(13) Scheidegger, A. M.; Strawn, D. G.; Lamble, G. M.; Sparks, D. L. The kinetics of mixed Ni-Al hydroxide formation on clay and aluminum oxide minerals: A time-resolved XAFS study. *Geochim. Cosmochim. Acta* **1998**, *62*, 2233−2245.

(14) Nachtegaal, M.; Sparks, D. L. Nickel sequestration in a kaolinite-humic acid complex. *Environ. Sci. Technol.* **2003**, *37*, 529−534.

(15) Peltier, E.; van der Lelie, D.; Sparks, D. L. Formation and stabiltiy of Ni-Al hydroxide phases in whole soils. *Environ. Sci. Technol.* **2010**, *44*, 302−308.

(16) Regelink, I. C.; Temminghoff, E. J. M. Ni adsorption and Ni-Al LDH precipitation in a sandy aquifer: An experimental and mechanistic modeling study. *Environ. Pollut.* **2011**, *159*, 716−721.

(17) Voegelin, A.; Kretzschmar, R. Formation and dissolution of single and mixed Zn and Ni precipitates in soil: evidence from column experiments and extended X-ray absorption fine structure spectroscopy. *Environ. Sci. Technol.* **2005**, *39*, 5311−5318.

(18) Shi, Z.; Di Toro, D. M.; Allen, H. E.; Ponizovsky, A. A. Modeling kinetics of Cu and Zn release from soils. *Environ. Sci. Technol.* **2005**, *39*, 4562−4568.

(19) Shi, Z.; Di Toro, D. M.; Allen, H. E.; Sparks, D. L. A WHAM-based kinetics model for Zn adsorption and desorption to soils. *Environ. Sci. Technol.* **2008**, *42*, 5630−5636.

(20) Tipping, E. WHAM—A chemical equilibrium model and computer code for waters, sediment, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comput. Geosci.* **1994**, *20*, 973−1023.

(21) Gaillard, J.-F.; Webb, S. M.; Quintana, J. P. G Quick X-ray absorption spectroscopy for determining metal speciation in environmental samples. *J. Synchrotron Radiat.* **2001**, *8*, 928−930.

(22) Kandegedara, A.; Rorabacher, D. B. Noncomplexing tertiary amines as "better" buffers covering the range of pH 3−11. Temperature dependence of their acid dissociation constants. *Anal. Chem.* **1999**, *71*, 3140−3144.

(23) Webb, S. M. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. *Phys. Scr.* **2005**, *T115*, 1011−1014.

(24) Livi, K. J. T.; Senesi, G. S.; Scheinost, A. C.; Sparks, D. L. Microscopic examination of nanosized mixed Ni-Al hydroxide surface precipitates on pyrophyllite. *Environ. Sci. Technol.* **2009**, *43*, 1299−1304.

(25) Shi, Z.; Allen, H. E.; Di Toro, D. M.; S., L.; Lofts, S. Predicting cadmium adsorption on soils using WHAM VI. *Chemosphere* **2007**, *69*, 605−612.

(26) Warnken, K. W.; Lawlor, A. J.; Lofts, S.; Tipping, E.; Davison, W.; Zhang, H. In situ speciation measurements of trace metals in headwater streams. *Environ. Sci. Technol.* **2009**, *43*, 7230−7236.

(27) Lofts, S.; Tipping, E. Solid-solution metal partitioning in the Humber rivers: application of WHAM and SCAMP. *Sci. Total Environ.* **2000**, 381−399.

(28) Isaure, M. P.; Laboudigue, A.; Manceau, A.; Sarret, G.; Tiffreau, C.; Trocellier, P.; Lamble, G.; Hazemann, J. L.; Chateigner, D. Quantitative Zn speciation in a contaminated dredged sediments by mPIXE, mSXRF, EXAFS spectroscopy and principal component analysis. *Geochim. Cosmochim. Acta* **2002**, *66*, 1549−1567.