

# SUPPORTING INFORMATION

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

*Zhenqing Shi,<sup>§ \* †</sup> Edward F. Peltier,<sup>‡</sup> and Donald L. Sparks<sup>†</sup>*

<sup>†</sup> Environmental Soil Chemistry Research Group, Department of Plant and Soil Sciences, 152 Townsend Hall, University of Delaware, Newark, DE 19717-1303

<sup>‡</sup> Department of Civil, Environmental & Architectural Engineering, University of Kansas, 1530 W. 15th St., Lawrence, KS 66045-7609

\*Corresponding author:

Email: zhenqing.shi@wsu.edu, Phone: 509-335-7857

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<sup>§</sup> Current address: School of Earth and Environmental Science, Washington State University, Pullman, WA

## S1. Details of EXAFS Experiments and Data Treatment

### (1) Materials and Methods

#### *EXAFS Data Collection and Processing*

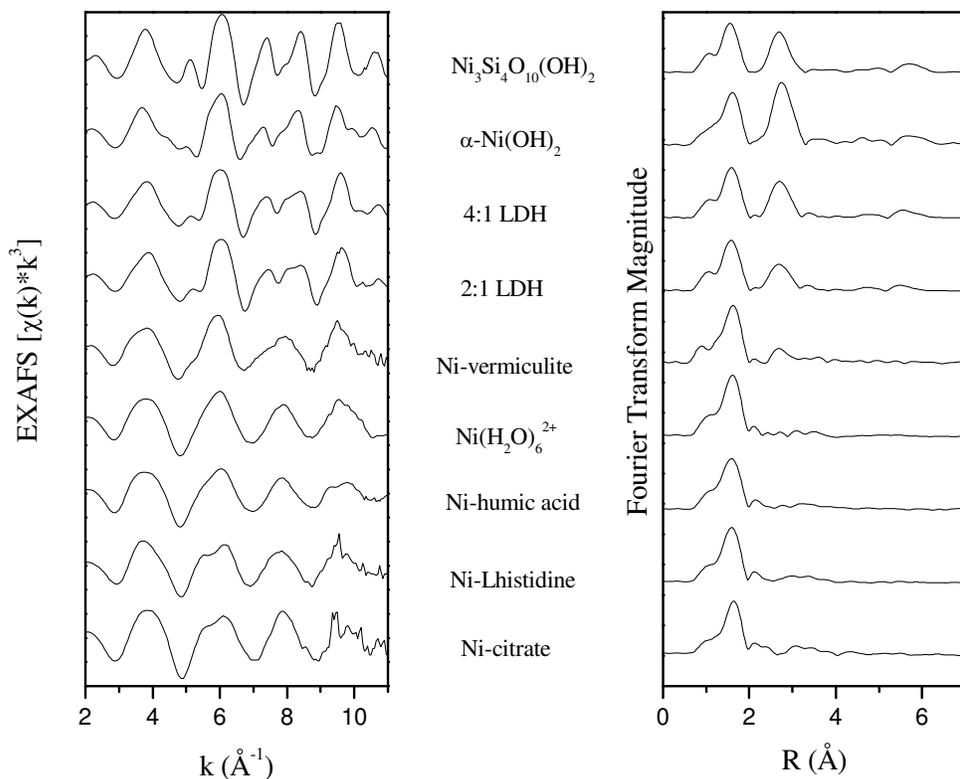
XAS experiments were conducted at beamline 5-BMB (DND-CAT) at the Advanced Photon Source at Argonne National Laboratory. For the short-term kinetic experiments, 10-15 mL of slurry was filtered onto a 0.22  $\mu\text{m}$  nylon filter and then washed with 3 mL of deionized water to remove entrained solution Ni. The filtering and washing process took approximately 10 minutes per sample. The filter cake on the nylon filter support was then mounted between two pieces of Kapton tape and immediately analyzed. The total time between the beginning of sample collection and the beginning of XAS analysis was never more than 30 minutes.

All spectra were collected under ambient conditions using a Si(111) monochromator detuned by 25% to reduce higher-order harmonic interference. Prior to data collection, the edge energy was calibrated to the first inflection point on the K adsorption edge of a Ni metal standard foil, with  $E_0 = 8333$  eV. Data were collected in fluorescence mode for all soil samples using a Stern-Heald type (Lytle) detector filled with a 95/5% mixture of  $\text{N}_2$  and Ar gas. In order to minimize elastic scattering and the fluorescence signal from lighter elements, particularly Fe, this fluorescence signal was filtered by a Co filter covered with 1 or 2 sheets of Al foil and by Soller slits. All reference spectra were collected in transmission using thin powder mounts. In order to obtain Ni-K edge spectra within 1.5 to 2 hours, a continuous-scanning QEXAFS mode was used.<sup>1</sup> For each sample, 16 scans were collected from 200 eV below to 800 eV above the absorption edge at a rate of 5 mins/scan, and averaged to produce a spectrum.

XAS data extraction was performed using the ATHENA software program.<sup>2</sup> Background subtraction and edge normalization were carried out using a 1<sup>st</sup> order polynomial fit to the pre-edge region from 150 to 50 eV below the Ni K-edge, and a 2<sup>nd</sup> order polynomial fit from 100 to 600 eV above the edge, respectively. Extraction of the EXAFS  $\chi$  function was performed by fitting a spline from 0.5 to 13.5  $\text{\AA}^{-1}$ , and the result was then weighted by  $k^3$  to compensate for dampening of the spectrum at higher  $k$ . Data were Fourier-transformed from 2-11  $\text{\AA}^{-1}$  using a Kaiser-Bessel window. Wavelet analysis of the combined  $k$  and  $r$  space dependence of the second FT peak was performed with HAMA,<sup>3</sup> using the Morlet wavelet function ( $\eta = 5.7$ ,  $\sigma = 1.0$ ).

Two freshly formed Ni-Al LDH phases with primarily nitrate interlayers were used as reference standards for linear fitting: i.) Ni-LDH with the chemical formula  $[\text{Ni}_{0.77}\text{Al}_{0.23}(\text{OH})_2[(\text{NO}_3)_{0.13}(\text{CO}_3)_{0.05}]] \cdot 0.60\text{H}_2\text{O}$ , and ii.) Ni-LDH with the chemical formula  $[\text{Ni}_{0.65}\text{Al}_{0.35}(\text{OH})_2[(\text{NO}_3)_{0.21}(\text{CO}_3)_{0.07}]] \cdot 0.42\text{H}_2\text{O}$ . Preparation and characterization of these phases was described in Peltier et al.<sup>4</sup> These phases were used to represent the two extremes of Al substitution in Ni-LDH phases, which can range from a Ni:Al ratio of  $\sim 4:1$  to  $\sim 2:1$ ,<sup>5</sup> and are thus referred to in the text as 4:1 LDH and 2:1 LDH, respectively. Other reference spectra used in the fitting included  $\alpha$ -Ni(OH)<sub>2</sub>, aqueous Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, Ni-citrate and Ni-Lhistidine complexes from McNear et al.,<sup>6</sup> a Ni phyllosilicate compound (Ni<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>) previously described in Peltier et al.,<sup>4</sup> and a Ni sorption standard formed by contacting 12 g/L of vermiculite clay with a solution of 3 mM Ni at pH 6 (to avoid the formation of surface Ni precipitates) for 48 hours using the same procedures described above for the soil sorption experiments. The spectrum for a Ni-humic acid complex was obtained from Matt Siebecker of the University of Delaware. This complex was prepared using humic acid purchased from Sigma Aldrich and reacted (after washing to remove Fe) with Ni at pH 7. The EXAFS spectra of each of these reference phases are presented in Figure S1.

A linear-fitting approach was used to estimate the percentage of Ni present as surface precipitates in the soil samples. Linear fitting was carried out using the linear fitting module of the SIXpack software package, version 0.68.<sup>7</sup> Initial screening of reference spectra was carried out using a matrix fit approach. Fit quality was assessed using the calculated r-value, which is the sum of the residuals of a given fit divided by the sum of squares of the dataset. For a perfect fit,  $r = 0$ . In evaluating the number of components used in a fit, it was assumed that the best fit used the minimum number of components necessary to achieve the minimum r-value. A component was added to the fit only if it resulted in an improvement of 20% or greater in the r-value for the fit. Once specific reference spectra were identified as potential fits for a sample, fitting was carried out on  $k^3$  weighted spectra from 2.5-10.5 Å<sup>-1</sup>. Fits were constrained to be non-negative, with  $e_0$  shifts of  $\leq 0.05$  eV (absolute value) allowed in the sample spectrum, and fits with fractional components summing to more than 1.2 were summarily rejected. A fit was considered superior to another fit if the reduced  $\chi^2$  value for the fit was at least 20% lower.



**Figure S1.** Spectra for reference phases used in linear combination fitting.

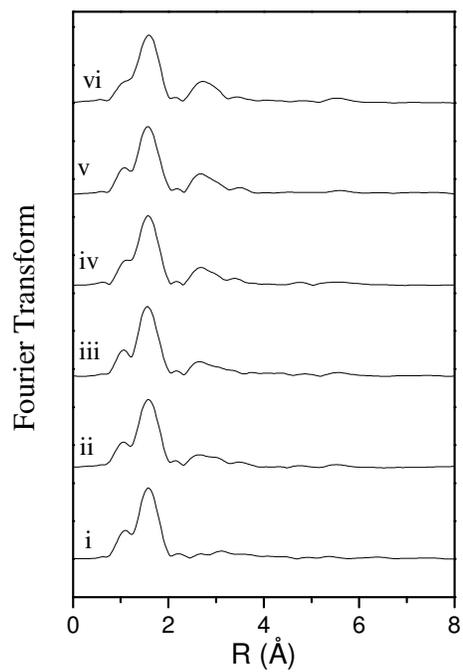
## (2) Additional Results and Discussions

### *Ni Speciation*

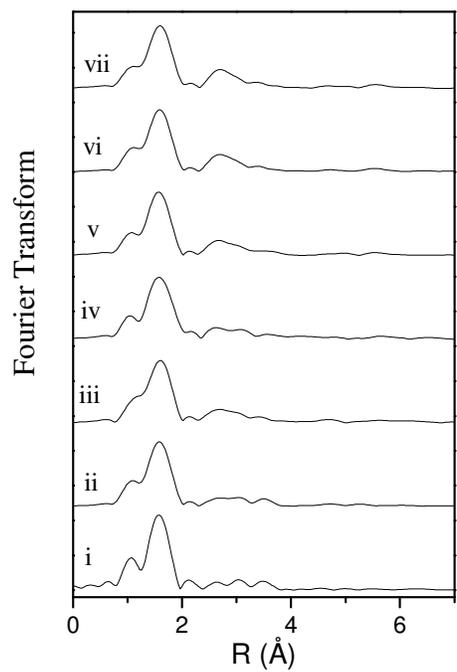
Figures S2 and S3 show the Fourier-transformed data for Berryland samples from the Ni sorption experiments taken within the first 24 hours after Ni addition. The exact onset of precipitate formation cannot be easily observed through this method, as the EXAFS technique provides information only on the average coordination environment of Ni atoms in the sample. An increase in precipitate formation can, however, be observed from the increase in the second-shell Ni-Ni interactions in the Fourier-transformed data. This second shell is visible from four hours onwards at both pHs, indicating substantial precipitate formation. The EXAFS spectra at

both pHs also begin to show features characteristic of precipitate formation, such as broadening of the  $8 \text{ \AA}^{-1}$  peak, as the reaction progresses.

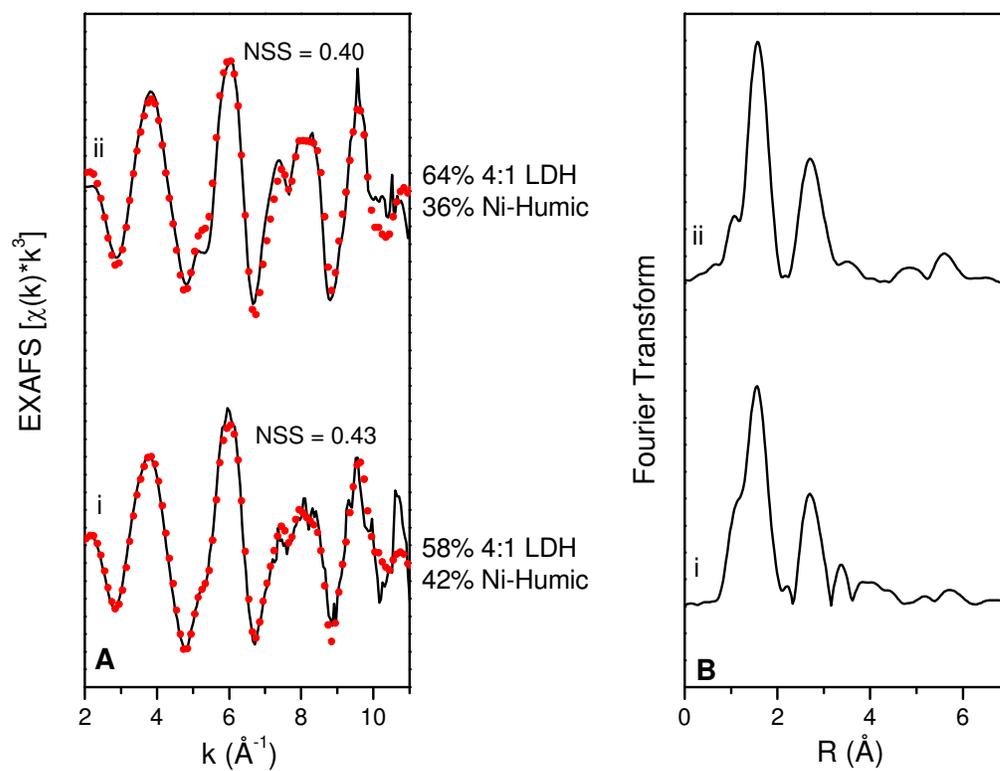
The linear fitting resulted in identification of five reference spectra that could contribute to best fits of the data: the 2:1 and 4:1 Ni-LDH precipitates, aqueous Ni ( $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ), Ni-vermiculite, and Ni-humic acid. Ni-vermiculite was only significant in fitting the samples collected 30 minutes after Ni addition, as described in the main text. Ni-citrate also met the criteria for inclusion, but was found to be generally indistinguishable from the Ni-humic acid sample and not included in the final fits. As described in the main text, the 4:1 Ni-LDH was chosen as the preferred reference for the LDH component because it produced a significantly better fit for some samples, and was never significantly worse than the 2:1 LDH reference. 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 all of these cases, the use of Ni-humic acid or aqueous Ni for the second component produced changes of less than 5% in the Ni-LDH fraction of the fit. Uncertainties in the fit were estimated at approximately 10% for each component, based on a previous similar fitting approach,<sup>8</sup> so this choice had a negligible effect on the estimated Ni-LDH concentration. Given this small effect, it is likely that the choice of best fit non-precipitated reference for a specific sample is primarily influenced by the noise in that sample spectrum. This noise is primarily due to the nature of the kinetics experiment, which did not allow for removal of water from the filtered soil samples prior to EXAFS analysis.



**Figure S2.** Fourier-transformed data for Berryland samples at pH 7.0 and various times after Ni addition: (i) 30 minutes, (ii) 4 hours, (iii) 8 hours, (iv) 12 hours, (v) 18 hours, and (vi) 24 hours.



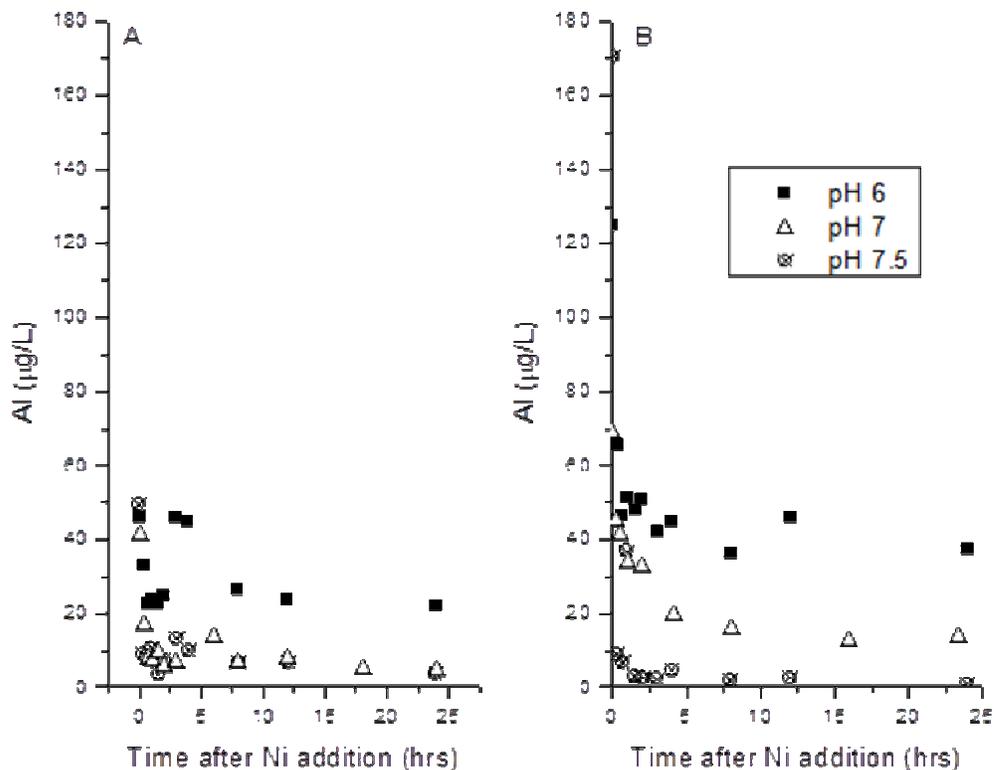
**Figure S3.** Fourier-transformed data for Berryland samples at pH 7.5 and various times after Ni addition: (i) 30 minutes, (ii) 2 hours, (iii) 5 hours, (iv) 9 hours, (v) 12 hours, (vi) 19 hours, and (vii) 24 hours.



**Figure S4.** Quick-EXAFs spectra, including best fit lines (●) from linear least-squares fitting (A), and Fourier-transformed data (B) for Matapeake samples at 24 hours: (i) pH 7.0, (ii) pH 7.5. NSS, or normalized sum of squares, is a quality of fit parameter, with NSS = 0 indicating a perfect fit.

## S2. Additional Information on Kinetic Modeling

### (1) Dissolved Al concentrations during sorption experiments



**Figure S5.** Dissolved Al concentrations in Ni sorption experiments. Data for the pH 7.5 samples are taken from Peltier et al.,<sup>9</sup> which also provides additional information on Al analysis methods.

### (2) WHAM Input Parameters and Additional Discussion

WHAM VI was used to calculate Ni adsorption equilibrium at different conditions. WHAM is capable of calculating the equilibrium chemical speciation in surface and ground waters, sediments, and soils, especially when the chemical speciation is dominated by organic matter.<sup>10, 11</sup> WHAM VI uses Model VI, a computer model, to describe the reactions of ions with humic substances, mainly through complexation which is modified by electrostatic reactions. WHAM VI also incorporates a clay cation-exchanger for non-specific interactions of ions with clay minerals.<sup>12</sup> The cation-exchange capacity of the clay minerals may be adjusted by altering

the surface area or the exchange capacity of clay minerals, which may differ according to clay mineral compositions in soils.

For Ni reaction with SOM, the input parameters for WHAM VI calculations include concentrations of particulate humic acid and fulvic acid ([HA] and [FA], respectively), solution cation concentrations or activities ( $[\text{Ni}^{2+}]$ ,  $[\text{Na}^+]$ ,  $\{\text{Al}^{3+}\}$ ,  $\{\text{Fe}^{3+}\}$ ), anion concentrations ( $[\text{NO}_3^-]$ ), and pH. Since SOM consists of a number of components different from humic substance, not all SOM is as active as humic substances for Ni binding. The percentage of active SOM responsible for Ni binding on both soils was obtained based on the linear regression model proposed in our previous study,<sup>13</sup> which indicated active percentages of 90% and 73% for the Matapeake soil and Berryland soil, respectively. The active SOM was input as 82% HA and 18% FA in WHAM VI.<sup>11</sup> The effect of dissolved organic matter was not considered since the solution concentrations of Ni in our experiments were high. The change in total soil concentrations due to sampling in the one month experiments was less than 5%. The solution pH was input as the experimental values. The Fe and Al competition effect on Ni partitioning was accounted for by assuming that Fe(III) and Al activities were controlled by the solubility of their metal hydroxides with solubility constant  $K_{s0}$ . Note that in our kinetic experiments at higher pH values, less Al was available at longer reaction times due to the formation of Ni-LDH phases. However, the Ni adsorption kinetic reaction was only dominant at short times when the Al release from two soils was rapid. At longer time when Ni concentrations in soils were high, the Al competition had little effect on  $K_p$  based on WHAM VI calculations. Thus, the solubility control of metal hydroxides seems to be a reasonable estimation to account for  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  competition with Ni adsorption, considering other uncertainties in the WHAM VI model parameters (e.g. Ni binding constants) discussed in the paper. Additional WHAM VI input parameters are summarized in Table S1.

There are some uncertainties in WHAM model parameters such as metal binding constants and the concentration of reactive organic matter,<sup>11, 13, 14</sup> that may affect the equilibrium partition coefficients predicted by WHAM. Since the accuracy of the adsorption/desorption kinetics model is affected by WHAM VI predicted partition coefficients ( $K_{p,SOM}$ ), we tested the model predictions with WHAM predicted  $K_{p,SOM}$  increasing with a factor from 2 to 4 ( $2K_{p,SOM}$  to  $4K_{p,SOM}$ ). The  $3K_p$  provided best model performance compared with sorption kinetics data at all

pHs and linear fitting results of XAS spectra. Thus the modeling results with WHAM-predicted  $K_{p,SOM}$  and the  $K_{p,SOM}$  increasing with a factor of three are presented in the manuscript. Considering the high concentrations of Ni used in this study and additional Ni precipitation reactions at high pHs, we only used one group of sites to account for the average adsorption/desorption rates of SOM to simplify this model.

For Ni binding to clay minerals, the exchange capacity of the clay minerals was set at  $2.7 \times 10^{-6}$  eq  $m^{-2}$ , based on previous Ni sorption study at pH 6.0 using the clay minerals extracted from the Matapeake soil under same experimental conditions.<sup>15</sup> As shown in Table 1, both Matapeake and Berryland soils have similar mineralogy of the clay fraction, so the same exchange capacity was used for both soils while the clay concentrations varied according to the clay content in soils. The Berryland soil may contain less vermiculite content based on the ECEC values in Table 1, so the Ni bound to clay minerals in the Berryland soil may be over-predicted. However, as shown in Figure S7, the contribution of clay minerals to Ni binding is relatively small compared with Ni binding to SOM for the Berryland soil. Therefore, we did not adjust the exchange capacity of the clay mineral for the Berryland soil, and the errors tend to be small for the model calculations.

Table S1. Additional WHAM VI input parameters

[HA]	[FA]	$\log K_{s0}$ (Al)	$\log K_{s0}$ (Fe(III))	[Na]	[NO <sub>3</sub> ]
g/L	g/L			M	M
Matapeake soil					
0.23	0.05	8.5	3	0.1	0.1
Berryland soil					
0.47	0.10	8.5	3	0.1	0.1

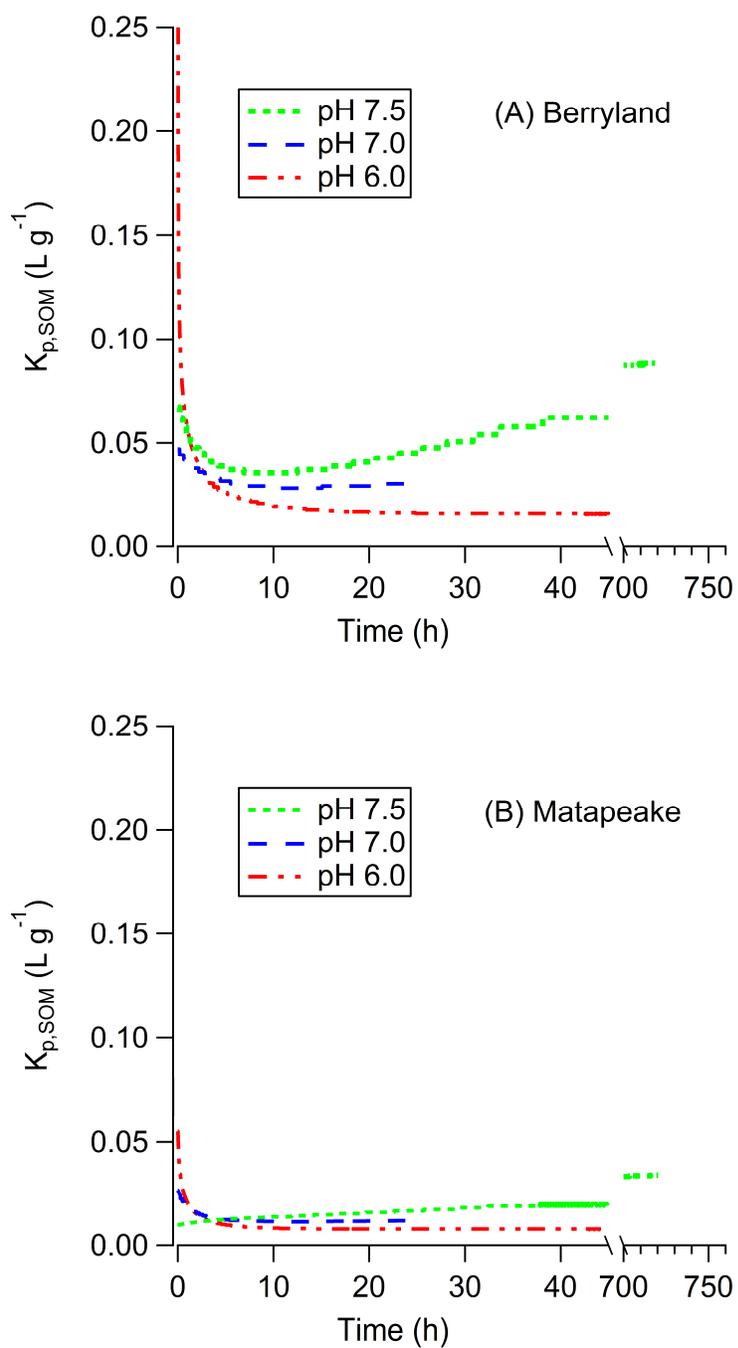
### (3) Initial Conditions of Model Calculations

During the initial Ni addition process, a portion of Ni was sorbed from the solutions. The 30 minute XAS spectra for the Berryland samples at both pH 7.0 and 7.5 indicate that Ni removal from solution during this period was primarily due to adsorption processes. Similar results were reported for short-term Ni sorption onto the clay fraction of Matapeake soils at pH 6.8 and 7.5.<sup>15</sup> For model calculations, the dissolved Ni concentrations at the end of the Ni addition process in the suspensions were set as the initial solution Ni concentrations ( $[\text{Ni}]_0$  ( $\text{mg L}^{-1}$ )) (Table S2). The initial Ni concentrations in SOM and clay minerals were computed based on total Ni adsorption during the spiking processes and instantaneous equilibrium of Ni binding to clay minerals. For the long-term sorption experiments, the transition from the fast precipitation and slow precipitation was set at 2000 min for both soils according to the change of solution Ni concentrations and model testing.

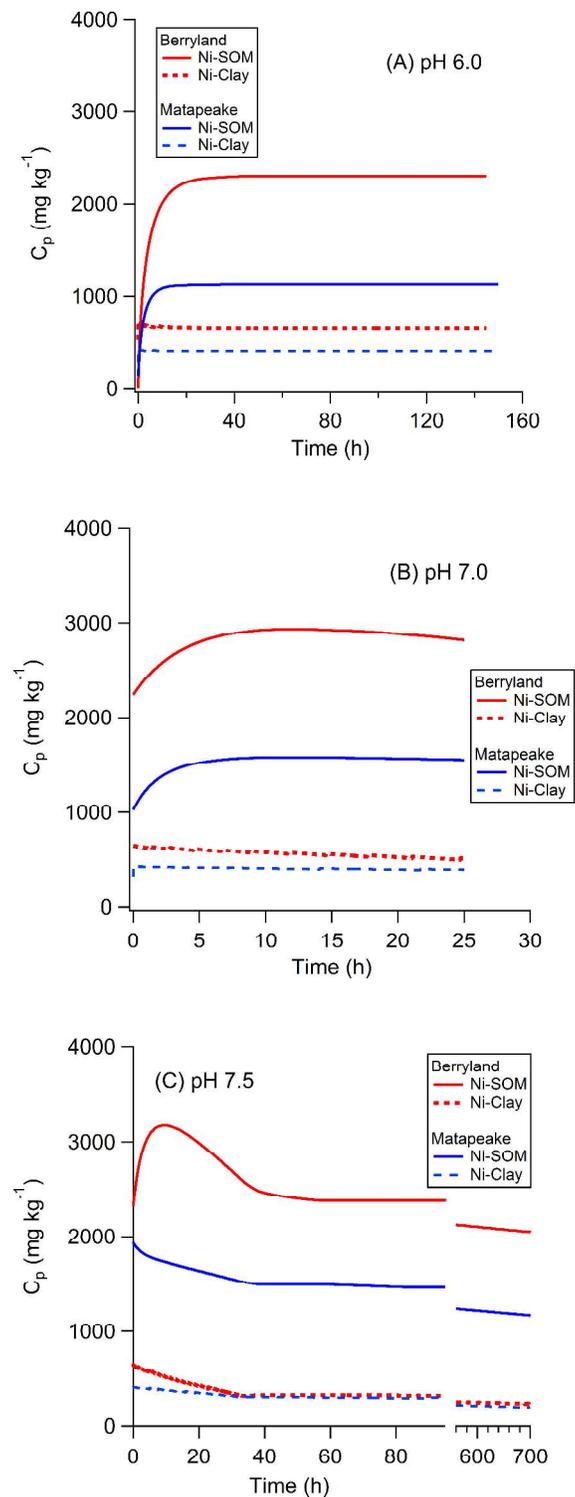
Table S2. Initial Ni concentrations in kinetic model calculations

Soil	pH 6.0	pH 7.0	pH 7.5
Matapeake ( $[\text{Ni}]_0$ ( $\text{mg L}^{-1}$ ))	151.0	154.2	140.8
Berryland ( $[\text{Ni}]_0$ ( $\text{mg L}^{-1}$ ))	171.4	138.6	139.3

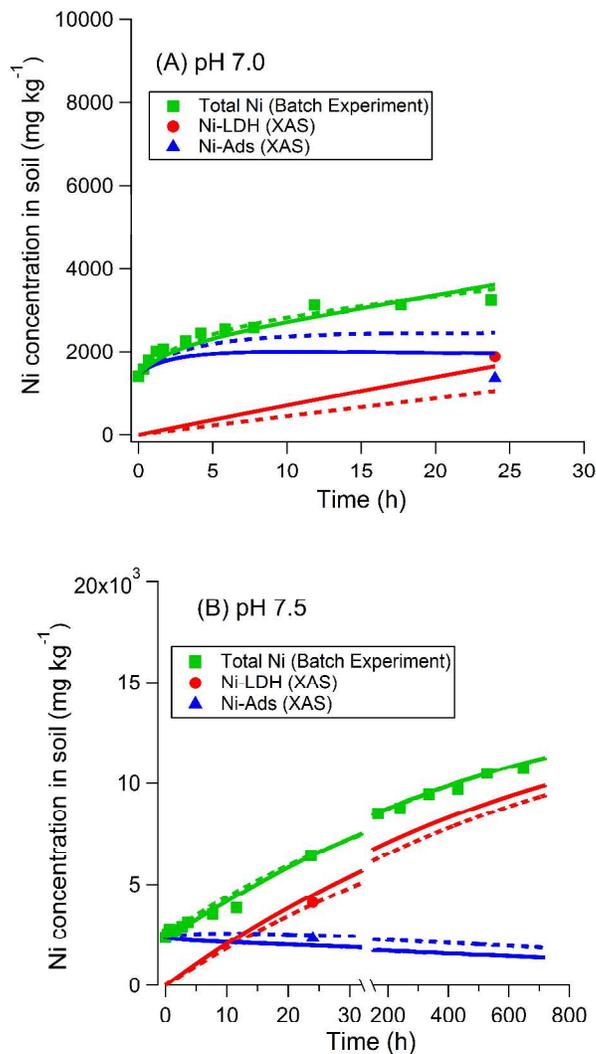
#### (4) Additional Modeling Results



**Figure S6.** Change of partition coefficient ( $K_{p,SOM}$ ), predicted by WHAM VI, during Ni sorption processes for (A) Berryland and (B) Matapeake soils at three different pHs.



**Figure S7.** Change of Ni concentrations in SOM (Ni-SOM) and clay minerals (Ni-Clay) at (A) pH 6.0; (B) pH 7.0; (C) pH 7.5 for both soils during sorption experiments. Model calculations used WHAM default  $K_{p,SOM}$ .



**Figure S8.** Change of Ni speciation (Ni-Ads, Ni-LDH, and total Ni) in the Matapeake soil at (A) pH 7.0 and (B) pH 7.5 during sorption experiments. Symbols are results calculated from batch sorption experiments (for total Ni) and from linear 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 three, respectively. Note that the x axis in plot (B) was split for a better presentation of results at different time scale.

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