

Formation and Stability of Ni–Al Hydroxide Phases in Soils

EDWARD PELTIER,^{§,*,*†}
DANIEL VAN DER LELIE,[†] AND
DONALD L. SPARKS[†]

Environmental Soil Chemistry Research Group, Department of Plant and Soil Sciences and Delaware Environmental Institute, 152 Townsend Hall, University of Delaware, Newark, Delaware 19716, and Brookhaven National Laboratory, Building 463, 50 Bell Avenue, Upton, New York 11973

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The formation of mixed metal–aluminum hydroxide surface precipitates is a potentially significant uptake route for trace metals (including Co, Ni, and Zn) in environmental systems. This paper investigates the effect of mixed Ni–Al hydroxide precipitate formation and aging on Ni solubility and bioavailability in laboratory contaminated soils. Two Delaware agricultural soils were reacted with a 3 mM Ni solution for 12 months at pH's above and below the threshold for mixed Ni–Al hydroxide formation. Ni speciation was determined at 1, 6, and 12 months using X-ray absorption spectroscopy (XAS). Precipitate solubility was examined through desorption experiments using HNO₃ and EDTA as desorbing agents, whereas metal bioavailability was assessed using a Ni-specific bacterial biosensor. For both soils, the formation of Ni–Al hydroxide surface precipitates resulted in a reduction in the fraction of desorbed and bioavailable Ni. However, precipitate dissolution was greater, particularly with EDTA, than in published studies on isolated soil clay fractions, and less affected by aging processes. These results suggest that mixed Ni–Al hydroxide phases forming in real world environments may be both longer-lasting and more susceptible to ligand-promoted dissolution than previously expected.

Introduction

The formation of hydrotalcite-like precipitates of Co, Zn, and Ni has been identified on a range of clay mineral and metal oxide surfaces (1–3). More recently, the existence of both mixed Ni–Al and Zn–Al hydroxides has been observed in field and laboratory contaminated whole soils (4–7). These precipitates have the general formula $M^{2+}_{1-x}Al_x(OH)_2(A^{n-})_{x/n} \cdot nH_2O$, where M is the metal cation (Co, Zn, or Ni), x , the extent of aluminum substitution, varies from 0.2 to 0.35, and A represents one of several possible anions. They are thermodynamically preferred to pure metal hydroxides at most typical soil conditions (8–10). Experiments with Ni–Al hydroxide phases formed on pyrophyllite and gibbsite surfaces have documented an increased resistance to dis-

solution as a result of precipitate aging (11–13). The primary source of this increased stability is silica substitution into the anion interlayer, with Ostwald ripening playing a more minor role (14). Based on these results, formation of these mixed hydroxide phases could significantly decrease metal mobility and bioavailability in contaminated soils. The limited amount of information currently available on the nature and stability of these precipitates in heterogeneous soils, however, limits our ability to adequately assess their actual impact on metal speciation in natural systems.

Soil mineralogy and organic matter content, in particular, could affect the nature and extent of mixed Ni–Al precipitate formation in the field. Some mineral surfaces that support mixed Ni–Al hydroxide formation, such as gibbsite, may not be effective competitors for Ni ions in heterogeneous systems (15). Competition from complexation reactions with organic ligands may also inhibit the formation of Ni–Al surface precipitates. Nachtegaal and Sparks (16) documented changes in the identity of Ni surface precipitate phases on kaolinite surfaces as the humic acid content of the system was increased. At 1% humic acid by weight, mixed Ni–Al hydroxide precipitates formed on the kaolinite surface after 4 days. At 5 wt % humic acid, however, precipitate formation was slower and resulted in Ni(OH)₂ precipitates that were less resistant to proton dissolution, even after six months.

The purpose of this paper is to investigate the effect of mixed Ni–Al hydroxide precipitate formation on Ni solubility and availability in contaminated soils. Soils were exposed to Ni solutions under laboratory conditions in order to control for environmental parameters affecting metal speciation and provide conditions favorable for the formation of the mixed hydroxide phases. Ni speciation in the soils was determined 1, 6, and 12 months after initial addition using X-ray absorption spectroscopy (XAS). The effect of surface precipitate formation on Ni solubility was examined as a function of soil aging through desorption experiments, while Ni bioavailability to soil microorganisms was estimated through the use of a bacterial biosensor. The results were compared to previous studies of Ni–Al hydroxide formation in simpler systems.

Materials and Methods

The <2 mm fraction of two Delaware agricultural soils, a Matapeake silt loam (Typic Hapludult), and a Berryland loamy sand (Typic Alaquod) were used in these experiments (Table 1). The Matapeake soil has been shown to support the formation of Ni–Al hydroxide precipitates at pH ≥ 7 (17). The Berryland soil was expected to be more amenable to Ni sorption due to the higher clay content and soil organic matter concentration.

Nickel Sorption. For each experiment, a 12 g/L slurry was created by mixing dried soil with deionized water containing 0.1 M NaNO₃ as a background electrolyte. The

TABLE 1. Soil Properties^a

	Matapeake	Berryland
pH	5.7	4.5
sand–silt–clay %	30–58–12	65–16–19
clay mineralogy	K+V	V
organic matter %	2	8
ECEC ^b (meq/100 g)	5.3	4.1

^a K = Kaolinite, V = Chloritized Vermiculite. ^b Effective cation exchange capacity.

* Corresponding author phone: 785.864.2941; fax: 785.864.5379; e-mail: epeltier@ku.edu.

[†] University of Delaware.

[§] Brookhaven National Laboratory.

[§] Current address: Department of Civil, Environmental & Architectural Engineering, University of Kansas, 1530 W. 15th St., Lawrence, Kansas 66045-7609

slurry pH was adjusted to either pH 6.0 or 7.5 using 0.1 M HNO₃ or 0.1 M NaOH and the soil was then hydrated for 24 h prior to Ni addition. Ni from a 0.1 M Ni(NO₃)₃ stock solution was added at a rate of 1 mL/min to achieve an initial solution Ni concentration of 3 mM, allowing for a maximum Ni soil loading of ~15 000 mg/kg. This concentration was selected to allow for direct comparison to previous experiments on Ni–Al hydroxide formation (2, 12, 13, 15–17). All experiments were conducted under an N₂ atmosphere using N₂-purged reagents to reduce the potential for NiCO₃ formation.

During the initial reaction stages (24 h at pH 6.0, 72 h at pH 7.5), solution pH was maintained to within ±0.1 units through the automated addition of 0.1 M NaOH. Subsequently, the bottles were sealed and continuously shaken at low speed in a constant temperature chamber set at 25 °C. Periodic adjustments were made to the solution pH through the addition of either 0.1 M NaOH or 0.1 M HNO₃. After 30 days, half of each sample was centrifuged at 15 000 rpm for 15 min and the supernatant removed. The wet soils were washed briefly with 0.1 M NaNO₃ to remove any entrained Ni solution, recentrifuged, and freeze-dried under vacuum for storage until XAS analysis. The other half of each sample was stored at 25 °C with no further stirring or pH adjustment. At 6 and 12 months after Ni addition, additional portions of the sample were centrifuged, washed, and dried in an identical manner.

Aqueous samples were collected during the first 30 days and analyzed for Ni, Al, and Si content. Ten mL of slurry were collected for each sample using a plastic syringe and filtered through a 0.22 μm nylon filter to remove particulates. Dissolved Ni was analyzed by flame atomic absorption spectroscopy, while Al and Si concentrations were determined using graphite furnace atomic absorption spectroscopy. In order to assess the effect of Ni addition on Al and Si release from the soils, sorption experiments with Ni-free slurries were also conducted for each soil at both pH 6.0 and 7.5.

Nickel Speciation. Determination of soil Ni speciation after 1, 6, and 12 months reaction time was carried out using X-ray absorption spectroscopy (XAS). XAS experiments were conducted at beamline X-11A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) and beamline 5-BMB (DND-CAT) at the Advanced Photon Source at Argonne National Laboratory. Linear combination fitting of the soil spectra to reference Ni standard phases was used to assess the percentages of precipitated and adsorbed Ni in the soils at pH 7.5. Additional details on XAS data collection, processing and analysis are provided in the accompanying Supporting Information (SI).

Desorption Studies. Desorption experiments were carried out using the batch replenishment technique described in Scheckel and Sparks (13). Two desorbing agents were used: 0.1 M HNO₃ at pH 4 (proton-promoted dissolution) and 1 mM EDTA at pH 7.5 (ligand-promoted dissolution). For each experiment, 30 mL of the desorbing solution was added to a volume of slurry containing ~0.3 g of the Ni-spiked soil in a 40 mL centrifuge tube and continuously shaken. For the first two replenishments, a contact time of 12 h was used to minimize potential resorption of Ni to the soil surface. For all subsequent replenishments, the contact time was 24 h. At the end of each extraction step, the samples were centrifuged and the supernatant collected for Ni analysis. The solids were then washed with deionized water and recentrifuged prior to the next desorption step.

Nickel Bioavailability. Approximately 20 g of each soil were reacted with Ni at pH 6.0 and 7.5 as described above, freeze-dried and then analyzed for Ni availability to soil microorganisms at Brookhaven National Laboratory using the BIOMET test procedure published by Corbisier et al. (18). The bacterial biosensor strain *Cupriavidus metallidurans* AE2515, which produces a luminescent signal in the presence

of Ni, was used to assess Ni availability. Soil suspensions were prepared at dilutions from 4:1 to 16:1 by mixing the dried Ni-spiked soil with reconstitution media and then added to the reconstituted cells. Light production from the biosensor was monitored every 30 min over a 12 h period using a Luminescan (Thermo Scientific) luminometer at 23 °C, as described previously (19–21). A constitutively light producing strain, *C. metallidurans* AE864 (pMOL82, nickel-resistant), was used to correct for sample toxicity and/or light quenching that could bias the interpretation of the test. Ni bioavailability data collected with strain AE2515 were only considered valid when, at the same time, strain AE864 showed a signal-to-noise ratio between 0.8 and 1.2. For each assay, metal standard solutions were repeated in duplicate, while soil experiments were repeated in triplicate.

Results

Nickel Sorption. At each pH, the Matapeake soil sorbed substantially less Ni (Figure 1). For both soils, a marked increase in total Ni loading, as estimated from loss of solution phase Ni, occurred as the pH increased. Ni sorption on the Matapeake soil was essentially completed after 24 h at pH 6, but continued at pH 7.5, at much reduced rates, throughout the experiment. This continued sorption is consistent with the growth of surface complexes and/or precipitate phases. The Berryland soil showed greater longer-term Ni sorption at both pHs, similar to other studies where higher soil organic matter (SOM) concentrations are present (16).

Ni addition resulted in a sharp decrease (>95%) in dissolved Al concentrations for both soils at pH 7.5, with concentrations below 10 μg/L throughout the experiment. (Al and Si concentration data are presented in the accompanying SI.) At pH 6, a more gradual decrease of 30–60% was observed in dissolved Al concentrations. In the Ni-free control samples, dissolved Al concentrations increased gradually over time in both soils. Dissolved Si concentrations increased for both the Ni-amended and Ni-free samples over the course of the experiment. At pH 7.5, however, Si release was enhanced by the presence of Ni relative to the control samples, especially within the first 24–72 h after Ni addition. The observed patterns of Al and Si release are consistent with the incorporation of dissolved Al into Ni–Al complexes and surface precipitates, resulting in increased dissolution of Al-containing soil materials and correspondingly higher rates of Si release to solution. This behavior also suggests Al release into solution as the rate-limiting step in Ni–Al precipitate formation, as observed in other studies (5, 22).

Ni Speciation. Ni speciation in both soils at pH 6 is dominated by adsorbed compounds, as evidenced by the lack of signal from second neighbor metal atoms in the 1 month Fourier transformed EXAFS data (Figure 2). (See SI for additional spectra.) These results are consistent with published results that indicate little to no Ni precipitate formation on mineral surfaces below pH 7 (17, 23).

At pH 7.5, the Fourier transformed spectra of both samples show longer range Ni–Ni interactions resulting from precipitate formation (Figure 2). Both spectra also contain features diagnostic for the presence of mixed Ni–Al hydroxide formation; namely the shoulder just above 5 Å⁻¹ and the splitting and dampening of the peak at 8–8.3 Å⁻¹ (14, 24–26). Wavelet analysis of the combined *k* and *r*-space dependency of the second Fourier transformed peak for both soils at pH 7.5 (Figures 3b and 3c) confirms the presence of both a lighter and a heavier backscattering atom in the precipitate structure (26–28). Fitted Ni–Ni coordination numbers and bond distances for the soils (available in the SI) are also within the range of published results for mixed Ni–Al-hydroxide surface precipitates (5, 17).

A more detailed speciation analysis can be obtained through linear fitting of the soil spectra with basis sets of

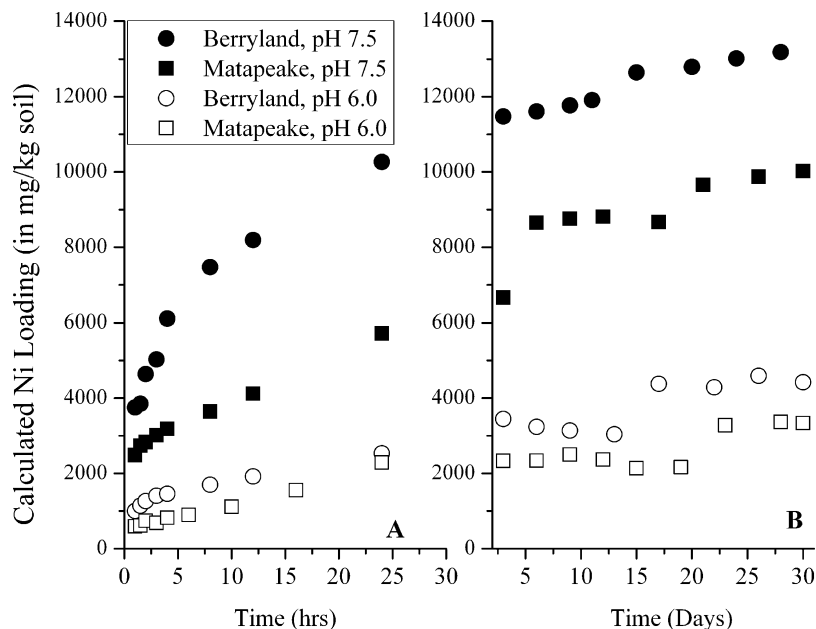


FIGURE 1. Nickel removal from solution at pH 7.5 (closed symbols) and 6.0 (open symbols) during soil sorption experiments: (A) 1st 24 h after Ni addition (B) 3–30 days after Ni addition.

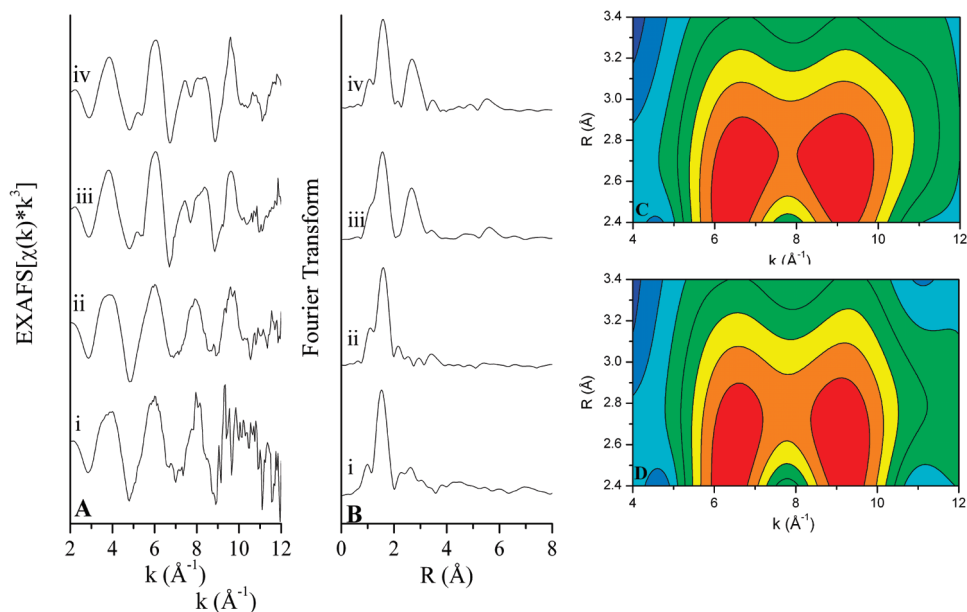


FIGURE 2. Ni EXAFS data for soil samples after 1 month sorption experiments (A) χ -extracted EXAFS spectra for (i) Matapeake soil, pH 6 (ii) Berryland soil, pH 6 (iii) Matapeake soil, pH 7.5 (iv) Berryland soil, pH 7.5 (B) Fourier transformed spectra of the same samples (C) and (D) Wavelet plots of 2.7-Å FT peak for soils iii and iv, respectively.

known Ni species. Figure 3 shows the results of this analysis for the 1 and 12 month Matapeake and Berryland soil samples at pH 7.5, as well as the large batch samples prepared for Ni bioavailability analysis. The major component of each spectrum ($\geq 75\%$) can be fit by one of the freshly precipitated Ni-LDH reference spectra. There is no evidence of significant adsorbed Ni in the Matapeake samples, as α -Ni(OH)₂ was the only other component to contribute to the best fit.

In the Berryland soil, approximately 15% of the fit was contributed by the aqueous Ni reference sample (Ni(H₂O)₆²⁺), which has a similar coordination environment to Ni adsorbed in weak (outer-shell) surface complexes. Many organic nickel complexes, however, also have similar EXAFS spectra, with little identifiable structure beyond the first shell. Replacement of the aqueous Ni standard with two of the organic Ni standards tested (Ni-histidine and Ni-citrate) resulted in only minimal ($\pm 4\%$) changes in the fraction of adsorbed Ni for all

three of the Berryland samples shown here. The rapid initial Ni sorption in the Berryland soil (Figure 1), followed by continuous uptake at a slower rate, suggests interaction with both soil organic matter and clay surfaces. It is likely, therefore, that the adsorbed Ni fraction observed in the EXAFS fitting results primarily from Ni-organic complexes.

In both soils, Ni speciation shows no dramatic changes between the 1 and 12 month samples. The best fit for the Berryland sample shifts from the 4:1 to the 2:1 LDH reference sample, but there is no change in the relative proportion of precipitated to sorbed Ni. The Matapeake sample does show a decrease in the LDH fitting and corresponding increase in α -Ni(OH)₂ between 1 and 12 months, but these phases have similar EXAFS spectra, and the shift could easily be driven by the effects of random noise in the signal.

Nickel Desorption and Availability. Results of the Ni desorption studies are presented in Figure 4 for both soils

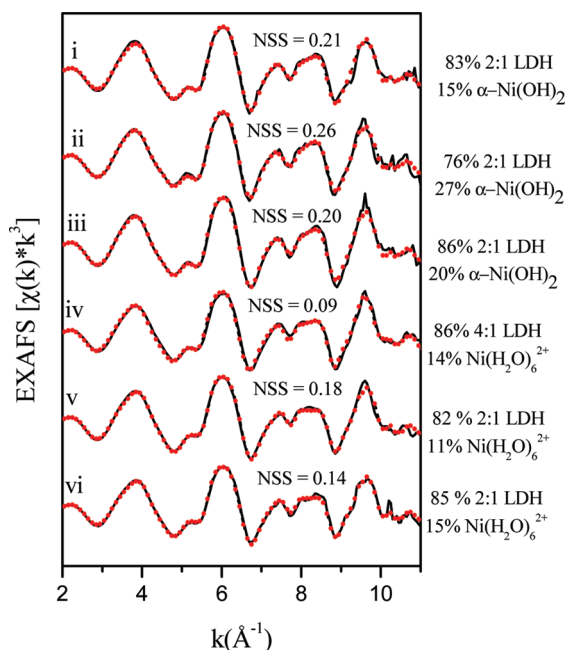


FIGURE 3. Ni speciation for soil samples at pH 7.5, showing EXAFS data (—) and best fit lines (●) from linear least-squares fitting: (i) Matapeake soil, 1 month, (ii) Matapeake soil, 12 months, (iii) Matapeake soil for bioavailability study, (iv) Berryland soil, 1 month, (v) Berryland soil 12 months, (vi) Berryland soil for bioavailability study. NSS, or normalized sum of squares, is a quality of fit parameter, with NSS = 0 indicating a perfect fit.

at pH 7.5 as the relative amount of Ni remaining on the surface, based on estimated Ni loadings at the end of the spiking experiment. Ligand promoted desorption was substantially more effective at removing Ni from both soils, with more than 50% of the total Ni removed in the first replenishment. This is substantially higher than the adsorbed Ni fraction in either soil, and must therefore include rapid dissolution of some of the mixed Ni–Al hydroxide surface precipitates. The slower rate of Ni release in subsequent replenishments suggests a mixture of more and less soluble Ni–Al hydroxide phases. Increasing the contact time between steps two and three had no apparent effect on Ni removal for the Matapeake soil, and only a small effect for the Berryland soil, so kinetic limitations do not appear to impact these results.

Ligand-promoted dissolution at 12 months show increased Ni retention as a function of soil aging in both soils. Ni released in the first replenishment, in particular, decreases significantly between 1 and 6 months. At these lower concentrations, desorption from secondary Ni species may account for a substantial portion of this initial release in both soils. While the total Ni retention at the end of the experiment increases substantially for the Matapeake soil between 1 and 6 months, further aging has no effect. In the Berryland soil, however, Ni retention continues to increase between 6 and 12 months.

With HNO₃ as the desorbing solution, Ni release in the two 12 h replenishment steps was less than 1 mg/L from both soils. Dissolved Ni concentrations were substantially higher in the remaining replenishments once the contact time was increased to 24 h. Average solution Ni concentrations were 2.6 mg/L from the Matapeake soil and 2.9 mg/L from the Berryland soil. For the Matapeake soil, these results are consistent with an initial fast desorption of small amounts of sorbed Ni, followed by a kinetically slower Ni release from relatively insoluble precipitate phases. Calculations based on previously published solubility product constants for a

pure NO₃ interlayer Ni–LDH phase (10) indicate an equilibrium solution Ni concentration of 3.6 mg/L in the nitric acid solution. This value, however, does not account for the effect of any other ions, such as Al, released from the soil substrate. Ni exchange from soil organic matter complexes may contribute to the higher rate of Ni release from the Berryland soil. Based on the patterns of dissolved Ni concentrations throughout the experiment, however, exchange of adsorbed species is not likely to be the primary source of Ni release to solution. Additional discussion of this topic is included in the SI.

Acid desorption at 6 and 12 months produced no significant change in the percentage of total Ni released for either soil. Low Ni release is observed in all aged samples in the initial 12 h steps compared to subsequent replenishments. In the 12 month samples, however, dissolved Ni concentrations during steps 3–10 average only 1.7 mg/L in both soils, increasing to 4.5 and 5.5 mg/L during the last two replenishments in the Matapeake and Berryland soil, respectively. These results suggest increased Ni stability on the soil at longer aging times. This could be caused by initial steps in the transformation of the mixed hydroxide phases into more stable structures, or by increased stability of the secondary Ni species.

Ni Bioavailability Using BIOMET Tests. Ni speciation results (Figure 3) and estimated soil loadings (Figure 5) in the larger batch samples used for BIOMET analysis were consistent with those from the initial 1 month samples. While the % Ni retained on the soils at pH 7.5 under acid-promoted dissolution is comparable to the original results, (71 and 80% for the Matapeake and Berryland soils, respectively), EDTA desorption left 19% of the sorbed Ni on the Matapeake soil and 14% on the Berryland soil. These higher values may be due to the freeze-drying process used to prepare the soils for BIOMET analysis. In both soils, bioavailable Ni is approximately 60% of the total soil Ni at pH 6, but only 25% at pH 7.5, although the higher overall loadings at this pH, result in greater total bioavailable Ni. The actual bioavailable concentrations are quite high for environmental systems, a result of the high total soil Ni loadings induced by this experiment. However, it is apparent that the formation of precipitate phases at the higher pH does correspond to a substantial decrease in the fraction of available Ni. The presence of adsorbed or organic-complexed Ni in the Berryland soil did not significantly increase the overall bioavailable fraction compared to the Matapeake soil.

Discussion

The extent of Ni retention on these soils is lower here for ligand-promoted desorption than in previous studies. Scheckel et al. (12) reported 41% Ni retention on pyrophyllite at 1 month after desorption with 1 mM EDTA and 28% retention on gibbsite. Retention increased to 75% on pyrophyllite and 50% on gibbsite at 1 year. This is a similar increase in Ni retention (~25%) to that observed here over the same time frame. Most of the increase in Ni retention in this experiment, however, occurred between 1 and 6 months, particularly for the Matapeake soil. Thus, it is likely that long-term Ni retention in these soils under these conditions will remain below 50%.

Increased precipitate susceptibility to ligand dissolution may be due to low Al substitution rates. Al release from vermiculites and kaolinites, the major clay minerals present in these soils, is relatively slow. While initial Ni–Al precipitate formation could incorporate existing dissolved Al ions, lower levels of available Al at longer times would result in a lower extent of Al substitution into the octahedral layers of later forming precipitates. The effect of Ni:Al ratio on LDH solubility ratio is small, but noticeable, within the typical Al

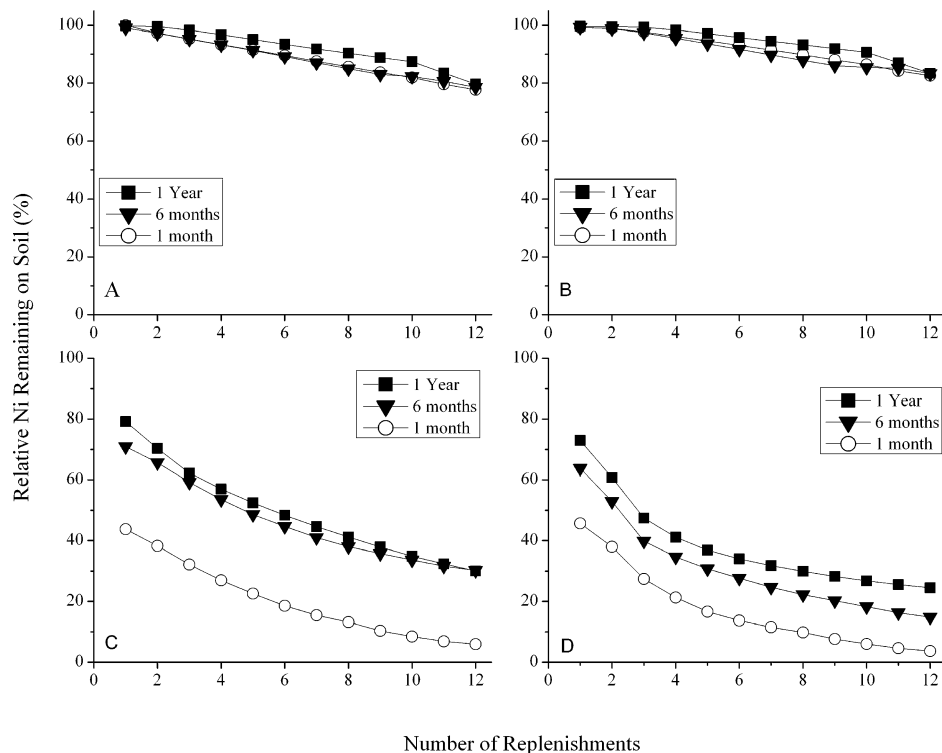


FIGURE 4. Ni dissolution behavior from soils aged at pH 7.5 showing the relative amounts of Ni remaining following extraction. Top: Matapeake (A) and Berryland (B) soils extracted with 0.1 mM HNO₃. Bottom: Matapeake (C) and Berryland (D) soils extracted with 1 mM EDTA.

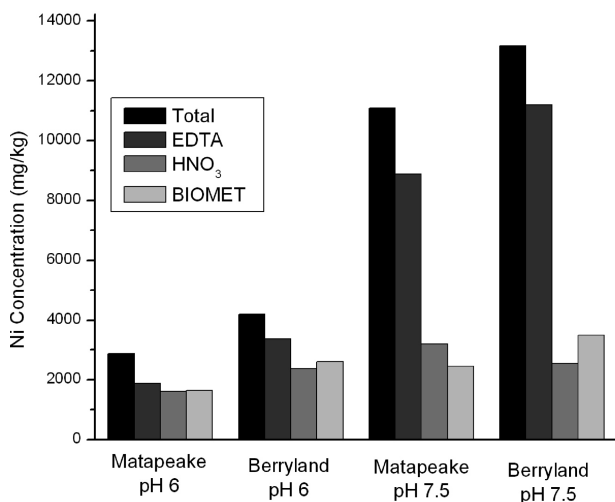


FIGURE 5. Comparison of bioavailable Ni concentrations using the BIOMET test to estimated total Ni loadings and the concentration extracted by EDTA and HNO₃ desorptions (12 replenishments).

substitution range of 20–33% (10). Below 20% Al substitution, the homogeneous structure of the cation sheets can begin to break down (29), with isolated Al deficient regions forming nuclei of atoms resembling Ni(OH)₂ that increase overall precipitate solubility.

The presence of Al deficient mixed hydroxide phases in the Matapeake soil could explain the presence of both mixed Ni–Al hydroxides and Ni(OH)₂ in the linear combination fitting results. In the Berryland soil, the higher soil organic matter content could have a similar effect on precipitate composition and stability. SOM concentrations in the Berryland soil are higher than those that prevented Ni–Al hydroxide formation in the study by Nachtegaal and Sparks (16), although this material is likely less reactive and less

evenly distributed in the soil than the humic acid used in that experiment. The SOM may nevertheless affect the nature of the Ni–Al precipitates formed, possibly by competing for dissolved Al or by retarding substrate dissolution.

The extent of Ni–Al hydroxide resistance to acid dissolution is strongly substrate dependent. Scheckel et al. (12) reported 97% Ni retention on pyrophyllite after 1 month, but only 78% retention on gibbsite. By contrast, Nachtegaal and Sparks (16) observed only 60% Ni retention on kaolinite. In leaching studies from soil columns, Voegelin and Kretschmar reported 80% Ni retention at pH 3 (5). The results presented here for the HNO₃ desorption experiments are thus well within the existing literature.

In the only similar experiment to assess Ni bioavailability in contaminated field soils, Everhart et al. (19) observed minimal bioavailable Ni in soils containing between 2000 and 4000 mg/kg total Ni. In these soils, however, the majority of Ni was present as solid Ni oxide phases, with secondary precipitates (including mixed Ni–Al hydroxides) accounting for only a small fraction of the total (4). Moreels et al. (21) analyzed the bioavailable fraction of Ni after sorption of aqueous NiCl₂ to soil columns at circumneutral pH. Bioavailable Ni percentages in that study ranged from <10 to 100% after approximately 7 months of exposure. The bioavailable fractions observed here are in line with those results. In both soils, bioavailable Ni concentrations were similar to the concentrations released by nitric acid dissolution. Decreases in metal bioavailability due to more extensive mixed hydroxide formation, therefore, may be correlated with increased resistance to acid promoted dissolution. This would provide a means of assessing changes in Ni bioavailability without access to bacterial biosensors.

The results from this study suggest that mixed Ni–Al hydroxide phases forming in real world environments may be longer-lasting than previously expected and more soluble with respect to organic complexes such as EDTA. The rate at which soil Al becomes available for surface reactions has a well-documented effect on the likelihood of mixed hy-

droxide precipitate formation (1, 2, 15, 30). These results indicate that, even in soils where formation of mixed Ni–Al hydroxides has begun, later limitations on the amount of dissolved Al will result in less stable Ni precipitates. Thus, soils in which Ni is slowly leached into solution (such as smelter-contaminated soils in which Ni is initially deposited in metal oxide phases) will have relatively high capacity for Ni incorporation into mixed hydroxide phases, as Ni release can be balanced out by substrate dissolution and release of Al. In soils where Ni contamination occurs rapidly and in easily soluble forms, a deficit of available Al would result in less stable mixed Ni–Al hydroxide phases with characteristics more similar to Ni(OH)₂. The presence of elevated concentrations of soil organic matter can directly influence both the amount of soluble Al present (through metal complexation) and the rate of Ni sorption to the soil. It is likely, therefore, that Ni–Al hydroxide formation will occur more slowly as the organic matter content increases.

Acknowledgments

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Supporting Information Available

Information related to Ni release during HNO₃ desorption studies, Al and Si release during the soil sorption experiments, and EXAFS data collection, analysis and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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