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Plutonium Immobilization and Remobilization by Soil Mineral and Organic Matter in the Far-Field of the Savannah River Site, U.S.

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Ⓢ *Supporting Information*

ABSTRACT: To study the effects of natural organic matter (NOM) on Pu sorption, Pu(IV) and (V) were amended at environmentally relevant concentrations (10^{-14} M) to two soils of contrasting particulate NOM concentrations collected from the F-Area of the Savannah River Site. More Pu(IV) than (V) was bound to soil colloidal organic matter (COM). A de-ashed humic acid (i.e., metals being removed) scavenged more Pu(IV,V) into its colloidal fraction than the original HA incorporated into its colloidal fraction, and an inverse trend was thus observed for the particulate-fraction-bound Pu for these two types of HAs. However, the overall Pu binding capacity of HA (particulate + colloidal-Pu) decreased after de-ashing. The presence of NOM in the F-Area soil did not enhance Pu fixation to the organic-rich soil when compared to the organic-poor soil or the mineral phase from the same soil source, due to the formation of COM-bound Pu. Most importantly, Pu uptake by organic-rich soil decreased with increasing pH because more NOM in the colloidal size desorbed from the particulate fraction in the elevated pH systems, resulting in greater amounts of Pu associated with the COM fraction. This is in contrast to previous observations with low-NOM sediments or minerals, which showed increased Pu uptake with increasing pH levels. This demonstrates that despite Pu immobilization by NOM, COM can convert Pu into a more mobile form.
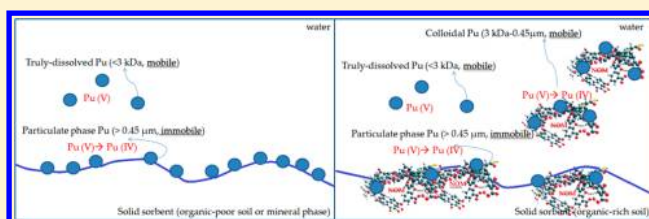
INTRODUCTION

Billions of cubic meters of soils, sediments, and groundwater at the Department of Energy (DOE) sites in the United States have been contaminated with plutonium (Pu) through activities related to nuclear weapons testing, nuclear materials production, radioactive waste reprocessing, reactor operations, the nuclear fuel cycling, and nuclear accidents.[1] The human and environmental risks associated with Pu disposal and remediation scenarios stems mainly from the very long half-lives of several of its isotopes ([238]Pu ($t_{1/2}$ = 88 yr), [239]Pu ($t_{1/2}$ = 24 100 yr), and [240]Pu ($t_{1/2}$ = 6560 yr)) and its radiotoxicity.[2,3] The environmental mobility of Pu can be affected by oxidation state, complexation, adsorption, precipitation, colloid formation, and microbial activity,[4−8] of which the first characteristic has the most profound influence. Pu can exist simultaneously in four different valence states (III, IV, V, VI) in a single groundwater or soil sample. The reduced forms (III, IV) are generally 2−3 orders of magnitude less mobile than the oxidized forms (V, VI) in most environments.[9−11] Numerous previous studies have shown that Pu has a high affinity to naturally occurring mineral phases, such as iron oxides and manganese oxides. In addition, it also has a strong propensity to undergo oxidation state transformations via surface-mediated interactions.[11−13] Under low organic matter vadose zone conditions (pH 5; 1 ×

10^{-15} M Pu), Pu speciation estimates based on thermodynamic calculations indicate that 94% of the aqueous Pu exists as Pu(V) (PuO_2^+) and 6% exists as Pu(IV) (as $Pu(OH)_4^0$ and $Pu(HPO_4)_4^{4-}$).[14]

Most field studies that have identified colloids as a vector for Pu subsurface transport have implicated inorganic mineral colloids as the carriers.[15−18] In contrast, Santschi et al.[19] revealed through field studies and laboratory experiments that 10−60% of the remobilized Pu from contaminated soils to streams in storm runoffs, pond discharge, and wind dispersion events at a particular DOE site was associated with colloidal organic macromolecules. The Pu-binding colloidal organic carrier was further characterized as containing strong hydroxamate siderophore binding sites specific to Fe(III) and Pu(IV) bound to a cutin degradation product cross-linked to hydrophilic moieties such as polysaccharides.[20] In contrast to promoting Pu mobility, natural organic matter (NOM) has also been reported to behave as a Pu sink in many sediment systems.[21−23] Therefore, the role of NOM in affecting Pu

mobility and transport is still unclear. Very likely, in the natural environment, it is the integrated interactions among a ternary system (mineral phase−NOM−Pu) that ultimately determines the fate of Pu.[24,25] Thus, it is necessary to obtain detailed knowledge of the various geochemical factors causing Pu fixation and remobilization in the presence of NOM, particularly at the low Pu concentration range of 10^{-12} to 10^{-18} M observed in the far-field of DOE sites.[15−17,26−28] Unfortunately, for analytical convenience, most Pu−NOM interaction laboratory experiments were performed at Pu concentrations orders of magnitude greater than ambient, thus exceeding those observed in the far-field, and were assuming that the results can then be simply extrapolated to the environmental concentrations. However, this assumption may be unrealistic because at higher concentrations, surface-mediated oxidation−reduction reactions sites and strong Pu-binding sites become limited, and Pu(IV) tends to form polymeric or colloidal Pu-oxide particles (i.e., intrinsic colloids).

The objectives of this study were thus to assess how the presence of soil NOM changes Pu behavior, by using soil−groundwater resuspension batch experiments, which were intended to mimic surface runoff and groundwater infiltration/exfiltration events. Particular attention was directed at evaluating the impact of initial Pu oxidation states (IV) and (V) on Pu partitioning to the three phases (particulate, >0.45 μm; colloidal, 3 kDa to 0.45 μm; and truly dissolved, <3 kDa) of two contrasting soil−groundwater systems (organic-rich soil vs organic-poor soil), as well as to different soil components of an organic-rich soil. The F-Area at the Savannah River Site (SRS), constructed in the early 1950s for the production of nuclear weapons, and containing one-third of the nation's Pu inventory ($\sim$ 40 t),[13] was chosen as a field site for this purpose, as the vadose zone sediments change abruptly from organic-poor loamy sand near the unlined, waste seepage basins to organic-rich loamy sand in the downgradient wetlands.[29] In addition, along a groundwater flow path between the seepage basins and the wetland area, a general increase in pH (pH 3.2 to 6.8) and decrease in E_h (654 to 360 mV) exists,[29−31] which was largely due to the acidic nature of the plume, basin closure activities, and ongoing in situ base-injection remediation efforts. Thus, another aim of this study was to rigorously assess the mechanisms that control how Pu partitions in a ternary system along a simulated groundwater pH gradient. As the role of NOM on Pu mobility across these geochemical gradients has not been previously studied, this study provides insights into Pu transformations and migration in this region, allowing for better predictions of its behavior in the natural environment. Most importantly, Pu was studied at relevant far-field concentrations (10^{-14} M).

■ MATERIALS AND METHODS

Sampling of Soils and Groundwater. One of the selected soil sampling sites was FSI18, which is in the path of the F-Area contaminant groundwater plume, and close to the wetland area (Supporting Information (SI) Figure S1). The other soil sample was located just north of the F-Area seepage basin (named "N Borrow"). Both soils were sampled from the same geological formation, yet with quite different organic matter contents (soil characterization provided in SI Table S1). The soil collected from FSI18 was termed as "organic-rich" soil, as it contained 24% organic carbon (OC), whereas the one collected from N Borrow was termed as "organic-poor" soil, as the OC content was barely detectable by our elemental analyzer (see

below). The soil samples were stored and shipped in a zippered bag under ice and immediately transferred to a 4 °C laboratory refrigerator. Soils were dried at 60 °C in an oven, then gently ground with a pestle and mortar to break up aggregates, and subsequently passed through a 2-mm sieve. A groundwater sample was collected from well FPZ6A in December 2011 (pH 4.9, SI Figure S1), filtered through a 0.45-μm polycarbonate filter, and kept frozen until use. Field parameter values of this groundwater include a pH of 4.95, E_h (SHE) of 487 mV, specific conductivity of 1231 μS cm^{-1}, and a dissolved O_2 concentration of 1.87 mg L^{-1} (additional characterization is provided in SI Table S2).

Kinetics of Pu(IV) and Pu(V) Uptake by the Two Soils. The experimental design included five contact times (days 1, 3, 7, 14, and 28), two Pu oxidation states (IV and V), two contrasting soils (organic-poor and organic-rich soils), Pu tracer controls without the soils, soil controls without the addition of Pu, and two replicates, for a total of 80 samples. A 1-g soil aliquot was pre-equilibrated with groundwater in a 15-mL polypropylene centrifuge tube for 48 h. Pu(IV) and Pu(V) stock solutions (see SI) was amended with piperazine-N,N″-bis(4-butane sulfonic acid) buffer (PIPBS, formula, $N_2C_4H_8(C_4H_8SO_3H)_2$, GFS Chemicals, Cat 2360) (0.02 M in 0.5 M NaOH), which is a noncomplexing buffer, to achieve pH $\sim$5.[32] Pu(IV) and Pu(V) working solutions were then immediately added to the slurry to achieve a final concentration of 8.4 × 10^{-14} M. The pH of the final solution was $\sim$5.0, mimicking background groundwater pH levels.[30] Suspensions with a final solid-to-water ratio of 1:4 were mechanically mixed in the dark with an end-over-end mixer. At each time point, samples (i.e., whole 15-mL centrifuge tubes) were taken from the mixer, centrifuged, and then filtered through a 0.45-μm polyethersulfone syringe filter to separate the aqueous phase from the "particulate" phase. The filtrate was further separated into "colloidal" and "truly-dissolved" phases, using 3 kDa-Amicon Ultra-4 centrifugal filter units.

The alpha-spectroscopy method for Pu activity determination was adapted, with some modifications, from Santschi et al.[19] and Ketterer et al.[33] Oxidation state analysis of Pu in the truly dissolved phase was performed by parallel extraction of the solution into 0.5 M thenoyltrifuloroacetone (TTA, Alfa Asear) in cyclohexane at pH 0.5 for Pu(IV), and 0.5 M bis-(ethyhexyl)-phosphoric acid (HDEHP, Alfa Asear) in heptanes at pH 0.5 for Pu(V).[9,11,12] Details are provided in the SI. OC contents in the colloidal (3 kDa to 0.45 μm) and truly dissolved (<3 kDa) fractions were determined with a Shimadzu 5000 total organic carbon (TOC) analyzer.

Kinetic Pu sorption (r_{uptake}, mol s^{-1}) by soil components (mineral, SOM, or COM) was described primarily with a kinetic sorption equation, that is a modification of an existing model.[34]

$$r_{uptake} = -k_m\left(C_i\frac{S_i}{K_d}\right)$$
(1)

where C_i is the aqueous Pu(IV) or Pu(V) concentration (mol L^{-1}), s_i is the sorbed Pu concentration on reactive sites (mol mol$_{site}^{-1}$), k_m is the mass transfer coefficient (L s^{-1}), and K_d is the distribution coefficient between solid and aqueous phase (L mol$_{site}^{-1}$). If the concentration of sorbate (aqueous Pu) is low enough to maintain the linear isotherm, this K_d-based kinetic sorption expression is mathematically convenient and scientifically valid.[35]
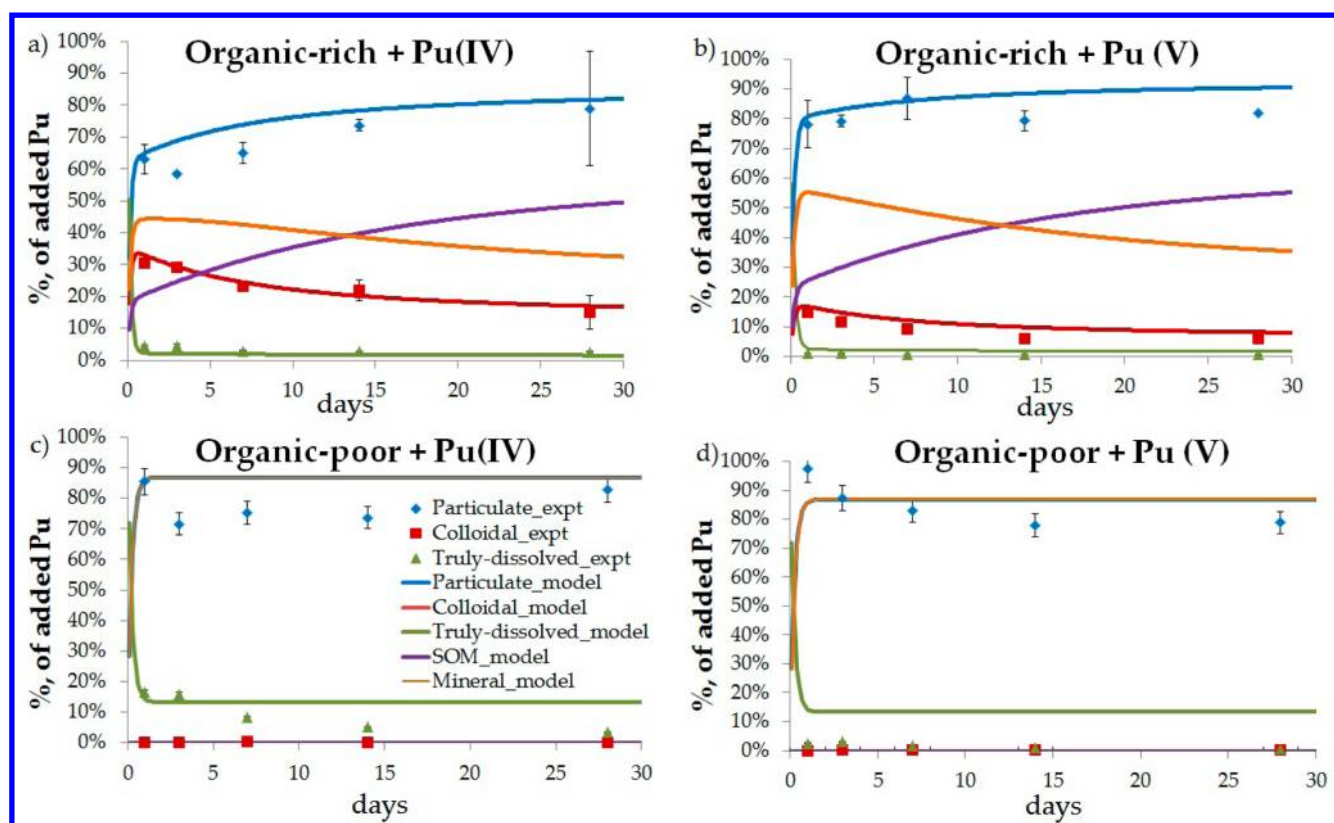
Figure 1. Kinetic distribution of Pu(IV) or Pu(V) in the particulate (> 0.45 μm), colloidal (3 kDa to 0.45 μm), and truly dissolved (< 3 kDa) fractions of a soil−groundwater resuspension (soil/water ratio 1:4, pH ∼5.0, amended Pu concentrations 8.4 × 10^{-14} M). (a) Organic-rich soil amended with Pu(IV); (b) organic-rich soil amended with Pu(V); (c) organic-poor soil amended with Pu(IV); (d) organic-poor soil amended with Pu(V). Two soils were used in this study, one was organic-rich (OC, 24% of total weight), and the other was organic-poor (OC, <0.01% of total weight). For organic-poor soil, the model simulation of the particulate Pu fraction (blue line) overlapped with that of the mineral Pu fraction (orange line).

Plutonium partitioning among particulate SOM, particulate mineral surfaces, and colloidal organic matter (COM) was modeled using eq 1 and the pH-redox-equilibrium-equation geochemistry code (PHREEQC-2) (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/). When a specific model parameter was not available, the value was optimized through a trial-and-error process in which simulated and experimental data were compared. In a few instances, a numerical optimization code was used (Parameter Estimation and Uncertainty Analysis (PEST), http://www.pesthomepage.org). The underlying rationale of the model development procedure is based on the component additivity (CA) approach, which was developed for the surface complexation modeling.[36−38] The CA approach primarily considers that each kind of sorption site in a system reacts independently with the sorbate. Therefore, by combining the sorption sites, based on mineralogy and surface area, it is possible to estimate the overall surface complexation reaction of the soil system. The Pu conceptual model proposed here adopted the notion of an independent reaction process of soil component from the CA approach. This is the first attempt to use the CA approach to explain Pu geochemistry. Through the development of the model, individual soil components were successively added as a sorption site to the system.

The major assumptions for the modeling were as follows: (1) The pH/pe of the system is constant during all experiments. (2) The metal oxides in the soil are the responsible minerals for Pu sorption. The site concentration was determined based on the dithionite citrate buffer (DCB)-extracted Al, Mn, and Fe concentrations in SI Table S1, representing Al oxide (Al_2O_3), Mn oxide (MnO_2), and Fe oxide ($Fe(OH)_3$), respectively. For organic-poor soil, the concentration was 1.14 × 10^{-3} mol g^{-1} soil, and for organic-poor soil was 3.63 × 10^{-3} mol g^{-1} soil. (3) The reactive site on the organic matter is assumed as carboxylate functional group, the amount of which is 11%, as estimated from previous NMR results.[39] (4) To simplify the modeling, regardless of the kinetic release of dissolved organic carbon (DOC) and colloidal organic carbon (COC) from the soil during the 28-day experiment (SI Figure S3), DOC and COC are assumed to be released at a fixed ratio of 0.41:0.59, which was calculated from equations in Figure 3b at pH ∼5. 5). The $K_{d\_mineral}$ values for Pu(V) and Pu(IV) were assumed to be similar over the experimental duration (28 days) according to the current study and Powell et al.,[40] since the sorbed Pu(V) converts to Pu(IV) on the surface of the mineral phase over time. That is, in the case of $K_{d\_mineral}$ for Pu(V), the $K_{d\_mineral}$ represents Pu(V) sorption/complexation + Pu(V) surface facilitated reduction. In the case of $K_{d\_mineral}$ for Pu(IV), the $K_{d\_mineral}$ represents Pu(IV) adsorption/surface facilitated precipitation.[40]

Comparison of Pu(IV) and Pu(V) Interactions with Original Humic Acid (HA), De-ashed HA (DA-HA), and the "Mineral Phase" from a Wetland Soil (FSI18). Details of the HA extraction procedures and mineral phase composition are provided in the SI (Figure S2 and Table S1). Briefly, HA was obtained based on the alkaline extraction

method recommended by the International Humic Substances Society (IHSS).[41] The difference between the original HA1 and DA-HA1 fractions was that the latter was extensively treated with HCl/HF (0.1/0.3 M) to remove the complexed metal ions, e.g., Ca^{2+}, Fe^{3+}. The "mineral phase" was created by extensively (>10 times) treating the soil with 30% hydrogen peroxide, which was intended to oxidize and decompose the labile organic matter fraction.[42−44] However, the "mineral phase" after treatment was not entirely free of organic matter. It contained about 6% OC, and the original, untreated soil contained 24% OC. It is likely that the treatment to create the "mineral phase" fraction only removed the OC associated with the exposed mineral surfaces, and left in place the occluded residual organic carbon fraction that was not solvent-accessible or oxidizable. Thus, in our study the "mineral phase" represents an OC fraction that may be more chemically recalcitrant and less available to interact with the introduced Pu.[4,45]

About 1 g of solid (original HA1, DA-HA1, mineral phase, and original soil) was pre-equilibrated with groundwater for 48 h. Pu(IV) or Pu(V) in noncomplexing PIPBS buffer solutions were amended to reach a final solid-to-water ratio of 1:4, a pH of ~5.0, and a Pu concentration of 8.4×10^{-14} M.

Four original HAs were sequentially extracted from the same soil (FSI18) using four repetitive NaOH extractions.[41] Thus HA1 represents the first extract, HA2 represents the second one, etc. In another experiment, 5−6 mg of these four original HAs, together with their corresponding four "de-ashed" HAs named DA-HA1, DA-HA2, DA-HA3, and DA-HA4, were pre-equilibrated in groundwater for 48 h. Pu(IV) PIPBS buffer solution was amended to reach a final volume of 4 mL and Pu concentration of 8.4×10^{-14} M. Two pH treatments were performed (4.4 and 7.1), with the addition of trace amounts of 1 M HCl or NaOH. Though less de-ashed HA was used in this experiment (solid-to-water ratio ~1:800), due to the limited sample quantity obtained from sequential extraction, the main purpose was to more systematically investigate the difference in Pu complexation by the two different types of HAs.

In both experiments, particulate (>0.45 μm), colloidal (0.45 μm to 3 kDa), and truly dissolved (< 3 kDa) phases were separated after 7-day dark incubation on end-over-end mixers. Each fraction was analyzed for Pu activity and OC contents, as described previously.

pH-Dependent Uptake of Pu(IV) by Organic-Rich Soil. A series of soil suspensions composed of 1 g of FSI18 soil and ~4 mL of groundwater were added to 15-mL polypropylene centrifuge tubes and pre-equilibrated in the dark for 48 h. Pu(IV) cocktails were prepared by mixing with trace amounts of HCl or NaOH to span the pH range of 3.7 to 8.7 in ~1.0 pH unit increments. Then the Pu tracer solution was added to the pre-equilibrated soil−groundwater system, to reach a final volume of 4 mL, and a Pu concentration of 8.4×10^{-14} M. pH values of the suspensions were maintained constant daily during the experiment by adding trace amounts of 1 M HCl or NaOH. Samples were incubated in the dark at room temperature on an end-over-end shaker for 14 days, after which they were processed as described above.

■ RESULTS AND DISCUSSION

Kinetic Study of Pu(IV) and Pu(V) Uptake by Organic-Rich (FSI18) and Organic-Poor (N Borrow) Soils from the SRS. Pu(IV) and Pu(V) uptake by the two soils are shown in Figure 1. For organic-rich soil, Pu amended as IV tended to increasingly partition to the particulate fraction (>0.45 μm)

from 63% at day 1 to 74% by the time it reached equilibrium on day 14 (Figure 1a). The variability of the measurements is within the uncertainty associated with the last contact period, 28 days, suggesting additional work is required to confirm this secondary trend in Pu uptake. However, several previous studies have also shown a slower Pu mineral sorption rate after an initial fast rate.[46−48] When Pu was added as V, the Pu-associated particulate fraction slightly increased from 78% on day 1 to about 87% by day 7, after which the distribution did not change for the remaining 21 days of the study (Figure 1b). It is noticeable that Pu added as IV more readily partitioned into the colloidal phase (~30% of the total added amount) on day 1 (Figure 1a), compared to only 15% of the Pu added as V (Figure 1b). In both cases, the decrease in colloid-associated Pu approximately corresponded to the increase noted in the particulate Pu percentages, suggesting a readsorption of the colloidal fraction. It was also confirmed by a decrease of the COC concentration toward the end of the experiment, and a relatively constant concentration of the truly dissolved DOC concentration throughout the experiment (SI Figure S3). At equilibrium, more Pu was present in the colloidal fraction (~15%) when Pu was initially added as Pu(IV) than when it was added as Pu(V) (~6%). It is likely that Pu was complexed with organic macromolecules which make up most of the colloidal fraction, e.g., humic acids, and were remobilized and released from the organic-rich soil, rather than any mineral type colloids. This is inferred from the fact that Pu was not associated with organic or inorganic colloids released from the organic-poor soil (Figure 1c and d). Approximately 2.6% and 0.5% of the total added Pu(IV) and Pu(V), respectively, partitioned into the truly dissolved phase (< 3 kDa) for the organic-rich soil−groundwater suspensions. However, it was not possible to use the solvent extraction method described above to determine oxidation states of Pu at trace levels in the organic-rich soil solution due to the fact that Pu was consistently collected at the interface between aqueous and organic phases (see the SI). Yet it is reasonable to assume that Pu associated with both particulate and colloidal phases was predominantly in the IV oxidation state.[9]

For the organic-poor soil, after one day, ~16% of total added Pu(IV) was present in the truly dissolved phase, which decreased to ~3% by the end of the 28-day experiment. In contrast, in the Pu(V)-amended treatment, much less Pu was present in the <3 kDa fraction at the beginning (3%), which then decreased to almost 0% after 28 days (Figure 1c and d). The particulate Pu fraction tended to remain rather constant in the Pu(IV) amended system (Figure 1c), whereas it appeared to consistently decrease until it reached steady state after 14 days in the Pu(V) amended system (Figure 1d). The kinetics of the partitioning of added Pu(V) to mineral surfaces has been previously shown to be proportional to the amount of Fe(II) present in the solid phase.[40,49] In our study with the organic-poor soil, the amount of Pu bound to the particulate phase after 28 days was similar, irrespective of whether Pu(IV) or Pu(V) was added to the system. This observation has previously been noted in Mayak sediments.[46]

A slight desorption of Pu(IV) and Pu(V) from the particulate phase observed during the experiment (especially for the organic-poor soil) likely occurred by sorption of Pu onto the reaction vessels, as no concomitant increases of Pu in the other two fractions (the truly dissolved and colloidal fractions) were observed. The mass balance (sum of Pu activity in the three fractions over the total amended activity) of Pu in the organic-
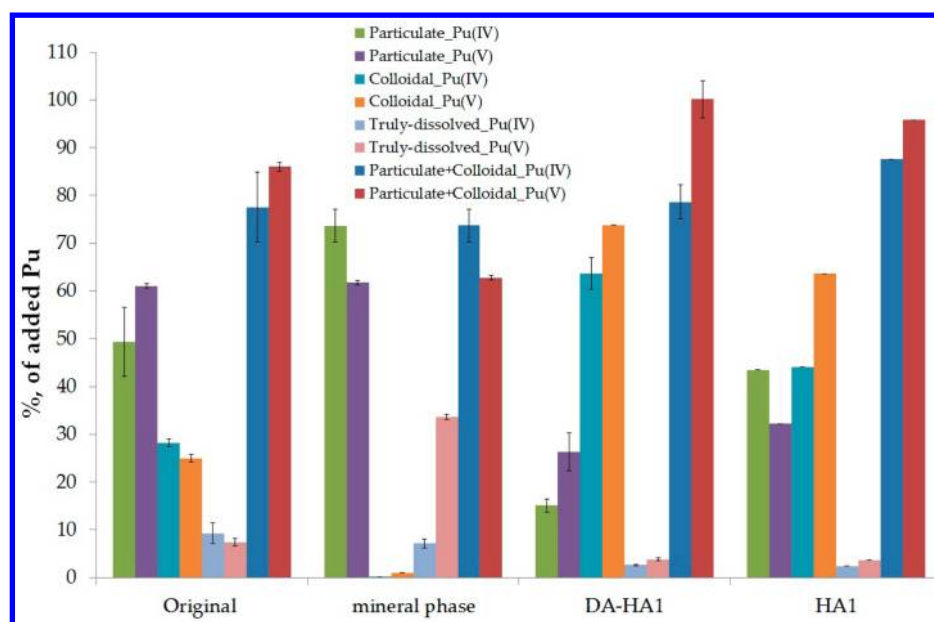
Figure 2. Pu(IV) and Pu(V) distribution in the (a) particulate (> 0.45 μm), (b) colloidal (3 kDa to 0.45 μm), and (c) truly dissolved (< 3 kDa) phases, and (d) particulate and colloidal phases (> 3 kDa) of four types of material: FSI18 soil, mineral phase, de-ashed humic acid (HA), and the original HA (soil/water ratio 1:4, Pu concentration 8.4 × 10^{-14} M, equilibrium time 7 days).

rich soil was higher (88−96%) than that in the organic-poor soil (79−86%). This suggests that slightly more Pu in the organic-poor soil−groundwater system partitioned to the reaction vessel walls, than that in the organic-rich system. This hypothesis was indirectly validated by the very high sorption of Pu onto reaction vessels in the tracer controls (> 70% in the soil-free controls, data not shown), as well as a much higher model calculated K_d values for SOM than those for the mineral phase (see below). But in the presence of a suspended sediment, it appears that the sediment surfaces can out-compete the reaction vessel walls for aqueous Pu(IV) or Pu(V),[40] and this effect was more pronounced when there was organic matter present.

It is noteworthy that almost the same amounts of Pu (between 79 and 83% of the Pu) were taken up by both soils at the end of the experimental period, irrespective of their contrasting organic matter contents or the initial oxidation states of added Pu, indicating that steady state had been achieved. The Pu activities distributed in the truly dissolved fractions were similar as well, whereas the colloidal organic matter (COM) of the organic-rich soil remobilized significant amounts of Pu (6−15%), under these typical background pH conditions of SRS groundwater.

Kinetic sorption modeling agrees very well with the experimental data (Figure 1) and provides some insight regarding the sorption processes that otherwise would not have been obvious. For the model, the $K_{d\_mineral}$ value used for the organic-rich soil was derived from the Pu sorption kinetic experimental data of organic-poor soil (Figure 1c and d), and the K_{d_COM} and K_{d_SOM} were estimated by model optimization. The Pu on the "particulates" (>0.45 μm) in the organic-rich soil was modeled as the sum of Pu associated with the SOM and the mineral surfaces. A ranking of solids by their K_d values is as follows: $K_{d\_COM} > K_{d\_SOM} > K_{d\_mineral}$ (SI Table S3). In the organic-rich soil, the modeling supports the conceptual model that there is a kinetic transition from Pu sorbed to the mineral phase (represented by "Mineral_Pu" in Figure 1a and b) to it being sorbed to the SOM (represented by "SOM_model" in

Figure 1a and b); this transition is driven by an order of magnitude greater K_{d_SOM} than $K_{d\_mineral}$ as the system approaches steady state (SI Table S3).

The optimized k_{m_COM} and K_{d_COM} values for Pu(IV) sorption on COM are more than twice as great as those for Pu(V) sorption on COM, which indicates the faster and greater sorption extent of Pu(IV) on COM compared to Pu(V) (SI Table S3). The early calculated peak of Pu partitioning to the particulate phase ("Particulate_model" in Figure 1a and b) was attributed to the rapid initial uptake of Pu to the particulate phase, and then the subsequent rapid kinetic release of COM and its associated Pu.

These results have significant implications on the efficacy of in situ remediation approaches based on most sorption processes, including adsorption, precipitation, and complexation. While SOM has little impact on the total amount of Pu bound to the particulate phase in this study, the SOM greatly increased the likelihood that it would desorb in a colloidal form. The finding that the presence of SOM can reduce the tendency for Pu(IV) or Pu(V) to bind to the immobile sorbent surfaces is novel, and needs to be considered in possible remediation strategies. Moreover, when Pu is initially discharged as IV to a system containing abundant NOM, more of the introduced Pu is going to be directly complexed to COM, thus becoming more mobile, compared to the case when it is introduced as Pu(V).

Comparison of Pu(IV) or Pu(V) Sorption to Different Soil Components of an Organic-Rich Soil. Figure 2 shows the Pu activity distributions in four fractions of the FSI18 sediment with originally high OC: (1) original (unadulterated) soil; (2) "mineral phase" in which the OC concentration decreased from 24% to 6%; (3) de-ashed HA1; and (4) original HA1. The "mineral phase" was not exactly the same as "N Borrow" soil (i.e., the organic-poor soil), as the latter had <0.01% OC (SI Table S1), where the former had 6% OC. The residual organic matter in the "mineral phase" likely existed in occluded locations in the aggregates where the H$_2$O$_2$ could not enter.[43] However, if one assumes this occluded OC was not

3190

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easily accessible to Pu, then its presence would not greatly affect Pu oxidation state transformation or sorption.

The original organic-rich soil sorbed more Pu(IV) than the "mineral phase", while both solids sorbed a comparable amount of Pu(V) (Figure 2). The presence of NOM in the F-Area soil thus did not enhance Pu fixation to the organic-rich soil due to the formation of COM-associated Pu. An appreciable amount of Pu(IV) (∼ 28%) was more readily complexed by the mobile COM, released from the original soil upon contacting the groundwater. In agreement with the results from N Borrow soil, there was no quantifiable colloidal Pu in the "mineral phase" slurry (Figure 2).

HA1 is the first HA in the repetitive extraction steps, which accounts for ∼47% of the total extractable OC of the original soil,[50] thus representing the majority of soil NOM. Without the mineral phase "anchor", more of the amended Pu(IV) (44−64%) or Pu(V) (64−74%) partitioned into the colloidal phase than that into the corresponding particulate phase for both HAs, in contrast to the case of the original soil (25−28% of added Pu(IV) or (V) into the colloidal phase versus 49−61% of added Pu(IV) or (V) into the particulate phase) (Figure 2). In addition, for both Pu oxidation states, particulate de-ashed HA1 scavenged less Pu (15−26%) than the original HA1 (32−44%). Conversely, colloidal de-ashed HA1 complexed more Pu (64−74%) than the original HA1 (44−64%) (Figure 2). Overall, when summing up both particulate and colloidal Pu, de-ashed HA1 and original HA1 complexed slightly higher amounts of Pu(IV) and much greater amounts of Pu(V) than the mineral phase or the original soil. This implies SOM has a greater amount of potential binding ligands for Pu than the mineral phase or the original soil, which was also confirmed by the ranking of the optimized K_d values (SI Table S3). One of the possibilities is that these binding sites were probably either "occupied" by the metals on the mineral phase, or inaccessible, potentially due to a "coiled" structure created when the SOM was bound to the mineral phase.[51−53]

De-ashing is a common practice to obtain NOM of higher purity. To investigate how the de-ashing step affects Pu complexation and mobility, a comparison was made between Pu uptake by de-ashed and non-de-ashed (original) sequentially extracted HA fractions (Table 1). To simplify this comparison, K_d and K_{dc} values are used (eqs 2 and 3):

$$K_d = \frac{\text{Pu in the particulate phase } (>0.45 \ \mu m)}{\text{Pu in the dissolved phase } (<0.45 \ \mu m) \times \text{ particle concentration}} \quad (2)$$

$$K_{dc} = \frac{\text{Pu in the particulate phase and colloidal phase } (>3 \text{ kDa})}{\text{Pu in the truly dissolved phase } (<3 \text{ kDa}) \times \text{ particle concentration}} \quad (3)$$

The traditional K_d value is the ratio of Pu concentration in the solids phase to that in the liquid phase, as operationally defined by phase separation using a 0.45-μm membrane. In the K_d construct, the colloidal fraction is treated as part of the dissolved fraction (as in eq 2). The K_{dc} construct treats the colloidal fraction as a part of the solid-phase fraction, and as such, this Pu colloidal fraction is included with the particulates. The hydrologist might be more interested in eq 2 because it attempts to separates the mobile from the immobile phase, whereas the chemist may be more interested in eq 3 because it provides a better estimate of dissolved (solubility values) versus surface-bound Pu.

Generally, slightly more HAs partitioned into the colloidal fraction after the de-ashing treatment (paired t test, df = 7, p =

Table 1. Comparison of Percentage of Colloidal Organic Carbon (COC, 3 kDa to 0.45 μm), K_d (eq 2) and K_{dc} (eq 3) of Sequentially Extracted HAs and Their De-Ashed HAs for Pu(IV) at pH 4.4 and 7.1

HA suspension pH	sequential extraction fraction	COC/total OC (%) de-ashed	COC/total OC (%) original	Pu(IV) Log $K_d{}^a$ de-ashed	Pu(IV) Log $K_d{}^a$ original	Pu(IV) Log K_{dc} de-ashed	Pu(IV) Log K_{dc} original
pH 4.4	HA1	1.69	1.58	3.09	3.26	4.99	5.14
	HA2	0.98	0.86	2.88	3.63	4.93	5.38
	HA3	0.97	0.40	2.92	3.44	4.89	5.49
	HA4	0.64	0.51	3.25	3.71	5.38	5.76
pH 7.1	HA1	6.68	4.05	2.13	2.34	5.30	5.37
	HA2	4.43	2.27	2.21	2.77	5.45	5.44
	HA3	1.39	1.22	2.58	2.90	5.39	5.47
	HA4	1.08	1.07	2.63	3.21	4.88	5.27
average				2.71	3.16	5.15	5.42

^{a}Pu(IV) amended concentration = 8.4 × 10^{-14} M, particle concentration = 1.25−1.5 mg/mL groundwater, reaction time = 7 days in dark at room temperature.

0.01; Table 1). Yet no significant increase in DOC was detected in the truly dissolved fraction after the de-ashing step (data not shown). This is consistent with the observations by Yang et al.,[54] who observed a decrease in the alkyl carbon content and an increase of polarity ((O + N)/C) at the surface of HAs after de-ashing. Such changes in chemistry tended to increase the surface hydrophilicity of de-ashed HAs compared to original HAs and thus are expected to enhance the solubility of HA. The significant decrease in K_d values of de-ashed as compared to original HA fractions (paired t test, df = 7, p < 0.001; Table 1) may be in part attributed to the observation that more de-ashed HAs were solubilized into the colloidal fraction than the original HAs. Moreover, the overall affinity of Pu for the de-ashed HAs, as estimated by K_{dc}, also decreased compared to the original HAs (paired t test, df = 7, p < 0.001). In contrast to an increase in surface polarity, increase in surface O content of HAs, and virtually no change in the bulk carboxylate groups of de-ashed HAs, Yang et al.[54] observed a decrease in the bulk oxygen-containing functional groups (not carboxylate but hydroxyl, hydroxamate, etc.) and nitrogen-containing functional groups (e.g., amide, N−OH in hydroxamate) after de-ashing. These functionalities have been proposed to serve as ligands to complex Type-A metals such as Pu.[55] This is evidenced by a decrease of the bulk O content and bulk (O + N)/C ratios of de-ashed HAs compared to their corresponding original HAs measured by elemental analysis.[54] It is likely that during the de-ashing processing O atoms bound to metal ions were diminished, and the surface reaction (e.g., hydrolysis by HF/HCl) could also lead to O attenuation. Furthermore, the content of Fe, which was still in great surplus over Pu, was greatly reduced after de-ashing. Some of that Fe, especially if bound as a polymeric species, could have been available to further bind Pu(IV). Thus, alteration of the functional groups, and, possibly, lack of binding possibilities to polymeric Fe hydroxide species, is another reason for the consistent decrease in K_d values of de-ashed HAs compared to those of the original HAs.

With their ease to be extracted from the soil by solvent water, the initially extracted HAs were considered more mobile than those in the latter extracts,[50] thus the sequentially extracted
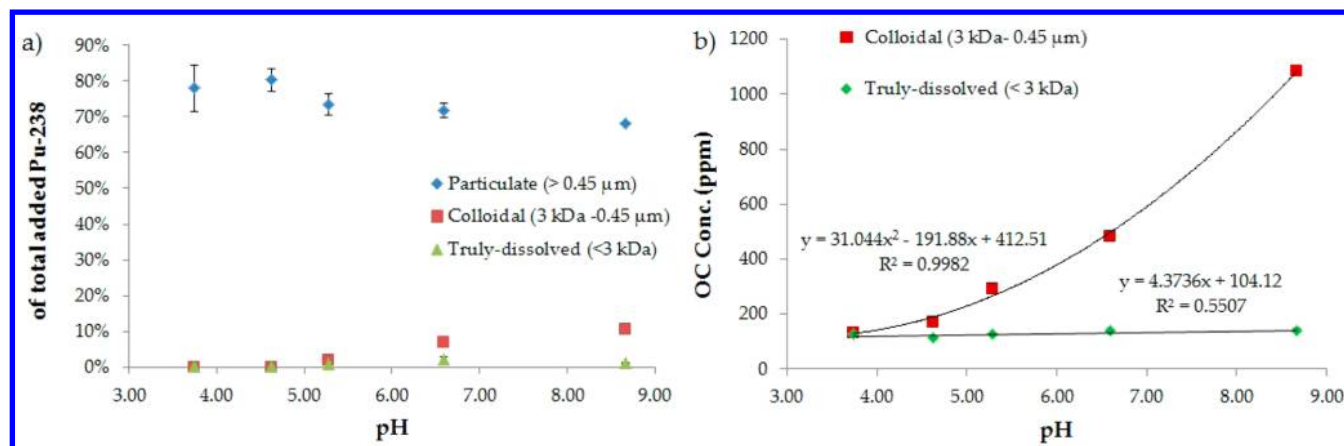
Figure 3. (a) pH-dependent Pu(IV) distribution in the particulate (> 0.45 μm), colloidal (3 kDa to 0.45 μm), and truly dissolved (< 3 kDa) phases of the FSI18 soil−groundwater resuspension; (b) pH-dependent on colloidal organic carbon and truly dissolved organic carbon of the FSI18 soil−groundwater resuspension (soil/water ratio 1:4, Pu concentration 8.4 × 10^{-14} M, equilibrium time 14 days).

HAs from the same source soil represent NOM of different solvent accessibility and thus potential mobility in the environment. This difference in mobility is consistent with their contributions of colloidal organic carbon (COC) to total OC (Table 1), which decreases with each successive extraction for the de-ashed HAs. However, there was no consistent trend for either K_d or K_{dc} values with the sequential extraction order for these eight NaOH extracts. It is also notable that the COM, even though accounting for only <7% of the total OC of the HAs, resulted in much greater log (K_{dc}) values, on average, than corresponding log (K_d) values (an average difference of 2.44 ± 0.55 for de-ashed HAs and 2.26 ± 0.45 for original HAs) (Table 1). Additional work is warranted to characterize this colloidal organic Pu carrier.

At lower pH levels (4.4), K_d values of both de-ashed and original HAs were significantly higher than those at higher pH (7.1) (Paired t test, df = 7, p < 0.001; Table 1). When pH levels are increased, HA becomes more deprotonated and the net charge becomes more negative, leading to intermolecular repulsion and greater dispersion (i.e., solubilization) into the aqueous phase. Nevertheless, the overall binding affinity (K_{dc}) of HAs were not appreciably changed with pH (Paired t test, df = 7, p = 0.606). This suggests that pH variations only affected the partitioning of the different components of NOM, and thus their associated Pu, but did not dramatically alter the overall binding capacity of NOM. To estimate the number of Pu binding sites associated with the NOM of SRS groundwater, we assume the minimum DOC value of 0.1 mg/L (the range is ~0.1−0.7 mg/L)[30] and an 11% carboxylate content in the total OC (the average carboxylate content of de-ashed HA1 to de-ashed HA4 measured by DPMAS-NMR[56]). The resulting concentration of potentially available Pu binding ligands is 9.2 × 10^{-7} mol/L. Comparing that to the Pu concentration in the far field groundwater of 10^{-16} to 10^{-12} M,[26] the concentration of available binding sites is thus in great excess.

Possible Influence of Increased pH Levels on Pu Mobility in the SRS F-Area Wetland Region: Implication on in Situ Immobilization Remediation Efforts. When the pH increased from 3.74 to 8.67, Pu in the particulate phase decreased from (78 ± 6)% to (68 ± 0)%, whereas Pu in the colloidal phase increased from (0 ± 0)% to (11 ± 0)% (Figure 3a). The increase of colloidal Pu (~ 11%) within the pH range is concurrent with an 8× increase in the OC concentration of

the colloidal fraction (pH 3.74 vs 8.67) (Figure 3b). There were no appreciable variations of OC or Pu in the truly dissolved fraction in the investigated pH range. This agrees well with the observation by You et al.[57] that an increase in pH would result in more colloid-associated organic matter (i.e., humic acid) partitioning into the defined soluble portion (<0.45 μm) for the soil-water suspension. Contrary to this, smaller organic matter molecules (i.e., fulvic acid) were less sensitive to pH changes due to their high solubility at any pH value.

Our observed decrease of particulate Pu with increasing pH (from 3.74 to 8.67) is in conflict with previous observations showing a general increase of Pu sorption within the same pH range to sediments or minerals with low concentrations or no NOM.[9,11,12,24,47,58,59] At low pH levels (more specifically, at a pH level below the zero-point-of-charge (ZPC) of the organic-poor SRS soils or sediments which was measured as ~4.2),[60] soil surfaces typically have an overall positive surface charge due to the protonated hydroxyl groups. At pH levels above the ZPC of the mineral phase, the surface hydroxyl groups deprotonate, causing an overall negative surface charge. Therefore, when NOM is absent, electrostatic attraction between Pu and mineral surfaces increases with increasing pH, yielding a greater attraction of the cationic Pu aqueous species and thus a higher sorption at higher pH.[11] However, the presence of NOM, capable of forming ternary complexes with the mineral phase and Pu, complicate Pu sorption to the soil. On one hand, NOM tends to "modify" the surface properties of the mineral phase by providing greater electron density near the mineral surface (e.g., quinone−hydroquinone content) for Pu redox transformation (usually from higher oxidation states (VI) or (V) to lower oxidation states (IV) or (III)), and more abundant and stronger binding sites (e.g., carboxylate, siderophoric hydroxamate, etc.). On the other hand, NOM moieties which usually have a much lower ZPC (pH ~3) than most common minerals,[61] are generally negatively charged at environmentally relevant pH values, and become more deprotonated with increasing pH. At higher pH levels, the SOM are more likely to desorb from the minerals, providing another vector for Pu to enter the mobile phase. For example, Buda et al.[24] showed that the presence of HAs can enhance the sorption of Pu(IV) onto kaolinite below pH 6, compared to the binary system consisting of only kaolinite and Pu(IV); whereas Pu(IV) sorption onto kaolinite

was substantially inhibited above pH 6 when HAs were present. In our current study, the presence of NOM did not significantly enhance the sorption of Pu(V) or Pu(IV) when compared to a typical F-Area organic matter depleted soil (Figure 1) or the mineral phase (Figure 2). Instead, higher amounts of Pu remaining in the mobile phase (i.e., colloid phases) were facilitated by the presence of soil COM, as demonstrated in all experiments. This is explained well by the consistent increase in release of COM and associated Pu accompanying an increased pH (Figure 3). Previous observations in a field study indicated that ^{239}Pu concentrations in a well (no. 4) downstream of the base injection remediation point decreased only slightly from 4 $\times$ 10^6 atoms kg^{-1} to 1 $\times$ 10^6 atoms kg^{-1} between 1998 and 2004, when the pH increased from 3.5 to 6.5 due to the recent base injection activity.[26,27] However, ^{239}Pu oxidation states appreciably shifted from Pu(V)-dominant to Pu(IV)-dominant and the colloidal fraction increased from <4% to >20%. Even though the properties of the colloidally enhanced transport of Pu were never further studied in the F-Area,[27] it is quite possible that ^{239}Pu, mainly discharged from the upstream seepage basins as Pu(V), was reduced to Pu(IV) more rapidly with increasing pH in the presence of humic substances.[47] The reduced Pu was subsequently complexed by colloidal natural organic matter, which is more easily released from the soil under less acidic conditions.

This research suggests that any natural or anthropogenic geochemical processes that may result in an increase in organic-rich soil pH in this acidic plume may also result in a shift from the NOM acting predominantly as a Pu sink at lower pH levels to a Pu source at the newly elevated pH levels. Moreover, the influence of oxidation state on Pu mobility in organic-rich far-field area is largely the opposite of that in low organic matter soils. Reduced Pu(IV) may become more mobile than oxidized Pu(V/VI), as a result of the tendency of Pu(IV) to bond more strongly to NOM that can form mobile colloids, and Pu(V) to sorb more readily to the prevailing solid surfaces possibly aided by reduction to Pu(IV) catalyzed by Fe(II) containing clay minerals.

ASSOCIATED CONTENT

(S) Supporting Information

Detailed descriptions of Pu(IV) and Pu(V) working solution preparation, extraction of the original humic acid (HA), de-ashed HA, and mineral phase from FSI18 soil, and Pu activity analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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3193

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3195

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