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# Plutonium Partitioning to Colloidal and Particulate Matter in an Acidic, Sandy Sediment: Implications for Remediation Alternatives and Plutonium Migration

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Plutonium partitioning within a bulk, freshwater sediment and to specific size fractions of the sediment was determined. Fission track analysis was used to observe the spatial heterogeneity of fissile isotopes of Pu and U in the sediment. For the bulk sediment, a six-step sequential extraction scheme was used to elucidate Pu partitioning. Although no direct Pu speciation is obtained from our sequential extraction scheme, this study demonstrates that the partitioning information obtained is more useful for evaluating ex-situ remediation treatments than information obtained from complete digestion and analysis of the bulk sediment. The majority of $^{238}$Pu and $^{239+240}$Pu appear to be partitioned in the oxidizable fraction, suggesting that Pu is primarily associated with organic matter in the bulk sediment or may exist as a discrete, oxidizable phase. By varying filter pore size used to separate the sequential extraction leachate solution from the remaining solid phase, a fraction of $^{238}$Pu associated with colloidal material was observed, and chemical evidence suggests that this colloidal material is relatively refractory. Pu partitioning to various size fractions of the bulk sediment was also compared to the percent organic carbon present in those size fractions. Interestingly, little correlation was observed between the percentage of organic carbon and concentrations of Pu isotopes in the various size fractions, although differences were observed in the distributions of $^{238}$Pu versus $^{239+240}$Pu in the size fractions. These results suggest that other sediment phases may also be important for Pu partitioning. Our observations are described in the context of feasibility of various remediation options.

## Introduction

Through activities ranging from nuclear weapons testing to plutonium production to nuclear accidents, significant quantities of soils and sediments have been contaminated with plutonium (Pu) and other actinides. For example, recent estimates suggest that over 73 million cubic meters of soils and sediments in the U.S. alone have been contaminated with actinides and fission products by Department of Energy defense nuclear activities (*1*), with even larger volumes of Pu contaminated soils and sediments generated in other countries such as the former Soviet Union (*2*). The costs for remediation of these environmental materials in the U.S. alone have exceeded \$5−7 billion dollars annually over the past several years (*3*). Developing safe and cost-effective remediation strategies requires an understanding of the chemistry that controls the sorption, or partitioning, of Pu to these natural matrices.

Soils and sediments are complex assemblages of oxides, clay minerals, silts, organic materials, and other coatings (*4*), presenting a variety of surfaces to which trace metals can sorb (*5*). These different surfaces each exhibit distinct reactivities, and cation sorption generally follows electrostatic trends, where $M^{4+}_{sorbed} > M^{3+}_{sorbed} > M^{2+}_{sorbed} > M^{+}_{sorbed}$ (*5, 6*). The chemical form, or speciation, of plutonium plays an important role in the extent to which it sorbs to a soil or sediment. Pu can exist in multiple oxidation states with a wide range of cationic charges extending from +1 (as the $PuO_2^+$ moiety) to +4 (as the simple tetravalent cation) (*7*). While speciation refers to the chemical form of the metal ion, we define partitioning within a soil or sediment as the distribution of Pu among the various components of the soil/sediment matrix, irrespective of the Pu valence state. In complex natural environments, speciation and partitioning are related to one another but are distinctly different parameters. In most natural aquatic systems contaminated with Pu, the majority of the Pu is associated with sediments, although much smaller but measurable quantities may be observed in the water column. This is frequently explained by Pu redox equilibria, where $Pu^{4+}$ in the solid phase (as either $PuO_2$ or $Pu(OH)_4$ or sorbed $Pu^{4+}$) can coexist with aqueous forms of $PuO_2^+$ (*8*).

Sequential extraction (SE) techniques are often used to study the partitioning of contaminant metals within a soil or sediment. Described by Tessier (*9*) and subsequently modified by many others (e.g., refs *10−15*), this approach is intended to selectively dissolve specific soil or sediment components using chemical treatments. As shown in Table 1, increasingly aggressive chemical treatments are applied sequentially, and the metal ions removed by each treatment are determined. Limitations to SE methods include the following: (1) the requirement that each soil or sediment phase targeted for dissolution by a treatment step is operationally defined; (2) possible incomplete extraction of an operationally defined solid phase; and (3) the potential for readsorption of the analyte(s) of interest to the remaining solid phase. However, SEs can provide useful information on the “environmental availability” of contaminants (*16−18*), which is essential for assessment of contaminated ecosystems and for evaluating site remediation alternatives and cleanup technologies.

In designing a SE approach, chemical and physical characteristics of the soil or sediment matrix must be considered along with the chemistry of the contaminant of interest. Because of the complexity of Pu environmental chemistry, this second consideration is quite important. Recently, significant effort has been devoted to defining an SE method for Pu and other actinides (Table 1) that optimizes dissolution of defined sediment phases while minimizing readsorption of the actinide contaminants to the remaining solids (*15, 16, 18, 19*). This method also allows discrimination between highly refractory Pu oxides such as that generated during weapons testing and other Pu-bearing solids that occur from releases of nonrefractory solids and/or contaminated aqueous waste effluents.

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**TABLE 1. Sequential Extraction (SE) Method Used in This Work (*15*)[a]**

| step | desired geochemical phase | extraction reagent | reagent: sample ratio | temp (°C) | time (h) |
|---|---|---|---|---|---|
| | | **Six-Step Method** | | | |
| 1 | exchangeable | 0.4 M $MgCl_2$ pH 4.5 | 15:01 | room | 1 |
| 2 | carbonate | 0.5 M $NH_4Ac$ (pH 5) | 15:01 | room | 2 |
| 3 | reducible | 0.1 M $NH_2OH-HCl$ in 25% HAc pH 2 ($HNO_3$) | 15:01 | 70 | 6 |
| 4 | oxidizable | 30% $H_2O_2$ in 0.02 M $HNO_3$ | 15:01 | 50 | 4 |
| 5 | acid/sulfide | 4.0 M $HNO_3$ | 15:01 | 90 | 4 |
| 6 | residual | $KF/Na_2SO_4$[34] | | 900 | |
| | | or $LiBO_2$/HF fusion[35] | | 1000 | |

[a] Separations of aqueous and solid phases were performed by centrifugation followed by filtration. To test the effect of filter pore size, two separate SE experiments were performed on sediment from pond B. In one case, a 0.45 $\mu$m filter was used; in the other case, a 0.1 $\mu$m filter was used. See text for more details.

Using this approach, Pu partitioning has been studied in a variety of soils and sediments. Working with an ocean sediment characterized and standardized by the National Institute of Standards and Technology (NIST), Smith (*15*) demonstrated that Pu was mostly associated (74%) with amorphous mineral phases and organic matter (OM). In an acidic, sandy lake sediment with minor quantities of OM, we have observed that Pu is partitioned primarily with OM and other oxidizable materials, while only small fractions of Pu appeared to be associated with iron oxide coatings (*20*). Although other studies have employed different SE methods, the importance of Pu-organic matter interactions has been demonstrated. For example, in Lake Kiziki (a mesotrophic lake in Japan) the amount of Pu partitioned to the organic fraction ranged from 44−66%, depending on the depth of the sediment. The percent of Pu found in the organic fraction of Lake Towada sediment (an oligotrophic lake in Japan) ranged from 5−54% (*10*). Sequential extraction results from a sediment taken from a small canal of the Venice Central area showed the majority of Pu was partitioned to the fraction associated with carbonates and only 10% was associated with OM (*11*). Similar to the ocean sediment studied by Smith, the dominant phases for Pu partitioning to a deep-sea sediment from Japan were identified as amorphous oxide materials, OM, and residual phases (*12*).

Colloids are operationally defined as microparticles and macromolecules of sizes or molecular weights between 1 nm and 1 $\mu$m (*21*). Many researchers (*22−24*) have demonstrated the impact of colloidal and particulate material on trace metal transport in hydrologic systems. Kersting et al. have demonstrated colloidal transport of Pu-bearing microparticles in the vadose zone at the Nevada Test Site (*25*). In oceanic and lake systems, there is evidence that colloids are a crucial link and reactive intermediary in the transfer of particle-reactive metal ions to particles sinking out of the water column (*24*). Colloids are also important in mobile phases in groundwater systems. Research by Kaplan et al. (*26*) suggested that Pu traveled through an aquifer in association with mobile colloids. Previous research by McCarthy et al. (*21*) focused on the mobility of natural organic material (NOM) in environmental systems. Their studies suggested that colloidal NOM would enhance the field-scale transport of contaminants, including organics, metals, and radionuclides.

Soil washing is a common method for the remediation of contaminated soils and sediments (*27, 28*). As an ex-situ process, the most contaminated soils are segregated and then washed with an aqueous solution. Generally, soil fines have a high concentration of contaminants, while coarse materials may be sufficiently clean that contaminant concentrations are below action levels. This permits coarse materials to be disposed of separately (*27*). Once fine material is separated from the coarse soils, the fines may be "washed" with a solution to enhance desorption and solubilization of the contaminant, or they may be solidified and disposed of as a secondary, solid waste. This technique is typically applied to soil particles <53 $\mu$m (*27, 28*).

The purpose of the work described herein is to evaluate the effects of colloidal and particulate matter on Pu partitioning within an acidic, sandy sediment. We have evaluated the impact of colloidal material on Pu partitioning results by varying the pore size of filters used to separate the dissolved fraction from the solid phase (0.10 $\mu$m and 0.45 $\mu$m). We have also studied Pu partitioning to various size fractions of the bulk sediment. This sediment was chosen because it was contaminated by two well-documented sources of different isotopes of Pu which were introduced by different physical processes (*29*). Despite these differences, no evidence for isotopic fractionation of Pu in these sediments has been previously reported (*20*). However, we demonstrate herein that consideration of the impact of colloids and particle size on the partitioning of the different Pu isotopes is necessary to elucidate the differences in the Pu geochemistry in this system. This kind of information is essential for developing safe and cost-effective remediation alternatives and for evaluating the feasibility of various remediation technologies.

## Experimental Section

**Sediment Sampling and Characterization.** Sediments were collected from pond B, at the Savannah River Site (SRS) near Aiken, SC, via a grab sampler in December 1996. Pond B was constructed in 1961 and used as a secondary cooling reservoir for two nuclear production reactors until the mid-1960s. Due to a combination of fuel element ruptures and leaks in the primary reactor cooling systems, water and sediments in the pond were contaminated with actinides and fission products. This resulted in $^{239+240}$Pu activities approximately five times greater than activities expected from global fallout in this region (*29, 30*). The primary source of $^{239+240}$Pu was a leaky reactor cooling system, resulting in Pu dispersal by an aqueous pathway (*41*). Refractory $^{238}$Pu contamination in pond B originated from production of satellite power sources at the SRS, and is believed to have been released via atmospheric inputs (*31*).

The location in the lake from which the sediments were collected is known to become anoxic during summer stratification. Initial characterization experiments were performed using samples dried at 60 °C. The methods used and results obtained are shown in Table 2. Organic carbon (OC) is directly correlated to the OM present in sediment and an OC measurement is often used for the basis for estimating the amount of OM present. However, depending on the type of soil or sediment, a different correction factor may be necessary (*32*). Because of this we have chosen to report OC, although our results will be discussed in terms of OM.

**Fission Track Analysis.** Fission track analysis (FTA) was completed using Washington State University's 1 MW TRIGA

**TABLE 2. Chemical and Physical Properties of Pond B Sediment**

| properties | |
|---|---|
| **Chemical Properties** | |
| organic carbon (*43*) | (2.58 ± 0.29) % |
| pH in 18 MΩ $H_2O$ (*44*) | (4.70 ± 0.02) |
| cation exchange capacity (*45*) | (114 ± 64) mol/kg |
| **Physical Properties** | |
| **Particle Size Distribution & Texture** | |
| sand (4.75 mm−53 μm) | (64.5 ± 2.8) % |
| silt (53−2 μm) | (17.6 ± 1.1) % |
| clay (<2 μm) | (17.90 ± 1.7) % |

fueled reactor as a neutron source. Isotopes with high fission cross sections [$^{239}$Pu ($\sigma_f$ = 750 barns) and $^{235}$U ($\sigma_f$ = 585 barns)] absorb neutrons, which induce fission and the subsequent fission events incur damage in a plastic detector. In this work, Lexan served as the detector.

To prepare the samples, a slurry with water was made and small drops were placed on the Lexan and allowed to dry. The samples were wrapped in Parafilm and packaged for irradiation in 2-dram plastic vials. The sample and detector were irradiated with a thermal neutron flux of $10^{12}$ cm$^2$ s$^{-1}$ for 7.5 min and allowed to cool for 30 min. The resulting fission tracks were etched by placing the Lexan in 6 M NaOH at 60 °C for 10 min. The Lexan was then rinsed with water and allowed to dry. The resulting tracks were viewed under a microscope at 10×, 40×, and 100× magnification levels.

**Sequential Extraction Methods and Analytical Methods.** Extraction conditions for the SE method are outlined in Table 1. The extraction procedure developed specifically for actinides (*15*) and analytical methods used have been reported elsewhere (*20*). Either a 0.45 μm or 0.10 μm filter was used to filter the leachate solutions between each extraction step, as indicated.

Samples were prepared differently for determination of the stable elements and actinide isotopes in the total and residual samples. For analysis of the stable elements, the total and residual sediment was digested using a modified version of the lithium metaborate fusion (*33*). For Pu isotope determinations, samples were digested using a KF/$Na_2SO_4$ fusion as described by Sill et al. (*34*). All reported uncertainties represent 1$\sigma$.

*Plutonium Determination.* The leachate solutions for isotopic Pu analysis were prepared as decribed by Kressin et al. (*35*), employing $^{242}$Pu (NIST SRM 4334F) as a monitor of the chemical yield. For leachates generated in the reducible treatment, an addition of $NaNO_2$ as a weak oxidizing agent was included prior to the drying step to eliminate the reducing effects of the hydroxylamine-hydrochloride. Pu was electrodeposited onto 5/8″ stainless steel planchets for alpha spectrometry (*36*).

$^{238}$Pu and $^{239+240}$Pu were determined using either an EG&G Ortec 576 or EG&G OCTETE alpha spectrometer. The samples were counted for 300 000 s with background correction. Typical detection limits for samples were approximately 0.05 dpm for $^{238}$Pu and 0.03 dpm for $^{239+240}$Pu.

*Stable Element Determination.* For elemental analyses, the leachates were dried and reconstituted in 50 mL of 2 M $HNO_3$ to minimize matrix effects during analysis. Stable elements were determined using a Jobin Yvon JY24 sequential inductively coupled plasma−atomic emission spectrometer (ICP-AES), equipped with a pneumatic nebulizer. The analyses were completed using matrix-matched standards.

**Particle Size Fractionation.** Particle fractionation was completed on two separate 80 g samples using the methods described in Jackson (*37*). Unlike typical particle size fractionation methods, sediment coatings such as organic matter or iron oxides were not removed to preserve the natural state of the sediment. The Pu isotope compositions of each size fraction were determined by digestion using a KF/$Na_2SO_4$ fusion as described by Sill et al. (*38*).

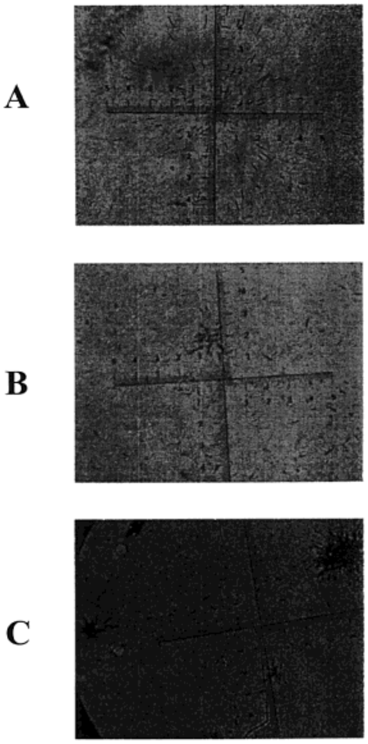

**FIGURE 1. Fission track analysis of Pond B sediment. Starlike bursts of lines represent the association of fissionable isotopes to a particle. Pictures show fission bursts in (A) nonfractionated pond B sediment, (B) 2−0.2 μm fraction, and (C) 20−5 μm fraction of pond B sediment. All images are at 40× magnification.**

## Results and Discussion

**Fission Track Analysis.** The physical distributions of fissile actinide isotopes in this sediment are shown in Figure 1. Notice that the tracks are not randomly distributed in the track detector but rather appear as discreet "star burst" patterns. This demonstrates that the $^{235}$U and $^{239}$Pu in this sediment are associated with specific particles and/or exist as discreet particles of various sizes (*39*). Previously, we have reported on the partitioning of U within this sediment, which is highly refractory. The $^{235}$U:$^{238}$U isotopic ratio of (0.808 ± 0.136)% suggests that it is primordial (*20*). Previous studies by Pinder et al. (*29*) suggest that Pu in the Pond B system is bound to particles in the water column that are cycled to the sediment via settling. As sedimentation occurs, these particles will become part of the sediment matrix.

**Sequential Extraction Results.** In previous work (*13, 20, 40*), we have studied the differences observed for the partitioning of actinides, fission products, and stable elements within this and other SRS sediments when two or more SE methods are applied, and, in general, the results obtained by different methods for a given soil or sediment are consistent with each other. Specifically, we have compared the partitioning of U and Pu observed by the method in Table 1 and an earlier method by Tessier (*9*). Recall that the SE method used herein is designed to discriminate between highly refractory Pu oxides that are only dissolved by fusion treatments (as in step 6, Table 1) from other relatively insoluble Pu solids that can be digested with an acid sulfide treatment (step 5). The consequence of including the acid sulfide treatment is that other relatively insoluble stable elements that are categorized as residual by other SE methods

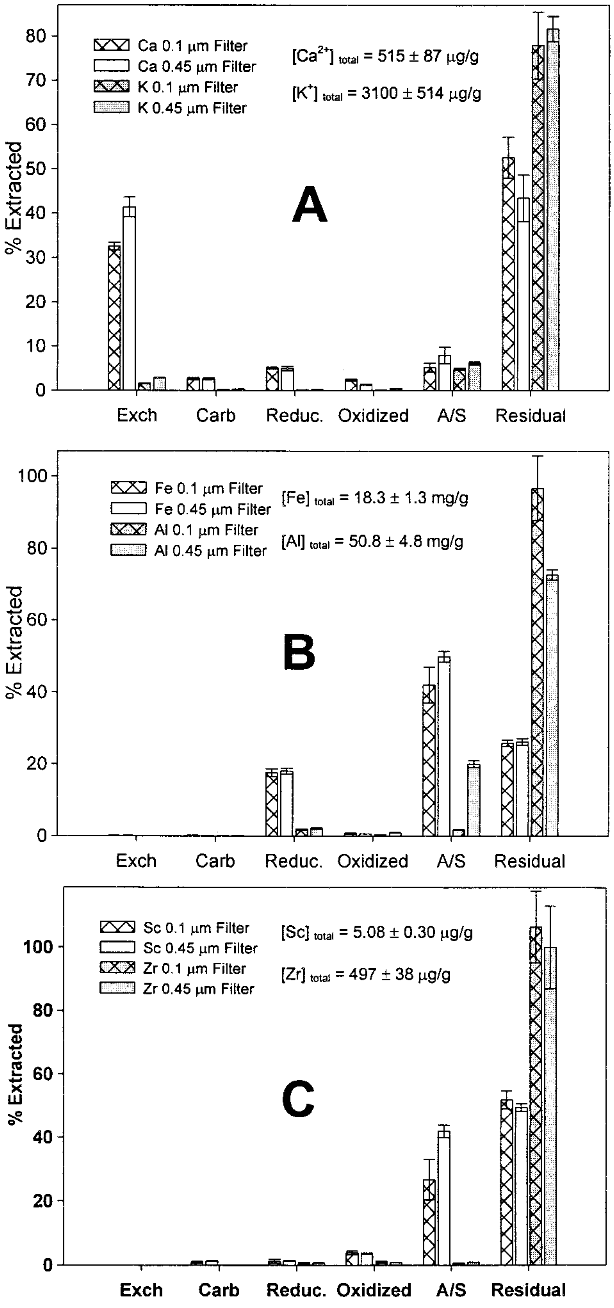

**FIGURE 2. Elemental partitioning within the pond B sediment using a six-step SE method with varying filter size. Hatched bars indicate the use of a 0.1 μm filter, solid bars are for 0.45 μm filter. (A) Ca and K, (B) Fe and Al (Note the differences in Al partitioning to the acid sulfide and residual fractions with different pore sizes.), and (C) Sc and Zr.**

can be extracted by the acid sulfide treatment (*20, 40*). It is important to note that SE methods have limitations, as described in the Introduction, and the partitioning suggested by a given SE method is operationally defined. Thus, the expectation of duplicating the exact partitioning information for a given sediment by two or more SE methods is not realistic.

The extraction of stable elements observed using the same SE method with two different filter sizes is shown in Figure 2. The elements are grouped according to their expected geochemical behaviors. Calcium and potassium were monitored because they tend to participate in exchange reactions. As shown in Figure 2a, a significant percentage of Ca is extracted in the exchangeable fraction with very small amounts extracted in the intermediate treatments when a 0.45 μm filter is used. Large fractions of both Ca and K are observed in the residual fraction; the Ca and K associated with this fraction are assumed to be part of the refractory clay mineral matrix. The predominance of K found in this fraction is explained by the presence of illite in the sediment. When a 0.10 μm filter was used, only small differences in the SEs of these two elements were observed. The overall trends in the partitioning of Ca and K do not appear to be affected by changes in filter pore size.

The partitioning of Fe was studied because of its redox chemistry; in the pond B system, water column concentrations of Fe (as well as other metals, including Pu) fluctuate seasonally with anoxia (*41*). Regardless of the filter pore size used, the majority of the Fe was refractory, with approximately 70% of the total Fe observed in the combined acid sulfide and residual extracts. This likely represents crystalline Fe oxides and Fe bound in the residual clay and silicate phases. Only 20% was partitioned in the reducible fraction; however, this is a significant concentration of Fe. It is some portion of this smaller fraction of reducible Fe that is assumed to participate in the seasonal cycling. For Fe, filter pore size seemed to have little effect, as only a slight decrease in Fe associated with the insoluble acid sulfide fraction was observed when the smaller filter pore size was used.

The partitioning of Al was studied because it is an important component of clay minerals, making up a significant part of the alumino-silicate matrix. Also, previous work on f-element sorption to similar southeastern coastal plain sediments suggested that gibbsite [$Al(OH)_3$] solubility plays an important role in the extent of sorption and the possibility of colloid formation (*42*). Like Fe, Al was also observed to be primarily refractory; however, the use of the 0.10 μm filter resulted in significant changes in the apparent Al partitioning within the sediment for the last two fractions. A small decrease in the amount of Al partitioned to the oxidizable fraction was observed with the smaller filter pore size. Al in the acid sulfide fraction was reduced by more than 90% when the smaller filter pore size was used, resulting in nearly 100% of the Al appearing as residual when the smaller filter pore size was used. This indicates that Al exists primarily as a colloidal species.

Scandium and Zr were both studied because they are typically refractory in most soils and sediments. Using the 0.45 μm filter, neither of these elements were extracted to any significant extent by the less aggressive chemical treatments, resulting in large amounts of Sc and Zr partitioned to the less soluble acid sulfide and residual fractions. Little differences were observed when a 0.10 μm filter pore size was used.

Figure 3 shows the partitioning of $^{238}Pu$ and $^{239+240}Pu$. Note that although OM in this sediment is low, it appears to be important in the partitioning of Pu for the bulk sediment. This is consistent with previous studies that have suggested the importance of OM in the chemistry of Pu in natural waters (*21, 22*). An alternative explanation for the extraction of Pu by the leachate intended to target oxidizable phases is that the Pu may exist as a discrete phase that is leached by extraction with an acidic solution of 30% $H_2O_2$. This treatment could oxidize the insoluble $Pu^{4+}$ to the more soluble $PuO_2^{+}$ or $PuO_2^{2+}$.

Although the sources and chemical forms of the $^{238}Pu$ and $^{239+240}Pu$ contamination were different, we see no evidence for isotopic fractionation in the partitioning of these isotopes to the sediment when the larger pore size filter was used. When a 0.10 μm filter was used, $^{239+240}Pu$ partitioning showed no changes in the any of the treatments. Similarly, little change was observed for the partitioning of $^{238}Pu$ in the first three fractions; however, the $^{238}Pu$ partitioning was reduced in the oxidizable and acid sulfide fractions with the

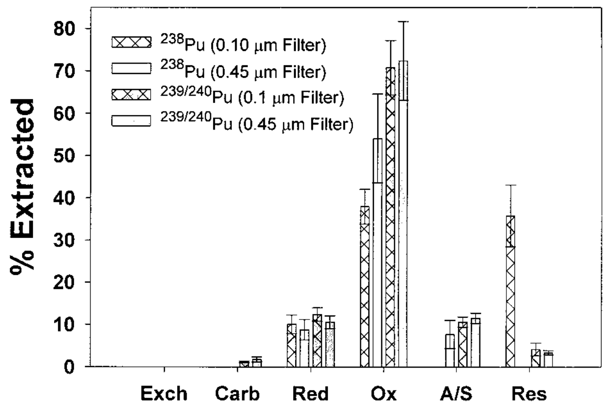

**FIGURE 3. Pu partitioning within pond B sediment using a six-step SE method with varying filter size. White bars indicate $^{238}$Pu; shaded bars indicate $^{239+240}$Pu. Hatched bars indicate the use of a 0.1 $\mu$m filter, solid bars are for 0.45 $\mu$m filter. Note the changes in $^{238}$Pu partitioning only when filter pore size was varied.**

smaller filter pore size. With lesser amounts of $^{238}$Pu extracted in the first five treatments, the amount of $^{238}$Pu remaining in the residual fraction was increased above the detection limit, resulting in approximately 40% of $^{238}$Pu appearing as residual.

The changes in partitioning observed with the smaller filter pore size may be due to colloidal material present in the sample or the creation of colloidal material during the SE of the samples. Nevertheless, our results suggest a correlation between $^{238}$Pu and Al partitioning as well as isotopic differences in Pu partitioning. Although FTA demonstrates that $^{239}$Pu is associated with specific particulates in this sediment, the filtration results suggest that none of these particles are colloidal in size. However, a significant fraction of the $^{238}$Pu does appear to be colloidal, which is consistent with its original dispersal as atmospheric particles (*29, 31*). These results demonstrate the importance of considering filter pore size when SEs are used to determine metal partitioning.

**Particle Size Fractionation.** The results of the particle size fractionation are shown in Figure 4A. The amount of OC present in each size fraction is shown in Figure 4 (parts b and c). Note that although surface area increases with decreasing particle size, the fraction of OC associated with each size fraction does not follow such a trend. As shown in Figure 4c, when the % OM was normalized to the total sediment, the 53−20 $\mu$m fraction had the highest amount of OM relative to the other fractions. Because our SE results suggested that the majority of the Pu in the bulk sediment was associated with OM, we focused on the fractions ≤53 $\mu$m for the Pu analyses.

Figure 5(parts A and B) shows the activities and percentages of $^{238}$Pu and $^{239+240}$Pu in each size fraction, respectively. The activities of $^{238}$Pu in the various size fractions were equally distributed, ranging from 2.5 to 6 mBq/g. However, the $^{239+240}$Pu appeared to be concentrated in the 5−2 $\mu$m fraction. When the concentration of Pu in each size fraction is converted to % Pu in the total sediment by size fraction, different trends are apparent. The $^{238}$Pu, assumed to be input in a particulate form (*31*), is found primarily in the smaller size fractions (2−0.2 $\mu$m and <0.08 $\mu$m). $^{239+240}$Pu, dispersed via an aqueous pathway (*41*), is more uniformly distributed among all the size fractions with exception of the 0.2−0.08 $\mu$m fraction of which very little material was present in the bulk sediment (Figure 4).

Comparison of the distribution of the OC among the various sediment size fractions (Figure 4) to the distribution of Pu isotopes in the size fraction (Figure 5) shows little correlation between OM and the percentage of $^{238}$Pu partitioned in each size fraction, whereas SEs indicate that as much as 45% of the $^{238}$Pu is partitioned to OM. Recall that application of the smaller filter pore size resulted in approximately 35% of this Pu isotope appearing as residual. Notice that more than 25% of the $^{238}$Pu is bound to the smallest sized clay fraction (<0.08 $\mu$m and 0.2−0.08 $\mu$m), which contain only minor amounts of OC. This suggests that some of the $^{238}$Pu may exist as discreet $PuO_2$ microparticles that are oxidized and dissolved by treatment with peroxide; this is consistent with knowledge of the contamination events for $^{238}$Pu. The $^{239+240}$Pu isotopes appear to be more closely correlated to the distribution of OC in the size fractions. The increase observed in the smallest size fraction may represent a small fraction of inorganic colloidal $^{239+240}$Pu that is difficult to discern from the SE/filter pore size results, or it may be an effect of the increased surface area associated with the smaller sized particles.

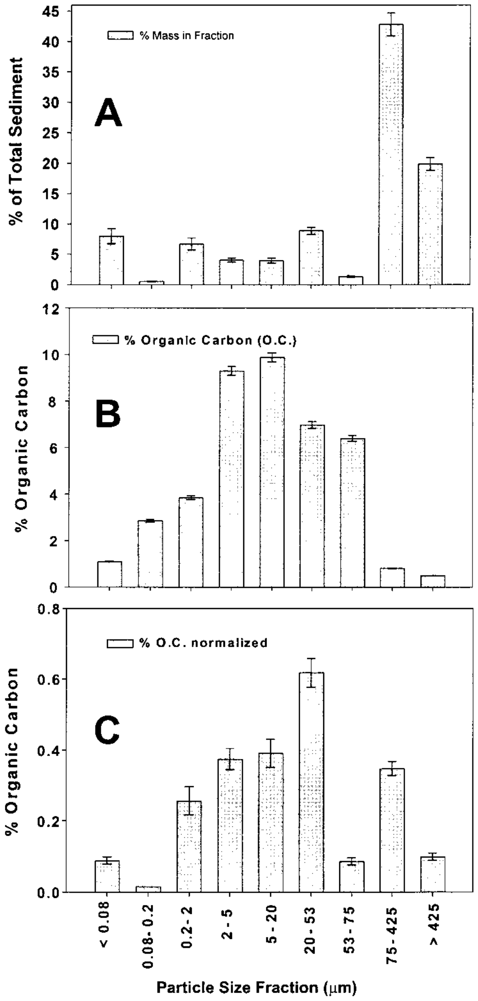

**FIGURE 4. (A) Particle size distribution of pond B sediment, (B) percent organic carbon in each fraction, and (C) percent organic carbon normalized to the weight percent of sediment in each size fraction.**

Although no direct Pu speciation information is obtained from SEs or determination of Pu in various sediment size fractions, our work clearly shows that such approaches provide much more useful information than determinations of total Pu from a complete digestion of the bulk sediment. For example, our results suggest that ex-situ soil flushing to remove clay materials that are less than 2 $\mu$m will only reduce the $^{238}$Pu concentrations in this sediment by 45% at most and will leave as much as 85% of the $^{239+240}$Pu behind. Other ex-situ treatments designed to remove OM and any associated

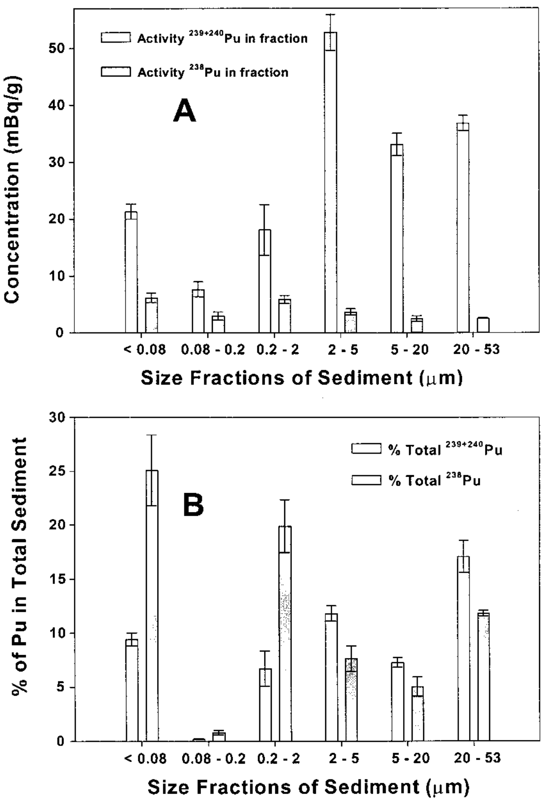

**FIGURE 5. (A) Plutonium activities in each size fraction <53 μm and (B) percent Pu in each size fraction normalized to the weight percent of sediment in each size fraction.**

Pu should reduce the $^{239+240}$Pu by more than 70% and the $^{238}$Pu by 50% or more. However, a significant fraction of the $^{238}$Pu in this system also appears to be colloidal and possibly linked to the chemistry of colloidal Al; therefore, such treatments may be less satisfactory if the colloidal material is not also removed by the treatment. Regardless, decisions on appropriate remediation approaches must be based on an adequate understanding of the chemistry of Pu in the system. Until more sensitive direct methods of determining Pu speciation are available, indirect approaches such as we have described here represent viable site assessment tools.

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## Literature Cited

(1) Ahearne, J. F. *Physics Today* **1997** June, 24.
(2) Bradley, D. J. *Behind the Nuclear Curtain: Radioactive Waste Management in the Former Soviet Union*; Battelle Press: Columbus, OH, 1997.
(3) MacDonald, J. A. *Environ. Sci. Technol.* **1999**, *33*, 314A.
(4) Kennedy, V. H.; Sanches, A. L.; Oughton, D. H.; Rowland, A. P. *The Analyst* **1997**, *122*, R89.
(5) Stumm, W. *Chemistry of the Solid-Water Interface*; John Wiley & Sons, Inc.: New York, 1992.
(6) Brady, N. C. *The Nature and Properties of Soils*; MacMillian: New York, 1990.
(7) Choppin, G. R.; Bond, A. H. *J. Anal. Chem.* **1996**, *51*, 1129.
(8) Choppin, G. R. *J. Radioanalyt. Nucl. Chem.* **1991**, *147*, 1.
(9) Tessier, A.; Campbell, P. G. C.; Bisson, M. *Anal. Chem.* **1979**, *7*, 51.
(10) Nagao, S.; Matsunaga, T.; Muraoka, S. *J. Radioanalyt. Nucl. Chem.* **1999**, *239*, 555.
(11) Testa, C.; Desideri, D.; Guerra, F.; Meli, M. A.; Roselli, C. *Czechoslovak J. Phys.* **1999**, *49*, 649.
(12) Haque, M. A.; Nakanishi, T. *J. Radioanalyt. Nucl. Chem.* **1999**, *239*, 565.
(13) Clark, S. B.; Johnson, W. H.; Malek, M. A.; Serkiz, S. M.; Hinton, T. G. *Radiochim. Acta* **1996**, *74*, 173.
(14) Schultz, M. K.; Burnett, W. C.; Inn, K. G. W. *J. Environ. Radioact.* **1998**, *40*, 155.
(15) Smith, G. E. M.S. Thesis, Florida State University, 1998.
(16) Schultz, M. K.; Burnett, W. C.; Inn, K. G. W.; Thomas, J. W. L.; Lin, Z. *J. Res. Natl. Inst. Stand. Technol.* **1996**, *101*, 707.
(17) *Assessing the environmental availability of uranium in soils and sediments: 1994*; U.S. Nuclear Regulatory Commission NUREG/CR-6232; PNL-9750; Pacific Northwest Laboratory.
(18) Schultz, M. K.; Burnett, W. C.; Inn, K. G. W. *J. Environ. Radioact.* **1998**, *40*, 155.
(19) Schultz, M. K.; Burnett, W. C.; Inn, K. G. W.; Thomas, J. W. L. *Radioact. Radiochem.* **1996,** *7*, 1.
(20) Loyland, S. M.; LaMont, S. P.; Herbison, S. E.; Clark, S. B. *Radiochim. Acta*, **2001**, *88*, in press.
(21) McCarthy, J. F.; Williams, T. M.; Liang, L.; Jardine, P. M.; Jolley, L. W.; Taylor, D. L.; Palumbo, A. V.; Cooper, L. W. *Environ. Sci. Technol.* **1993**, *27*, 667.
(22) Guo, L.; Santschi, P. H.; Baskaran, M. *Colloids Surf. A: Physicochem. Eng. Aspects*, **1997**, *120*, 255.
(23) Santschi, P. H.; Lenhart, J. J.; Honeyman, B. D. *Mar. Chem.* **1997**, *58*, 99.
(24) Baskaran, M.; Santschi, P. H. *Mar. Chem.* **1993**, *43*, 95.
(25) Kersting, A. B.; Efurd, D. W.; Finnegan, D. L.; Rokop, D. J.; Smith, D. K.; Thompson, J. L. *Nature* **1999**, *397*, 56.
(26) Kaplan, D. I.; Bertsch, P. M.; Adriano, D. C.; Orlandini, K. A. *Radiochim. Acta* **1994**, *66/67*, 181.
(27) *Innovations in Ground Water and Soil Cleanup*; National Research Council, National Academy Press: Washington, DC, 1997.
(28) *Ground Water & Soil Cleanup*; National Research Council, National Academy Press: Washington, DC. 1999.
(29) Pinder, J. E., III; Alberts, J. J.; Bowling, J. W.; Nelson, D. M.; Orlandini, K. A. *J. Environ. Radioact.* **1992**, *17*, 59.
(30) Alberts, J. J.; Halverson, J. E.; Orlandini, K. A. *J. Environ. Radioact.* **1986**, *3*, 249.
(31) Alberts, J. J.; Bowling, J. W.; Orlandini, K. A. In *Environmental Research for Actinide Elements*; DOE CONF-841142; 1986.
(32) *Methods of Soil Analysis: Part 3 Chemical Methods*; Soil Science Society of America; 1996; Chapter 34.
(33) Cantillo, A. Y.; Sinex, S. A.; Helz, G. R. *Anal. Chem.* **1984**, *56*, 33.
(34) Sill, C. W.; Puphal, K. W.; Hindman, F. D. *Anal. Chem.* **1994**, *46*, 1725.
(35) Kressin, I. K. *Anal. Chem.* **1977**, *49*, 842.
(36) Glover, S. E.; Filby, R. H.; Clark, S. B.; Grytdal, S. P. *J. Radioanalyt. Nuclear Chem.* **1998**, *1/2*, 234.
(37) *Soil Chemical Analysis Advanced Course*, 2nd ed.; Jackson, M. L., Ed.; 1973.
(38) Sill, C. W.; Puphal, K. W.; Hindman, F. D. *Anal. Chem.* **1994**, *46*, 1725.
(39) Center, B.; Ruddy, F. H. *Anal. Chem.* **1976**, *48*, 14.
(40) Loyland, S. M.; Yeh, M.; Phelps, C.; Clark, S. B. *J. Radioanalyt. Nucl. Chem.* in press, **2001**, *248*.
(41) Pinder, J. E., III, Alberts, J. J.; Bowling, J. W.; Nelson, D. M.; Orlandini, K. A. *J. Environ. Radioact.* **1992**, *17*, 59−81.
(42) Bryce, A. L.; Clark, S. B. *Colloids Surfaces A* **1996**, 107.
(43) Sparks, D. L. In *Methods of Soil Analysis, Part 3 Chemical Methods;* 2nd ed.; Soil Science Society of America: 1996; p 961.
(44) Sparks, D. L. In *Methods of Soil Analysis, Part 3 Chemical Methods;* 2nd ed.; Soil Science Society of America; 1996; p 475.
(45) Sparks, D. L. In *Methods of Soil Analysis, Part 3 Chemical Methods;* 2nd ed., Soil Science Society of America: 1996; p 1201.

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