

Organic Nature of Colloidal Actinides Transported in Surface Water Environments

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Elevated levels of ^{239,240}Pu and ²⁴¹Am have been present in surficial soils of the Rocky Flats Environmental Technology Site (RFETS), CO, since the 1960s, when soils were locally contaminated in the 1960s by leaking drums stored on the 903 Pad. Further dispersion of contaminated soil particles was by wind and water. From 1998 until 2001, we examined actinide (^{239,240}Pu and ²⁴¹Am) concentrations and phase speciation in the surface environment at RFETS through field studies and laboratory experiments. Measurements of total ^{239,240}Pu and ²⁴¹Am concentrations in storm runoff and pond discharge samples, collected during spring and summer times in 1998–2000, demonstrate that most of the ^{239,240}Pu and ²⁴¹Am transported from contaminated soils to streams occurred in the particulate ($\geq 0.45 \mu\text{m}$; 40–90%) and colloidal (~2 nm or 3 kDa to $0.45 \mu\text{m}$; 10–60%) phases. Controlled laboratory investigations of soil resuspension, which simulated storm and erosion events, confirmed that most of the Pu in the $0.45 \mu\text{m}$ filter-passing phase was in the colloidal phase ($\geq 80\%$) and that remobilization of colloid-bound Pu during soil erosion events can be greatly enhanced by humic and fulvic acids present in these soils. Most importantly, isoelectric focusing experiments of radiolabeled colloidal matter extracted from RFETS soils revealed that colloidal Pu is in the four-valent state and is mostly associated with a negatively charged organic macromolecule with a pH_{IEP} of 3.1 and a molecular weight of 10–15 kDa, rather than with the more abundant inorganic (iron oxide and clay) colloids. This finding has important ramifications for possible remediation, erosion controls, and land-management strategies.

Introduction

Surficial soils of the Rocky Flats Environmental Technology Site (RFETS), CO, contain elevated levels of ^{239,240}Pu and ²⁴¹Am due to wind dispersal of soil particles contaminated in the 1960s by leaking drums stored on the 903 Pad. During storm runoff and pond releases, Pu concentrations are often above the discharge limit of 0.15 pCi/L (1–3). Such a situation is typical for many nuclear waste facilities in the United States,

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where some usually small fraction is dispersed through physical and chemical erosion of surface soils through the action of wind and water. A better understanding of the process(es) that control the phase and, if possible, the chemical speciation of filter-passing forms of Pu is crucial for evaluating actinide transport from the vadose zone to surface waters. A wide range of work at Rocky Flats has demonstrated that “particulate” forms of Pu and Am make up a significant fraction of actinides in surface waters (e.g., refs 1–3) and that particle transport is greatest during rainfall events (4). We suggest here that surface water transport of Pu and Am is dominated, during soil erosion events, by aggregation and disaggregation processes of colloids, not just by particle erosion and transport. Clearly, knowledge of the phase speciation of actinides is a prerequisite for the development of defensible cleanup strategies. Questions concerning the environmental forms of Pu and Am have direct bearing on evaluating the importance of their various migration pathways.

Organic matter can modify the surface charge and characteristics of particle and colloid aggregates. Depending on the type of natural organic matter, particles and colloids can aggregate (“coagulate”) or disaggregate. For example, small organic molecules such as fulvic acid and other organic acids can increase dispersion and disaggregation of soil colloids through their effect on particle charge, while large surface-active organic molecules such as polysaccharides act to bind colloid particles together (e.g., refs 5–7). Colloid/particle partitioning is an important colloid characteristic because it reflects the affinity of colloidal material for suspended particles and immobile soil media, and thus, colloid stability. Therefore, contaminant partitioning between particles, colloids, and truly dissolved phases is a primary parameter for (1) estimating colloid mobility and (2) development of engineering and management strategies for removing colloidal-associated actinides from surface water.

Our hypothesis is that the elevated ^{239,240}Pu and ²⁴¹Am concentrations in Rocky Flats runoff are related, besides hydrodynamic conditions (i.e., storm surface runoff vs base flow), to the nature and types of organic matter present in soils, stormwater and pond water at the time of sampling. To test our hypothesis, we have examined the oxidation state and elemental associations of the dominant Pu species generated via resuspension during storm runoff through filtration, cross-flow ultrafiltration, chemical analysis, and gel isoelectric focusing experiments. In addition, laboratory soil resuspension experiments were carried out using actinide-contaminated soil treated with either commercially available or soil-extracted natural organic compounds to investigate mechanisms of colloid formation during stormwater runoff and to relate colloid stability to organic matter composition.

Materials and Methods

Study Area and Sampling. The selected sampling sites were Pond B5 pond release waters at compliance point GS03 (Walnut Creek at Indiana Street) and stormwater runoff at GS10 (near the most heavily contaminated 903 pad), South Walnut Creek at the B-series bypass (Figure 1). Grab samples were collected by bailing water from the pond or stream using a small container followed by compositing the water into clean 15–20 L carboys (PE, Nalgene) for processing and analysis in the laboratory. In addition, soil samples were collected for extraction of natural organic matter fractions and used in the soil erosion/colloid stability experiments in the laboratory.

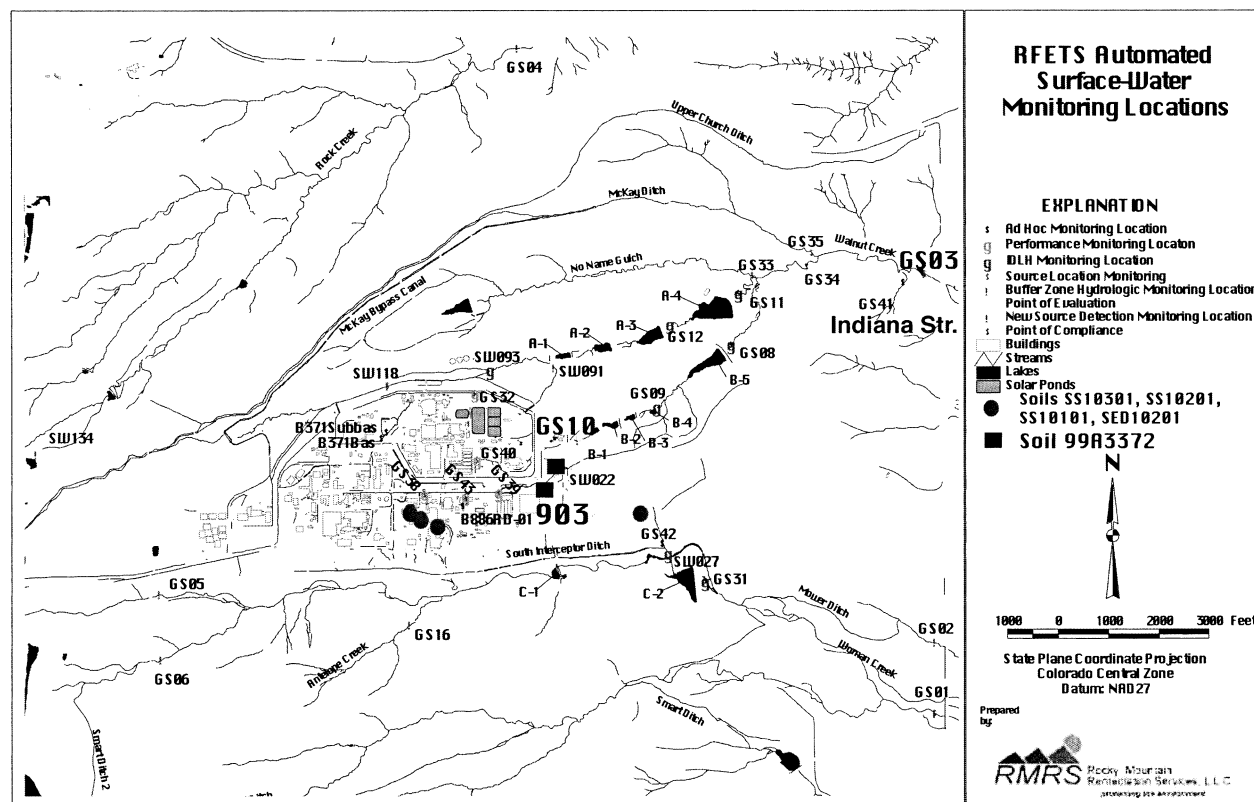


FIGURE 1. Map of sampling locations. Stream stations include GS10 at the upstream end of the B-series ponds and GS03 on Walnut Creek near Indiana Street. Soil samples SED10201, SS10101, and SS10201 were collected near GS27 and soil sample SS10301 near GS42 in the Woman Creek watershed, all in 2001; sample 99A3372 was taken in 1999 from soil near the 903 pad.

Total water samples were collected on August 26 and 27, 1998; April 27, 1999, and April 27, 2000, from a discharge event; and on April 20, 1999, and May 08, 2000, from a storm runoff event. They were size fractionated by filtration and ultrafiltration in a nearby laboratory at the Colorado School of Mines (CSM) for further measurements of $^{239,240}\text{Pu}$, ^{241}Am and organic carbon concentrations at Texas A&M University at Galveston (TAMUG). For both discharge and storm runoff samples, approximately 200 L of water were taken from GS03 and GS10, respectively.

Field samples were also quantified for dissolved organic carbon (DOC), particulate organic carbon (POC), colloidal organic carbon (COC), pH, alkalinity, nutrients (phosphate, silicate, nitrate), suspended particulate matter (SPM), and Fe, Al, Mn, and U concentrations. Methods for measuring DOC, POC, and COC were previously described in Guo and Santschi (8), whereas standard methods were followed for pH, alkalinity, nutrients, SPM measurements. Metals (Fe, Al, Mn, U) were determined using ICP-MS (9, 10).

Phase and Chemical Speciation Determination of Actinides. Both discharge and storm runoff samples were size fractionated in duplicate. About 12–18 L of total water (unfiltered) was set aside for each sample for total $^{239,240}\text{Pu}$ and ^{241}Am measurements. The remaining water was filtered consecutively through a 20 μm and a 0.5 μm filter cartridge to isolate the >20 μm and the 0.5–20 μm particles. About 20 L of the filtered water (<0.5 μm) was set aside for later analysis of the dissolved (<0.5 μm) fraction. The remaining 0.5 μm filtered water was used for ultrafiltration to isolate the 3 kDa (or 100 kDa) to 0.5 μm colloidal fractions using cross-flow ultrafiltration techniques (11–13). Ultrafiltration was carried out within 4–6 h of sample collection. About 30–40 L of filtered (<0.5 μm) water was run through a 3 kDa spiral-wound filter membrane (Amicon S10Y3), and another

30–40 L were run through a 100 kDa filter membrane (Amicon S10Y100). All size fractions, including the <3 kDa and the <100 kDa permeate fractions, the 3 kDa–0.5 μm and the 100 kDa–0.5 μm retentate fractions, the <0.5 μm fraction, and the unfiltered total water sample, were processed by $\text{Fe}(\text{OH})_3$ precipitation in the laboratory at CSM, after ^{242}Pu and ^{243}Am yield tracer additions. The resultant precipitate was sent to TAMUG for radiochemical analysis of $^{239,240}\text{Pu}$ and ^{243}Am (14).

During the first year (1998), flat filters were used. However, due to filter clogging, 25 cm polypropylene spiral-wound cartridges (Sparkling Clear Industries) were used in subsequent years. Errors from replicate sampling and counting errors were usually larger than any differences from applications of slightly different pore size filters (e.g., 0.45 vs 0.5 μm).

It needs to be pointed out that filtration and cross-flow ultrafiltration are the only methods suitable for the separation and analysis of the environmental forms of actinides present in these waters in the 10^{-3} – 10^{-1} pCi/L concentration range. Other methods, such as field-flow fractionation (15), not only require sample volumes that are 5 orders of magnitude smaller than analyzed here but also rely on the use of foulable membranes as well. However, through extensive calibration tests of cross-flow ultrafiltration, we had previously determined the optimal conditions that minimize artifacts and maximize the reliability of determinations of colloidal species concentrations. For example, extensive calibration and cleaning of cartridge membranes before ultrafiltration, the use of high concentration factors (e.g., >20), was previously shown to be most beneficial for separating colloidal chemical species from large volumes of prefiltered water (11–13).

Aliquots of colloidal samples (the >3 kDa fraction) were then freeze-dried to get powdered colloidal samples for

further chemical characterization, radiolabeled isoelectric focusing experiments, and transmission electron microscopy (TEM) imaging analyses.

Determinations of oxidation states of Pu in the 0.5 μm filter-passing fraction were also attempted using previously described methods (16–18) for Pu concentrations that were 6–9 orders of magnitude higher than concentrations encountered in our field study.

Soil Resuspension Experiments. Laboratory soil resuspension experiments were conducted using Rocky Flats soils (99A3372–002.006, sampled in 1999; SS10101, SS10201, SED10201, and SS10301, all sampled in 2000) as a source of Pu and Am to the surface water to mimic the corelease of dissolved and colloidal organic matter (DOM and COM) and actinides from contaminated soils and to investigate colloid formation and associated actinide partitioning during storm runoff. Experimental protocols used for the soil resuspension experiments are similar to those of sediments described in Guo and Santschi (19).

The soil was first sieved through a 1 mm sieve to reduce inhomogeneity of the Pu activities. This fine soil fraction was added to a Teflon jar containing 0.5 μm filtered tap water, which was rapidly stirred using a stir bar on a stir plate. The resuspension experiments were carried out with variable amounts of commercially available organic matter compounds (i.e., Aldrich humic acids, copolymers of microorganisms, such as alginic acids or Xanthan) and soil extracts (e.g., humic acids). Pu-contaminated soils from the RFETS site were resuspended in the presence or absence of these natural organic substances and then filtered through 0.45 μm polypropylene membrane filters. The solutions were analyzed for DOC, Pu, and Am to determine the extent of colloidal Pu and Am liberation from the soils. Soil concentrations, resuspension times, as well as type and quantity of organic substances were varied to assess colloid formation effects on <0.5 μm filter-passing $^{239,240}\text{Pu}$ activities. In select cases, the filtered fraction was fractionated further using 1 kDa stirred cell ultrafiltration or a 3 kDa Amicon Miniplat system to determine the extent of Pu colloid formation. After resuspension and equilibrium, the slurry solution was prefiltered (0.45 μm) followed by ultrafiltration through a 3 kDa membrane to isolate colloidal materials for surface chemistry, including radiolabeled isoelectric focusing experiments and other characterization.

Column Chemistry and Measurements of $^{239,240}\text{Pu}$ and ^{241}Am . The methods for isotope separation were adapted from EPA method 908.0 (14), U.S. DOE (20), U.S. EPA (21), and Yamato (22). Briefly, each sample was acidified with concentrated nitric acid to pH < 2 and allowed to sit for at least 16 h. For each sample, concentrated HCl was added at 5 mL/L, and ^{243}Am and ^{242}Pu yield tracers were added. The samples were placed on a stir plate, and 5 mL of 40 mg/mL Fe(III) carrier was added. The pH was measured, and concentrated HCl added until pH is < 1. The sample was covered and stirred for 30 min, and the pH was measured again.

Once the pH was < 1, concentrated ammonium hydroxide was added until turbidity remained constant, and then an additional 50 mL was added. The sample was again covered and stirred. After 30 min, the sample was removed from the stir plate, the stir bar was removed, and the precipitate was allowed to settle. The supernate was decanted until the precipitate slurry could be transferred to 250 mL centrifuge tubes. The samples were centrifuged for 30 min at 3000 rpm. The supernate was decanted, and the precipitate was dissolved in concentrated HCl to which 75 mL of 9 N HCl and 2 mL saturated sodium nitrite were added. The samples were then run through a series of three anion-exchange columns (23). The first column separated the Am from the Pu fractions. The Pu was then microprecipitated (as LaF₃) on

a Pall Gelman Metricel 0.1 μm filter, mounted on a stainless steel planchet, and α -counted. The Am fraction was carried through a methanolic anion-exchange column followed by a TEVA resin column. The Am fraction was microprecipitated (LaF₃), mounted on a stainless steel planchette, and α -counted.

All retentate samples from ultrafiltration experiments were first treated with strong acids (HCl and HNO₃) and evaporated after tracer addition prior to the column chemistry.

Isoelectric Focusing Experiments. To determine colloid charge and mobility, colloids were also radioactively tagged with ^{234}Th (IV), ^{14}C , and ^{59}Fe (III) (^{14}C -dimethyl sulfate on the –OH sites of sugars, ^{59}Fe on –OH sites of Fe oxyhydroxides and clay minerals), according to Wolfenbarger and Crosby (24) and Quigley et al. (25). The ^{14}C labeling is a methylation reaction and labels mainly the hydroxyl groups of both neutral and amino sugars (24). Generally, both isotopes were added to a small aliquot of colloids in a batch reactor. Each isotope was measured in the different filter fractions separately using liquid scintillation counting (LSC). Small volumes of ^{14}C or ^{59}Fe radiolabeled colloids were then used in isoelectric focusing gel electrophoresis experiments. The charged molecules migrate through the gel toward one of the electrophoresis electrodes until protonation or deprotonation within the pH gradient results in a net neutral charge for the molecule. A Multiphor II system, purchased from Amersham Pharmacia Biotech, was used. The pH values of the isoelectric focusing system, which applies a high voltage (~2 kV) with very low current across a gel that contains regions of varying pH, maintained on the carrier ampholytes by the applied electric field, were also calibrated using small pH electrodes (25). The gradient sodium dodecyl sulfate–polyacrylamide gel electrophoresis (SDS–PAGE) system, used for molecular weight determination, was calibrated using protein standards, ranging from 10 to 100 kDa, according to manufacturer's specifications. Typically, sample detection within the gel was made using liquid scintillation counting. The gel was sectioned into 1 cm sections and each section was put in a glass liquid scintillation vial with 3 mL 1% SDS. The SDS solution worked as a detergent to wash the molecules out of the gel matrix, which greatly increased counting recovery of the radiolabels. The gel sections were allowed to soak in the SDS solution for 24 h before liquid scintillation fluid was added and the vials counted. For Pu analysis, gel sections were treated with concentrated HCl and HNO₃, after soaking in SDS, and then passed through anion-exchange columns and α -counted.

Results and Discussion

Concentrations and Phase Speciation of $^{239,240}\text{Pu}$ and ^{241}Am . $^{239,240}\text{Pu}$ and ^{241}Am phase speciation results are shown in Table 1, and additional water, organic matter, particle, or colloid parameters are in Tables 1a–c, Supporting Information. The lower end of the $^{239,240}\text{Pu}$ activities in RFETS surface waters, taken on August 26–27, 1998, from Walnut Creek at GS03, is indistinguishable from bomb fallout levels measured in various freshwater and seawater environments (Table 2). Total $^{239,240}\text{Pu}$ and ^{241}Am concentrations in the storm runoff samples taken in 1999 and 2000 were near the discharge limit of 0.15 pCi/L. Pu and Am activity concentrations in storm runoff were always higher than in pond discharge samples. Contrary to the 1998 samples, however, both storm runoff and pond discharge sampled in 1999 showed a large percentage (~60%) in the 0.5 μm filter-passing fraction, which was determined to be mostly colloidal (Table 1). Higher total and 0.5 μm filter-passing Pu and Am activity concentrations measured in 1999 are likely due to physicochemical or biological processes which operate under oxic conditions.

In general, most of the Pu and Am in the water was found in the particulate phase, with most of the remainder in the

TABLE 1. Summary of ^{239,240}Pu and ²⁴¹Am Data in Pond Discharge and Storm Runoff Samples at RFETS^a

| sample ID | size fraction | ^{239,240} Pu activity | | | ²⁴¹ Am activity | | | | % |
|------------------------|---------------|--------------------------------|--------|----|----------------------------|--------|--------|----|-----|
| | | pCi/L | SD | | pCi/L | SD | | | |
| 4/27/00 discharge GS03 | <0.5 μm | 0.0207 | 0.0014 | M | 36 | 0.0112 | 0.0008 | S | — |
| | >0.5 μm | 0.0364 | 0.0020 | D | 64 | — | — | — | — |
| | total | 0.0571 | 0.0021 | M | 100 | — | — | — | — |
| | <3 kDa | 0.0131 | 0.0012 | M | 23 | 0.0030 | 0.0005 | M | 27 |
| | 3 kDa–0.5 μm | 0.0116 | 0.0017 | M | 20 | 0.0082 | 0.0006 | M | 73 |
| 5/8/00 storm GS10 | <0.5 μm | 0.0089 | 0.0018 | M | 10 | 0.0092 | 0.0009 | M | 12 |
| | 0.5–20 μm | 0.0612 | 0.0026 | M | 69 | 0.0406 | 0.0022 | M | 53 |
| | >20 μm | 0.0190 | 0.0067 | D | 21 | 0.0270 | 0.0057 | D | 35 |
| | total | 0.0891 | 0.0061 | M | 100 | 0.0768 | 0.0052 | M | 100 |
| | <3k Da | 0.0010 | 0.0009 | M | 1 | 0.0012 | 0.0007 | M | 2 |
| 3 kDa–0.5 μm | 0.0151 | 0.0018 | M | 17 | 0.0112 | 0.0020 | M | 15 | |
| 4/29/99 dischargeGS03 | <0.5 μm | 0.0174 | 0.0019 | M | 60 | 0.0106 | 0.0011 | M | 65 |
| | 0.5–20 μm | 0.0045 | 0.0006 | M | 15 | 0.0019 | 0.0004 | M | 12 |
| | >20 μm | 0.0073 | 0.0006 | M | 25 | 0.0037 | 0.0005 | M | 23 |
| | total | 0.0292 | 0.0021 | S | 100 | 0.0162 | 0.0013 | S | 100 |
| | <3 kDa | 0.0002 | 0.0006 | M | 1 | 0.0004 | 0.0003 | M | 3 |
| 3 kDa–0.5 μm | 0.0138 | 0.0011 | M | 47 | 0.0096 | 0.0010 | M | 60 | |
| 4/30/99 storm GS10 | <0.5 μm | 0.1372 | 0.0112 | M | 66 | 0.0431 | 0.0030 | M | 51 |
| | 0.5–20 μm | 0.0251 | 0.0018 | M | 12 | 0.0109 | 0.0009 | M | 13 |
| | >20 μm | 0.0468 | 0.0025 | M | 22 | 0.0303 | 0.0022 | M | 36 |
| | total | 0.2091 | 0.0115 | S | 100 | 0.0843 | 0.0038 | S | 100 |
| | <3 kDa | 0.0011 | 0.0009 | M | 5 | 0.0006 | 0.0004 | M | 1 |
| 3 kDa–0.5 μm | 0.1430 | 0.0078 | M | 68 | 0.0488 | 0.0020 | M | 58 | |
| 8/26/98 discharge GS03 | <0.45 μm | 0.0009 | 0.0002 | M | 12 | 0.0005 | 0.0002 | M | 7 |
| | 0.45 μm–20 μm | 0.0030 | 0.0016 | M | 39 | 0.0019 | 0.0020 | M | 25 |
| | >20 μm | 0.0037 | 0.0003 | M | 49 | 0.0051 | 0.0007 | M | 68 |
| | total | 0.0076 | 0.0016 | S | 100 | 0.0075 | 0.0021 | S | 100 |
| | <100 kDa | 0.0006 | 0.0002 | D | 8 | 0.0002 | 0.0001 | M | 3 |
| 100 kDa–0.45 μm | 0.0003 | 0.0001 | M | 4 | 0.0003 | 0.0002 | D | 4 | |
| 8/27/98 discharge GS03 | <0.45 μm | 0.0004 | 0.0001 | M | 7 | 0.0007 | 0.0005 | M | 20 |
| | 0.45 μm–20 μm | 0.0042 | 0.0007 | M | 52 | 0.0010 | 0.0004 | M | 29 |
| | >20 μm | 0.0033 | 0.0005 | M | 41 | 0.0018 | 0.0004 | M | 51 |
| | total | 0.0079 | 0.0009 | S | 100 | 0.0035 | 0.0008 | S | 100 |
| | <100 kDa | 0.0003 | 0.0001 | M | 4 | 0.0004 | 0.0001 | M | 11 |
| 100 kDa–0.45 μm | 0.0002 | 0.0004 | M | 2 | 0.0008 | 0.0001 | M | 23 | |

^a Average of duplicate measurements used when possible. (M) = measured value; (–) = low tracer recovery; (D) = calculated by difference; (S) = calculated as sum.

TABLE 2. Comparison of ≤0.45 μm Filter-Passing Concentrations of ^{239,240}Pu in Different Water Bodies

| ≤0.45 μm filter-passing plutonium (fCi/L) | water body | ref |
|---|---|-----------|
| 0.4–150 | ≤0.45 μm, at GS03 and GS10 | this work |
| 37 | average total concentration at Walnut Creek at GS03 | 1 |
| 0.1–0.5 | ≤0.45 μm, Great Lakes, 1977 | 26 |
| 0.3–1.1 | ≤0.45 μm, Narragansett Bay, 1976–1978 | 27 |
| 0.3–1.1 | New York Bight, 1976–1977 | 27 |
| 0.1–0.3 | ≤0.7 μm, Ob and Yenisey Rivers, 1995 | 28 |

colloidal phase (Table 1). Pu activity concentrations in the particulate fractions (>20 μm and 0.5–20 μm) amounted to about 30–90% in the different years. In most cases, most of the Pu and Am in the 0.5 μm filter-passing fraction was colloidal (i.e., it was filtered out by 100 kDa or 3 kDa ultrafilters, with 20% or less of 0.5 μm filter-passing Pu and Am passing a 3 kDa ultrafilter (Table 1)). During the spring 1999 and 2000, we observed higher fractions of Pu and Am as colloidal forms than in August 1998, a time when Pu

concentrations in the water were close to bomb fallout levels (Table 2). ^{239,240}Pu/²⁴¹Am activity ratios in both particles as in the 0.5 μm filter-passing “dissolved” phases were low (i.e., ~1–3; Table 1), significantly lower than those in RFETS soils, which are 5–7. This could indicate a higher mobility of ²⁴¹Am than ^{239,240}Pu in the watershed.

Chemical, Surface Chemical, and Morphological Characterization of Colloidal Pu. Colloidal Pu concentrations, ranging from 0.3 to 1.6 pCi/g, were similar in concentration to those in suspended matter, which ranged from 0.3 to 1.5 pCi/g (Figure 2a; Table 2, Supporting Information), suggesting that particles and colloids have similar Pu activities and chemical composition. The amounts of colloidal mass (Figure 2b; Table 2, Supporting Information) is also similar to that of particle mass suspended in the water (Table 1, Supporting Information), whereby at GS03 colloid concentrations are slightly more abundant and, at GS10, less abundant than particles. The most striking finding is, however, that there is no significant difference between the colloidal and particulate Pu concentrations at GS10 versus those at GS03 (Figure 2a). Surface soils in the vicinity of the source region (i.e., 903 pad) near GS10 have 10²–10³ pCi/g of Pu, while soils surrounding GS03 have Pu concentrations close to 1 pCi/g. Thus, the most likely source for suspended and colloidal Pu is resuspension of stream bed and bank sediments rather

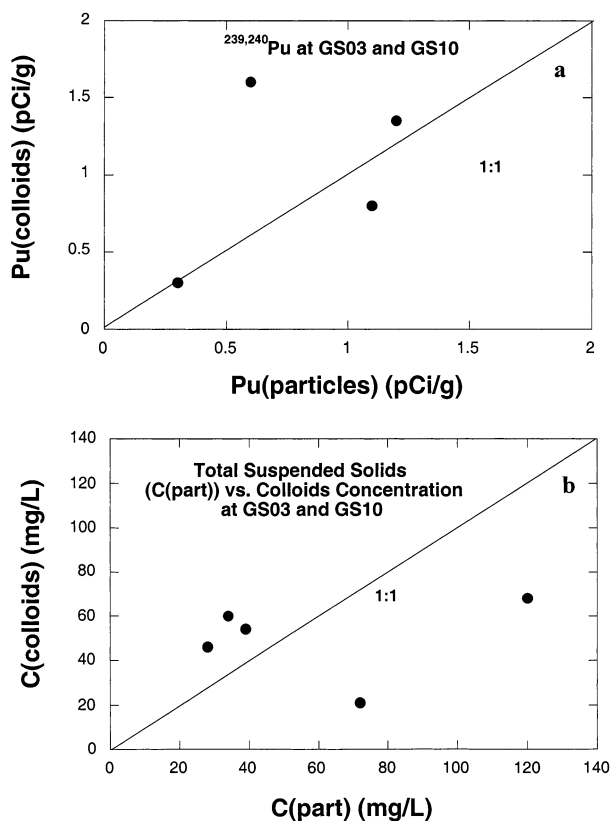


FIGURE 2. Relationship between (a) Pu concentration in particles and colloids and (b) mass concentration (C) of particles and colloids from sample sites GS03 and GS10 collected from 1998 to 2000.

than directly from soils. Linear correlations between concentrations of total Pu and TSS (total suspended solids, C_p) in the water at many measuring stations (I) suggest that total $^{239,240}\text{Pu}$ concentrations in streamwater from the Walnut Creek area at GS03 or GS10 area can be predicted from those of total suspended solids (TSS) concentration. Assuming that the particulate Pu concentration accounts for the majority, the slopes of best-fit lines correspond to Pu concentration of 0.5–0.7 pCi/g (I). However, the scatter around the least-squares lines is often plus/minus a factor of 2–4 away from the least-squares value; a deviation, as we showed previously, was likely produced by having variable amounts of colloidal Pu, in addition to particulate Pu, in the water. More than 50% of $^{239,240}\text{Pu}$ and ^{241}Am in water samples from GS03 and GS10 in 1999 was in a colloidal rather than particulate form (Table 1). Even at other times (i.e., in 1998 and 2000), some samples showed up to 30% of colloidal Pu and Am but, on average, were generally lower.

Colloids were primarily composed of clay and organic matter (0.05–4.7% Fe, 0.07–9.3% Al, 3.1–11.9% OC; see Table 1, Supporting Information), similar to those from soil particles. TEM/EDAX analyses also confirmed that colloid sample RF157 (storm discharge at GS10 on 5/8/00 with 11% OC, 1% Fe, 1.2% Al) was more mineralized and richer in Fe-containing clays than sample RF137 (pond discharge at GS03 on 4/27/00). Using graphite furnace atomic absorption spectroscopy, we found that the pond discharge sample at GS03 on 4/27/00 had 3% OC, 0.2‰ Fe, 0.1‰ Al (see Table 1, Supporting Information). As was evident from elemental analyses and TEM and energy dispersive X-ray microprobe (EDAX) images, these clay- and organic-matter-rich colloids (3 kDa–0.5 μm) were present in microparticles of different sizes (Figure 2, Supporting Information). Results from colloidal TEM and EDAX analysis demonstrated that the main colloids in these two samples were clays (some of which

contained Fe), microbes (mainly bacteria), microbe parts, debris, biogenic silicates, membranous structures (probably biological), titanium microcrystals, and extremely small colloids aggregated into complex structures. These latter aggregates of extremely small colloids could not be properly analyzed morphologically because the samples had been processed as dehydrated powders. Thus, the fractal arrangements and long range associations would likely have been artifactually altered (29).

Colloids from the storm discharge contained higher Al, Fe, Mn, and % OC (Table 1, Supporting Information). The same was true for % OC in suspended particulate matter (Table 1, Supporting Information). While there is a relationship between metal content of colloids and total metal concentration in the 0.5 μm filter-passing fraction, variations in major ion content are clearly not correlated with colloidal composition (Table 1, Supporting Information). Variations in colloidal Pu concentrations also did not co-vary with dissolved or particulate organic matter concentrations (Table 1, Supporting Information).

The colloidal nature of Pu was also demonstrated in the oxidation state determinations. Attempts to determine Pu oxidation states in 0.5 μm filter-passing water samples failed. This was likely due to the 6–9 orders of magnitude lower Pu concentration in field samples than the test samples because of the predominant colloidal and surfactant-like nature of the Pu, which caused it to become enriched at the interface between water and organic phase rather than distribute between aqueous and organic phases. The data from this 2-thenoyltrifluoroacetone extraction is summarized in Table 3, Supporting Information. The results show that the Pu was neither found in the organic nor the aqueous phase but in the interfacial fraction which contained parts from either phase (50 of 300 mL), including the interface. The Pu was thus recovered in exactly the fraction that one would predict if the Pu is indeed associated with surfactant-like colloids and is nonexchangeable (i.e., from the interfacial region).

More information on chemical speciation and oxidation state of Pu could be gained from isoelectric focusing experiments. First, these results (Figure 1, Supporting Information) reveal that colloidal organic matter, extracted from streamwaters, ^{14}C -labeled at the sugar-OH sites, and rich in acid moieties, exhibits strong acid functional groups with $\text{p}K_a$ of 3 or less, imparting these colloids a negative charge and, therefore, allowing the majority of labeled organic matter to migrate to the anode ($\text{pH} \leq 3$) (Figure 1, Supporting Information). Furthermore, ^{59}Fe -labeled iron hydroxides and clay minerals in these stream colloids show isoelectric points between $\text{pH} 8$ – 9.5 , in agreement with literature values (30). The gel electrophoresis results thus suggest that the colloids are mainly composed of strongly acidic organic matter (^{14}C -labeled) and inorganic clay and iron oxide minerals (^{59}Fe -labeled) with more basic functional groups. Isoelectric focusing results from the soil colloids (Figure 3b) are in general agreement with those from stream colloids sampled in 2000 and 1999 (Figure 1, Supporting Information).

The most significant results were, however, obtained from soil colloids extracted from RFETS surface soil 99A3372 (which had sufficiently high Pu concentrations for this experiment; see later section). $^{239,240}\text{Pu}$ in these soil colloids followed more the ^{14}C -labeled organic matter (Figure 3a), rather than the mineral phases (labeled with ^{59}Fe). ^{59}Fe -labeled colloids, likely associated with iron and aluminum hydroxide surface sites, showed isoelectric points (pH_{IEP}) between $\text{pH} 8$ – 9.5 (Figure 3a), in agreement with literature values for these iron oxyhydroxide phases. The pH_{pzc} of PuO_2 is ~ 8 – 9 (30). Thus, PuO_2 colloids should have migrated to pH of 8–9. Ambient $^{239,240}\text{Pu}$ in these soil colloids showed the same electrophoretic distribution as added $^{234}\text{Th}(\text{IV})$ (Figure 3a) and $^{240}\text{Pu}(\text{IV})$ (not shown), added to rehydrated soil or stream colloids in

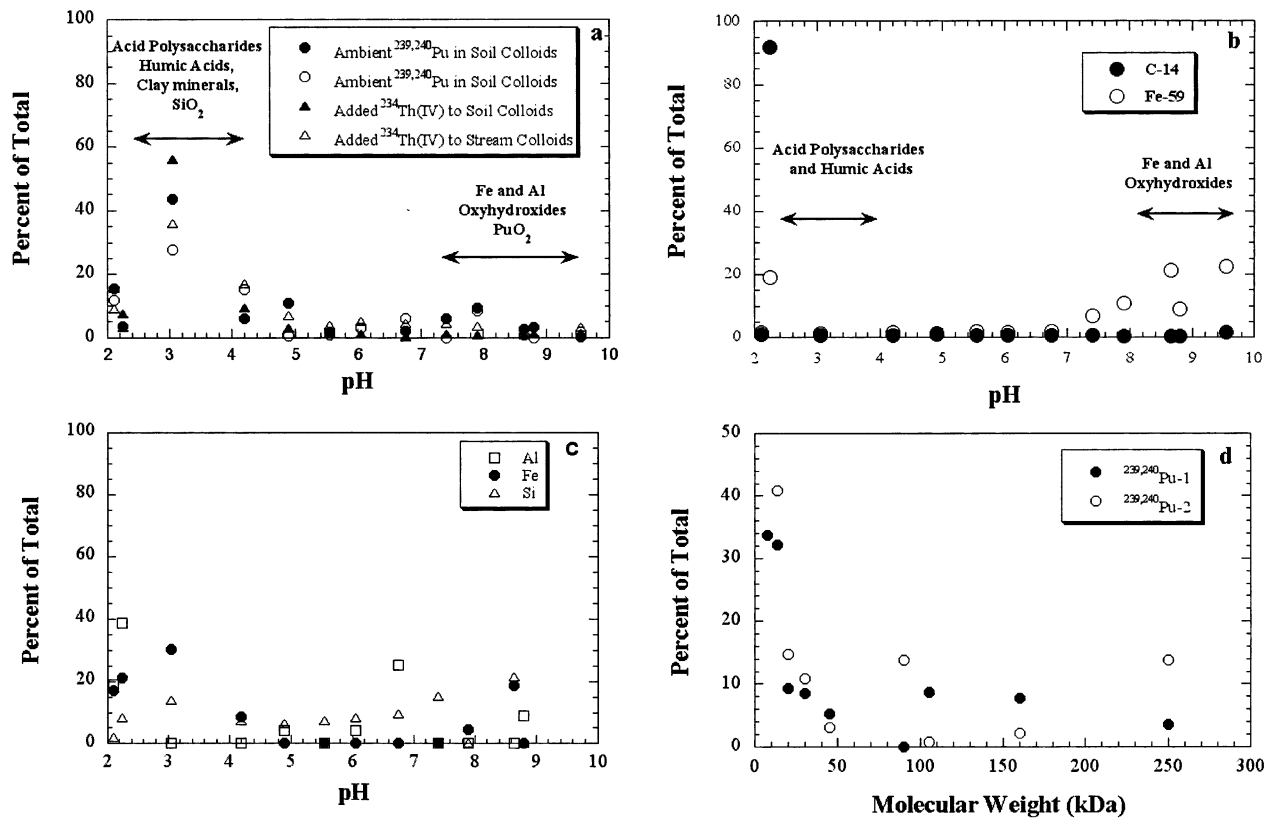


FIGURE 3. (a) Isoelectric focusing results (in duplicate) for ambient colloidal $^{239,240}\text{Pu}$ and $^{234}\text{Th(IV)}$ added to these colloids isolated from RFETS soil #99A3372 through resuspension into water; (b) Isoelectric focusing results (duplicate) for ^{14}C (to sugar-OH groups) and ^{59}Fe labeled colloids from soil resuspension experiment; (c) Isoelectric focusing results for Al, Si, and Fe in soil Pu colloid, determined by AAS; (d) average molecular weight determined of Pu colloid by gradient SDS-PAGE electrophoresis.

separate experiments, demonstrating that ambient $^{239,240}\text{Pu}$ in these colloids is four-valent and dispersed much like the added four-valent actinide tracers.

An important question is the nature of the carrier phase for the “pseudocolloidal” Pu(IV). While organic macromolecules are more likely, inorganic sorbents are possible, too. Some clay minerals, such as montmorillonite and kaolinite, also have pH_{IEP} values between 2.5 and 3.5 and, thus, could have been carrier phases for Pu. However, based on separate Al analysis, we can rule out the presence of Al in the gel electrophoretic region where Pu peaked (pH of 3.1). Aluminum, even though present in the colloid samples and many sections of the gel electrophoresis strips, was depleted in the region where Pu peaked (Figure 3c). Furthermore, Si was present at low concentrations throughout the gel electrophoresis spectrum (Figure 3c) but with no enrichment in the Pu region. Because the colloid sample was initially applied evenly to each pH section of the gel electrophoresis strip, this indicates that Si is still evenly distributed after electrophoresis and therefore was deemed immobile. Also, the pH_{IEP} value of SiO_2 is 2.0 and, thus, would be below the Pu peak region. The fact that small amounts of Fe, shown in Figure 3c, were found focused at the pH_{IEP} of the Pu maximum (pH 3.1, Figure 3a), is contrary to what would be expected from the pH_{IEP} values of all known iron oxyhydroxides, which are higher than 6 (31), and the ^{59}Fe -labeling results (Figures 1 and 3b, Supporting Information). This indicates that stable Fe was not located on the surface of the colloid, where it could have exchanged with ^{59}Fe , and that the Fe species associated with this low pH_{IEP} compound was not the charge determining species. Rather, organic molecules with a low pH_{IEP} of about 3.1, such as some humic or fulvic acids or lipopolysaccharides (31), are determining the negative surface charge. Thus, the organic macromolecule is negatively

charged, as shown in Figure 3a, and of medium molecular weight (i.e., 10–15 kDa) based on the gradient SDS-PAGE results (Figure 3d).

Interestingly, this macromolecule appears to have a similar pH_{IEP} and molecular weight as the strongly Th(IV) binding acid polysaccharide molecule isolated from marine colloidal macromolecular organic matter (25).

These combined electrophoresis results (Figure 3a–d) provide unequivocal evidence for a Pu association to natural organic matter. Even though there are previous reports of Pu association with natural organic matter in soils, the previous evidence was mainly inferred based on colloid size (e.g., refs 32–34) or sequence in sequential leaching schemes (e.g., refs 35–37) rather than chemical or charge determination. To our knowledge, this is the first direct demonstration of an association of Pu with negatively charged macromolecular organic matter in the surface environment. Our evidence strongly argues against the presence of mobile colloidal microparticles consisting mainly of PuO_2 , even though such particles have been documented within some soil profiles (38, 39) near the 903 pad source region. This would make sense, because Fe- and Al-containing or organic colloids are present in the water at $1\text{--}10^2 \mu\text{M}$ concentrations, while colloidal Pu concentrations are at $1\text{--}10^1 \text{fM}$, resulting in Fe- (or Al, organic carbon) to-Pu atomic ratios of $10^8\text{--}10^{11}$. Most likely, the PuO_2 , if it exists, is imbedded in a matrix of organic matter and some Fe and with organic matter determining the surface charge and migration behavior of the 10–15 kDa colloid.

Our evidence also argues against a major presence of Pu in siderophore desferrioxamine-B, which has been shown to be important in bioaccumulating Pu (40) in the laboratory. Even though we did not analyze this compound, it could have been present in our samples. However, such sidero-

phores are expected to have a pH_{IEP} of 8 or higher, as they contain mostly basic N-containing functional groups.

Colloidal Pu Release Potential from Soil Resuspension Experiments: Importance of the Type of Organic Matter for Pu Remobilization through Surfactant Effects. Pu concentrations above the action level (≥ 0.15 pCi/L) occur predominantly during storm runoffs in early spring and summer. During these events, elevated concentrations of colloidal Pu, accompanying those in the particle phase, are being observed (Table 1). We hypothesize that colloidal Pu, as a pseudocolloid (i.e., Pu associated with a different carrier phase), is generated by soil erosion and transport and that remobilization of colloid-bound Pu during soil erosion events is likely aided by elevated concentrations of humic acids in soil waters. This hypothesis was tested using soil resuspension experiments with RFETS soils. Soil resuspension experiments were carried out with varying amounts of RFETS soil 99A3372 (726 ± 68 pCi/g $^{239,240}\text{Pu}$, 4.9% OC) (e.g., 0.5 g of the fine fraction (<1 mm) in 190 mL of filtered tap water). These experiments demonstrate that Pu that is released during these experiments is mostly of colloidal nature (Figure 3, Supporting Information). Colloidal Pu is occurring as a pseudocolloid (i.e., Pu associated with a different carrier phase). As shown in Figure 4a, colloidal Pu concentrations increase over a resuspension time of 1–7 days, in the presence and absence of additional humic or fulvic acid. Thus, there is a significant kinetic effect during the release of colloidal Pu.

Soil resuspension experiments were also conducted at DOC concentrations typical of soil solutions, but elevated compared to typical stream concentrations (4–14 mg of C/L) to examine the role of soil humic acids in the formation of colloidal Pu. When the results from the control experiment with soil 99A3372 (and soil-generated DOC of about 2–3 mg of C/L) are compared with those with increasing Aldrich humic acid concentrations, it is evident that colloidal Pu concentrations significantly increase with increasing added humic acid concentrations. Soil humic acids, extracted from uncontaminated Rocky Flats soils and containing 16% OC, turned out to be considerably more effective than the commercial Aldrich humic acids in remobilizing Pu from contaminated soils into the water (Figure 4b). Most effective were, however, fulvic acids, possibly due to their higher carboxyl group concentration (31), releasing up to 1.2% of Pu from this soil, and citric and oxalic acids (which, however, were added at about 10^3 times ambient concentrations of these molecules).

The increase in % Pu is not due to a shift in pH during soil resuspension, as the pH values during 3-day soil resuspension experiments did not change by more than a few tenths of a pH unit (i.e., pH increased from 8.2 to 8.6 in the controls and from 8.5 to 8.6 in the presence of commercial and extracted humic acids (120 ppm)).

The bacteria-derived acid polysaccharide Xanthan may act as a particle glue, namely, it exhibited strong particle aggregation effects (e.g., strong filter clogging) but only slightly reduced the colloid production potential of resuspended soils (not shown), consistent with its more aggregating nature. The strongest effect of Xanthan was in acting as a particle glue by increasing the cohesiveness of particles and effective particle size of aggregates, thus reducing soil erosion. Pu release from resuspended particles slightly decreased also as a function of alginic acid (an excretion product of algae and bacteria) concentrations in the water (Figure 4b).

Soil 99A3372 was taken from a vegetated area, while soils SS10301, SS10201, SS10101, and SED10201 were taken from soils with little vegetative cover. There was a 10-fold decrease of the amounts of colloidal Pu released at equivalent fulvic acid concentrations from these soils without vegetative cover (Figure 4c). Thus, while vegetation greatly reduces particle erosion rates (by an order of magnitude; 41), soils with

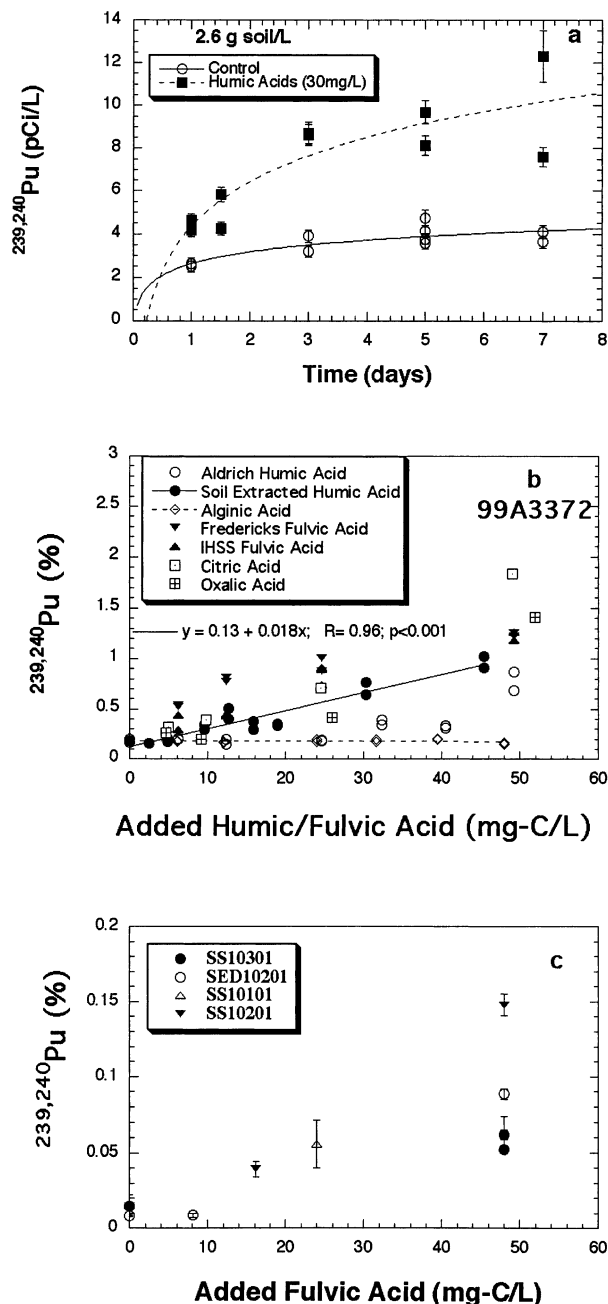


FIGURE 4. (a) Kinetics of colloidal Pu remobilization during soil resuspension (soil 99A3372) with and without addition of Aldrich humic acid ([DOC] = 12 mg/L) to the experimental solution (0.5 g/190 mL). DOC concentrations in solution, resulting from soil resuspension alone, ranged from 2.5 to 2.7 mg/L DOC (0.5 g/190 mL); (b) Percent Pu released from resuspending RFETS soil (99A3372) in the presence of different types of organic acids, such as Aldrich humic acid (41% OC), RFETS soil extracted humic acid (16% OC), fulvic, citric, oxalic and alginic acid, at resuspension times ranging from 3 to 7 days (0.5 g/190 mL). DOC concentration shown is concentration added to the solution; (c) Pu colloids from soils SS10301, SS10201, SS10101, and SED10201 in the presence of Fredericks fulvic acid.

vegetative cover can increase the release of colloidal Pu by an order of magnitude.

However, the fraction of remobilized colloidal Pu, at most 1% in these soil resuspension experiments, was much smaller than what was observed during storm runoff or pond discharge, where the fraction of colloidal Pu passing a 0.5 μm filter was as much as 66% (Table 1). This shows that

suspended matter and colloids are likely derived less from eroding soils directly but more likely from sediment resuspension of stream beds and banks. Such a conclusion agrees with the observation of similar Pu concentrations in colloids and particles at GS03 and GS10 (see earlier discussion) and with the results of soil erosion modeling (41).

Interestingly, a consistent particle concentration effect was observed for both percent of $^{239,240}\text{Pu}$ released and phase partition coefficient (ratio of filter-retained to filter-passing concentration, R_p) decreasing with increasing particle concentration (Table 2 and Figure 4 of the Supporting Information), an observation that has previously been ascribed to the presence of colloidal analyte binding species (42).

One of the conclusions of these soil resuspension experiments is that type and concentration of DOC can have a major effect in remobilizing colloidal Pu into solution. The fact that DOC concentrations measured in 1998, 1999, and 2000 stream samples, which varied from 4 to 13 mg of C/L, showed no obvious correlation with Pu concentrations argues against DOC concentration alone as the major determinant for colloidal Pu release from soils. Compositional differences of DOM between spring and summer, that is, pedogenic organic matter (e.g., humic and fulvic acids) in the spring versus aquagenic organic matter (e.g., acid polysaccharides) in the summer, could be most important in controlling the extent of soil aggregation/disaggregation and, thus, of colloidal Pu remobilization. Most importantly, as we show here, the formation of colloidal Pu species, associated with a negatively charged macromolecule with a pH_{IEP} of about 3.1 and a molecular weight of 10–15 kDa, can become one of the most important vectors for enhancing Pu dispersion in contaminated surface soils.

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Supporting Information Available

Ancillary field data on DOC, POC, PON, SPM, C/N, Fe, Al, Mn, F, Cl, NO_3 , PO_4 , SO_4 , Si, pH, temperature, SC, DO, Alk in the water, and OC, ON, C/N, Fe, Al, Mn, mass concentration in particles and colloids from streamwater, nutrient, gel electrophoretic results of radiolabeled colloids extracted from streamwater, an example of a TEM/SEM picture of colloidal material, as well as the colloidal partitioning (R_p) of Pu during lab soil resuspension experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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