

Actinide Migration from Contaminated Soil to Surface Water at the Rocky Flats Environmental Technology Site

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Abstract:

Surficial soils of the Rocky Flats Environmental Technology Site (RFETS) contain elevated levels of $^{239,240}\text{Pu}$ and ^{241}Am due to wind dispersal of soil particles, contaminated in the 1960's by leaking drums stored on the 903 Pad. Over the past 4 years, actinide mobility in the surface environment at RFETS, Golden, Colorado, USA, was examined through field and laboratory experiments. From measurements of total $^{239,240}\text{Pu}$ and ^{241}Am concentrations in storm runoff and pond discharge samples, collected during spring and summer times, it was established that most of the actinide transport from contaminated soils to streams occurred in the particulate ($0.45\mu\text{m}$) and colloidal ($3\text{kDa} - 0.45\mu\text{m}$) phases. Controlled laboratory investigations of soil resuspension, indicated that remobilization of colloid-bound Pu during soil erosion events can be enhanced by humic acids¹⁾.

2-D Polyacrylamide Gel electrophoresis (PAGE) experiments of radiolabeled colloidal organic and inorganic matter, extracted from RFETS soils, suggested that colloidal Pu, which was focused at pH_{IEP} of 4.5, is mainly associated with organic (humic acids) colloids of 10-15 kDa molecular weight. Pu(IV) oxide and inorganic colloids such as iron and aluminum oxides have pH_{IEP} of 8-10. While some clay minerals also have pH_{IEP} of 3-5, no Al was found coincident with Pu. This finding has important ramifications for possible remediation, erosion controls, and land-management strategies.

Keywords: Plutonium, colloids, natural organic matter, humic acids, gel electrophoresis

I. Introduction

Surficial soils of the Rocky Flats Environmental Technology Site (RFETS), Colorado, USA, contain elevated levels of $^{239,240}\text{Pu}$ and ^{241}Am due to wind dispersal of soil particles, contaminated in the 1960's by leaking drums stored on the 903 Pad. During storm runoff and pond releases, Pu concentrations are often above 0.15 pCi/L, the discharge limit. A better understanding of the process(es) that control the speciation of filter-passing forms of Pu is crucial for evaluating their transport. 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, and that particle transport is greatest during rainfall events [1, and references therein]. We suggest that surface water transport of Pu and Am is dominated by aggregation and disaggregation processes of colloids, not only particles, during soil erosion events. Clearly, knowledge of the phase and chemical speciation of actinides is a prerequisite for the development of defensible closure strategies.

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 be stabilized by humic and fulvic acids²⁾.

Our hypothesis is that the colloidal $^{239,240}\text{Pu}$ and ^{241}Am concentrations are produced by organic matter present in soils. To test our hypotheses, we have examined the nature of

the dominant colloidal Pu species generated via soil resuspension in laboratory experiments using two-dimensional polyacrylamide gel electrophoresis (2-D PAGE).

II. Materials and Methods

In order to determine colloid charge and mobility, colloids were also radioactively tagged with ^{14}C and ^{59}Fe (^{14}C -Dimethyl sulfate on the -OH sites of sugars ^{59}Fe on -OH sites of Fe oxyhydroxides and clay minerals)¹⁾. The labeling is a methylation reaction and labels mainly the hydroxyl groups of both neutral and amino sugars. The ^{14}C radiolabeled organic matter was stored in dH_2O in a sterilized bottle at 4°C . 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. Typically, sample detection within the gel was made using liquid scintillation counting. The gel was sectioned into 1cm sections and each section was put in a glass liquid scintillation vial with 3 ml 1%

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sodium dodecylsulfate (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, spiked with ²⁴²Pu for chemical yield determination, and then passed through anion exchange columns and alpha counted. Metal analysis was carried out using GF-AAS¹⁾.

III. Results and Discussions

Colloids were primarily composed of clay and organic matter colloids (0.02-1 % Fe, 0.02-1.3 % Al, 3.1-11.9 % OC) similar to soil particles. Colloids from the storm discharge contained higher Al, Fe, Mn, and %OC¹⁾ [Table 1]. The same was true for % OC in suspended particulate matter. 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. Comparison of organic carbon, nitrogen, Fe, Al, and Mn content, and C/N atomic ratio in colloids (1.5-500 nm) from RFETS surface waters¹⁾ and soils.

Sample ID	Colloid. Mass (mg/L)	OC (%)	ON (%)	C/N atom ratio	Fe (mg/g)	Al (mg/g)	Mn (μg/g)	^{239,240} Pu (pCi/g)	
								Colloids	Particles
Field									
1998-2000	21-68	3-11	0.2-0.6	12-20	1-47	1-13	60-450	0.3-1.6	0.3-1.2
Resuspension Experiments									
99A3372	-	2.3	0.15	17.8	0.3	0.1	6	1460	750

Isoelectric focusing results (Fig. 1a-c) reveal that colloidal organic matter, ¹⁴C-labeled at the sugar-OH sites, and rich in acid moieties, exhibits strong functional groups

with pKa of less than 4, imparting these colloids a negative charge, and therefore, allowing the majority of organic matter to migrate to the anode (pH 3.5).

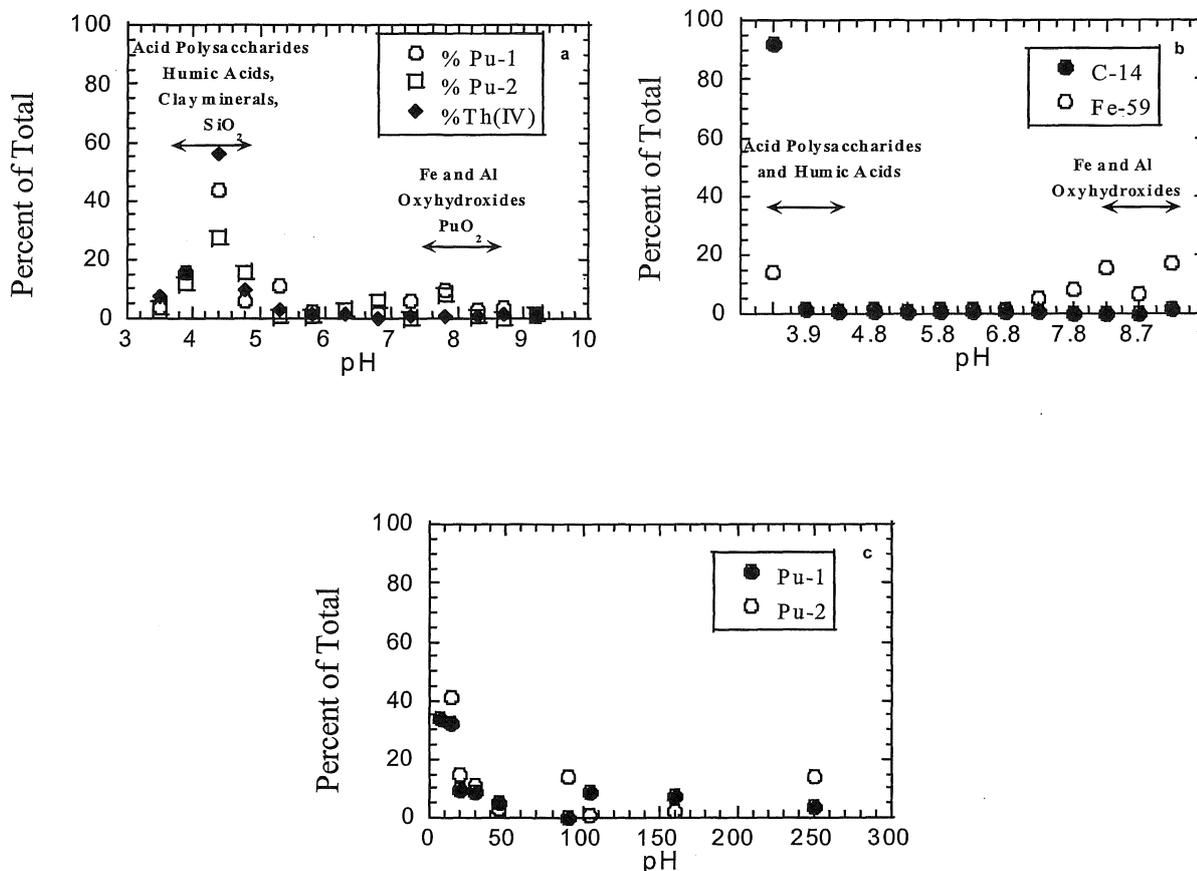


Fig. 1. Gel electrophoresis separation of colloidal ^{239,240}Pu (in duplicate) and radiolabeled colloids.

Furthermore, ^{59}Fe -labeled colloids, likely to iron and aluminum hydroxide surface sites, show isoelectric points (pH_{IEP}) between pH 8 - 9.5, in agreement with literature values for these mineral phases (Table 2).

The gel electrophoresis results thus suggest that the colloids are mainly composed of organic matter (^{14}C -labelled) with acid functional groups and thus, low isoelectric points, pH_{IEP} , and inorganic aluminum and iron oxide minerals (^{59}Fe -labelled) with more basic functional groups and higher pH_{IEP} .

Table 2. Isoelectric points^{2,3}.

Mineral	pH_{IEP}
SiO_2 (quartz)	2
SiO_2 (gel)	1-2.5
$\delta\text{-MnO}_2$	2
Montmorillonite	2.5
Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$)	3.5
Apatite ($10\text{CaO} \cdot 6\text{PO}_2 \cdot 2\text{H}_2\text{O}$)	5
Magnetite (Fe_3O_4)	6.5
Anatase (TiO_2)	7.2
Hematite (Fe_2O_3)	8.5
Goethite (FeOOH)	6.5
Alumina (Al_2O_3)	8.5
PuO_2	8.5

Pu, extracted from RFETS surface soils 99A3372 followed the ^{14}C -labeled organic matter (Figure 1b), rather than the mineral phases (labeled with ^{59}Fe). The point of zero charge, pH_{PZC} of PuO_2 is $\sim 8\text{-}9^3$. Thus, PuO_2 colloids should have migrated to pH_{IEP} of 8-9. This is strong evidence for a Pu-association to natural organic matter or to some clay minerals (Table 2). Ambient $^{239,240}\text{Pu}$ in these soil colloids showed the same electrophoretic distribution as added $^{234}\text{Th}(\text{IV})$ (Fig. 1b), added to rehydrated colloids in a separate experiment, demonstrating that ambient $^{239,240}\text{Pu}$ in these colloids is four-valent and dispersed much like the added four-valent actinide tracers.

Some clay minerals such as montmorillonite and kaolinite also have pH_{IEP} values between 2.5 - 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 (pH of about 4.5) where Pu peaked. Al, even though present in the colloid samples and many gel electrophoresis strips, was depleted in the region where Pu peaked. Furthermore, Si was present at low concentrations throughout the gel electrophoresis spectrum, but with no enrichment in the Pu region, indicating that Si, though present, was relatively immobile. The fact that small amounts of Fe, were found focused at the pH_{IEP} of the Pu maximum (pH 4.4), is contrary to what is expected from the pH_{IEP} values of all known iron oxyhydroxides, which are higher than 7². This indicates that Fe was not the charge determining species in that region, but rather organic molecules with a low pH_{IEP} of 4 - 5, such as humic or fulvic acids or lipopolysaccharides².

The molecular weight of the major Pu polymer species was determined as 10-15 kDa (Fig. 1c), suggesting that Pu mobility is enhanced by the presence of a negatively charged organic species of medium molecular weight.

Previous reports of Pu association with natural organic matter in soils was mainly based on evidence inferred from colloid size, or sequence in sequential leaching schemes, rather than chemical or charge distribution¹. Our results suggest an association of Pu with negatively charged species, likely macromolecular organic matter. Our evidence therefore strongly argues against the presence of mobile intrinsic colloidal PuO_2 microparticles, and excludes clay minerals. Our evidence also argues against the association of Pu with siderophore desferrioxamine-B, which recently has been shown to be important in bioaccumulating Pu⁴ in the laboratory. Even though we did not analyze them, they could have been present in our samples. However, siderophores are expected to have a pH_{IEP} of 8 or higher, as they contain mostly basic functional groups. The most common organic molecules with a low pH_{IEP} of less than 5 are fulvic or humic acids².

Preliminary evidence from separate oxidation state determinations¹ indicates strong association of Pu with colloids with strong surfactant qualities, as Pu was only found in the interfacial regions during solvent extraction procedures.

IV. Summary and Conclusions

The addition of colloidal Pu from sediment resuspension and soil erosion to stream water during pond discharge and storm run-off can increase the total Pu concentration, over that of particulate Pu alone, by a factor of 2 to 4¹. Thus, colloidal Pu formation can become one of the most important vectors for enhancing Pu dispersion at Rocky Flats. Results from 2-D PAGE experiments of radiolabelled colloids extracted by fresh water from surface soils revealed that colloidal Pu, which was focused at pH_{IEP} of 4.5, was associated with organic (humic acid) colloids of 10-15 kDa molecular weight. Pu(IV) oxide and inorganic colloids such as iron and aluminum oxides have higher pH_{IEP} values of 7-10. This finding has important ramifications for possible remediation, erosion controls, and land-management strategies.

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