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Speciation and Structural Characterization of Plutonium and Actinide-Organic Complexes in Surface and Groundwaters

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Research Objective

Our proposed research is designed to study the association of actinides with dissolved organic complexes in subsurface waters. This study expands considerably on prior work due to the combination of Pu oxidation studies (for Pu speciation/chemical reactivity information), Pu isotope ratio work (for Pu source function information), and the detailed characterization of organic matter in size-fractionated groundwater samples. We have postulated that actinide associations with organic matter may be enhanced due to colloidal biopolymers.

Research Progress and Implications

This report summarizes work completed after less than 2 years of a 3-year project. Activities thus far have included: 1) the development of sampling techniques to minimize contamination and artifact formation, 2) the separation of Pu isotopes by oxidation state in groundwater, 3) the development of techniques for the separation and identification of organic constituents from natural waters, 4) a study of background Pu and organic carbon concentrations at the proposed study sites, and 5) field work at the Savannah River site (SRS).

Sampling

Our proposed research calls for field work at the Savannah River and Hanford Sites (SRS and HS, respectively). Towards this end, we have established protocols for the sampling and analyses of organics and actinides in groundwaters using ultra-clean (fg level) cross-flow filtration (CFF) techniques suitable for thermal ionization mass spectrometric (TIMS) analysis of Pu. A series of tests have been completed and the results have shown that no Pu contamination from the CFF system was observable as long as the system was rigorously cleaned with acid, base and nano-pure water. We have also processed samples from a fresh water pond in Woods Hole, MA, from the groundwater in Falmouth, MA and from the Gulf of Maine (GOM) in order to test blank conditions in the field, to determine CFF mass balances, and to estimate the Pu colloidal association and isotopic ratio in these contrasting geochemical environments. Our CFF mass balance was generally $100 \pm 10\%$ for both ^{239}Pu and ^{240}Pu (Table 1). CFF is known to be prone to both sorptive losses and contamination effects, hence these results are encouraging for the success of the project because CFF will be the major sampling tool we will use to study natural Pu-organic complexes. Also shown in the table are the size fractionated Pu data. In seawater, the majority of Pu was found in the low molecular fraction (<1 kD). Colloidal Pu varied from 8 % of the total in surface waters to $<1\%$ in the deepest (250m) seawater sample. In contrast, in a freshwater pond at Woods Hole, all of the Pu was associated with the high molecular weight fraction, most likely due to complexation with organic material. In the groundwater in Falmouth, colloidal Pu represented 57% of the total Pu. These results suggest that the association of Pu with colloidal organic material is highly variable, depending presumably upon the speciation of Pu and the quantity and quality of organic matter in a given aqueous sample.

	Dissolved (< 1 kD)		Colloidal (1 kD - 1 µm)		Particulate (> 1 µm)		CFF Recovery (%)
	dpm/1000kg	% of Total	dpm/1000kg	% of Total	dpm/1000kg	% of Total	
GOM (1m)	0.2205	92.0	0.0099	4.1	0.0094	3.9	99
GOM (15 m)	0.1462	58.5	0.0206	8.2	0.0832	33.3	99
GOM (37m)	0.2106	85.7	0.0165	6.7	0.0187	7.6	87
GOM (65 m)	0.3492	92.1	0.0149	3.9	0.0152	4.0	110
GOM (200 m)	0.4442	88.3	0.0142	2.8	0.0447	8.9	103
GOM (250 m)	0.4512	85.6	0.0003	0.1	0.0758	14.4	96
Nobska Pond	0.04259	0.20	21.3544	99.8	N/A	N/A	110
Falmouth							
groundwater	0.00105	10.1	0.00592	57.1	0.00341	32.9	71

Preliminary results from the SRS and HS

We collected a suite of samples from SRS and HS for preliminary analyses of total actinide levels and Pu isotope ratio work (in collaboration with the Jim Kelley and John Wacker at PNNL). The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in a sample taken from the 100-K area at HS was 0.0498, indicating a local Pu source in this area (global fallout $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio avg. = 0.18). At area F at SRS, $^{240}\text{Pu}/^{239}\text{Pu}$ ratios ranged from 3.9 to 0.18, signifying various sources at this one site. The excessively high ratios may be related to the decay of Cm-244 and Cm-243 from wastes.

Organic analyses

CFF organic matter samples collected locally are being used to develop methodologies for sample fractionation and biopolymer identification. We have found that the major organic constituents of our water sample are biopolymers similar in composition to those we have previously identified in seawater. Given that >80% of the dissolved Pu is in this fraction, this result supports our original hypothesis that biopolymeric rather than humic substances may account for a large fraction of actinide-organic matter associations. Specifically, 60% of the carbon in our sample is bound in a mixture of structurally related acyl-polysaccharides. We have made a preliminary investigation of polysaccharide stereochemistry, and are presently conducting analyses of the monosaccharide composition and linkage patterns. In parallel, we are testing chromatographic procedures in an effort to develop protocols to further purify the mixture for more comprehensive spectrometric analyses.

About 35% of our sample is made up of dissolved proteins. We have made a preliminary characterization of these proteins, and we are preparing to make further analyses of protein amino acids and specific components by SDS-PAGE and similar techniques. Finally, only 5% of the carbon in our sample is made up of what are traditionally classified as humic material. NMR spectrometric analyses of this fraction shows a high degree of aromatic character, but a significant acylpolysaccharide component as well. It may be that the humic substances in our sample are derived from the acyl-polysaccharides described above, or that the humic substances are difficult to purify in the presence of high relative concentrations acyl-polysaccharides.

Comprehensive sampling activity at SRS (April 1998)

Field sampling for at SRS was completed in April 1998 at 8 monitoring wells in F area.

Planned Activities

We are planning to sample at HS this Summer or early Fall. In the lab, the large suite of samples (> 200) from SRS are being processed both for organic and Pu isotopes in the size fractionated samples.

Other Access To Information

- Dai, M., J.M. Kelley, K.O. Buesseler et al. (1998) Size fractionated Pu isotopes in the ocean, a pond and groundwater, AGU Spring meeting, May 1998, Boston.
- Dai, M., J.M. Kelley, K.O. Buesseler et al. (1998) Size fractionated Pu isotopes in the Gulf of Maine. (in preparation for submission to Journal of Environmental Radioactivity)