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Speciation and structural characterization of Plutonium and Actinide-organic complexes in surface and ground waters

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Our proposed research is designed to study the association of actinides with dissolved organic complexes in subsurface waters. Actinide-humic matter associations in natural waters have been investigated previously, but we have postulated that much of the actinide binding activity may be supported by colloidal biopolymers. To investigate this, we are developing techniques to sample and identify organic constituents in groundwater, and to measure the Pu associated with different fractions of organic matter. Year 1 activities have focused on: 1) sampling techniques to minimize contamination and artifact formation, and to establish mass balances, 2) separation of Pu isotopes by oxidation state, and 3) analytical development of techniques for separation and identification of organic constituents from natural waters.

Sampling - Our proposed research calls for field work at the Savannah River and Hanford Sites (SRS and HS, respectively). Towards this, we have been working on establishing protocols for ultra-clean (fg level) cross-flow filtration (CFF) techniques suitable for thermal ionization mass spectrometric (TIMS) analysis. A series of tests have been completed and the results have shown no Pu contamination from the CFF system was observable as long as the system is rigorously cleaned with acid, base and nano-pure water (Table 1). We have also collected a water sample from a pond near our laboratory in Woods Hole, MA to test blank conditions in the field, and to determine system mass balances. Blank levels were found to be satisfactory, and our mass balance is 100 $\pm$10 % for both ^{239}Pu and ^{240}Pu, the only two isotopes measurable in the sample. This is one of the major assurances for the success of the project because CFF will be the major sampling tool we will use to study natural Pu-organic complexes. Another important result from our field test is that > 80 % of the dissolved Pu (based on the TIMS measurements) is in colloidal form.

Well pumping test - This test was made in preparation for the comprehensive field work that will be conducted at SRS and at Hanford, where samples will be drawn from monitoring wells surrounding contaminated sites. We used our CFF system to sample groundwater from a local monitoring well, giving us practical experience in many aspects of sampling (balancing well flow and CFF sampling rates, exposure of the

sample to air, etc.). A great deal has been learned from this experiment, leading to some modifications in our sampling equipment and protocols. This information is being considered in our discussions of sampling strategy with liaison offices at SRS and HS.

Table 1. Blanks of Pu isotopes Concentration(fg/l).

Sample	Vol(liter)	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
1	4	0.005	0.002	0.002	0.002
2	4	0.017	0.001	0.001	0.001
3	4	0.002	0.002	0.002	0.001
4	4	0.002	0.002	0.001	0.001

We have contacted liaison offices at SRS and HS and arranged for a suite of samples to be collected and shipped to us for preliminary analyses. We plan to use the data on Pu and organic matter from these samples to select monitoring wells for comprehensive sampling. Samples are being analyzed for Pu isotopes and concentration levels, as well as total organic carbon. We have discussed our sampling needs with personnel at each site. Our needs lie outside routine sample requests and therefore have raised important new issues about operating on site that need to be resolved. Discussions are continuing and we are optimistic we will be able to visit and sample at the SRS in the spring of 1998, followed by a visit to HS in early summer.

Pu analyses - Three samples have been processed to assess the separation efficiency and the source tracer preparation. Preliminary data show our separation technique results in an 80 % separation of Pu(III,lV) from Pu(V, VI), and indicates there is still some room to improve the separation efficiency. We are continuing to work on this problem and feel we will be able to achieve better separations in the coming year. In addition, Pu oxidation state analyses of samples collected from the local pond (surface water) and monitoring well (groundwater) to determine potential differences in CFF processing.

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. As >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 Iarge 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.

Some 35% of our sample is made up of dissolved proteins. We have made a preliminary characterization of these proteins, and 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.

Summary - We believe our research effort is progressing on the schedule outlined in our proposal. We have developed and tested our sampling system, and Pu blank levels and mass balances are within acceptable limits. In parallel we have established laboratory protocols for actinide and organic matter characterization, and have initiated contacts with both the SRS and HS facilities to organize future sampling. Finally, we are preparing to present our results on ultra-clean Pu CFF sampling at the AGU spring meeting (Boston, 1998).