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

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RESEARCH OBJECTIVE

Our proposed research is designed to study the association of actinides with dissolved organic complexes in subsurface waters.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work after 3 years of the project. Activities so far included: 1) development and testing of sampling and analytical techniques for both actinides and organic constituents from natural waters, 2) confirmation of Pu and organic carbon concentrations, 3) field work at the Savannah River site (SRS) and at Hanford site (HS), and sample analysis, and 4) preparation of publications. While activities 1-2 have been summarized in prior reports, we are focusing on activity 3 in this report.

Hanford 100-K sampling in March/April 1999

Comprehensive field sampling activities at the Hanford Site were completed March 22-April 6, 1999. Initial groundwater samples from wells near the 100 K reactor building indicate a local Pu source (see annual report in 1998). It was our intent to further define the plume and model Pu transport through comprehensive sampling activities. In addition to acquiring samples through the normally scheduled site sampling efforts at four groundwater wells (199-K-107A, K-28, K-30, and K-109A), we performed comprehensive sampling at four additional wells (199-K-27, K-32A, K-36, and K-110A).

During these comprehensive sampling activities, samples were processed on-site using an ultraclean cross-flow filtration (CFF) system. About 40 Pu isotopic composition samples, 50 Pu oxidation state samples (processed on-site), and 4 concentrated colloidal fractions were collected during this field effort along with other ancillary samples. A water sample was also taken from the Columbia river downstream of the 100-K area. Although the Pu levels in the groundwater at 100-K area are extremely low and would not pose a direct threat to the environment, it is important to know the migration potential of the contaminant into the Columbia River in order to establish the longer term risk assessment at this site. Processing of samples from this field work is in progress.

Results from Savannah River Site Seepage Basin F-Area

Our study was focused on the seepage basins at the SRS in the F-area (Fig. 1). The F-area was one of two main sites where chemical separations facilities were located. It has been reported that the seepage basin received on the order of 150000 Ci ^3H , 18 Ci ^{239}Pu , 0.22 Ci ^{241}Pu , 0.24 Ci $^{234,244}\text{Cm}$, and 12.6 Ci ^{238}U (Kaplan et al., 1994). As a result of the highly acidic chemical wastes released into the unlined basins, the groundwater underneath the site is characteristically acidic ($\text{pH} \approx 3-4$).

Figure 1: Groundwater well locations in F-Area at Savannah River Site sampled in 1997 and 1998

Our first results were from unfiltered samples collected in August 1997. In one of the three wells, we were surprised by the elevated $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 3.9 (well 78) vs. 0.15-0.20 in the other two wells (92D & 103C; see Figure 2a for data). Values typical of fallout and nuclear materials are always <1 , with the global fallout average being 0.18. Hence this high ratio is indeed unusual for most Pu sources. As will become clearer with the 1998 SRS samples, we attribute the highest $^{240}\text{Pu}/^{239}\text{Pu}$ ratios to samples that have been impacted by the decay of ^{244}Cm ($t_{1/2} = 18.1$ yrs.) to ^{240}Pu in the seepage basin wastes. Cm is predicted to be more mobile in groundwater than at least the reduced forms of Pu, hence we need to consider in our interpretation of these results the possible dissimilar behavior of ^{239}Pu and ^{240}Pu since one of these isotopes, namely ^{240}Pu , has a unique source term which has different geochemical properties (see below).

Figure 2. a) $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in unfiltered well samples collected at SRS in August 1997. **b)** size fractionated $^{240}\text{Pu}/^{239}\text{Pu}$ data from samples collected in May 1998. Note two of the well sites are the same, and that for well 108D (Figure 2b), $^{240}\text{Pu}/^{239}\text{Pu}$ ratio is only available for an unfiltered sample at this time.

Downstream from the seepage basins, the $^{240}\text{Pu}/^{239}\text{Pu}$ ratios increase in all size classes, with the highest ratios being found most distant from the potential source. We speculate that most of the ^{240}Pu in the farthest wells originates from the decay of ^{244}Cm . As stated above, Cm would be more mobile in groundwater, thus earlier Cm releases should have separated from the original Pu plume. This effect would be most evident the further one moves towards Fourmile Branch. The presence of Cm at this site is not surprising. During the mid 1960's, 3 kg of Cm was produced at the SRS and most relevant to our observations, the Cm produced was primarily ^{244}Cm (Seaborg and Loveland, 1990). As noted

earlier, it is also estimated that 0.24 Ci of Cm was released into these seepage basins. Assuming discharge in the mid-60's, our results can be used to predict ^{244}Cm levels in well 79 around 4 pCi/kg, which is roughly the same order as observed in well 79 by Kaplan et al. (1994).

Figure 3. Percent oxidized ^{240}Pu in May 1998 at SRS. Size classifications are the same as in Figure 5.

Our oxidation state studies provided further evidence of why there might be preferential mobility of ^{240}Pu relative to ^{239}Pu at this site. For ^{240}Pu , we find that >75-95% of the Pu is in the oxidized form in all of the size classes (Figure 3). Specific isotopic analyses on these oxidized fractions show even higher enrichment in ^{240}Pu than in the bulk permeate and filtrate phases ($^{240}\text{Pu}/^{239}\text{Pu} = 11.2$ and 27.1 in oxidized fractions at wells 78 and 79, respectively). Typical groundwater is reducing, and the high abundance of oxidized ^{240}Pu is at first surprising. However, if we consider that the source of much of the ^{240}Pu is from ^{244}Cm decay, it is consistent with known processes. The Pu progeny of the Cm isotopes, by the Szilard-Chalmers process, are born deficient in electrons and hence would be enriched in the penta and hexavalent oxidation states. It should be noted that given these higher valence states, one would predict a significantly lower distribution coefficient (K_d), and hence a lower tendency to adsorb to soil particles and natural colloids.

For ^{239}Pu , production from Cm is not considered significant, as source ratios of $^{234}\text{Cm}/^{244}\text{Cm}$ are typically on the order of 10^{-4} . Instead, the likely source of most ^{239}Pu is from the Site operations, since ^{239}Pu (with ^{238}Pu) was a main product at the SRS (Carlton et al, 1996). In the downstream wells, oxidized forms of Pu represent only 20-50% of the total in the different size classes. We found ^{239}Pu predominantly in the higher oxidation states in the “background” well 108D, and the upstream well 92D (>90% oxidized). Some of these wells are strongly oxidizing in general, due to the nature of the liquid wastes deposited in the seepage basins. For example, dissolved oxygen was >3.0 mg/l at well 92D vs. <1 mg/l at well 78 during our sampling period. We do not yet have a single explanation for this variability.

The Pu concentration data for both ^{239}Pu and ^{240}Pu show that only a small fraction of the total Pu is in the colloidal fraction (<5% in general for both isotopes). A low colloidal abundance is consistent with the higher oxidation states, and with overall low natural colloidal organic carbon levels at this site (see below).

Overall, our data suggest that redox speciation can vary considerably, and that most of the Pu is in a more oxidized form <1 kD in size in the SRS wells. We attribute this to the unique ^{240}Pu source from ^{244}Cm , but even ^{239}Pu appears less associated with colloids than data from prior studies using different techniques would imply. We note that the forms of Pu found at the SRS would be significantly more mobile than standard models predict. The highly varied $^{240}\text{Pu}/^{239}\text{Pu}$ ratio can only point to ^{240}Pu being enhanced downstream due to its production from the more mobile Cm precursor and its own enhanced mobility in the oxidized form.

Kaplan et al. (1993), reports groundwater DOC values in the F area of 0.86 mg C/l. Our samples collected in May of 1998, consistently had lower values of 0.36 mg C/l (well 108D; background well), 0.60 mgC/l (well 78), 0.48 mg C/l (well 79), and 0.60 (well 92D). Most of the groundwater organic carbon was in the small size fraction, with less than 10% of total organic carbon in the > 1 kD size fraction. These results are unlike most surface water environments where the > 1kD colloidal fraction contributes > 30% of the total carbon.

Particularly striking is the complete absence of aromatic resonances (7.0-7.5 ppm) characteristic of humic substances. Instead, we observe major resonances characteristic of acylpolysaccharides (APS; 3.3-4.3 ppm), acetate (2.0 ppm), and deoxysugars/lipids(1.3 ppm). On the basis of NMR data, we calculate 50-65% of the carbon in this size fraction may be

APS. We are currently completing our NMR spectral analysis for this sample and will soon begin molecular level characterization. If we observe the same distribution of neutral sugars, then we will have confirmed the presence of a persistent, microbially derived biopolymer in our samples similar in composition to APS in surface fresh and marine waters. By documenting the presence of remnant biopolymers in ground water from the Savannah River and Hanford Sites, we will have established that the mobilization of groundwater contaminants, including actinides, may not be determined by the chemistry of humic substances as previously assumed. Confirmation of APS in groundwater will also demonstrate further the pervasiveness of APS in the environment. Our ongoing chemical characterization of APS suggests that it is a family of structurally related biopolymers. We have made a partial determination of geometry and stereochemistry of the polysaccharide component in this biopolymer, and have demonstrated its synthesis by microorganisms (Aluwihare et al., 1997, Aluwihare and Repeta, 1999). Our current efforts are focussed on the purification of APS for complete structural analysis.

Publications and Presentations Generated From This Project

Dai, M., J.M. Kelley, K.O. Buesseler, R.A. Belastock, T.C. Maiti and J.F. Wacker (1998). Size fractionated Pu isotopes in the ocean, a pond and groundwater, AGU Spring meeting, May 1998, Boston, EOS, 79(17), pg.138.

Dai, M.H., J.M. Kelley, K.O. Buesseler, R.A. Belastock, T.C. Maiti and J.F. Wacker (1998). Size fractionated Pu isotopes in surface and subsurface waters, ACS/DOE EMSP workshop, July 27-30, Chicago.

Dai, M., J.M. Kelley, K.O. Buesseler et al. (1999). Isotopic composition, speciation and mobility of Pu in the groundwater at DOE Savannah River Site, AGU Spring meeting, May 1999, Boston.

Dai, M., K.O. Buesseler, J.M. Kelley, et al. (1999). Size fractionated Pu isotopes in a coastal environment (submitted to *J. Environmental Radioactivity*).

Dai, M., J.M. Kelley, K.O. Buesseler et al. (1999). Isotopic composition, speciation and mobility of Pu in the groundwater at DOE Savannah River Site (in preparation for submission to *Environmental Science and Technology*).

Repeta, D.J. and T.M. Quan (1999) A comparison of chemical characteristics of dissolved organic matter in fresh and marine waters. *Limnol. Oceanogr.* (in preparation).

Repeta, D.J., T.M. Quan, L.I. Aluwihare and A. Accardi (1999) Dissolved organic matter in fresh and marine waters. Amer. Soc. Limnol. Oceanogr. Annual meeting, Santa Fe, N.M.

PLANNED ACTIVITIES

We have been recommended for funding for a new EMSP proposal entitled "Speciation, mobility and fate of actinides in the groundwater at the Hanford Site" by K.O Buesseler, M. Dai and Dan Repeta with the continuous collaboration with J.M. Kelley and J. Wacker from PNNL. This new proposal will serve as a renewal of the ongoing EMSP project. We are currently processing the large amount of samples collected from the HS 100-K area. We are expecting to complete the sample analysis and data processing within the next 6 months. Based on the information, we will be conducting new research at HS as proposed in the proposal. Our main focus remains on Pu speciation, mobility and the potential role that colloidal material may play in the Pu transport in the subsurface water.

INFORMATION ACCESS

Groundwater Pu studies at <http://cafethorium.whoi.edu>