

**Speciation and structural characterization of Plutonium and Actinide-organic complexes in surface and ground waters (Sept. 1996-Sept. 1999) & Speciation, Mobility and Fate of Actinides in the Groundwater at the Hanford Site (Sept. 1999-Sept. 2002)**

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## **INTRODUCTION**

This report summarizes work on our EMSP project: "*Speciation and structural characterization of Plutonium and Actinide-organic complexes in surface and ground waters*" (Sept. 1996-Sept. 1999) and work after 6 months on: "*Speciation, Mobility and Fate of Actinides in the Groundwater at the Hanford Site*" (Sept. 1999-Sept. 2000). One post-doctorate and one part time graduate student have been involved in the project.

## **SIGNIFICANCE TO DOE EMSP**

Migration of Plutonium in the environment is a major issue at several DOE sites. As such, fundamental data concerning the interactions between various chemical forms of plutonium with compounds in the environment are essential for predicting Pu's behavior in the aqueous environment. Our research has focused on two important DOE sites, namely the Savannah River Site (SRS) and the Hanford Site (HS). Earlier assumptions that contaminants would migrate very slowly in the vadose and groundwater zones have been demonstrated to be incorrect based upon findings of prior monitoring programs and independent review. At this point in time, extensive cleanup and stabilization programs are underway at many DOE sites. These important DOE activities are challenged by the immense scope of the cleanup and the overriding need for more streamlined and focused solutions to the cleanup problem. The results of our research program would:

- i) provide the basis for accurate modeling and prediction of actinide transport;
- ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the vadose/groundwater zone
- iii) identify specific Pu sources and the extent of far field, or long-term migration of actinides in groundwater. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies.

## **RESEARCH OBJECTIVES**

Our first project focused on the development and testing of appropriate sampling and analytical techniques to study the association of actinides with dissolved organic complexes in subsurface waters. Our ongoing project is designed for: (1) the determination of the speciation of plutonium and other actinides (Np, U) in groundwater at the 100 and 200 areas at the Hanford Site. This includes the separation of Pu into particulate, colloidal and <1 kilo-Dalton dissolved phases and the determination of redox states and isotopic composition in each fraction; (2) the characterization of groundwater colloids, which includes submicron-sized inorganic particles and organic macromolecules (3) the prediction of the rate of transport and fate of actinides in the groundwater of the Hanford Site using a three-phase (dissolved-colloid-particulate) model.

## **RESEARCH PROGRESS AND IMPLICATIONS**

### **1) Development of sampling and analytical techniques**

Technique development in the project included work on well sampling and field processing procedures, cross-flow filtration (CFF) for the collection of groundwater colloids, plutonium oxidation state separations, actinide analysis by thermal ionization mass spectrometry (TIMS), and methodologies for characterizing the organic constituents of groundwater colloids. We have made use of a "micro-purge", low pumping rate procedure for groundwater sampling and on site cross-flow filtration (CFF) for the collection of groundwater colloids. The application of CFF to groundwater speciation studies requires considerable care to minimize the potential of colloid formation and/or redox shifts during sample processing. We have developed and tested a suite of procedures which include extensive flushing and CFF preconditioning steps, in order to minimize these artifacts. Our experience is that if such steps are not taken, colloid precipitation and contamination can occur. We also separated our ultrafiltration samples on site into oxidized and reduced fractions. This is done immediately in the field after sample collection under N<sub>2</sub> gas, which is crucial to minimize any alteration of ambient redox characteristics.

The high sensitivity of the TIMS facility at the Pacific Northwest National Laboratory (PNNL collaborative effort with Wacker/Kelley) has been extremely important to the success of all of our studies. Subfemtogram ( $<10^{15}$  g) detection limits are critical for following the far-field transport of Pu in the environment, and for determining Pu isotopic abundances in small subfractions of the total groundwater sample. TIMS is advantageous over more commonly used alpha-spectrometric techniques due to its higher sensitivity and its ability to quantify multiple Pu isotopes.

## **2) Results from Savannah River Site Seepage Basin F-Area**

Our field study at SRS was focused on the F seepage basin area of SRS. Sampling was undertaken by following a groundwater plume downstream of the seepage basin as well as in a background monitoring well upstream from the basin. The F-area was one of two main sites where chemical separations facilities were located. We determined highly variable  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios (vs. the global fallout average of 0.18), with the most elevated values downstream. We attribute the highest  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios to samples that have been impacted by the decay of  $^{244}\text{Cm}$  ( $t_{1/2} = 18.1$  yr.) to  $^{240}\text{Pu}$  in the seepage basin wastes. Redox speciation experiment shows that  $>75\text{-}95\%$  of the  $^{240}\text{Pu}$  is in an oxidized form. This supports the hypothesis that a unique  $^{240}\text{Pu}$  rich source from the more mobile precursor  $^{244}\text{Cm}$ , leads to enhanced mobility resulting in increased  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios downstream. A low  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio in the background well signifies a Pu source other than global fallout and is most likely due to weapons grade Pu waste of some local origin.

Most of the Pu at SRS is in the oxidized  $<1\text{kD}$  forms, which would be significantly more mobile than standard models predict. Size fractionation studies show only  $< 5\%$  of the Pu as colloidal form, which is consistent with the higher oxidation states, and with overall low natural colloidal organic carbon levels at this site. In contrast to prior studies, we therefore conclude that colloids do not play a significant role in groundwater Pu transport at this site.

**These findings suggest that Pu at SRS would be significantly more mobile than standard models predict.**

## **3) 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, and results will be presented at the EMSP national workshop in April, 2000.

## **4) Publications and presentations generated from this project**

Dai, M., J.M. Kelley, K.O. Buesseler, R.A. Belostock, 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. Belostock, 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, *J. Environmental Radioactivity* (accepted)

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

Buesseler, K.O., Dai, M. et al., (1999) Speciation, mobility and fate of actinides in the groundwater at the Hanford Site, EMSP PI workshop, Nov. 16-18, Hanford.

## **PLANNED ACTIVITIES**

We are currently processing a large number of samples collected from the HS 100-K area. We are expecting to complete the bulk of the sample analysis and data processing during the first half of 2000. Based on the

information, we will be conducting new field research at HS as detailed 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 groundwater.

**INFORMATION ACCESS**

Results from these EMSP projects can also be found at: <http://cafethorium.who.edu>