Annual Progress Report : DE-FG07-96ER14733

Speciation, Mobility and Fate of Actinides in the Groundwater at the Hanford Site (Sept. 1999-Sept. 2002)

May 31, 2001

Lead PI: K.O. Buesseler, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, 508-289-2309, kbuesseler@whoi.edu
Co-PI: M. Dai, WHOI, Woods Hole, MA 02543, 508-289-3466, mdai@whoi.edu
Co-PI: D.J. Repeta, WHOI, Woods Hole, MA 02543, 508-289-2635, drepeta@whoi.edu

INTRODUCTION

This annual report summarizes work on our EMSP project: *"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

The objectives of this project are: (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 TO DATE 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. These methods have been optimized and reported on in prior annual reports, meetings and publications. During year 2000 isotopic analyses of more than 70 new size fractionated redox state groundwater samples were completed. Sample processing was performed at WHOI and returned to PNNL for TIMS ananlysis.

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. We find that < 5% of the Pu at SRS is colloidal, and thus conclude that at least at this site, colloids do not play a significant role in groundwater Pu transport. We measured the highest isotopic ratio of $^{240}Pu/^{239}Pu$ (≈17) ever reported for environmental samples and attribute

this to a unique source of Pu at SRS, namely the decay of waste curium (^{244}Cm, t½ = 18.1 y) to ^{240}Pu which leads to enhanced mobility and increased ^{240}Pu/^{239}Pu ratios downstream.

To our knowledge, this is the first report of groundwater Pu results with a combination of both size class, redox states and isotopic composition information. There is no evidence from our study pointing to a strong association between Pu and groundwater colloids that prior studies using different techniques have implied. We also document a dissimilar behavior between ^{239}Pu and ^{240}Pu in the SRS, F-area groundwater, since one of these isotopes, namely ^{240}Pu, was generated *in situ* from the decay of a unique, ^{244}Cm source. This dissimilar behavior can only be resolved by mass spectrometric techniques such as TIMS, rather than by alpha spectrometry. The Cm related Pu forms we have found at SRS would be significantly more mobile than standard models predict. In general, **our data demonstrate both redox and size speciation are essential in order to predict the long term fate and mobility of Pu and other actinides in groundwater.**

3) Results from Hanford 100-K area

We have completed comprehensive field sampling activities at 100 K area of the Hanford Site. Initial groundwater samples from wells near the 100 K reactor building indicated a local Pu source (see annual report in 1998 & 1999). We defined the plume through comprehensive sampling performed at four groundwater wells: 199-K-107A, K-28, K-30, and K-109A. In addition samples were obtained through the normally scheduled site sampling efforts at four groundwater wells (199-K-107A, K-28, K-30, and K-109A).

Our Pu analyses from the 100-K area are now essentially complete and the results suggest:

- Pu from Hanford operations is found in all groundwater samples from 100K area at very low levels (fg/l, 10^{-4} to 10^{-6} pCi/l)
- Colloidal Pu is minor fraction of total Pu in 100-K groundwater-<5-15% colloidalPu is primarily in reduced form near source, with a trend towards more oxidized forms further from sourceThere is likely a source of high ^{241}Pu/^{239}Pu in wells K-109A and K-27 due to N-reactor waste (the K-East reactor basin is currently being used to store irradiated fuel from the N-reactor).
- The isotopic ratio in the other wells reflects the K-reactor signal, possibly mixed with fallout.

PLANNED ACTIVITIES

We are currently preparing for an extensive field sampling of the HS 100-N area in July 2001. Comprehensive sampling will be conducted at six groundwater wells: 199-N-16, N-25, N-26, N-47, N-71 and N-72). We also intend to obtain groundwater samples through normally scheduled site sampling at seven additional wells: 199-N-3, N-18, N-19, N-56, N-62, N-65 and N-73. During the second half of 2001 we are expecting to continue analyses and data processing of 2001 samples. 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.whoi.edu and in the following publications and reports:

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. (2001). Size fractionated Pu isotopes in a coastal environment, *J. Environmental Radioactivity*, **53 (1)**, 9-25.)

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.

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.

Dai, M.H., J.M. Kelley, S. Pike, K. O. Buesseler, T. C. Maiti and J.F. Wacker (2000) Isotopic composition, speciation and mobility of Pu in groundwater at the DOE Savannah River Site, DOE EMSP national workshop, April 2000, Atlanta.

Buesseler, K.O., M.H. Dai and J.M. Kelley, S. Pike, R. Nelson, S. Goodwin and J.F. Wacker (2000), Speciation and isotopic composition of plutonium in the groundwater at the Hanford Site DOE EMSP national workshop, April 2000, Atlanta.

Dai, M.H., J.M. Kelley and K. O. Buesseler (2000) Do colloids facilitate Pu migration in groundwater? (submitted Environmental Science and Technology).