Project 90075

Sources, Speciation and Mobility of Plutonium and Other Transuranics in the Groudwarter at the Savannah River Site

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RESULTS TO DATE: Annual Progress Report: DE-FG02-03ER63659 Sources, Speciation and Mobility of Plutonium and Other Transuranics in the Groundwater at the Savannah River Site (Sept. 2003-Sept. 2006) May 31, 2005

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INTRODUCTION This annual report summarizes work to date on our EMSP project: ?Sources, Speciation and Mobility of Plutonium and Other Transuranics in the Groundwater at the Savannah River Site? (Sept. 2003-Sept. 2006 ABSTRACT Our research focus is to further evaluate the sources and fate of Pu and other transuranics in groundwater at the Savannah River Site (SRS). Our overarching goal is to understand Pu speciation and mobility well enough to support safe remediation, containment and long term stewardship at any site with transuranic wastes and sources. Methods developed under prior funding for the determination Pu isotopes, oxidation state and size fractionation in groundwater are providing the best direct evidence for rejecting or not, hypotheses concerning whether colloids enhance the transport of Pu and other transuranics in groundwater. Survey samples collected in the fall of 2003 from F-area well FSB 78 had a 240/239 Pu atom ratio 7.087 +/-0.048 and reflects the continued presences of decayed 244Cm. In October 2004, we returned to the F-area and completed comprehensive field sampling of 7 wells. Field experiments included 6 different extraction rates at well 92D to test sensitivity to artifacts related to well pumping rates, and an aging experiment to evaluate Pu behavior by re-oxidation of reducing groundwater. Sampling of Pond B was included in the site visit to explore unique conditions of redox potential on Pu within the pond. To date, more than 70 Pu redox and whole water samples have been processed and are awaiting analysis at PNNL. Also, five samples from our 1998 visit are undergoing chemistry at PNNL to directly measure Cm with analysis of 2004 samples to follow. Work is continuing to evaluate particle affinity under controlled conditions and a site specific groundwater transport model which we will apply to our lab and field data to obtain a better understanding of the importance of these processes on Pu transport.

SIGNIFICANCE TO DOE EMSP Migration of plutonium in the environment is a major issue at several DOE sites (Riley and Zachara, 1992). 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 and the Hanford Site, and at both sites we see no need to invoke colloid facilitated transport to explain Pu groundwater distributions. This conclusion has important practical implications because much of the uncertainty associated with Pu subsurface transport, including at the Hanford Site (Mann et al. 1998) and the SRS (McDowell et al., 2000) is attributed directly to the uncertainty associated with the role that mobile colloids may or may not play in transporting Pu.

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 goal of our research program is to: 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 groundwater zone; iii) identify specific Pu sources and the extent of far field, or long-term migration of transuranics in groundwater; iv) reduce costly uncertainty in performance and risk assessment calculations. 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.

The original definition of the transuranic waste category, TRU, was created in 1970 by the Atomic Energy Commission (AEC) to define those wastes with concentrations of long-lived transuranics greater than 10 nanocuries per gram (AEC raised this limit to 100 nanocuries per gram in 1984). Waste below this ceiling and the shorter lived transuranics, can be treated as low-level waste and disposed of with much less consideration. At SRS, we have shown that 244Cm, a short-lived transuranic, is the dominant source of the long-lived 240Pu that is of concern in TRU wastes. TRU wastes are common to many DOE sites and the releases are often poorly documented in terms of total radioactivity and relative transuranic activities (Fioravanti et al., 1997). Since little quantitative field data exists documenting in-situ speciation and forms of transuranics in groundwater, the data collected in this study will go a long way to test predictive models of long-term migration patterns and thus assess risk and design containment strategies appropriate for transuranics in groundwater originating from the many differing sources on DOE sites.

RESEARCH OBJECTIVES The objectives of this project are: (1) the determination of the speciation of plutonium and other transuaranics (Am, Cm) in groundwater at the F and H areas at the Savannah River 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 prediction of the rate of transport and fate of actinides in the groundwater of the Savannah River Site using a three-phase (dissolved-colloid-particulate) model, (3) conduct laboratory tests using site-specific sediment and groundwater to compare plutonium and curium sorption (e.g., cation exchange, surface complexation, or precipitation) and derive sorption mechanism constants, (4) conduct reactive transport modeling using the sorption mechanisms and constants constructed from the laboratory data to provide a first approximation of how well the field data supports the hypothesis.

RESEARCH PROGRESS TO DATE AND IMPLICATIONS Research activities during year 2004-05 The major field effort for this project occurred in October/November 2004. Wells sampled during our site visit were based on results from survey analysis. Whole water survey samples from the F and H area seepage basins of SRS show that samples from F-area wells 92D and 78 contained 106 atoms/l 239Pu and a high atom ratio of 240Pu/239Pu =7 (weapons testing fallout for example has a ratio of 0.18) "downstream" from trenches (well 78), indicating 244Cm source. These atom concentrations and ratios look similar to 1998 levels we have published previously. The highest concentration of 108 atoms/l 239Pu was found near the source (well 92D). In H-area, well 110D had >106 atoms/l 239Pu with enriched 240Pu/239Pu = 2.7. Remaining H-area wells fell in two groups, all <106 atoms/l 239Pu conc.- in the NE sector of H-Area, wells 102-D, 105-D, 104-D, have low 239Pu, and 240/239 = 0.05-0.07. While this suggests a local source (i.e. non-fallout Pu), the extremely low concentrations of Pu found in these H area wells forced removal of the seepage basin from our sampling strategy.

We performed comprehensive sampling of 7 wells over a 14 day visit to F area seepage basin. Sampling methods included low flow rate pumping (150 ml/min) for determination of Pu isotopes, oxidation state and size fractionation. To support our argument that high flow rate extraction from aquifers may artificially mobilize Pu in the groundwater, we conducted field experiments which included 6 different extraction rates (150-16000 ml/min) at well 92D. Additionally, an aging experiment was conducted at this same well evaluate Pu behavior by re-oxidation of reducing groundwater. We collected an additional 140 liter sample from this well at the initial low flow rate and allowed it to age for 5 days exposed to ambient air. After aging, we conducted our standard CFF sampling until 70 liters of permeate were processed.

While on site, samples were also collected from Pond B. Pond B is one of the former reactor cooling ponds located on SRS which contains low level radionuclide contamination within the lakebed sediments and waters of the impoundment. Pond B is characteristically stratified during the summer months and during survey collection was found to have dissolved oxygen levels of 5.16 mg/l in the surface layer contrasted by 0.33 mg/l at 8 meters depth. Levels of 239Pu measured from these depths were 3.9 x107 atom/l and 1.6 x108 atom/l respectively. Given the unique difference in redox potential and measurable Pu concentrations, a sampling effort was designed for the site visit to explore the potential effects on Pu speciation within the

pond. A complete CFF experiment was performed at 1 meter depth with 30 liter of permeate processed. Unfortunately, due to heavy organic loading of prefilters at 8 meter which prevented CFF processing, only whole water samples collected. To date, WHOI has processed, 48 redox samples and 24 corresponding whole water samples. for TIMS analysis.

PLANNED ACTIVITIES Processing at WHOI is continuing which includes remaining whole water fractions from CFF processing and redox samples precipitated in the field. Assessment of blanks and carry over between well sampling will be addressed from Q-H2O field blanks along with CFF cleaning solutions. Methods and analysis for Cm/Am will continue at PNNL with processing of October 2004 samples. TIMS analysis of size fractionated and redox/speciation Pu samples will continue as instrument time is made available.

INFORMATION ACCESS Results from these EMSP projects can be found at: http://cafethorium.whoi.edu and in the following publications and reports: Journal Articles - M.H. Dai, K.O. Buesseler and S.M. Pike. Plutonium in the groundwater at the DOE Hanford Site. Journal of Contamination Hydrology,76, 167-189. Hassellov, M., K.O. Buesseler, S.M. Pike and M. Dai (2004) Application of cross flow ultrafiltration to determine the abundance of colloids and associated elements in anoxic ferrous-rich ground waters, Journal of Contamination Hydrology, in review. M. Dai, K.O. Buesseler, (2004) Cross Flow Ultrafiltration, Water Research, in review.