Project 90075

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, 2004 Lead PI: K.O. Buesseler, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, 508-289-2309, kbuesseler@whoi.edu 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 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. he 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 2003-04 Our major effort over the past 9 months was focused on collection and analysis of whole water survey samples from the F and H area seepage basins of SRS. Results from this survey analysis (and one in May) will direct our field efforts later this year. Results to date 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. Note that 110-C, a deeper well at the same site, has below detectable Pu. Other 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. This suggests a local source (i.e. non-fallout Pu), but at extremely low concentrations. Two other wells have equally low 239Pu concentrations, and 240/239 ratios of 0.13-0.14. This includes one sample across Fourmile Branch river, and another from well 101D, "upstream" from the other H-area wells in the NE sector. Initial assessment of these two wells suggest they contain some combination of very low levels of fallout and a local source Pu with the low ratio. There are vanishingly low concentrations of Pu in the NW sector of the H-area (wells 115 & 137). Six additional survey samples are to be collected during June to aid in establishing a sampling strategy for the site visit in fall 2004. PLANNED ACTIVITIES We are currently in preparation for the major field operation of this project in the fall of 2004. INFORMATION ACCESS Results from these EMSP projects can be found at: http://cafethorium.whoi.edu and in the following publications and reports: Journal Articles - 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, S.M. Pike (2004) Speciation and isotopic composition of plutonium in the groundwater at the DOE Hanford Site, Journal of Contamination Hydrology, in review. M. Dai, K.O. Buesseler, (2004) Cross Flow Ultrafiltration, Water Research, in review.