Annual progress report of project # 86845

"Linking Chemical Speciation, Desorption Kinetics, and Bioavailability of U and Ni in Aged-Contaminated Sediments: A Scientific Basis for Natural Attenuation and Risk Assessment"

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1. Project Goals and Objectives

The extent to which heavy metals and radionuclides pose an environmental hazard depends on their potential for release to and transport in the environment, i.e., environmental availability, and their potential for introduction into biological systems, i.e., bioavailability. Although there exists a substantial body of literature pertaining to the fate, distribution, and bioavailability of contaminant metals in model laboratory systems, few studies have examined the biogeochemical cycling of heavy metals in complex aged-contaminated soils and sediments at a fundamental level. Even fewer have coupled detailed information on chemical speciation from state-of-the-art microscopic analytical and spectroscopic techniques with macroscopic observations obtained using indirect chemical extractions, metal desorption and leaching experiments, and biological uptake and toxicity assays.

Consequently, a major knowledge gap exists in translating basic geochemical science performed in simple model systems, short duration sorption/desorption laboratory experiments, and decoupled aqueous and solid phase speciation studies to real world systems that reflect the complexity arising from interaction of mixed waste contaminant source terms, long term aging reactions, multiple mineral surfaces, and naturally occurring organic matter. Moreover, the fundamental reactions governing contaminant aging, environmental availability, and bioavailability of metals and radionuclides, which dramatically influence the efficacy of environmental remediation and management strategies, remain poorly defined and understood.

The overall **goal of this project** is to address these fundamental knowledge gaps by investigating specific aging mechanisms for U (an actinide) and Ni (a transition metal) released to the Savannah River Site (SRS) environment from a compositionally and temporally defined source term and aged in dynamic riparian/wetland sediments for over 30 years. Another unique feature of the study site is the distinct sediment stratification resulting from variable hydrologic regimes during processes discharges which created discrete zones of sediment deposition that vary significantly in organic carbon and Fe oxide contents while having relatively similar total U and Ni concentrations. Knowledge about the timing and composition of past contaminant discharges coupled with the unique sediment stratification provides a tremendous opportunity to examine the relative role(s) of reactive mineral and organic phases in metal sequestration processes.

The proposed research represents a unique opportunity to establish clear linkages between aging, soil/sediment properties, chemical speciation, environmental availability, and bioavailability of U and Ni. These linkages are essential for developing rational and scientifically sound risk assessment methods, evaluating the potential of natural attenuation processes (MNA) and engineered remediation strategies for reducing metal toxicity and environmental risk, and understanding the fundamental processes governing cycling of heavy metals and radionuclides in the environment. Specifically, the information generated in this project will be important to developing final remediation strategies and approaches for a >7 km stretch of stream and associated riparian zone on the SRS that is received more than 40 metric tons of U and Ni, which in the case of U, represents more than 97% of the gross alpha emissions from the SRS to the environment over 51 years of operations.

Thus, the principal objectives of this study are to:

I. Define and explain the primary mechanisms of contaminant aging responsible for redistributing U and Ni into less available forms in terms of metal biogeochemistry (i.e., actinides and transition metals), important sediment properties (e.g., Fe oxide coatings and organic matter) and key environmental conditions (e.g., pH, Eh, and ionic strength).
II. Relate chemical lability (solubilities and desorption kinetics) of U and Ni back to chemical speciation in aged-contaminated sediments at a fundamental molecular level through a unique integration of indirect and direct, macroscopic and microscopic, and solid and solution phase chemical speciation methods.
III. Correlate chemical speciation and lability of U and Ni in aged-contaminated sediments with relevant bioavailability metrics, i.e., bioaccumulation and toxicity in the sediment-detritus-detrivore trophic system.

The proposed work is divided into 3 phases that corresponds to our 3 research objectives and corresponding hypotheses. The **Research Phases** are:

I. Investigation of contaminant aging mechanisms
II. Linking contaminant (heavy metal, radionuclide) aging mechanisms and chemical speciation to fate and transport endpoints, i.e., leaching and desorption kinetics, pH and redox cycling
III. Linking results from Phases I and II with biological endpoints, i.e., bioavailability of heavy metals and radionuclides, through chronic and acute exposure assays within the sediment-detritus-detrivore trophic system

Implicit in our experimental approach is the integration of (1) indirect and direct speciation techniques, (2) aqueous and solid phase speciation and bioavailability data, (3) macroscopic observations from desorption and leaching experiments and microscopic level information on molecular contaminant speciation and sediment properties for defining and interpreting the linkages between heavy metal (and radionuclide) aging, speciation, desorption kinetics, and geochemical cycling and the biological responses to sediment and solution phase metals/radionuclides.

2. Research Progress and Implications for the period September 26, 2002 through June 16, 2003.

Phase I. As of June 16, 2003 (nine months into the project), we have completed much of the basic and more traditional physical and chemical characterization of contaminated sediments in the Tims Branch (TB) corridor , and have collected speciation data from more advanced methods. Accordingly, we have narrowed our analytical focus on the use of direct, spatially resolved speciation methods for determining how aging impacts the homo- and heterogeneous distribution and speciation of metals (and radionuclides) in complex environmental media as a function of mineralogy, organic carbon, and other geochemical controls.

We dedicated 16 days of our participating research team (PRT) beam time at beamline X-26A at the National Synchrotron Light Source (NSLS) to examine thin sections of sediments collected from the high and low organic C zones in the contaminated sediments by micro-X-ray fluorescence spectroscopy and micro-XANES. We were also successful in receiving 3 days of beam time at sector 13 (GSE-CARS) at the Advanced Photon, Source, Argonne, IL for the period covering January – April, 2003 with the proposal entitled "Spatially resolved EXAFS on uranium in aged-contaminated riparian sediments."

SXRF mapping, μ-XANES, and electron microprobe characterization of thin-sections. Completed SXRF and XANES characterization of sediment thin-sections, which involved multiple sessions at NSLS beamline X26A, use of electron microprobe facilities at the University of Georgia, and incorporation of laser ablation-ICP-MS setup at SREL. This work confirmed preliminary results that suggested distinct distribution patterns for the major contaminants U and Ni within sediments. Uranium is concentrated in organically derived sediment features, while Ni is predominately associated with Fe-rich mineral matrix. This heterogeneity appears at the 10 um scale, which on the order of the spatial resolution available at X26A. Evidence for a connection between detritial degradation and changing U and Ni partitioning is also suggested by the extensive work performed at NSLS, i.e., U appears to be completely excluded from living or fully-intact plant roots and becomes increasingly concentrated within organic structures as root integrity is compromised and mineralization begins. Further mineralization also results in substantial Ni accumulation as Fe coatings and cementations fill the void spaces left by decaying plant matter. Further evidence for the presence of refractory Ni phases, which may represent source term artifacts, was also observed, corroborating earlier SEM observations with whole soils.

MicroEXAFS at APS. More advanced XAS work was initiated on the same thin-sections employing the capabilities available at GSE-CARS (sector 13) at the APS. Instead of yielding the expected information on local chemical environment for U (i.e., nearest neighbors), the high flux beam appears to strongly influence

the speciation of U in the thin-sections. However, an interesting pattern was observed for these beam artifacts, namely that the two predominate populations of U undergo beam induced reduction, i.e., organically bound versus mineral matrix associated, at distinctly different rates. Consequently, these apparent deleterious effects may be useful in themselves as probes of local geochemical environment based the reduction kinetics. More work is required to examine the ability to use the extent and kinetics of U reduction as a probe to examine spatially variable chemical speciation.

Phase II. As of June 16th we have initiated preliminary batch desorption experiments in order to link aging effects to relevant geochemical endpoints (solubility, desorption kinetics). Collaboration with Jon Chorover's research group was initiated as a result of a DOE-SC sponsored workshop. Chorover's group has existing and extensive experience with redox cycling experiments with soils and sediments in a specially designed controlled reactor cell. Sediments are being characterized for shipment to Arizona as per DOT regulations to initiate desorption experiments as a function of changing redox.

Phase III. As of June 16th, we have completed the development of a Field Flow Fractionation (FFF) and Size Exclusion Chromatography (SEC) coupled with ICP-MS for the chemical speciation of soluble U and Ni complexes. We have also completed initial experiments examining the influence of chemical speciation on the bioavailability of U and Ni as assessed by the microbial assay MetPLATE.

SEC- and FFF-ICP-MS speciation of aqueous phase complexes: Initiated work coupling aqueous speciation with information on solid phase partitioning and speciation patterns for U and Ni in sediments. Preliminary results from SEC and FFF chromatography coupled with ICP-MS detection, clearly indicates two distinct populations of U: one associated with colloidal material and one with fulvic acid complexes. In contrast, the majority of Ni appears to be associated with low molecular weight complexes but major differences in the proportion of inorganic and low molecular wt. organic complexes are observed between different locations on the Tims Branch corridor and these differences in speciation correlated to observations of bioavailability and toxicity (*vide infra*).

MetPLATE toxicity assay: The aqueous speciation work correlates nicely with toxicity screening assays performed on the same sediment-water extracts using the commercially available MetPLATE test kit. Toxicity trends did not appear to follow expended increases in total and dissolved metal concentrations. Instead, toxicity appears to track the source of sediments (upstream vs. downstream), which would reflect physical and chemical aspects such as particle size effects, redox cycling and exposure to oxidizing conditions, local sediment conditions (e.g., pH), etc. These dramatic and unexpected trends were fully borne out in SEC and FFF chromatographic separations.

3. Ongoing and Planned Acitivities:

In the upcoming year we plan to continue the thin section work using advanced spectroscopic methods to interrogate spatially variable U and Ni solid phase speciation, to complete batch desorption experiments, to initiate the experiments examining the role of redox on U an Ni sorption dynamics, and to expand the solution phase speciation approach using SEC- and FFF-ICP-MS techniques on a wider range of port waters. We also will initiate toxicity experiments utilizing two important detritivores, earthworms and nematodes. We have also begun to establish a collaboration with D. van der Lelie and his group at Brookhaven National Lab (BNL), who has developed an extremely sensitive microbial biosensor to predict bioavailable Ni in soils and we hope to incorporate this bioindicator into future studies.

4. Information Access:

Publications

A. G. Sowder, B. P. Jackson, and P. M. Bertsch, and A. Lanzirotti. 2003. Spatially-resolved characterization of U and Ni partitioning and speciation in riparian sediments. To be submitted to *Geochimica et Cosmochimica Acta.* In preparation.

A. G. Sowder, P. M. Bertsch, and P. J. Morris. 2003. Partitioning and Availability of Uranium and Nickel in Aged-Contaminated Riparian Sediments. *Journal of Environmental Quality.* **32**(3):885-898.

Papers/Posters at Professional Meetings

A.G. Sowder, B. P. Jackson, and P. M. Bertsch. 2002. Organic Carbon and Iron Oxides as Geochemical Controls of Uranium and Nickel Availability in Contaminated Riparian Sediments. 2002 Soil Science Society of America Annual Meeting, Indianapolis, IN, November 10 –14, 2002.

P. M. Bertsch, A.G. Sowder, and B.P. Jackson. 2003. Linking Chemical Speciation, Desorption Kinetics, and Bioavailability of U and Ni in Aged-Contaminated Sediments: A Scientific Basis for Natural Attenuation and Risk Assessment. EMSP Annual PI meeting, Richland, WA, May 6, 2003.

Published Abstracts

A. G. Sowder and P. M. Bertsch. 2002. Elemental Distribution of U and Ni in Contaminated Riparian Sediments. National Synchrotron Light Source activity

report for period covering October 1, 2001 – September 30, 2002. Brookhaven National Laboratory, Upton, NY.

A. G. Sowder and P. M. Bertsch. 2002. Spatially Resolved XANES Analysis onU and Ni in Aged-Contaminated Savannah River Site Sediments. National Synchrotron Light Source activity report for period covering October 1, 2001 – September 30, 2002. Brookhaven National Laboratory, Upton, NY.

Reports

A.G. Sowder, P.M. Bertsch, B.P. Jackson, and A. Lanzirotti. 2002. Partitioning and Speciation of U and Ni in Aged-Contaminated Riparian Sediments. *In*: Molecular Environmental Science: An Assessment of Research Accomplishments and Needs. Draft Whitepaper on Molecular Environmental Science prepared by EnviroSync.