Final report of project # DE-FG02-08ER64609 -11/7/2013 Project period: 7/1/2008-6/30/2009

"Environmental Remediation Science at Beamline X26A at the National Synchrotron Light Source"

Report # 110713

PI: Paul M. Bertsch University of Kentucky

Executive Summary- The goal of this project was to provide support for an advanced Xray microspectroscopy facility at the National Synchrotron Light Source, Brookhaven National Laboratory. This facility is operated by the University of Chicago and the University of Kentucky. The facility is available to researchers at both institutions as well as researchers around the globe through the general user program. This facility was successfully supported during the project period. It provided access to advanced X-ray microanalysis techniques which lead to fundamental advances in understanding the behavior of contaminants and geochemistry that is applicable to environmental remediation of DOE legacy sites as well as contaminated sites around the United States and beyond.

1. Project Goals and Objectives

The extent to which heavy metals and engineered nanomaterials 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 and nanomaterials 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, engineered nanomaterials and radionuclides, which dramatically influence the efficacy of environmental remediation and management strategies, remain poorly defined and understood.

The overall **goal of this project** was to provide technical support for the hard Xray microprobe beamline, X26A, at the National Synchrotron Light Source (NSLS). Beamline X26A has been developed by a consortium led by the University of Chicago since the 1980s. It is a critical resource for investigators conducting fundamental research in environmental remediation science. This beamline has capabilities that include X-ray fluoresce microscopy, micro-X-ray absorption spectroscopy, micro-X-ray computed tomography, and micro-X-ray diffraction. These capabilities enable the elucidation of the fundamental mechanisms underlying contaminant behavior at the molecular level.

2. Research Progress to date:

The beamline supported numerous research activities either performed by researchers at the University of Kentucky, our collaborators at the University of Chicago, or by general users from a variety of institutions. Some of the scientific accomplishments from our group include the first evidence for bioavailability of engineered nanomaterials in soil invertebrates (Unrine et al., 2008, 2010a, 2010b). Insights into the bioavailability of molybdenum in soils (Wichard et al., 2009), metal homeostasis in plants (Punshon et al., 2009) and arsenic mineralogy at a contaminated site (Wallker et al., 2009) are among the many topics which were investigated at X26A during the grant period. These research activities are likely to lead to fundamental advances in environmental remediation science that will benefit the DOE environmental remediation missions. A list of publications produced as a result of work performed at the beamline during the period of support, or resulting from research conducted during this time is listed in section 4.

3. Ongoing and Planned Research Activities:

Support for the beamline has been maintained through a combination of DOE grants and support from the University of Kentucky office of the vice president of research and will continue until the decommissioning of the NSLS in November 2014. The PI and collaborators are working to establish support for a transitional hard X-ray microprobe beamline at the NSLS-II in order to continue to support these fundamental advances.

4. Information Access:

Publications

Cottrell, E., Kelley, K., Lanzirotti, A., and Fischer, R. (2009) High-Precision Determination of Iron Oxidation State in Silicate Glasses Using XANES, *Chemical Geology*, v. 268, p. 167-179.

Castro, J., Cottrell, E., Tuffen, H., Logan, A. Kelley, A. (2009) Spherulite crystallization induces Fe-redox redistribution in silicic melt, *Chemical Geology*, v. 268, p. 272-280.

Duff, M.C., Hunter, D.B., Burger, A., Groza, M., Buliga, V., Bradley, J.P., Graham, G. Dai, Z.R., Teslich, N., Black, D.R., and Lanzirotti, A. (2009) Characterization of

heterogeneities in detector-grade CdZnTe crystals, Journ. of Materials Res., v. 24, p. 1361-1367.

Eaton, M., Jones, K., and Mahajan, D. (2009) Mimicking natural systems; methane hydrate formation-decomposition in depleted sediments. *Geological Society Special Publications*, v. 319, p. 121-130.

Flynn, G., Sutton, S., and Lanzirotti, A. (2009) A Synchrotron-Based Facility for the In-Situ Location, Chemical and Mineralogical Characterization of ~10 micrometer Particles Captured in Aerogel, *Advances in Space Research*, v. 43, p. 328-334.

Flynn, G., Lanzirotti, A., and Sutton, S. (2009) Elemental and Mineralogical Compositions of Cluster IDPs: A Possible Analog to the Wild 2 Particles Collected by Stardust, *40th Lunar and Planetary Science Conference*, Vol 40, p. 1166, sponsored by Lunar and Planetary Institute (2009).

Jackson, B., Pace, H., Lanzirotti, A., Smith, R., and Ranville, J. (2009) Synchrotron X ray 2D and 3D elemental imaging of CdSe/ZnS quantum dot nanoparticles in Daphnia Magna, *Analytical & Bioanalytical Chemistry*, v. 394, p.911-917.

Kastyak, M. (2009) Chemical Characterization and Imaging of Creatine Deposits in Human Central Nervous System Tissues with Infrared and X-Ray Fluorescence Spectromicroscopy, Ph.D Thesis. University of Science and Technology, Krakow.

Kelley, K. and Cottrell, E. (2009) Water and the Oxidation State of Subduction Zone Magmas, *Science*, v. 325, p.605-607.

Khodja, H., Reapsaet, C., Burchell, M., Flynn, G., Gainsforth, Z., Herzog, G., Keller, L., Lanzirotti, A., Rao, W., and Sutton, S., (2009) Characterization of 81P/Wild 2 Particles C2103,1,98,1,0, C2103,1,98,2,0, and C2065,1,97,1,0, *40th Lunar and Planetary Science Conference*, Vol 40, p. 1746, sponsored by Lunar and Planetary Science Institute (2009).

Lange, K. (2009) Investigation Into the Attenuation of Metals in GCLS Intended for Mine Waste Containment, PhD Thesis. Queen's University, Kingston.

Leskovjan, A., Lanzirotti, A., and Miller, L. (2009) Amyloid plaques in PSAPP mice bind less metal than plaques in human Alzheimer's disease, *NeuroImage*, v.47, p. 1215-1220.

Morrissey, J. and Guerinot, M. (2009) Iron Uptake and Transport in Plants: The Good, the Bad, and the Ionome, *Chemical Reviews*, v. 109, p. 4553–4567.

Punshon, T., Guerinot, M. and Lanzirotti, A. (2009) Using Synchrotron X-ray Fluorescence Microprobes in the Study of Metal Homeostasis in Plants, *Ann. Bot.*, v. 103, p. 665-672.

Seiter, J. (2009) The Fate and Speciation of Arsenic in Soils and Poultry Production Systems, Ph.D Thesis. University of Delaware, Newark.

Unrine, J., Bertsch, P., and Hunyadi, S. (2008) Bioavailability, Trophic Transfer and Toxicity of Manufactured Metal and Metal Oxide Nanoparticles *in* Terrestrial Environments, Nanoscience and Nanotechnology: Environmental and Health Impacts, p. 345-360, John Wiley & Sons, Hoboken.

Unrine, J., Tsyusko, O., Hunyadi, S., Judy, J., and Bertsch, P. (2010a) Effects of particle size on chemical speciation and bioavailability of Cu to earthworms (*Eisenia fetida*) exposed to Cu nanoparticles. *Journal of Environmental Quality*, v. 39, p. 1942-1953.

Unrine, J., Hunyadi, S., Tsyusko, O., Rao, W., Shoults-Wilson, W., and Bertsch, P. (2010b) Evidence for Bioavailability of Au Nanoparticles from Soil and Biodistribution within Earthworms (Eisenia fetida). *Environmental Science and Technology*, v. 44, p. 8308–8313.

Walker, S., Parsons, M., Jamieson, H., and Lanzirotti, A. (2009) Arsenic mineralogy of near-surface tailings and soils: influences on arsenic mobility and bioaccessibility in the Nova Scotia mining districts, *Canadian Mineralogist*, v.47, p.533-556.

Wichard, T., Mishra, B, Myneni, S., Bellenger, J., and Kraepiel, A. (2009) Storage and bioavailability of molybdenum in soils increased by organic matter complexation, *Nature Geosciences*, v.2, p.625 - 629.