Developing EnviroSuite Resources at the National Synchrotron Light Source

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1. Research Objective:

The objective of Brookhaven National Laboratory's EnviroSuite Initiative is to develop the facilities, user support infrastructure, and techniques necessary to conduct world-class molecular environmental science research at the NSLS. This is intended to benefit the research of ERSD-supported scientists, both through direct access and assistance and through the indirect benefits of a broader network of environmental scientists as collaborators and users. Much of the EnviroSuite research involves close collaboration with members of the Center for Environmental Molecular Science (CEMS), an EMSI based at BNL and nearby Stony Brook University and jointly supported by ERSD (Project 1023761, P. Kalb) and NSF. This offers unique opportunities to benefit from both national laboratory facilities and university resources. Other collaborators, from around the US and the world, investigate various aspects of the underlying molecular-scale processes in complex natural systems. In general, synchrotron techniques are ideal for studying the molecular-scale structures, chemical/physical interactions, and transformations that govern the macroscopic properties and processes (e.g. transport, bioavailability) of contaminants in the environment. These techniques are element-specific, non-destructive, and sensitive to the very low concentrations found in real-world samples.

2. Research Progress and Implications:

This project is in its third year of funding by ERSD which provides full support for Dr. Paul Northrup and provides partial support for Dr. Mark Fuhrmann. Over the course of this project EnviroSuite has worked to enhance user support and develop resources for molecular environmental science research at the NSLS through capital investment in facilities and operational support including scientific expertise to conduct leading research and develop advanced techniques.

Facilities: ERSD support for EnviroSuite, in combination with the efforts of EnviroSuite staff to form collaborative teams for facility and research projects, has enabled the development of a number of NSLS resources and techniques for use by ERSD-supported researchers. The combination of beamlines now available provides an array of tools for environmental science research that covers a wide range of spatial resolution and energy. A multi-method approach is encouraged to better understand complex environmental systems. Access to these facilities is available through collaborations with the EnviroSuite group and through the NSLS General User (GU) Access Program. It is important to note that the active participation of EnviroSuite in the management and operation of beamlines has significantly increased the capacity of user beamtime at beamlines optimized for environmental science research. This increased capacity has principally resulted from EnviroSuite assuming management roles in three of the beamlines described below, including (1) the microprobe beamline at X27A which is a new beamline built in collaboration with the NSLS and Stony Brook University, (2) the low energy x-ray absorption spectroscopy (XAS) beamline at X15B which was previously operated by Lucent Technologies, and (3) the high energy XAS beamlines at X11A and X11B which were previously managed by the Naval Research Laboratory. EnviroSuite management/user support in each case is made possible by ERSD funding and user demand at these beamlines continues to exceed capacity.

Beamline X27A Microprobe:
Specifications: spot size ~10 microns, energy range 4-23 keV, multi-element Ge detector.
Research techniques: elemental mapping by X-ray fluorescence (XRF) including elemental associations; microbeam X-ray absorption spectroscopy (XAS) for oxidation state determination, phase fingerprinting, and local structure/speciation of precipitated, incorporated or adsorbed contaminants in environmental samples; and relationship of microscale to bulk measurements from other beamlines.
Access: As "Contributing User" (CU), 25% of beamtime is allocated to the EnviroSuite group in return for capital investment (detector, electronics, etc.) and continuing user support, in collaboration with the NSLS. J. Fitts is CU Spokesperson, P. Northrup is Beamline Scientist. An additional 50% of beamtime is allocated to the NSLS General User program.

Beamlines X11A and X11B:
Specifications: spot size 1x10 mm, energy range 4-35 keV.
Research techniques: bulk XAS for oxidation state, speciation and local-structure determination of trace components in environmental and other materials.
Access: As managers of the beamline "Participating Research Team" (PRT), 20% of beamtime is allocated to the EnviroSuite group, 20% to other environmental science collaborators, 25% to General Users, and 35% to materials science programs. M. Fuhrmann is PRT Spokesperson.

Beamline X15B:
Specifications: spot size 1x1 mm, energy range 2-5 keV standard or 0.8-10 keV extended, helium atmosphere.
Research techniques: bulk XAS of light elements (e.g. P, S) and other trace elements (e.g. U, Pu, Cd) in environmental and biological materials.
Access: PRT management and operation, 40% of beamtime is allocated to the EnviroSuite group, 35% to supporting environmental science collaborators, and 25% to General Users. P. Northrup is PRT Spokesperson and Beamline Scientist.

Beamline X1: Soft X-ray microscopy and microspectroscopy, 30 nm resolution, used for sub-cellular structure and elemental sequestration in environmentally relevant microorganisms. Access is through PRT membership and the General User program.
Beamline X26A microprobe: Similar to X27A but includes microdiffraction. GU access.
Beamline U10B: IR microscopy, microspectroscopy of organic, inorganic materials. GU access.
Beamline X18B: Quick XAS capability is under development. GU access.

Technique Development:

The personal research of P. Northrup has focused on development of new synchrotron techniques and applications for environmental science. These include:

Development of M5-edge XAS for Uranium Oxidation State Determination: Facility capabilities, measurement procedures, sample-mounting techniques, and data-processing methods have been developed for measurement of U oxidation state in mineral, sediment, biological or solution samples. Beamline X15B has been adapted to low-energy (2-5 keV) XAS of environmental samples. One focus of this is the U M5 absorption edge at 3.5 KeV, which shows a ~1 eV shift between U(IV) and U(VI). Samples are sealed in polypropylene film and analyzed under a He atmosphere, which, combined with careful sample-collection and preservation protocols, allows measurement of sediment and soil samples as they exist at the field site. Successful measurements have been made at U concentrations as low as 3 ppm. This is an advantage over the more commonly used L3 absorption edge, which is less sensitive and suffers interference from common trace elements. In addition, the M5-edge spectra are dominated by the 3d to 5f electron transition, which results in a strong easily-fit peak. This provides the opportunity to quantify mixtures of oxidation states. In addition, samples can be simultaneously examined at the S, P and Fe absorption edges to evaluate organic and mineral species and sulfate-reduction processes. Further efforts include characterization of possible U(V) species and extension of the technique to the Pu M5 edge.

Phosphorus and Sulfur XAS: Improvements to X15B and corresponding development of analytical techniques have made possible XAS of low-energy phosphorus (2.1 keV) and sulfur (2.5 keV) K edges. This can be used to determine oxidation state, speciation, and local structure in complex environmental or laboratory samples. EXAFS (extended x-ray absorption fine structure) can be used to determine local structure (identity, number, and interatomic distance of neighbors out to ~6A). Phosphate and sulfate may strongly influence metal and radionuclide mobility and toxicity by altering solution and mineral surface speciation and solubility. In addition, S is involved in both biologic and abiotic redox processes. Phosphorus XAS can identify organic (e.g. phosphine, phosphonate, polyphosphate) and inorganic (dissolved, adsorbed, crystalline, or coprecipitated phosphate) species. A collaboration with J. Brandes (Skidaway Institute of Oceanography, Georgia Tech.) and D. Hesterberg (NC State) is producing an extensive database of P spectra that has been utilized by ERSD researchers to identify U-phosphate complexes during microbial processes. Sulfur XAS, due to the rich variety of S species and oxidation states, can be utilized to identify and quantify organic and inorganic species in mixed sediments. This is useful to track diagenetic processes including reduction/oxidation and biological activity. Deconvolution of a typical organic-rich sediment spectrum can be accomplished with peaks fit representing sulfide/thiol, thiophene, sulfoxide, sulfite/sulfone, sulfonate, and sulfate. Such P and S XAS require beamline stability, resolution, optical quality, and sensitivity that are unique to X15B among worldwide synchrotron facilities.

Single-crystal microbeam and surface XAS: EXAFS has a strong orientation dependence within and on the surface of crystalline materials. This is not a consideration in bulk samples with random orientation of particles, but can be very important in microbeam XAS, where beam size is comparable to grain size. It can also be used effectively to study the nature of adsorption and reaction at mineral surfaces. A collaboration with J. Rakovan (Miami Univ. of Ohio) uses the X27A microprobe to develop orientation-dependent micro-EXAFS of U- and Th-doped apatite crystals. Work with D. Strongin (Temple U.) investigates processes on calcite crystal surfaces.

In addition, J. Fitts is participating in collaborations developing environmental-science applications for "quick XAS" capabilities the NSLS is developing at X18B. P. Northrup and J. Fitts have begun a collaboration with G. Waychunas (LBNL) to develop grazing incidence XAS at X15B.

Support for ERSD-funded users:

In addition to optimizing these beamlines for environmental science research, a significant portion of EnviroSuite effort involves providing support to users before, during, and after their experiments. Support provided by EnviroSuite Scientist P. Northrup includes beamline optimization and setup, beamline safety training, beamline operations training and on-call troubleshooting. Part of beamline training includes graduate student and post-doctoral education. In addition to hands-on beamline support, significant support is provided prior to arrival with regard to experiment design, preparation of GU proposals (18 during FY06), safety reviews, sample preparation, preservation and transport procedures, and following experiment completion with regard to data analysis and interpretation. EnviroSuite personnel supported 55 ERSD-funded experimental runs in FY06, and provided beamline training for 28 new users and students during these experimental runs. EnviroSuite also offers collaboration opportunities and short-term beamline access for feasibility studies.

A significant effort has been made to educate current and potential users, through seminars, workshops, and meetings. EnviroSuite was represented at Spring NABIR and ERSP PI meetings in Warrenton VA 2004-6, FRC meetings at Oak Ridge 2005-6, and American Chemical Society and Geological Society of America national meetings. J. Fitts, P. Northrup and M. Fuhrmann were guest lecturers for the ERSD-supported 2006 Nuclear Chemistry Summer School.

ERSD-funded users (PIs only) and projects directly supported by EnviroSuite personnel:

J. Fitts, BNL Environmental Science Department

1) Project 1023761. Phosphate sorption on iron oxide nanoparticles using P K-edge XAS, X15B.

2) Project 1024830, Composition of Microbial Communities Used for In Situ Radionuclide Immobilization: Natural Gene Transfer to Develop Resistance to Metal Toxicity. X27A, X15B, X11, and X1 Characterization of U distribution and oxidation state in sediments from of the NABIR Field Research Center Area 2 prior to induced microbial activity, X27A microprobe, U and S XAS at X15B

AJ Francis, BNL Environmental Science Department, Project 1024831

. U and Pu in Nevada Test Site soils, X27A, U and Pu XANES at X15B.

M. Fuhrmann, BNL Environmental Science Department, Project 1023761.

West Valley project grouts, X27A microprobe, U XAS at X15B, X-ray diffraction at X7.

G. Halada, SUNY Stony Brook. Project 90258

Microbial Transformations of TRU and Mixed Wastes: Actinide Speciation and Waste Volume Reduction. Structure and redox processes in molybdate coatings on U metal, X15B.

P. Northrup, BNL Environmental Science Department, Project 1023762.

Characterization of U in organic-rich sediments under redox gradients; X27A microprobe; U, Fe and S XAS at X15B, U XAS at X11, IR microspectroscopy at U10B.

P. Sobecky, Georgia Tech, Project 1024775.

Using P EXAFS to investigate the role (and mechanism) of microbial phosphatases in non-reductive sequestration of U(VI), X15B.

G. Waychunas, LBNL, Project 1024944.

Grazing incidence Si K-edge spectroscopy of silicate adsorbed on metal oxide surfaces, X15B.

3. Planned Activities:

In FY 2007 and beyond, the EnviroSuite program will continue operations, user support, publications, and program development. It will remain focused on development of techniques and applications most useful to ERSD-supported research. Additional upgrades to beamline facilities will be pursued as permitted by budget, leveraging other funding sources wherever possible. We will continue to educate and reach out to experienced, novice and potential synchrotron users within the community.

EnviroSuite personnel have and will continue to actively participate in planning for the future of the NSLS and the next generation of synchrotron facility at BNL. P. Northrup, with input from environmental science users, worked with NSLS administration to develop the enviroscience portion of the NSLS 5-Year Strategic Plan. This plan was submitted by the NSLS to DOE in spring 2006. Northrup also is participating in design/planning for the proposed NSLS-II project, and contributed to the NSLS-II Conceptual Design Report which was submitted to DOE in November 2006. When operational, NSLS-II would have the potential to become a world-class facility for ERSD synchrotron-based research.

4. Information Access:

EnviroSuite Web Page: (http://www.bnl.gov/envirosuite/)

Publications generated by the research program of P. Northrup supported by this contract (publications by supported researchers and users are listed under their individual projects):

A. Frenkel, L. Menard, P. Northrup, J. Rodriguez, F. Zypman, D. Glasner, S. Gao, H. Xu, J. Yang, R. Nuzzo, "Geometry and charge state of mixed-ligand Au13 nanoclusters," American Inst. of Physics XAFS Conference Proceedings, 2006.

F. Einsiedl, T. Schaefer, P. Northrup. "S XANES spectroscopy and stable isotope studies on fulvic acids sulfur and groundwater sulfate for mapping anoxic processes in otherwise oxic soils." In press, Global Biogeochemical Cycles, 2006.

P. Northrup, EnviroSuite: Environmental Science at the NSLS. NSLS Newsletter, Spring 2005. http://www.nsls.bnl.gov/newsroom/publications/newsletters/2005/05-april.pdf

L. Mgrdichian, Students Experience NSLS via Webcast, NSLS Newsletter, Summer 2006. http://www.nsls.bnl.gov/newsroom/publications/newsletters/2006/06-july.pdf

Invited presentations:

P. Northrup, National Synchrotron Light Source Symposium, 3/28/06, "An introduction to X-ray absorption spectroscopy in enviro- geo- and biosciences."

P. Northrup, "Nuclear Science and the Environment" symposium at the Summer School in Nuclear and Radiochemistry, 7/18/06, "An overview of synchrotron techniques for studying synchrotron processes." (http://www.bnl.gov/ncss/Symp_Environment.asp).

P. Northrup, Stony Brook University Geosciences Colloquium, 2/9/06, "X-ray absorption spectroscopy in environmental and geosciences."