Environmental Science Program at the Advanced Light Source
FY05 Annual Report

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Project objective

Synchrotron Radiation (SR)-based techniques have become an essential and fundamental research tool in Molecular Environmental Science (MES) research. MES is an emerging scientific field that has largely evolved from research interactions at the U.S. Department of Energy (U.S. DOE) SR laboratories in response to the pressing need for understanding fundamental molecular-level chemical and biological processes that involve the speciation, properties, and behavior of contaminants, within natural systems. The role of SR-based investigations in MES and their impact on environmental problems of importance to society has been recently documented in *Molecular Environmental Science: An Assessment of Research Accomplishment, Available Synchrotron Radiation Facilities, and Needs* (EnviroSync, 2003).

The Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) is one the U.S. DOE SR laboratories with special experimental capabilities for MES. An active, diverse portfolio of MES research is performed at the ALS, some of which is supported by the Environmental Remediation Science Division (ERSD) of BER, such as the EMSP and the NABIR programs. The ALS, similar to the other U.S. SR laboratories, does not have the optimal level of user support that is needed to most efficiently support ERSD researchers.

The primary objective of the project is to provide support to NABIR and EMSP PI's who wish to use the Advanced Light Source. Based on expressed and documented ERSD PI research needs, this program offers support across a suite of environmental beamlines at the ALS. The capabilities of the facility include infrared spectromicroscopy on beamline 1.4.3, micro-tomography on beamline 8.3.2, micro-X-ray absorption spectroscopy and micro-diffraction on beamline 10.3.2, and scanning transmission X-ray microscopy (STXM), X-ray photoelectron spectroscopy, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy on beamline 11.0.2. These beamlines provide an energy range from sub-eV to 30 keV while covering a length scale from tens of nanometers to centimeters. Beam line 8.3.2 was in commissioning most of the FY05. As of the end of the year, the beamline completed commissioning and is now available for use by interested PI's. The new capabilities of this beam line will allow for the rapid three dimensionally imaging of solid samples through computed X-ray tomography. This represents a new and powerful capability of the facility.

Additional components of the Environmental Program at the ALS include raising the awareness within the environmental community about the utility of the environmental beamlines for ERSD research, and developing methods (such as approved programs) that increase access for environmental scientists to the chosen beamlines. The bulk of the funds in this project are allocated to support Dr. Peter Nico, the scientist in the Earth Sciences Division of LBNL who is leading the Environmental Program at the ALS.

Project progress and implications

This report summarizes the progress as of 1 year of a 4 year initial project for the development of the ALS environmental science program at LBNL. Progress on the project can be divided into the four areas listed below: the research conducted at the facility by EMSP, NABIR, and EMSI PIs, recruitment of the new scientific lead of the environmental science

program, the development of the facility's technical capabilities, and outreach to the potential user community.

Research Activities

Even in this early stage, the Environmental Program at the ALS has assisted several EMSP, NABIR, or EMSI projects during FY05, including several investigators who were new to the facility or to one of its beam lines as of this year. Below, we provide a brief description of some of the projects that Dr. Nico has supported. A more complete list of ERSD researchers who have been assisted by this program is provided in the section entitled 'Optional Additional Information'.

Dr. Mary Neu of LANL (EMSP, NABIR; 24 hours of beam time) and co workers wished to study the effects of microbial metabolism on the chemical speciation of U and Pu. The STXM on beam line 11.0.2 was identified as the appropriate instrument to address this question because of its ability to gather spatial and oxidation state information on both light elements such as carbon (important in imaging bacterial cells) and heavy elements such as U and Pu with spatial resolution of approximately ten nanometers. The samples were shipped to LBNL where Dr. Nico assisted in preparing the samples for analysis and collecting the data on the 11.0.2 STXM. This was the first time Dr. Neu was able to utilize beam line 11.0.2 in support of her research program.

Drs. A.J. Francis and Cleveland Dodge of BNL (EMSP, EMSI; 24 hours of beam time) and co workers were interested in conducting a similar experiment as Dr. Nue. They wished to look at Pu speciation on soils from the Nevada Test Site, and compare that to Pu speciation on the same soils after biostimulation of the natural microbial consortium through carbon additions, e.g., glucose and citrate. The soils arrived at LBNL where Dr. Nico prepared them for analysis on the STXM. The data acquisition proved challenging because the absolute concentration of Pu was relatively low and because the Pu was not present in discrete grains but was dispersed throughout the sample in thin absorbed layers. This was also the first time that Drs. Francis and Dodge had been able to utilize the capabilities of the facility.

An example of the data collected during this experiment is shown in Figures 1 and 2.

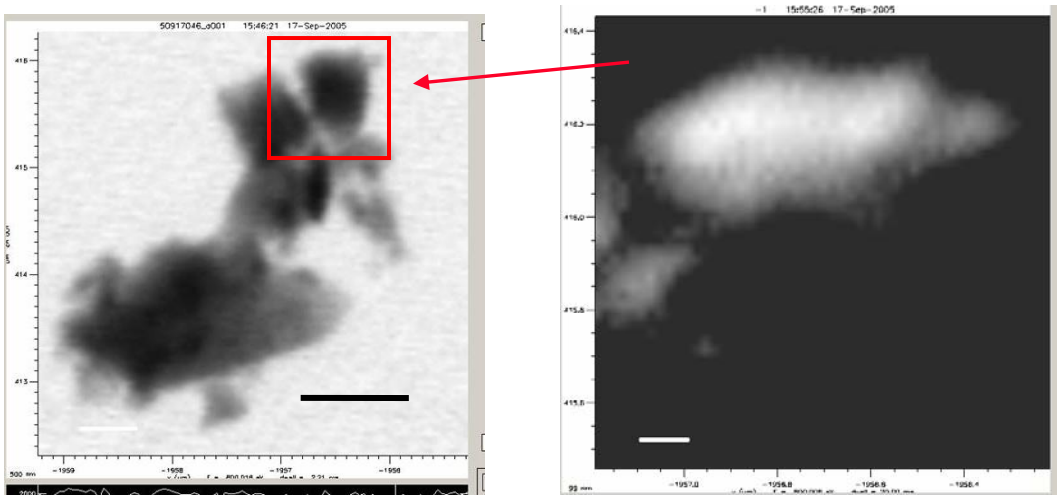

Figure 1a: Optical density map of a particle @ 800 eV. Scale bar 1 μm.

Figure 1b: Map of Pu concentration in selected region. Scale bar 0.1 μm.

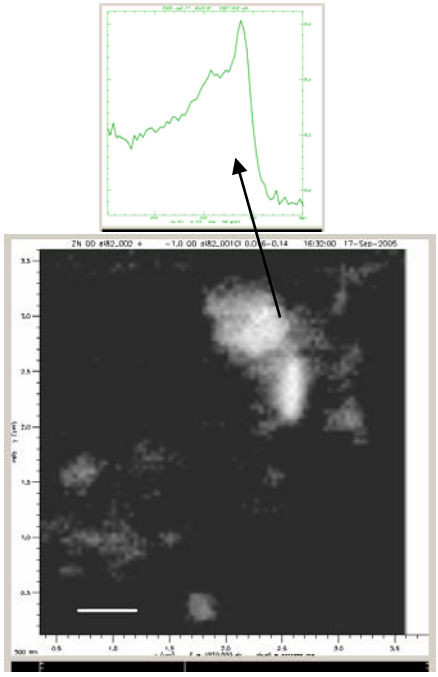

Figure 2a: Al map and NEXAFS spectra of particle from Figure 1a. Scale bar 0.5 μm.

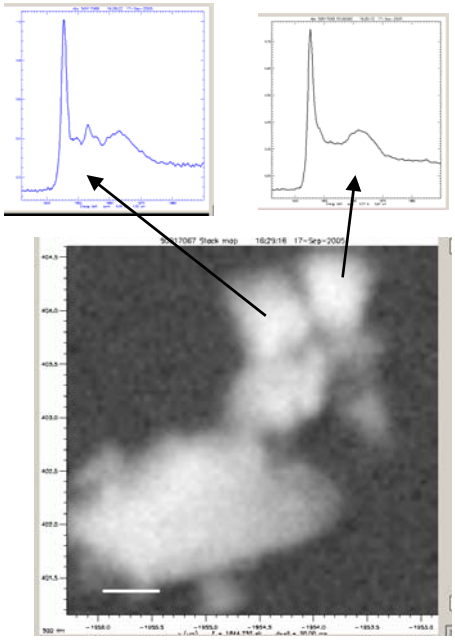

Figure 2b: Si map and NEXAFS spectra of particle from Figure 1a showing two different types of Si present. Scale bar 0.5 μm.

Dr. Nico also assisted in the STXM data collection for **Dr. Carl Steefel of LBNL (EMSP, EMSI; 12 hours of beam time**) and coworkers, who are studying the rates and mechanisms of clay dissolution in order to remove the long standing discrepancies between experimental data and field simulations, as well as for **Dr. David Shuh of LBNL (EMSP; 12 hours of beam time)** and co workers who are investigating the fundamental chemistry of technetium.

The limited amount of available beam time is a perennial problem for researchers wishing to use synchrotron facilities. Since his arrival at LBNL, Dr. Nico has been able to increase the overall amount of useable beam time for ERSD researchers by carefully matching the capabilities of the facility to the needs of the researchers. For example, "two-bunch mode" is a specific experimental arrangement of the electron storage ring at the ALS that is important to experimenters wishing to conduct ultra-fast timing experiments. Unfortunately, it also reduces the flux of X-rays emitted from the ring by an order of magnitude. Because of this decrease, two bunch mode is usually considered inadequate for use by researchers with environmentally relevant samples with low analyte concentrations. However, this year Dr. Nico was able to identify two projects of **Dr. Scott Fendorf's of Stanford University (NABIR, EMSP, and EMSI; 16 hours of beam time)** that could effectively be advanced during two-bunch mode. In this way, the total amount of beam time utilized by NABIR, EMSP, and EMSI users was increased. The first project looked at As and Cr spatial distribution on soils from contaminated sites. The second project involved studying the effects of Fe(II) on the transformations of Fe(III) minerals and the subsequent effect on contaminant transport. Beam line 10.3.2 was used to collect an Fe oxidation state speciation map that could be correlated with Fe mineral forms and contaminant mobility and chemical state. An example of this oxidation state map is shown in Figure 3.

A)

B)

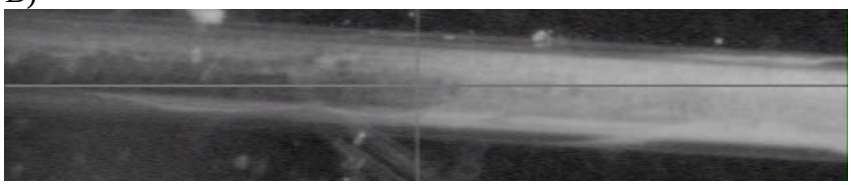

Figure 3: A) The decrease in Fe(II) content from left to right can be seen in the transition from blue/purple to red (Fe(II) is shown in blue, Fe(III) is shown in red). B) Optical image of capillary showing left to right transition from magnetite (dark) to ferrihydrite (light).

Dr. Liviu Tomutsa was supported by the program to assist EMSP and NABIR users wishing to use the new tomography beamline, 8.3.2. He worked with **Drs. Susan Hubbard, Ken Williams, and Jillian Banfield (UBC and LBNL; EMSP)** and co workers on designing and building flow cells for constructing micro-sand packs. A number of such sand packs have been prepared and cultures of sulfur reducing bacteria are incubating. Beamline 8.3.2 is being utilized to examine how the growth of the bacteria alter the three dimensional structure of the pore spaces within the sand packs. Initial data have been collected using iodine K-edge imaging. Data are still being acquired and processed for this experiment.

Through the efforts of Drs. Tomutsa and Hubbard, an Approved Program (AP) for beamline 8.3.2 has been established. The AP allocates ~11% of the available experimental time on this line to environmental science research for the next several years. This program will be used to support the research programs of EMSP, EMSI, and NABIR PI's.

Dr. Glenn Waychunas of LBNL (EMSI; 24 hours of beam time) and co workers were interested in the characterization of novel radionuclide complexing dedrimers by studying the nitrogen NEXAFS of these compounds. Dr. Nico assisted Dr. Waychunas' team in data collection and trouble shooting of this novel research approach. Very few nitrogen NEXAFS spectra of compound in aqueous solution have ever been collected so this was a difficult experiment that resulted in preliminary data that will be very helpful in obtaining the further beam time and external financial support necessary for a more detailed study. This study utilized the spectroscopy branch line of 11.0.2 and the specialized end station built by Dr. Satish Myneni.

Recruitment

Project PIs Susan Hubbard and David Shuh worked with a recruiting committee at LBNL during FY05 to identify the new scientific lead for the program. An international search was conducted in order to recruit the largest, most highly qualified group of potential candidates possible. After an initial screening of applicants, a short list was identified and three of the candidates were invited to the laboratory for interviews. The result of this process was the hiring of Dr. Peter Nico as the new scientific lead of the program. Due to the requirements of his current academic position, Dr. Nico began his employment at LBNL on August 1st, 2005.

Laboratory Access

Dr. Nico oversees an Environmental Program at the ALS laboratory, which can be used for sample preparation and manipulation. The efficient functioning of this laboratory space will be a great asset to researchers needing to conduct beamline and laboratory operations simultaneously in order to achieve their research objectives.

User Community Outreach

In addition to assisting ERSD researchers at the ALS who are already familiar with the facility, another important contribution of the program is to inform those who are less familiar about the capabilities of the ALS for environmental research and to advise them on the mechanisms for accessing the beamlines. The outreach component of the program has included personal contacts, development of a website and a brochure, and giving oral presentations at conferences.

The program has established a website for the Environmental Science Program at the ALS. http://esd.lbl.gov/ALS_environmental/index.html The site serves as a central information repository for researchers interesting in using the facility. It contains information to help researchers decide how to best take advantage of the facility, including: beam line specifications, sample research projects, and contact information for Dr. Nico and other scientists that may be of assistance to potential users.

In addition, the program has sent representatives to several important meetings to make contact with PI's who are not currently using the ALS, but have research projects that could benefit from the facilities capabilities. Drs. Hubbard and Shuh represented the program at the annual NABIR PI meeting, and participated in an oral presentation about the Environmental Program at the ALS. Dr. Nico was the program representative at Synchrotron Environmental Science III and also presented a talk and posted on facility capabilities at the annual PI workshop of the Field Research Center at Oak Ridge National Lab. A brochure that explains the program and provides contact information has been developed and was distributed at these meetings.

Dr. Nico has also been facilitating communication with ERSD funded scientists serving in similar positions at the three other major synchrotron sources: Stanford Synchrotron Radiation Laboratory, the Advanced Photon Source, and the National Synchrotron Light Source. Since each facility has particular strengths and specialties, close communication between the facilities representatives will help potential users identify which facility is best equipped to address their specific research questions. In this way, the efficacy of the four facilities as whole is increased to the great benefit of the outside MES user community.

Importantly, development of the program has raised awareness within the ALS about the importance of the facility for environmental research. To ensure that environmental beamline proposals are given sufficient consideration, Sam Traina (UC Merced) has recently been added as a new member of the Proposal Study Panel. The addition of such expertise to the review panel is expected to increase the access for environmental users across the ALS.

Planned activities

The activities for next year will focus on continuing to increase the benefit to MES researchers from the capabilities of the ALS facility. The goal is to ensure that current users are able to use the facility in an increasingly efficient manner as well as to inform the community about the research conducted at the ALS, and to increase the number and variety of MES projects undertaken there. The outreach activities will continue with representation of the program at annual PI meetings as well as continued development of the website as a single point of contact for interested researchers. A few specific activities are outline below.

Research development

Dr. Nico has been in contact with **Dr. Gill Geesey** (Montana State University) and coworkers at PNNL and has been developing an experimental approach to use the IR beamline, 1.4.3, to conduct studies on microbial colonization of mineral surfaces in real time. He has also been in contact with **Drs. Jaimin Wan and Tetsu Tokanaga** (LBNL) about their desire to access to the ALS. These collaborations will result in the development of general user beam time proposals to be submitted with the December 1st call for proposals at the ALS.

Increasing Access for environmental science users

Access to sufficient experimental time at the ALS is a continuing obstacle faced by many ERSD researchers whose projects could benefit from the facilities capabilities. Each call for proposals inevitably brings requests for many times more experimental time than is available. In order to help alleviate this problem, a program goal for the upcoming year is the establishment of an Approved Program (AP) for environmental science at the ALS. As was described above, such a program has already been developed at one particular beamline in the environmental beamline suite. Dr. Nico will take the lead on writing this proposal in conjunction with collaborators from the EMSP and NABIR programs. A successful AP will guarantee a certain amount of beam time over several years for environmental research in areas of interest to ERSD.

Capital Expenses

Beam line 8.3.2 was inoperable for several months this past year because the CCD camera had to be returned to the manufacturer for repair. Operating with only one camera wastes considerable researcher time. Redundancy needs to be built into the system regarding critical components before maximum usage is obtainable. A spare camera was identified (PCO400 from Cooke Corp) but was not ordered due to lack of capital equipment funds. It would be a great benefit for researchers wanting to use the facility if some of the capital equipment funds initially requested in the proposal were able to be restored for next year. The camera cost is approximately $40,000.

Beam Time Tracking

As of Dr. Nico's arrival at LBNL in August, the existing beam line staff at the four beam lines in the consortium did not collect information on the funding agencies supporting the users of their beam line. In the up coming year, Dr. Nico will work with the existing beam line staff to implement a simple reporting mechanism in order to better track which BER funding projects are being supported by the ALS and the percentage of time allocated to each project.

Information Access

Environmental Science at the Advanced Light Source webpage: http://esd.lbl.gov/ALS_environmental/index.html\

Appendix:

The following is a partial list of environmental researchers supported by BER who utilized the facility in the past year and who received varying degrees of program assistance.

Research Projects Supported

Drs. Hendrick Bluhm of LBNL (EMSI), Gordon Brown of Stanford University (EMSP, EMSI), Anders Nilsson of Stanford University (EMSI) and co workers studying chemical and microbiological interactions at solid-aqueous solution interfaces in Earth's near-surface environment, where natural waters, natural organic matter, and biological organisms interact with natural solids and environmental contaminants. (Beamline 11.0.2)

Dr. Scott Fendorf of Stanford University (EMSP, NABIR, EMSI) and co workers were studying coupled geochemical and hydrological processes governing the fate and transport of radionuclides and toxic metals beneath the Hanford tank farms. (Beamline 10.3.2)

Dr. Andrea Foster of the USGS (EMSI) and coworkers were studying Arsenic speciation in mine wastes and sorption onto mica grains. (Beamline 10.3.2)

Drs. A.J. Francis and Cleveland Dodge of BNL (EMSP, EMSI) and co workers were studying natural and biostimulated transformation of Pu in soils. (Beamline 11.0.2)

Drs. Terry Hazen and Hoi-Ying Holman (Genomics: GTL) and co workers used the facility to explore issues related to molecular mechanisms of microbial transformation of metal oxyanions and aromatic organic compounds as they relate to bioremediation. (Beamline 1.4.3)

Drs. Susan Hubbard, Ken Williams (LBNL) and Jillian Banfield (UCB/LBNL) (NABIR, EMSP) and co workers used the facility to examine samples solid samples and how microbial community activity and geochemical reactions alters the pore spaces in the material. (Beamline 8.3.2)

Dr. Satish Myneni of Princeton University (EMSP, EMSI) and co workers conducted studies on H-bonding in water, coordination chemistry of Al^{3+} in aqueous solutions and in amorphous precipitates, and on the functional group chemistry of bacteria surfaces. They also examined the functional groups of C, N, and O in siderophores and their metal complexes. (Beamlines 11.0.2, 10.3.2)

Drs. Mary Neu of LANL (EMSP, NABIR) and co workers were studying plutonium and uranium speciation and mobility in soils and the subsurface. (Beamline 11.0.2)

Drs. Klaus Pecher, Don Baer, and Yuri Gorby and co workers of PNNL (NABIR). (Beamline 11.0.2)

Drs. David Shuh and Wayne Lukens of LBNL (EMSP) and co workers investigated the fundamental chemistry of technetium. (Beamline 11.0.2)

Dr. Carl Steefel of LBNL (EMSP, EMSI) and coworkers were studying the rates and mechanisms of clay dissolution in order to remove the long standing discrepancies between experimental data and field simulations. (Beamline 11.0.2)

Dr. Glenn Waychunas of LBNL (EMSI) and co workers studied the characterization of novel radionuclide complexing dedrimers. (Beamline 11.0.2)

Time Allocations Reporting

Supported Staff Members and Allocation of Time

Staff Member	Percentage of Total	Allocation of *Environmental Science Program at the ALS* Supported Time

	Time Supported by *Environmental Science Program at the ALS* funding[1]	Support of ERSD Researchers	Technology Development and Personal Research	All Other Activities
Atkinson, Maria	2.5%	0%	0%	100%
Hubbard, Susan	7.5%	0%	0%	100%
Nico, Peter	100%[2]	85%	10%	5%
Shuh, David	1.7%	0%	0%	100%
Tomutsa, Liviu	21.4%	60%	30%	10%

[1] Estimates based on 1,848 hour working year
[2] Percentage of time since start of employment August 1st, 2005