

Justification for the Development of a Bending Magnet Beamline at Sector 10 at the APS

prepared by
Biosciences Division
Argonne National Laboratory

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by
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JUSTIFICATION FOR THE DEVELOPMENT OF A BENDING MAGNET BEAMLINE AT SECTOR 10 AT THE APS

EXECUTIVE SUMMARY

The long-planned and much-needed merger of EnviroCAT into the Materials Research Collaborative Access Team (MR-CAT)¹ will provide dedicated state-of-the-art facilities that are critical to research on a broad range of issues in environmental sciences. These CATs will focus on developing a bending magnet (BM) beamline for x-ray absorption fine structure (XAFS) and micro x-ray analysis of environmental samples through integration with existing insertion device (ID) capabilities in XAFS, micro x-ray analysis, and x-ray scattering. In addition, the expanded MR-CAT will serve as the hub of personnel and laboratory infrastructure support for molecular environmental science and biogeochemical science at the Advanced Photon Source (APS). In conjunction with the merger of EnviroCAT into MR-CAT, the U.S. Environmental Protection Agency (EPA) will become a member institution of MR-CAT, joining the present members (University of Notre Dame, Illinois Institute of Technology, University of Florida, British Petroleum, and Argonne's Chemical Engineering and Biosciences Divisions).

The motivation for blending capabilities meeting the needs of EnviroCAT users into the MR-CAT facilities is the explosion of synchrotron-radiation-based research in the field known as molecular environmental science (MES). This research is driven largely by the need to remediate contaminated environmental materials and to understand the scientific foundations that govern contaminant transport in the environment. Synchrotron radiation is playing a crucial role in solving environmental science problems by offering x-ray-based analytical techniques for detailed molecular- and atomic-level studies of these systems.

This document focuses on the scientific justification for developing a specific type of BM beamline capability at Sector 10 for XAFS and micro x-ray analysis to support the growing MES community. However, the modification of Sector 10 will meet other future needs by providing (1) an existing undulator beamline with an experimental station for bulk XAFS applications and x-ray microbeam applications (XRF, XAFS, and XRD) and (2) a BM beamline with an experimental station for large-sample XAFS spectroscopy and XRF elemental mapping on submillimeter to centimeter length scales.

Development of the BM beamline at Sector 10 will increase the availability of needed capabilities for MES at the APS. Moreover, increasing the MES component of MR-CAT research and giving the MES community an APS sector suitable to their research will create a natural conduit to the APS for these researchers. MR-CAT further intends to enhance laboratory and personnel infrastructure for MES research.

¹ With the increased profile of environmental science at MR-CAT, we have considered renaming the consortium the Materials and Environmental Research Collaborative Access Team (MERCAT). For continuity and to avoid confusion, we have at least temporarily tabled this change.

Presently available funds for the modification of the BM first optical enclosure (FOE) for bulk XAFS capabilities include \$250 K/year from the DOE Office of Biological and Environmental Research (DOE-BER) for salary support for a beamline scientist (Dr. Bruce Ravel), ~\$750 K for capital equipment from the EPA, a \$250 K/year pledge of salary support from the EPA, and a \$250 K pledge of capital equipment from DOE-BER. Though development of the FOE will provide only a rudimentary capability at present, it is an important interim step toward complete build-out of the 10-BM beamline. Upon receipt of encouragement from the Scientific Advisory Committee to develop the FOE for XAFS measurements, the CAT will pursue additional funding for complete build-out of the BM from the DOE-BER Environmental Remediation Sciences Division (ERSD), Argonne LDRD funds, and the EPA. Finally, the long-range design for the BM beamline will accommodate future incorporation of a canted undulator setup at Sector 10.

Sector 10, with the support of the APS, will seek to spearhead the solution of key issues in environmental science and human welfare faced by our nation and the world, while continuing the strong program of materials science research that has been ongoing at MR-CAT for nearly a decade.

In the following pages describe our rationale for merging MES research into MR-CAT. Our intention is to make a strong scientific case for establishment of a home for MES research at Sector 10 at the APS.

1 ENVIRONMENTAL SCIENCE RESEARCH

The need to understand how to remediate contaminated environmental materials has led to a fairly recent explosion of research activity in the field known as molecular environmental science. This term has emerged from the realization that solutions to the challenges associated with environmental contamination require knowledge of material properties and processes at the molecular level. The research involves investigations of chemical speciation, reactions at surfaces that modify speciation, the inherent mobility and bioavailability of contaminants, and physical processes (such as fluid flow) that control transport. This research leads to advances in fundamental environmental science issues, and it also provides essential input to national and international environmental policy development.

The processes investigated in MES range from the dissolution of mineral particles in soils — with potential release of natural contaminants into pore waters — to the binding or sorption of metal and organic compounds to mineral surfaces — which can effectively immobilize contaminants and reduce their bioavailability. Contaminant elements such as chromium, arsenic, uranium, and selenium can undergo oxidation or reduction when they interact with mineral surfaces and organic compounds. In addition, microorganisms and plants can have a profound influence on chemical reactions occurring at Earth's surface. For example, microorganisms often play a major role in the degradation of organic contaminants and in the oxidation and reduction of heavy metals and radionuclides. The root-soil interface, where organic acids, sugars, and other organic compounds are exuded by live plant roots, is another area of particularly intense

chemical and biological activity. Thus, mineral weathering and the solubility of natural and anthropogenic contaminants are generally increased in surface soils, where plant and microbial activity are higher than in deeper parts of the soil and geologic column. An understanding of the molecular-scale mechanisms and rates of these processes requires knowledge of the types, spatial distribution, and reactivity of contaminant species; the nature of mineral surfaces (including coatings that affect their reactivity) and colloidal particles; the types and distribution of organic compounds and microorganisms in soils and pore water; and the effect of a host of variables on the rates of dissolution, adsorption, desorption, precipitation, degradation, and redox reactions.

The importance of MES lies in the crucial role played by speciation in determining the toxicity, mobility, and bioavailability of contaminants in the environment. The molecular form or speciation of environmental contaminants such as chromium, arsenic, lead, uranium, and plutonium determine their toxicity and availability to organisms. A good example of the importance of chemical speciation on properties is chromium, which occurs in two dominant forms in nature — hexavalent chromium (Cr^{VI}), which is typically coordinated by four oxygen atoms in aquatic systems, and trivalent chromium (Cr^{III}), which is coordinated by six oxygen atoms. The hexavalent Cr^{VI} is highly toxic, mutagenic, teratogenic, and carcinogenic to organisms and is highly soluble in aqueous solution, and thus it is mobile in groundwater. In contrast, Cr^{III} is non-toxic and occurs in solids that are highly insoluble in groundwater. Thus, a relatively subtle difference in electronic and molecular configuration leads to a major difference in the impact of chromium exposure on human health.

Research in MES directly affects the core missions of many federal agencies, including DOE-BER and the EPA (both of which have pledged financial support to the MR-CAT), through investigations related to (1) discovery of fundamental knowledge about environmental materials and chemical interactions between these materials and environmental pollutants, microbial communities, and natural waters; (2) remediation of heavy-metal contamination at U.S. sites and cities; (3) quantitation of radionuclide transport and risk assessment at high-level waste disposal and radioisotope production sites; (4) science-based stockpile stewardship; (5) design of plant species to remediate contaminated soils; and (6) photooxidation of crude oils (Brown, 2002). For example:

- XAFS studies of core samples from the DOE-BER Field Research Center (FRC) at Oak Ridge National Laboratory (ORNL) are revealing depth-dependent changes in the average local chemical environment of U. This information will be critical for understanding the results of future biostimulation experiments planned for the FRC site.
- While this document was being written, floodwater sediments from the recently flooded streets of New Orleans were being prepared for Pb and As XAFS and XRF analysis at the MR-CAT ID beamline by EPA scientists. Membership of the EPA in MR-CAT, enabling regular access to the APS, is critical for these scientists to respond quickly to future disasters of national importance.

Synchrotron radiation (SR) plays a crucial role in solving environmental science problems. The advent of high-brilliance synchrotron sources has led to x-ray-based analytical

techniques that can accomplish what is otherwise impractical. The most common environmental problem being addressed at SR sources in the United States and abroad is the molecular-level speciation of metal contaminants and pollutants in complex environmental samples. The very high flux of SR sources enables dilute levels (<50 ppm) of metals to be detected and characterized. Foremost among the techniques used to address molecular-level speciation of metal contaminants and pollutants is XAFS, which yields atomic-level information on oxidation state, coordination, bond lengths, and the identity of nearest neighbors surrounding the element of concern.

The research scientists of the MR-CAT member institutions and other key scientists will conduct the research program and scientific outreach program described in Appendix A.

2 A CALL TO ACTION FROM THE MES COMMUNITY AND ENVIROSYNC

Synchrotron radiation techniques are important on a national level in the area of MES. This statement was confirmed by the results of various workshops, one held at Airlie, Virginia, in July 1995 (see *Report of DOE Molecular Environmental Science Workshop*) and another held at the Stanford Synchrotron Radiation Laboratory (SSRL) in January 1997 (see report *Molecular Environmental Science and Synchrotron Radiation Facilities: An Update of the 1995 DOE Airlie Workshop on MES*). More recently, the Synchrotron Environmental Sciences (SES-I) workshop (April 1999) and follow-up workshop, SES-II (May 2002) were organized by Ken Kemner of Argonne (MR-CAT member) and held at the APS. These SES workshops, attended by ~100 and 150 participants, respectively, brought synchrotron scientists together with environmental scientists to explore opportunities for using SR in environmental science research. A more recent workshop was a short course *Applications of Synchrotron Radiation to Low Temperature Geochemistry and Environmental Science*, sponsored by the Mineralogical Society of America and the Geochemical Society and held in Monterey, California, in December 2002, with 75 attendees.

These efforts have been formalized with the formation of EnviroSync, a national organization representing the growing community of MES SR users in the United States. EnviroSync is modeled after two existing organizations, GeoSync and BioSync, that represent U.S. SR users in the geological and biological sciences, respectively. The main purposes of EnviroSync are to (1) serve as an advocate for the MES SR user community, (2) assess the state of existing SR facilities for MES research on a continuing basis, (3) assess the SR needs of the MES community on a continuing basis, and (4) serve as an advisory group to federal agencies concerning the need for new SR facilities to serve MES research (Brown, 2004). The present chair and secretary of EnviroSync are Rich Reeder (Stony Brook) and John Bargar (SSRL), respectively. Both were elected during the SES-III Conference, held at Brookhaven National Laboratory in September 2005. Previous chairs of EnviroSync include Gordon Brown (Stanford) and Steve Sutton (University of Chicago, GSE-CARS).

A recent survey by the EnviroSync committee (see below and <http://envirosync.org>) indicated that 45 experimental stations at the 4 DOE-operated synchrotron facilities (APS, SSRL,

NLS, ALS) were being used for MES research. However, only 2 stations are dedicated to MES research. The MES activity at the remainder varies from a few experiments per year to half time; the vast majority fall at the low end of the range. The level of usage is estimated at 10-15% of the total available shifts at each synchrotron, a remarkable level of activity considering that only half a dozen stations were used in this field in 1995. The MES community is continuing to expand, yet the experiment stations currently used in the field are fully subscribed or oversubscribed in virtually all cases. In a recent white paper titled *Molecular Environmental Science: An Assessment of Research Accomplishments and Needs*, prepared on behalf of EnviroSync by Gordon E. Brown, Jr. (Stanford University), Stephen R. Sutton (University of Chicago), and others (Brown, 2004), representatives of the EnviroSync community outlined a number of recommendations to U.S. funding agencies and directors of SR laboratories.

An abbreviated presentation of the recommendations from the EnviroSync white paper follows. Next is an analysis of beamlines at the APS that are dedicated, in some form, to support of MES research. Finally, a proposal for the enhancement of MES capabilities at Sector 10 at the APS to address some of the specific recommendations of EnviroSync is presented.

3 RECOMMENDATIONS OF THE ENVIROSYNC COMMITTEE

The MES community has continued to experience strong growth at U.S. SR laboratories in recent years. There have been steep rises in the number of beam time proposals submitted in the MES area, the number of 8-h shifts awarded to MES researchers, and the number of publications resulting from MES research (Brown, 2004). Approximately 100 proposals, requesting more than 950 8-h shifts, were submitted to the APS for General User (GU) MES SR beam time for the 2004-1 and 2004-2 periods. The number of proposals submitted for beam time to perform MES research increased by 33% between these two periods. In addition, more than 250 proposals were submitted to the APS during the 2004-1 and 2004-2 periods for GU beam time for earth, biological, and life science studies. The EnviroSync committee made the following statements (Brown, 2004; these are direct quotes with bold font added for emphasis):

- **Introductory comments:**

With the exception of the GSECARS-CAT, which serves a national group of earth science users including MES researchers, there are no PRT-style beamline stations devoted primarily to MES research.... Many high-quality, peer-reviewed experimental programs in MES and other research areas do not receive access to SR beam time. In addition, many of the programs that do receive beam time do not receive sufficient experimental time on a regular basis to warrant the development of long-term research programs that require regular access to SR facilities.... The learning experience and experimental success of MES students at SR labs are also dependent on the scientific and technical staff members who maintain and support beamlines. Without such beamline maintenance and support, particularly for inexperienced students

and research groups new to MES SR-based research, it is very unlikely that beam time will be used efficiently or that high quality data will be obtained during a typical 3-7 day SR experiment.... **There are opportunities to re-task existing BL stations such that they will serve a broader scientific community, including MES. (One) example includes MR-CAT at the APS....** The challenge is to develop new beamlines, enhance the capabilities of existing beamlines, and enhance infrastructure support to meet the current and future needs of the MES community in a coherent and responsible manner.

- **On the need for infrastructure support for dedicated and non-dedicated SR facilities essential to MES:**

Overall support for MES BL facilities is low compared to that in other scientific fields. This is true for both staffing and equipment. Often, the equipment available at stations is not adequate for MES investigations. For example, XAFS studies of very dilute MES samples require beamlines with very high fluxes and stations with solid-state detectors that can isolate weak x-ray fluorescence signals for the element of interest from background scattering, which can be quite high.... Additionally, the available support staff at beamlines is frequently unfamiliar with MES samples or experimental protocols and needs. **EnviroSync concludes that there is a critical need for increased personnel and equipment support for all dedicated MES SR facilities in the US.**

- **On the need for non-beamline facilities for MES research:**

The quality of scientific output from SR beamlines is often limited by the quality of materials investigated or by the ability to use particularly fresh or unique samples. Although this is true in most fields, in no other field is this consideration more critical than MES where unique samples range from radioactive ones requiring special precautions and handling, to natural samples that must not be subjected to unnecessary preparation because of the possibility of alteration of their compositions or structures.... Infrastructure facilities and capabilities often enable a class of experiments at a synchrotron radiation source across several beamlines. A particularly important example in MES research are nearby laboratory facilities in which biological specimens can be prepared and transported over a short distance to a beamline for experiments.... **EnviroSync concludes that there is a critical need for nearby laboratory facilities for preparing biological and biogeochemical samples for SR studies.**

4 BEAMLINES AT THE APS THAT SUPPORT MES RESEARCH

The APS is a third-generation SR source specifically designed to accommodate IDs and BMs as x-ray sources. Qualified users have access to the APS either as members of CATs or as GUs. Each CAT is responsible for building and operating the beamlines in one or more of the APS's 34 sectors. The CATs are required to provide at least 25% of their sector beam time to GUs. Allocation of GU beam time is determined by a review committee's rankings of competitive proposals submitted by GU scientists. The CATs that have provided beam time for environmental studies are described below. The focus is on the three sectors (GSECARS-CAT at Sector 13, PNC-CAT at Sector 20/XOR-20, and MR-CAT at Sector 10) that have explicitly identified MES as part of their core scientific focus. Some descriptive titles of recent investigations are included, as are discussions of beam time allocations and oversubscription rates for each CAT that has focused a significant amount of effort on environmental research.

4.1 GeoSoilEnviroCARS-CAT

GeoSoilEnviroCARS-CAT (GSECARS-CAT; Sector 13) is operated by the Consortium for Advanced Radiation Sources (CARS) as a national user facility (supported by DOE, the National Science Foundation, and the W.M. Keck Foundation) for state-of-the-art research on earth materials. All beam time at GSECARS is allocated to members of the geological, soil, and environmental science communities through the APS GU proposal-based system. The undulator beamline (13-ID) contains a Kirkpatrick-Baez (KB) mirror-based x-ray microprobe (3-50 keV, 3- μ m beam spot, for micro-XRF, micro-XAFS, fluorescence computed microtomography, x-ray standing wave-fluorescence yield spectroscopy), a general purpose kappa diffractometer (for surface diffraction and spectroscopy with fully focused undulator radiation, microcrystallography), and a high-pressure apparatus. Fluorescence radiation is measured with a 16-element Ge detector, a vortex detector, or a high-resolution wavelength-dispersive spectrometer. The BM beamline (13-BM) includes instrumentation for computed microtomography, micro-XRD, XAFS, and high-pressure experiments.

Recent MES investigations at GSECARS-CAT include "Investigations of Pu sorption to Yucca Mountain tuff"; "Crystal truncation rod investigation of U^{VI} adsorption on alpha-Fe₂O₃"; "High resolution imaging of porous media systems"; "As speciation and coordination in the As-hyperaccumulating fern *Pteris vittata*"; "The role of Fe and Mn oxides in biosolids-amended soils on metal binding"; "U distribution and speciation within biomineralized surface and subsurface environments"; "Using XAS to understand the formation, structure and reactivity of microbially formed Mn oxyhydroxides in acid rock drainage biofilms"; "Defining bioreductive transformations controlling the fate and transport of Cr and U within sediments"; "XAFS studies of goethite nanoparticle reactivity"; "Investigation of metal speciation products associated with secondary mineral formation on *in situ* reactive barrier materials"; "Intragranular diffusion of U^{VI} in Oak Ridge sediments: Direct testing using fluorescence microtomography, "U distribution and speciation within biomineralized surface and subsurface environments"; "Aqueous speciation of Hg in simulated mine-impacted fresh and marine waters"; "Heterogeneity in Fe (bio)mineralization within surface and subsurface environments"; "Examination of Hg

interactions with Fe in the presence of chemical agent simulant using EXAFS and XANES”; “Investigation of the geochemical relationships governing dissimilatory bacterial reduction of U^{VI} from solid uranyl mineral phases”; and “Reactions and phases controlling Cr transport in the vadose zone beneath the Hanford tank farms.”

Analysis of the allocation of beam time, relative to the total amount of beam time requested by GUs, indicates oversubscription rates of approximately 2.5 for x-ray microspectroscopy, -tomography, and -diffraction and for surface and interface scattering, as well as full subscription for bulk XAFS at the GSECARS-CAT (Steve Sutton, personal communication).

4.2 X-ray Operations and Research (XOR-20)

X-ray Operations and Research at Sector 20 (XOR-20), also referred to as Pacific Northwest Consortium (PNC-CAT), has developed ID and BM beamlines. Pacific Northwest National Laboratory (PNNL) and its Environmental Molecular Sciences Laboratory are affiliated with this CAT. PNNL scientists who have had samples measured at XOR-20 or have personally performed research there include J. Amonette, J. Fredrickson, J. Fulton, Y. Gorby, N. Hess, E. Ilton, P. Long, J. McKinley, J. Zachara (Steve Heald, beamline scientist at XOR-20, personal communication). The BM beamline at Sector 20 is primarily a dedicated bulk XAFS beamline. The ID beamline capabilities include an experimental setup dedicated to x-ray microprobe studies. Ion, solid-state, wavelength-dispersive, and bent Laue detectors in the setup provide great versatility for detecting fluorescence radiation emitted from various elements in a wide variety of matrices and make the setup very useful for a range of environmental studies.

More than 50% of the beam time at XOR-20 is used for microbeam and imaging applications (Steve Heald, personal communication). Operational responsibility for the sector has shifted from PNC-CAT to XOR-20 (operated by the APS). With this transition, GU beam time at the ID is 25%. The remainder of the beam time is allocated through a number of approved Partner User Proposals and to beamline staff and commissioning studies (Robert Gordon, personal communication). Any increase in the percentage of GU time would be at the expense of the present institutional members of the CAT, who would be required to compete in the GU pool for that beam time. Such new GUs will presumably still need access to SR for their research, and thus any additional increase in GU time at XOR-20-ID will be diluted by the need for former members to apply for that time. Some 70–80% of beam time at the BM beamline is available for GU time.

Titles of recent MES investigations at XOR-20 include the following: “X-ray investigations of supercritical fluids”; “Delineating areas of As conversion in plant roots”; “EXAFS investigation of metal sorption on ruthenium oxide”; “Soil Cr in the roots, shoots and the rhizosphere zone during phytoremediation by *Brassica juncea* (Indian mustard)”; “A crystal truncation rod study of U^{VI} adsorption on alpha-Fe₂O₃ surfaces”; “Microbially influenced degradation of solidified radioactive waste: Micro-XAS to overcome heterogeneity and chemical complexity”; “Bacterial influence on Pb adsorption to kaolinite — a pH-dependent study”; “Cu and Au abundance and speciation in hydrothermal fluids”; “U distribution and speciation within

biomineralized surface and subsurface environments”; “Chemical speciation of As in U mill tailings using synchrotron microbeam techniques”; “EXAFS spectroscopic studies of Cd-extremophile bonding”; “Micro-XAFS studies of geologic materials”; and “Chemical and coordination structure of radionuclides and metals in spent nuclear fuel and its alteration products: understanding release pathways.”

During the 2004-1 scheduling cycle, XOR-20 BM beamline was oversubscribed by a factor of 2.5 (Steve Heald, personal communication). During the 2005-2 scheduling period, the BM line was oversubscribed by ~25–50% for bulk XAFS experiments (Steve Heald, personal communication). Similarly, the ID microprobe typically has been oversubscribed by a factor of ~2.5 by MES scientists for most of the scheduling periods during the last two years (Steve Heald, personal communication).

4.3 Materials Research CAT (MR-CAT; Sector 10)

The MR-CAT at Sector 10 has a developed ID beamline. Emphasis is on XAFS, scattering, and reflectivity studies. A 19-element solid-state Ge detector or several bent Laue analyzers enable detection of fluorescence radiation in XAS-based experiments on dilute environmental samples. A KB mirror setup enables XRF elemental mapping, micro-XAFS, and microdiffraction studies with x-ray spot sizes as small as ~2 μ m. In addition to MES GU experiments, many other MES experiments have been performed directly or through collaborations with the Kemner group at Argonne, the Chemical Engineering Division at Argonne, and the University of Notre Dame (UND). Recent investigations at MR-CAT include “Sequestration of Sr and Cs by caustic waste-soil weathering reaction products”; “XAFS investigations of ferrous iron sorption to mineral surfaces”; “XAFS investigations of radionuclide and metal sorption to bacterial surfaces”; and “Interfacial reduction — oxidation mechanisms governing fate and transport of contaminants in the vadose zone.”

The MR-CAT ID beamline was oversubscribed by a factor of 3 in 2005 (Carlo Segre, personal communication). Furthermore, during the last year, no GU-proposed experiment requesting beam time for a bulk XAFS experiment at 10-ID has received a beam time allocation.

Some of the MES investigations performed by members of MR-CAT are listed below. The descriptive title of each investigation is followed by the last names of investigators collaborating on the project, including their home institutions. *The italicized names are members of MR-CAT.* These MES investigations are as follows:

- “X-ray microprobe investigations of uranyl in ancient caliche” — *Kelly, Kemner, Kropf, Rasbury* (Stony Brook)
- “Coordination chemistry of Ca-UO₂-CO₃ aqueous complexation by EXAFS” — *Kelly, Kemner, Brooks* (ORNL), *Fredrickson* (PNNL)

- “Microbial reduction of U^{VI} at the solid-water interface” — *Kelly, Kemner, Roden* (Univ. Wisconsin, Madison)
- “Humic materials inhibit biological uranium reduction by *Shewanella putrefaciens* CN32” — *Kelly, Kemner, Roden* (Univ. Wisconsin, Madison), *Burgos* (Pennsylvania State Univ.)
- “U XAFS characterization of U valence state and chemical speciation in ORNL Field Research Center (FRC) sediments before and after biostimulation experiments” — *Kelly, Kemner, Jardine* (ORNL), *Watson* (ORNL), *Istok* (Oregon State Univ.)
- “Reduction of Ag, Au, Cu, and Hg by Fe²⁺/Fe³⁺ hydroxysulfate green rust” — *O’Loughlin, Kelly, Kemner*
- “Inhibition of bacterial U^{VI} reduction by Ca” — *Brooks* (ORNL), *Fredrickson* (PNNL), *Zachara* (PNNL), *Fendorf* (Stanford Univ.), *Kelly, Kemner*
- “Microbial populations stimulated for U^{VI} reduction in U mine sediment” — *Kelly, Kemner, Banfield* (Univ. California, Berkeley)
- “Reduction of U^{VI} by mixed Fe²⁺/Fe³⁺ hydroxide (green rust): Formation of nanoparticles” — *O’Loughlin, Kelly, Kemner*
- “Adsorption of Cd to *B. subtilis* bacterial cell walls: A pH-dependent XAFS spectroscopy study” — *Boyanov, Kemner, Fein, Bunker*
- “XAFS determination of pH-dependent U-bacterial cell wall interactions” — *Kelly, Kemner, Fein*
- “Nonmetabolic reduction of Cr(VI) by bacterial surfaces under nutrient-absent conditions” — *Fein, Boyanov, Bunker, Kemner*
- “Environmental applications of self-assembled monolayers on mesoporous supports (SAMMS)” — *Fryxell* (PNNL), *Kemner*
- “Immobilization of radionuclides and heavy metals through anaerobic bio-oxidation of Fe(II)” — *Coates* (Univ. California, Berkeley), *Kelly, Kemner*
- “XRF analysis of nondenaturing electrophoretic gels to investigate metalloprotein expression in bacteria” — *Giometti* (Argonne), *Kelly, Kemner*
- “Actinide-specific interfacial chemistry of monolayer coated mesoporous ceramics” — *Fryxell* (PNNL), *Kelly, Kemner*
- “XAFS investigations of the interactions between contaminant tetrahedral anions and self-assembled monolayers on mesoporous supports” — *Fryxell* (PNNL), *Kelly, Kemner*

- “Enzymatic U^{VI} reduction by *Desulfosporosinus* species” — Banfield (Univ. California, Berkeley), *Kelly, Kemner*
- “U-XAFS investigations of U speciation on microbial coupons from the ORNL FRC” — Geesey (Montana State Univ.), *Kelly, Kemner*
- “XAFS investigations of the local structure around Cr³⁺ ions in dilute acetate and perchlorate aqueous solutions” — *Boyanov, Bunker, Kemner*
- “Investigations of the use of x-ray fluorescence spectroscopy for the study of biochips” — Chandler (Argonne), *Kemner*
- “U XAFS investigations of interactions between *S. putrefaciens* CN32 and *S. oneidnesis* MR-1 EPS and uranium” — Gorby (PNNL), *Kemner*
- “Cu XAFS investigations of heavy metal tolerant *Ralstonia* sp.” — Marsh (Michigan State Univ.) — *Kemner, Kelly*
- “Fe K edge XAFS investigations of Fe(VI)” — Nealson (Univ. Southern California) — *Kemner, Kelly*
- “The effect of acidic solutions and growth conditions on the adsorptive properties of bacterial surfaces” — *Fein, O’Loughlin, Kemner*

4.4 Basic Energy Sciences Synchrotron Radiation Center (BESSRC-CAT; Sectors 11 and 12)

Basic Energy Sciences Synchrotron Radiation Center (BESSRC-CAT, Sectors 11 and 12) has capability for mineral surface studies (reflectivity, CTR, and XSW) and electrochemical experiments on actinides (XAS and scattering). BESSRC-CAT also is the home base of the actinide-handling facility, which is the responsibility of Lynn Soderholm (Chemistry Division at Argonne). This facility provides support to all scientists requesting assistance with measurement of radioactive samples. Recent investigations at BESSRC-CAT include “Mechanisms of actinide sorption by minerals,” “Pu interactions with redox-active mineral surfaces,” “Evolution in As bonding environment during growth of Fe oxide nanoparticles,” and “Complexants for actinide element coordination and immobilization.”

4.5 XOR(2)-CAT (formerly SRI-CAT)

XOR(2)-CAT (formerly SRI-CAT) has well-developed BM and ID beamlines dedicated to x-ray imaging. The BM beamline is dedicated to x-ray microtomography (resolution 1-2 μ m) in both transmission and phase-contrast modes. The ID beamline has three end stations. All make use of Fresnel optics zone plates (ZPs) and are typically used in experiments requiring submicron spatial resolution. One of the ID end stations focuses on the use of low-energy (1- to 4-keV)

x-rays for a variety of imaging and spectroscopic needs (scanning transmission x-ray microscopy with simultaneous fluorescence detection), with x-ray beam sizes as small as 60 nm. This beamline is optimized for fluorescence excitation of light elements at intermediate energies. The other two end stations focus on the use of hard x-rays for x-ray fluorescence imaging, micro-XANES, and microdiffraction studies. The 2-ID-D hard x-ray microprobe achieves a spot size of ~100 nm. The 2-ID-E microprobe operates in parallel with 2-ID-D at somewhat relaxed resolution (250 nm). Presently, either the two high-energy end stations or the low-energy end station may operate at a single moment. During operation, access to the 2-ID-E microprobe is limited to times when the 2-ID-D user permits access. Much of the work performed at 2-ID-D that is related to MES research has been performed by members of the Kemner MES Group. Recent investigations at XOR(2)-CAT include “Formation of sphalerite (ZnS) deposits in natural biofilms of sulfate-reducing bacteria,” “X-ray microbeam analysis of bacteria: Elemental and redox analysis of single cells,” “X-ray microbeam investigations of correlations between metal concentration and respiration of *S. oneidensis* bacterial cells,” “Fe micro-XANES investigations of internal biomineralized products in *S. putrefaciens* CN32,” and “Development of x-ray microbeam analysis to investigate metalloprotein localization in dissimilatory metal reducing bacteria.”

Both DND-CAT (Sector 5) and BIO-CAT (Sector 18) have XAFS instrumentation for environmental studies and have been used for such studies on a limited basis. The DND-CAT BM beamline (5-BM-C) can be used for microtomography on a broad range of materials.

5 DEVELOPMENT OF ENHANCED CAPABILITIES FOR MES STUDIES AT SECTOR 10 AT THE APS AND AN EXPLANATION OF HOW THAT DEVELOPMENT ADDRESSES THE SPECIFIC RECOMMENDATIONS OF ENVIROSYNC

The demand for beam time for MES experiments is of two kinds. First, increasing numbers of new users are entering the field for the first time with exciting new research. Second, many researchers have sufficient experience to have developed established research programs that need regular, extended access to synchrotron-based analytical facilities. **A major goal of the MR-CAT is to address the increasing demand for access by these two types of users by offering extended access to institutions and single-experiment access to individual scientists.**

To adequately demonstrate APS support for MES, a home base for MES must be established at an APS sector. A concentration of MES researchers in one location increases the probability of interaction between these researchers and improves the integration of scientific disciplines involved with MES. In addition to being tailored to the needs of the MES community, the sector must be available to MES researchers on emergency or high-profile basis.

In response to the recommendations of EnviroSync, as well as to improve beamline capabilities, increase beam time availability, increase user support, and improve infrastructure

support for MES research at the APS, we propose a number of improvements at and to the MR-CAT sector. Specifically, we propose to (1) initially develop in the isolated portion of the FOE of the BM beamline at MR-CAT a capability for XAFS and XRF measurements; (2) create non-beamline infrastructure in the form of laboratory facilities in the MR-CAT wet and dry laboratory space and in the MES Group laboratories in Building 203 at Argonne to aid GUs; and (3) support beamline scientists stationed at Sector 10 who will work closely with and participate in both the Kemner MES Group and EPA research groups.

5.1 Developing the Monochromatic Portion of the FOE BM Beamline at MR-CAT for Spectroscopy Experiments

The FOE for the BM beamline at MR-CAT has been constructed. A lead wall in the FOE created an experimental end station measuring 6 ft by 10 ft. The beamline presently supports x-ray lithography work with a polychromatic (white) x-ray beam. Funds for the purchase of a monochromator have been provided by ERSD. This monochromator will be based on the Daresbury double-crystal design that we have used with great success on the ID beamline. The monochromator has been ordered, and delivery is expected in 2006. Some of the standard items needed for transmission-mode and fluorescence-mode XAFS experiments (ion chambers, current amplifiers, etc.) are already available at the MR-CAT sector. Additional funding for the build-out of the BM FOE for bulk XAFS capabilities is available via an interagency agreement between DOE and the EPA. ERSD has also pledged an additional \$250 K of capital equipment support in the future.

Although the spectroscopy capabilities being developed at the FOE are relatively rudimentary, they are viewed as a necessary interim step toward complete build-out of the BM beamline. Planned improvements to the BM beamline include (1) creation of an XAFS beamline separate from the x-ray lithography beamline, thus doubling the amount of available monochromatic and white-light beam time and (2) inclusion of focusing optics to increase photon flux on the sample and enable microbeam studies. An additional capability of the beamline end station and a unique capability at the APS is a dedicated, controlled-environment sample chamber capable of (1) scrubbing oxygen from the chamber (for anoxic or anaerobic samples), (2) flooding the chamber with a variety of free-flowing inert gases (either to reduce the absorption of fluorescence x-rays before the x-ray fluorescence detector or to remove moisture from the sample environment), or (3) freezing the sample to reduce the migration of free radicals generated by radiation-induced chemical interactions.

Upon receipt of encouragement from the Scientific Advisory Committee to develop the FOE for XAFS measurements, MR-CAT will pursue additional funding for complete build-out of the BM from ERSD and the EPA. When appropriate, additional Argonne LDRD funds will be solicited for salary support of scientists associated with the project. Finally, the long-range development of the BM beamline will be designed to accommodate future incorporation of a canted undulator setup at Sector 10.

5.2 Creating Non-Beamline Facilities to Aid MES General Users

The quality of scientific output from SR beamlines is often limited by the quality of materials investigated or the ability to use particularly fresh or unique samples. Although this is true in most fields, in no other field is this consideration more critical than in MES, where unique samples range from radioactive materials requiring special precautions and handling, to biological materials that are time or oxygen sensitive, to natural samples that must be protected from unnecessary preparation that could alter their compositions or structures. Infrastructure facilities and capabilities often enable a class of experiments at an SR source across several beamlines. Particularly important examples in MES research are facilities for handling radioactive samples in SR laboratories and nearby laboratory facilities where biological specimens can be prepared before transport over a short distance to a beamline for experiments. Presently, a radioactive material handling facility is available to GU MES researchers working at the APS. Additional support is available via collaboration with current institutional members of MR-CAT. Much of the laboratory infrastructure required for measurement of biogeochemical and MES samples at the APS can be made available by the Kemner MES Group.

To increase the quality of scientific output and improve the infrastructure facilities and capabilities at Sector 10 and throughout the APS, we propose to create critical non-beamline infrastructure in the form of laboratory facilities in the MR-CAT wet and dry laboratory spaces that will aid MES GUs who use time-sensitive materials. To optimize the benefits relative to costs, we propose to include only the most urgently and frequently needed items in the MR-CAT laboratory space, such as a microcentrifuge, a large high-speed centrifuge with multiple rotors, a shaker, an analytical balance, a refrigerator-freezer, an anoxic chamber, a pH meter, heat and stir plates, a spectrophotometer, and a limited number of room-temperature and low-temperature sample holders. To our knowledge, these items are not regularly available to MES or biogeochemical science researchers working at the APS. We further propose modest maintenance support for some of the more specialized pieces of equipment already available in the Kemner MES laboratories in Building 203 for occasional use by MES GUs at the APS, such as a bench-scale x-ray diffractometer, shakers, incubators, refrigerator, laminar flow hood, kinetic phosphorescence analyzer, -80°C freezer, Coy anaerobic chambers, spectrophotometer, scanning UV-VIS spectrophotometer, Olympus microscope, HPLC, sonicator, autoclave, high-speed centrifuges, microcentrifuges, ovens, autotitrator, balances, and pH meters.

5.3 Hiring Beamline Scientists at MR-CAT to Benefit MES Scientists

With the increased amount of beam time available for x-ray spectroscopy research at Sector 10 when the BM beamline becomes available, the support staff will necessarily be increased. The current beamline support staff at the MR-CAT has broad experience in materials science and some experience in environmental science. Around the storage ring most beamline support staff are unfamiliar with MES samples and experimental protocols and needs. Members of the Kemner MES Group have often provided beamline (MR-CAT) and infrastructure (DND-CAT, GSECARS-CAT, PNC-CAT) support to MES GUs. An increased level of support at MR-CAT and other CATs is a critical need for MES researchers. To alleviate this need, the Kemner MES Group hired a staff beamline scientist (Dr. Bruce Ravel) who (1) provides support

to MES scientists performing experiments at MR-CAT and occasionally at other beamlines throughout the ring, (2) will maintain the non-beamline infrastructure at MR-CAT that supports MES GUs at the APS, (3) will work to develop x-ray techniques and computer software at MR-CAT that are beneficial to MES scientists, and (4) is building his own MES-based research program. Dr. Ravel also will work closely with Dr. Kemner to help coordinate his support efforts with the support provided by other members of the Kemner MES Group. In conjunction with the full build-out of the BM beamline, the EPA (the newest member of MR-CAT) is expected to hire a person with a similar background and research interests.

6 SUMMARY

The developments at Sector 10 described above will provide the dedicated state-of-the-art facilities that are critically needed for research on a broad range of environmental science problems, with a focus on developing a multifaceted bulk and microanalysis facility using both ID and BM beamlines. **MR-CAT will be unique at the APS in several ways:**

- **Dedication to Environmental Science Research:** MR-CAT will be one of the APS sectors most dedicated to MES research. MR-CAT will serve as a home base for synchrotron-based MES and biogeochemical science by its members. The members themselves will function as an interface between the APS and less experienced GUs performing MES investigations. This approach will alleviate the inefficiencies of current research, which is typically done in a parasitic, but symbiotic, fashion around the ring. More importantly, the scientific staff at Sector 10 (beamline scientists and scientific program leaders) will have expertise in both environmental science problems and technical aspects of SR experiments and techniques.
- **MES and Biogeochemistry Laboratory Infrastructure Support:** The MR-CAT will provide a service to the MES and biogeochemical science communities by providing laboratory infrastructure required for proper preparation of environmental and biogeochemical samples to be measured at all APS beamlines. This infrastructure includes an optical microscope for submicron x-ray microscopy (already based at Sector 2), basic MES and biogeochemical science laboratory equipment (to be based at Sector 10), and more comprehensive MES and biogeochemical laboratory infrastructure (based in the MES Group laboratory space in Building 203 at Argonne).
- **Concurrent Scheduling of Bulk and MicroXAFS Beam Time:** When appropriate, MR-CAT will promote simultaneous micro- and bulk XAFS studies by individual groups. This approach will allow samples to be studied across the most relevant spatial scales in a given experimental session, an extremely powerful capability required for understanding the components in an environmental sample.

- **Dedicated Controlled Sample Environment:** The MR-CAT will develop a controlled-environment sample chamber capable of (1) scrubbing oxygen from the chamber (for anoxic or anaerobic samples), (2) flooding the chamber with a variety of free-flowing inert gases (either to reduce the absorption of fluorescence x-rays before the x-ray fluorescence detector or to remove moisture from the sample environment), or (3) freezing the sample to reduce the migration of free radicals generated by radiation-induced chemical interactions.
- **Advance the State of the Art in Synchrotron-Based Environmental Science Research:** The MR-CAT will advance the state of the art in chemical- and physical-state studies of environmental materials and, in collaboration with GSECARS-CAT and EnviroSync, will be an advocate for these studies through training and scientific workshops.

Together, these unique capabilities and value added in support of MES at the APS demonstrate the value of developing the Sector 10 BM beamline for XAFS and XRF analysis.

APPENDIX A: SCIENTIFIC PROGRAM

A.1 Core Research Program

The research scientists of the MR-CAT member institutions and other key scientists will conduct a core research program. It is this group that will drive the design, construction, commissioning, operation, and utilization of the sector. The following are some of these individuals and brief descriptions of their research interests:

- **Bruce Bunker** (UND): Nanoscale materials, ordering phenomena, binding and adsorption of heavy metals to bacterial and mineral surfaces, metal complexation and biomineralization at surfaces. *Equipment required:* Bulk XAFS, x-ray reflectivity and reflection-mode XAFS, microprobe for XAFS and elemental mapping.
- **Jeremy Fein** (UND): Effect of bacteria on heavy metal mobility in contaminated groundwater; mechanisms and extent of metal-bacteria adsorption reactions. *Equipment required:* Bulk XAFS.
- **Robert Ford** (EPA): Redox disequilibria of metal speciation in sediments. Uptake mechanisms of inorganic contaminants by permeable reactive barriers. *Equipment required:* Bulk XAFS, microprobe for XAFS, XRF and imaging; microcrystallography; and controlled-environment sample chamber.
- **Christopher Impellitteri** (EPA): Speciation of inorganic contaminants in drinking water waste residuals, drinking water distribution systems, wastewater residuals, mine wastes and hazardous wastes. *Equipment required:* Bulk XAFS, microprobe for XAFS, XRF and imaging
- **Shelly Kelly** (Argonne): Changes in speciation and valence state of uranium (and other trace metals) in groundwater and sediment systems by biogeochemical processes such as microbial reduction, adsorption, and coprecipitation. *Equipment required:* Bulk and microprobe XANES, XRF, and EXAFS.
- **Kenneth Kemner** (Argonne): Behavior of toxic and radioactive species in the environment, including sorption and reactions on mineral and biological surfaces, migration of contaminant metals and radionuclides through the biosphere, as well as stabilization and remediation processes. Bioavailability of toxic species in the environment. Specific focus has entailed the investigation of the role of metal-microbe-mineral interactions and microbial exopolymers in the transport of heavy metal contaminants through the subsurface. *Equipment required:* Bulk XAFS; microprobe for XAFS, XRF, and imaging; and controlled-environment sample chamber.

- **Jeremy Kropf** (Argonne): Works extensively with the Yucca Mountain Project and the related Science and Technology program studying the speciation of fission products and their sorption and reactions on mineral surfaces and high level waste. *Equipment required:* Bulk XAFS, microprobe for XAFS, XRF imaging, radioactive materials handling.
- **Charles Kulpa** (UND): Research and collaborations in the areas of microbial physiology, environmental microbiology and microbial community (biofilms). *Equipment required:* Microprobe for XAFS, XRF, and imaging
- **Ed O’Loughlin** (Argonne): Processes controlling contaminant fate and transport in aquatic and terrestrial environments. Current research focuses on biogeochemical processes affecting biotic and abiotic transformations of a range of organic and inorganic contaminants including halogenated hydrocarbons, metals, metalloids, and radionuclides. *Equipment required:* Bulk XAFS; microprobe for XAFS, XRF, and imaging; and controlled-environment sample chamber.
- **Bruce Ravel** (Argonne): X-ray absorption spectroscopy technique, data analysis, and data analysis software development; determination of the chemical speciation of heavy-metal and radionuclide contaminants. *Equipment required:* Bulk XAFS; x-ray microprobe for XAFS and imaging; and controlled-environment sample chamber. (See Appendix B.)
- **Kirk Scheckel** (EPA): Application of macroscopic kinetic and thermodynamic studies coupled with in-situ microscopic and spectroscopic techniques to elucidate metal reactions within the natural environment. *Equipment required:* Bulk XAFS; microprobe for XAFS, XRF and imaging; and controlled-environment sample chamber.

A.2 Scientific Applications

The breadth of potential scientific applications is large. In this section, example applications are given in several research areas:

- Mineral-microbe-metal interactions
- Mineral-water interface reactions
- Chemical speciation, mobility, bioavailability, and toxicity of contaminants
- Remediation of contaminated sediments
- Metal sequestration by plants and association with plant structure
- Surface reactivity of phyllosilicates and other minerals

Each example presents the significance of the scientific problem, results of recent work, proposed new research, and the need for proposed EnviroCAT capabilities.

Adsorption of Aqueous Actinide and Heavy Metal Cations onto Bacterial and Algal Cell Walls: X-ray Absorption Spectroscopy Measurements

Collaborators: J.B. Fein, B. Bunker, C.F. Kulpa, Jr. (UND), K.M. Kemner, S.D. Kelly, B. Ravel (Argonne)

Liquid and solid wastes from industry and nuclear activities have severely contaminated groundwater aquifers and surface waters at hundreds of sites worldwide. The inability to accurately predict the mobility and fate of aqueous metal contaminants in the environment often results in costly, ineffective remediation efforts, and is a major problem in planning effective waste disposal scenarios. Improving the accuracy of contaminant transport models is one of the biggest challenges facing environmental geochemists. A lack of understanding of the controls on contaminant-bacteria and contaminant-algae interactions represents some of our most significant gaps in knowledge. Bacteria are ubiquitous in the subsurface, even to depths of several kilometers, and bacteria and algae are ubiquitous in surface waters. Both types of microbes have an extremely high affinity to adsorb aqueous metal cations, potentially dominating the speciation of the metals in the environment. We have a poor understanding of the molecular-scale processes that control contaminant-microbe adsorption reactions, and without this understanding, our ability to quantitatively model contaminant transport in the environment is severely hampered.

Bulk adsorption measurements, conducted as a function of pH and solute:sorbent ratio, provide the best means of determining the thermodynamic stability constants for the important surface complexes in a system (e.g., Fein et al., 1997; Fein, 2000). However, these types of experiments typically do not provide constraints on the stoichiometry of the surface complexes. X-ray absorption spectroscopy (XAS) is ideally suited to complement bulk adsorption measurements in constructing quantitative models of adsorption. XAS provides detailed information concerning the binding environment of a metal, and thereby yields rigorous constraints on the adsorption reaction stoichiometry. Taken together, bulk adsorption measurements and XAS experiments represent a powerful approach for determining and modeling metal speciation and distribution in microbe-water-rock systems.

Recently, we have used the APS for initial studies of metal-microbe XAS measurements of U-*B. subtilis* and Cd-*B. subtilis* systems (Kelly et al., 2001; 2002; Boyanov et al., 2002). For example, Kelly et al. (2001; 2002) exposed *B. subtilis* (a Gram-positive aerobic bacterial species) to aqueous uranyl solutions at pH 1.67, 3.22, and 4.80. The Extended X-ray Absorption Fine Structure (EXAFS) analysis indicated that uranyl binding occurs exclusively to protonated phosphoryl functional groups at pH 1.67. At the higher pH values (3.22 and 4.80), inclusion of C atoms is required to accurately simulate the uranyl-binding environment. These results indicate an increase in the number of carboxyl bonds with increasing pH. Our EXAFS results confirm the surface complexation models proposed by Fein et al. (1997) and Fowle et al. (2000), which were based solely on bulk adsorption measurements. XAS provides similar confirmation of our surface complexation model of Cd adsorption onto *B. subtilis* cells (Boyanov et al., 2002). Boyanov et al. (2002) found that relatively low pH adsorption of Cd is caused by carboxyl

binding of Cd, with Cd-phosphoryl binding becoming important above approximately pH 7. However, Boyanov et al. (2002) found additional surface complexes that were only detectable through the sensitivity of the EXAFS analysis. These studies identify the mechanism of binding of metals onto bacterial surfaces using XAS, and they are the first to examine the pH dependence of the adsorption mechanism and to interpret these results in a surface complexation framework.

We propose to extend the use x-ray absorption spectroscopy to conduct three types of experiments: (1) using XAS to constrain the distribution of metal in complex bacteria-water-rock systems; (2) using XAS to determine the binding mechanism of heavy metals and actinides to a wider range of bacterial and algal species than we have studied to date; and (3) using XAS to determine the binding mechanism of these elements to natural consortia of bacteria and algae from a wide range of environments. The overall objective of the research is to test whether surface complexation modeling can account for the observed metal distributions under a range of conditions and complexities. In the first type of experiments, we will measure the bulk extent of adsorption, and we also will use XAS to determine the distribution of a metal in a mixed bacteria-mineral-water system. We will use equilibrium constants that characterize the adsorption of the metal onto each sorbent in order to construct geochemical models of the adsorption behavior in the mixed systems, and we will use the XAS results to test the accuracy of those models. We will test a range of systems, from bacteria-dominated adsorption to mineral-dominated adsorption. The second and third types of experiments will determine the range of metal adsorption behaviors exhibited by natural populations of bacteria. Our experimental studies over the past few years suggest that a wide range of bacterial surfaces exhibit nearly identical metal adsorption properties (Yee and Fein, 2001). Universally similar adsorption between bacterial species implies a common mechanism of adsorption between aqueous metal cations and bacterial cell walls. It is possible that due to similar cell wall structures, algae and bacteria may exhibit similar adsorption behaviors as well. In the proposed research, we will rigorously test the universality of the adsorption behavior, using natural populations of bacteria from a wide range of environments. We will also use x-ray absorption spectroscopy to determine the dominant adsorption mechanisms in natural bacterial populations, and we will test the ability of a range of advanced surface chemistry models to account for the adsorption behavior that we observe. We will compare the behavior of the bacterial populations with that observed for single isolated species of bacteria and algae in parallel experiments.

Quantifying the effects of bacteria on adsorption reactions in water-rock systems has direct applications not only to contaminant transport modelling, but also to bioremediation engineering and to the understanding of bacterial pathogen mobility. The research that we will conduct in this project will ultimately lead to more accurate predictions of the mobility of aqueous metals in contaminated groundwater systems.

Because the amount of biomass material generated for these experiments is typically small (hundreds of microliters), the high-brilliance APS is extremely well suited for biomass experiments such as these that require small beam size. This facility also enables “quick-scan” XAS that will enable an energy scan to be measured in tenths of a second (for spectra in the vicinity of the absorption edge) or in tens of seconds (for an entire extended-energy scan). This quick-scan capability will allow us to repeatedly scan and monitor the microstructure of the sample and to better identify any radiation-induced chemical effects that may occur in our

samples. These proposed measurements will be conducted in fluorescence mode, thereby enabling studies of samples with very low metal concentrations.

Structural Characterization of Halogenated Sorbents Used for Capture of Vapor Phase Mercury – Understanding the Nanoscale Binding Mechanisms between Hg and H (Cl, Br, I)

Collaborators: N. Hutson, R. Ford, K. Scheckel (EPA Office of Research and Development), J. Wilcox (Worcester Polytechnic Institute)

Background. Mercury (Hg) is present in coal in trace amounts (approximately 0.1 ppm on average) and coal-fired power plants are known to be the major source of anthropogenic Hg emissions in the U.S. As such, the U.S. Environmental Protection Agency (EPA) has recently promulgated the Clean Air Mercury Rule (CAMR) to reduce emissions of mercury from these plants.

During combustion of the coal, mercury is released into the exhaust gas as elemental mercury vapor, $\text{Hg}^0(\text{g})$. This vapor may then be oxidized to Hg^{2+} species via homogeneous (gas-gas) or heterogeneous (gas-solid, surface catalyzed) reactions. The primary homogeneous oxidation mechanism is the reaction with gas-phase chlorine to form HgCl_2 . While this reaction is thermodynamically favorable, it is thought to be kinetically limited due to rapid cooling of the flue gas stream. The heterogeneous oxidation reactions occur on the surface of fly ash, unburned carbon, and metal ductwork. One proposed heterogeneous oxidation mechanism involves the chlorination of carbon by HCl as a first step toward heterogeneous oxidation of Hg^0 to HgCl_2 , and subsequent adsorption onto the carbon.

Mercury control via injection of powdered activated carbon (PAC) into the flue gas stream of coal-fired boilers is under development and is being demonstrated on selected full-scale systems. However, in many situations, the effectiveness of standard PAC is limited due to inadequate free chlorine in the flue gas. As a result, halogenated PAC sorbents have been developed to overcome some of these limitations. Iodated carbon has been used for mercury capture in fixed beds and chlorinated carbons have been developed and tested at the bench-scale at the EPA/RTP Laboratories. However, to date, only brominated PAC sorbents have been evaluated in full-scale field tests. These full-scale tests have shown the brominated PACs to be quite effective for Hg capture.

Additional mercury and multi-pollutant sorbents are being developed and tested in the EPA/RTP laboratories. One sorbent, which is derived from bauxite residue, an industrial waste from the aluminum extraction industries, has been shown to have very good mercury capture after going through a bromination procedure.

Research Objectives. The research objectives of this proposed work are to use advanced XAFS analysis to characterize the structure and binding mechanism at nanoscale sorbate-sorbent local environments.

The 10-BM beamline will be ideally suited to look at the oxidation state of Hg because the L_{III} -edge, which is very sensitive to the oxidation state and the local symmetry, is at 12284 eV and falls in the energy range covered by the newly purchased monochromator. Additional studies at the Br edge will also be performed. In situations when Hg concentrations are found to be too low for XAFS analysis at the BM line, we hope to make use of the ID beamline for either bulk or x-ray microprobe investigations.

Expected Outputs. At least one, but likely more, peer-reviewed journal articles would be expected to result from this work. Further, the results from this work will serve as input to molecular-level modeling of Hg-Br interactions.

Projected Impact/Outcomes. The ultimate goal will be to establish relationships between the physical and chemical characteristics of the halogenated adsorbents and the sorption capacity and selectivity. The ability to directly link the physical and chemical nature of binding sites in the materials with the performance of those materials is the key to developing new or improved adsorbents with performance properties that exceed those that have conventionally been used. Understanding the interactions between mercury and halogens on the surface of adsorbents will help in the further development of more effective and, possibly, more cost-effective sorbents.

Uniqueness of the Work. Much work is being done now on determining the mercury capture capacity of various halogenated carbons and additional mercury adsorbents are being developed at the EPA/RTP laboratories and elsewhere. However, limited work had been done in the area of chemical and physical characterization of the local environment/binding sites of these sorbents. Huggins et al. (1999) reported the results of XAFS characterization of mercury sorption on three activated carbons, including sulfur- and iodine-impregnated carbons. The XAFS results showed that each type of activated carbon behaved differently with respect to the sorption of mercury. Li et al. (2002) have also reported XAFS results from Hg adsorbed on activated carbon.

Relating Metal Speciation to Bioavailability in Contaminated Sediments

Collaborators: Kirk Scheckel, Aaron Williams, and James Ryan (EPA Office of Research and Development)

Metal contaminated sediments have been an important environmental issue for the EPA for decades. Previous research has relied on basic laboratory tools to investigate the relationship of total metal content to impacts on biological receptors. The purpose of this research is to apply state of the art spectroscopic techniques to determine the chemical speciation of metals in contaminated sediments from various locations around the country and correlate the metal form to biological availability via assays. This project will entail examination of multiple metal contaminated sediment sites which will be updated in the QAPP via periodic addendums. As such, the total number of samples to be analyzed is unknown at this point in time. Biological assay studies will likely be conducted via contracts and the extent and type of assay have yet to be determined. The primary objective of this research is to determine the speciation of metals in contaminated sediments.