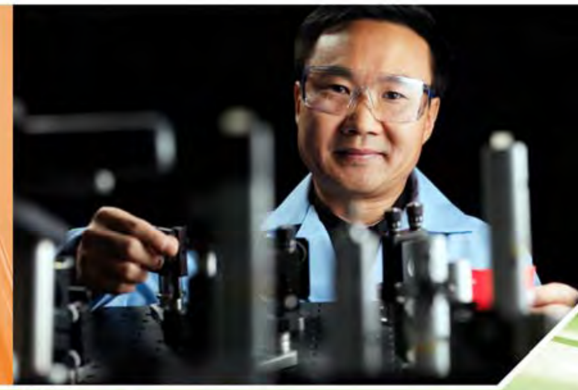
Environmental Molecular Sciences Laboratory

Science and Operational Review



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EMSL

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Science and Operational Review 08

Dr. Allison A. Campbell

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Richland, Washington 99352

Acronyms

AAAS	American Association for the Advancement of Science
ACS	American Chemical Society
AD	Associate Director
AES	Auger electron spectroscopy
AFM	atomic force microscope
AVS	American Vacuum Society
BER	(DOE's) Office of Biological and Environmental Research
BID	Biological Interactions and Dynamics (science theme)
BioMAS	bio-magic angle spinning
CAARI	Conference on the Application of Accelerators in Research and Industry
CaNS	Computing and Networking Services
CARS	Coherent Anti-Stokes Raman Scattering
CB	cell body
CCSEM/EDX	computer controlled scanning electron microscopy with energy-dispersed analysis of x-rays
CF-MAS	constant-flow, magic-angle-spinning (probe)
CPIC	Capital Planning and Investment Control
cryo-EM	cryo-electron microscopy
CSM	Cognizant Space Manager
CT	carbon tetrachloride
DFT	density functional theory
DOE	U.S. Department of Energy
EC	Executive Committee (PNNL)
Ecce	Extensible Computational Chemistry Environment
EDX	energy-dispersive x-ray spectroscopy
EMSL	Environmental Molecular Sciences Laboratory
EPR	electron paramagnetic resonance spectroscopy
ERS	EMSL Resource System
ESH&Q	environmental, safety, health, and quality
EUS	EMSL Usage System
FIB/SEM	focused ion beam scanning electron microscope
FPGA	field programmable gate array
FT	Fourier transform
FT-ICR	Fourier transform ion cyclotron resonance
GB&SS	Geochemistry, Biogeochemistry, and Subsurface (science theme)
GPP	General Plant Project
HPCS-3	High-Performance Computing System-3 (Chinook)

HPLC	high-performance liquid chromatography
HREELS	high-resolution electron energy loss spectroscopy
IDL	Instrument Development Laboratory
IIC	Institute for Interfacial Catalysis
IMS	ion mobility spectrometer
LC	liquid chromatography
LC/MS-MS	liquid chromatography-coupled mass spectrometry
LNAPL	light non-aqueous phase liquid
MBE	molecular beam epitaxy
MOA	Memorandum of Agreement
MRI	magnetic resonance imaging
MRS	magnetic resonance spectroscopy
MSC	Molecular Science Computing
MS/MS	tandem mass spectrometry
MS^3	Molecular Science Software Suite
NHMFL	National High Magnetic Field Laboratory
NIH	National Institutes of Health
NMR	nuclear magnetic resonance
NPUA	Nonproprietary Use Agreement
NSF	National Science Foundation
NWChem	Northwest Computational Chemistry Software
OMB	Office of Management and Budget
PD	pseudopodium
PEEM	photoemission electron microscope
PIXE	proton-induced x-ray emission
PNNL	Pacific Northwest National Laboratory
PNSO	Pacific Northwest Site Office
POZ	primary ozonide
PRP	pentapeptide repeat proteins
PS-SFR	Particle-on-Substrate Stagnation Flow Reactor
PTM	post-translational modifications
RFR	repeating five-residues
SAC	Science Advisory Committee
SCZ	Secure Collaboration Zone
SDC	samaria doped ceria
SEM	scanning electron microscopy
SFG	sum frequency generation
SHG	second harmonic generation
SIP	Science of Interfacial Phenomena (science theme)
SMERF	Systems Microbiology Extremophile Research Facility

SOA	secondary organic aerosol
SOFC	solid-oxide fuel cell
SOZ	secondary ozonide
SPLATII	Second-generation Single Particle Laser Ablation Time-of-Flight
SPM	scanning probe microscopy
STM	scanning transmission microscope
STOMP	Subsurface Transport Over Reactive Multiple Phases
STXM/NEXAFS	scanning transmission X-ray microscopy with near edge X-ray absorption fine structure spectroscopy
TEM	transmission electron microscopy
TOF	time-of-flight
TOF-SIMS	time-of-flight secondary ionization mass spectrometry
TPD	temperature programmed desorption
TRLIFS	time resolved laser induced fluorescence spectroscopy
UCSD	University of California, San Diego
UHV	ultrahigh vacuum
USB	universal serial bus
USO	User Support Office
VPP	(PNNL's) Voluntary Protection Program
WBS	work breakdown structure
WU	Washington University in St. Louis
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction

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1.0 Pacific Northwest National Laboratory Director's Statement

Mike Kluse
PNNL Director

Welcome to EMSL, a premier U.S. Department of Energy (DOE) national scientific user facility operated by Pacific Northwest National Laboratory (PNNL). We very much appreciate your participation in the operational review of EMSL and look forward to further strengthening the user facility and user program through the feedback that you—the review committee—will provide.

Last October, EMSL celebrated its first decade of operation as a user facility. Since opening its doors, EMSL has provided researchers from across the nation and the world a unique collaborative environment and state-of-the-art instrumentation.

Through the support of DOE's Office of Science, EMSL's expert scientific staff and impressive suite of computational and experimental resources have enabled many of these researchers to make great scientific strides. For example, Grand Challenge research integrating instrumentation across all of EMSL has provided insights into nature's methods for carbon sequestration and nitrogen fixation. Research on these and many other extraordinary user research projects continue to lead to publications in prestigious journals such as *Nature, Science*, and *Proceedings of the National Academy of Sciences.*

As EMSL enters its second decade of operation, DOE's Office of Science continues to show confidence in PNNL's operation of the user facility. Investments are being made in recapitalization to keep EMSL capabilities at the forefront of science and meet users' emerging needs. Such investments include EMSL's third-generation $24-million supercomputer, Chinook, a 163-peak teraflop system that will advance DOE's missions in energy, environment, and national security. Support for development of new capabilities—a hallmark of EMSL—is leading to unique tools such as *NWChem*, EMSL's premier computational chemistry software that allows users to address a wide range of challenging scientific problems. We also are making progress in bolstering EMSL's user program through key hires and development of the Wiley Research Fellowship, designed to attract distinguished users who will advocate the user facility.

Once again, welcome and thank you for participating in this review. Your guidance and input are critical to ensuring that EMSL's user program continues to serve the scientific community efficiently and effectively for years to come. The future is indeed very exciting for EMSL and the science produced here.

2.0 EMSL Director's Statement

Allison A. Campbell
EMSL Director

Welcome to the 2008 EMSL Science and Operational Review. We look forward to the opportunity to highlight past accomplishments at EMSL as well as future opportunities. The past three years have been full of achievement. The past three years have been full of achievement. We formally launched the EMSL Sciences Themes; launched a major recapitalization effort to revitalize many of our capabilities as well as propel EMSL through development of unique transformational tools; centralized our user support activities; and worked towards an integrated problem-solving environment through calls for proposals that encourage use of multiple capabilities, including combined theory, modeling, and simulation with experiment. In fact, some very exciting science performed at EMSL in recent years that have taken advantage of our capabilities. For example:

- A protein map of a mouse brain was compiled, the first study to ever apply quantitative proteomics to imaging. Such maps may help in early detection of neurological diseases such as Alzheimer's or Parkinson's. The research was published in *Genome Research* and featured in *Nature* online Neuroscience Gateway.

- EMSL's computational chemistry software, *NWChem*, and nuclear magnetic resonance spectrometry capabilities enabled users to derive a molecular theory that describes the electronic environment of the metal-amino acid motif. Many critical biological functions, including DNA repair, depend on proteins with reactive metal centers. Understanding the structure of these proteins at the molecular level gives researchers insight into how those proteins carry out their functions. The research was published in *Journal of the American Chemical Society.*

- Using a combination of EMSL spectroscopic and computational modeling capabilities, researchers discovered a class of gold atom clusters that are the first-known metallic hollow equivalent of the buckyball. In very minute quantities, gold becomes highly reactive and exhibits very good catalytic properties. Combined with another atom in the center of the buckyball, materials with novel chemical, magnetic, or optical properties could be achieved. The research was featured on the cover of *Proceedings of the National Academy of Science.*

As we look toward EMSL's next decade of operation, we will build upon our excellent progress made so far to strongly focus on strategies of scientific innovation, development of capabilities that transform science, outstanding management and operations, and engaged and proactive users—strategies that will continue to strengthen EMSL as one of the U.S. Department of Energy's premier national scientific user facility. I expect that, with such a strong strategic focus, the future will continue to bring some great scientific discoveries, strong leaders, and users at the top of their fields. In all areas of operational excellence, we will continue to strive for continuous improvement. Through your participation in this review, I have no doubt the value you provide will help us to be one of the best scientific user facilities available to the scientific community. I look forward to meeting with all of you in September.

3.0 EMSL History

The genesis of EMSL can be traced to 1986 when Pacific Northwest National Laboratory (PNNL) Director William R. Wiley and several of his senior managers met to discuss how PNNL could respond to the nation's scientific challenges that were critically dependent on fundamental advances in chemistry. Of particular concern were the growing challenges related to environmental cleanup, energy efficiency, and health.

William R. Wiley

In 1993, EMSL's project team, led by PNNL Director William R. Wiley (center, holding plaque), celebrate approval to proceed with construction of EMSL.

The resulting concept was that of a center for molecular science research, located at PNNL, that would bring together theoreticians with expertise in computer modeling of molecular processes with experimentalists from the physical and life sciences. Wiley and others at PNNL, knowing the tremendous advances that were occurring and would continue to occur in the ability of scientists to characterize, manipulate, and create molecules, believed molecular-level research would significantly contribute to solving significant challenges. This center would provide PNNL researchers and the nation with advanced instrumentation for molecular-level chemistry.

Battelle, which operates PNNL for the U.S. Department of Energy (DOE), approved funding to establish the facility; develop research programs; and obtain the equipment, facilities, scientists, and staff to support these programs.

PNNL was authorized by DOE in October 1993 to proceed. Construction began in July 1994. The facility was dedicated in Wiley's honor in October 1996, a few months after he unexpectedly passed away. Construction was completed in August 1997, and EMSL opened on October 1, 1997, for full operation as DOE's newest national scientific user facility.

In October 1996, Gus Wiley, wife of the late William R. Wiley, cuts the ribbon at the dedication of EMSL.

4.0 Organizational Relationships and Governance

4.1 Organizational structure

4.1.1 Office of Science Organizational Structure

EMSL is a national scientific user facility supported by the U.S. Department of Energy (DOE) Office of Biological and Environmental Research (BER), under the Deputy Director for Science Programs within the Office of Science. Within BER, EMSL funding and oversight is under the responsibility of the Climate and Environmental Sciences Division. Figure 4-1 shows the organizational relationship of EMSL stewardship within DOE. In addition, the Pacific Northwest Site Office (PNSO) works closely with BER, the Climate and Environmental Sciences Division, and EMSL on operational, performance, and contractual needs.

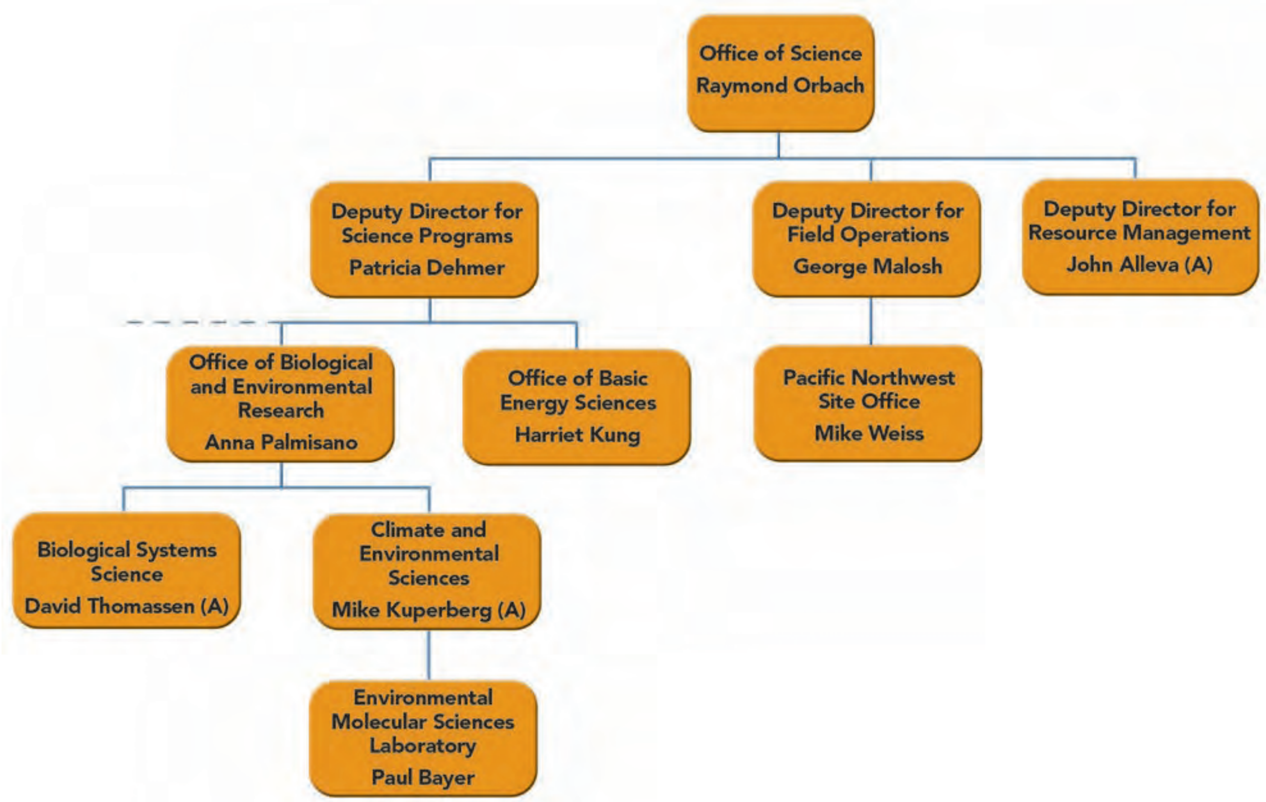


Figure 4-1. Organizational Relationship of BER within the DOE Office of Science.

4.1.2 Pacific Northwest National Laboratory Organizational Structure

Within Pacific Northwest National Laboratory (PNNL), EMSL is one of four research directorates (Figure 4-2). The EMSL Director reports directly to the PNNL Laboratory Director and is a member of the PNNL Executive Committee (EC).

Figure 4-2. Organizational Relationship of EMSL within PNNL.

4.1.3 Engagement

4.1.3.1 PNNL and EMSL Interactions

The EMSL Director is a member of PNNL's EC. The EC is composed of the senior leadership at PNNL and is responsible for setting PNNL's vision and strategy, setting priorities, and allocating resources, setting expectations for institutional performance, strengthening customer relationships, and reviewing and responding to assessments. The EC meets weekly. At these meetings, the EMSL Director has the opportunity to raise issues relative to EMSL's performance, request and defend fiscal year budgets, and ensure that EMSL's strategy is aligned with PNNL's future outcomes. In addition, the EC meets monthly with the PNSO senior leadership team to discuss issues, actions, upcoming events, and strategy. Formal reports required by EMSL to PNNL are listed in Table 4-1.

Table 4-1. Required Reports Sent by EMSL to PNNL.

Quarterly	Annually
Changes in Business Projections	Business Plans
Assessment Update	Annual Assessment Plans
EMSL Dashboard[(a)]	Electronic Prep and Risk
Performance Evaluation and Measurement Plan assessment	Input on Performance Evaluation and Measurement Plan

(a) Reporting of the dashboard is not required but provided to the PNNL Director for their information.

4.1.3.2 Engagement with BER and PNSO

EMSL management works closely with both BER and PNSO staff to ensure that the user facility is meeting performance expectations and to address issues and future opportunities (Table 4-2). Most interactions occur during weekly conference calls between the EMSL Core Team (see page 4-4), BER, and PNSO or between the EMSL Director, BER, and PNSO. Formal agendas for these meetings are provided by BER with input from EMSL. In addition, BER has established an EMSL Management Team comprised of the BER Director, Chief Scientist, and Operations Manager as well as members of BER's two divisions. The EMSL Director and a member from PNSO travel to BER's location quarterly to brief the management team on EMSL status and progress. On occasion, BER staff travel to EMSL to meet with EMSL staff to obtain a more detailed understanding of operations. Finally, monthly teleconferences are held between the EMSL computer operations group and BER to discuss issues and approaches to EMSL supercomputer procurement and management.

In addition to teleconferences and visits to BER, EMSL management provides, at BER's request, various reports either monthly, quarterly, or annually. Table 4-3 outlines these reports and interactions.

Table 4-2. Interactions Between EMSL, Office of Biological and Environmental Research, and Pacific Northwest Site Office.

Biweekly	Monthly	Quarterly
Core Team Telecon	Molecular Science Computing Telecon	Management Team Meeting
EMSL Director Telecon	Pacific Northwest Site Office Monthly Meetings	

Table 4-3. Formal Reports Provided by EMSL to BER at BER's Request.

Monthly	Quarterly	Annually
MSC High-Performance Computing System-3 Project Monthly Report	Operating Hours (C)	List of Major Resources
EMSL Capital Status	Resource Usage Report (D)	Cost of EMSL Resources by Funding Agency
MSC Status Sheet	Proposal and User Statistics (E)	Field Work Proposal
MSC Operational Assessment Response Plan	Resource Summary Report	Annual Highlights (F)
	Quarterly Highlights (F)	Hours per Quarter Estimate, and Planned Outages
	User Survey and Summary (biannually) (G)	MSC Risk Management Plan
	Performance Plan Charts	MSC Alternatives Analysis
	EMSL Dashboard (H)	MSC Archive Storage Analysis
	Financial Profile (I)	OMB Exhibit 300
	Building-Based Management (J)	MSC Dashboard
	CPIC Quarterly	

The letters in parentheses indicate the appendix in this report where examples of the reports can be found.
CPIC = Capital Planning and Investment Control
MSC = Molecular Science Computing
OMB = Office of Management and Budget

4.2 EMSL organizational structure

As shown in Figure 4-3, EMSL management consists of a director with five direct reports and the front office administrative team with responsibility for line management, science programs and capability development, user outreach, and support and operations. Associate Directors steward the bulk of EMSL science and technology staff, research capabilities, and user scientific consulting. The Chief Science Officer and Chief Technology Officer are responsible for setting the science and capability development strategy and priorities. The Chief Operations Officer is responsible for business planning and assessment, and all the operational aspects of EMSL including environmental compliance, safety, space, and construction. The User Support Office is responsible for supporting outreach, proposals calls, and peer review. Reporting to the Associate Directors are Capability Stewards who are responsible for the day-to-day operations of their respective capability suites including user training and support, instrument development and maintenance, and instrument utilization. The EMSL Core Team (outlined in red in Figure 4-3) is accountable to the EMSL Director for EMSL-wide efforts. Working together, they produce EMSL's vision and strategy, set EMSL's priorities and allocate resources, set expectations for EMSL's performance and outcomes, maintain strong customer relationships, review and respond to assessments, and solve problems. Finally, two external advisory committees, the Science Advisory Committee and the User Advisory Committee, provide expertise and direction to EMSL management.

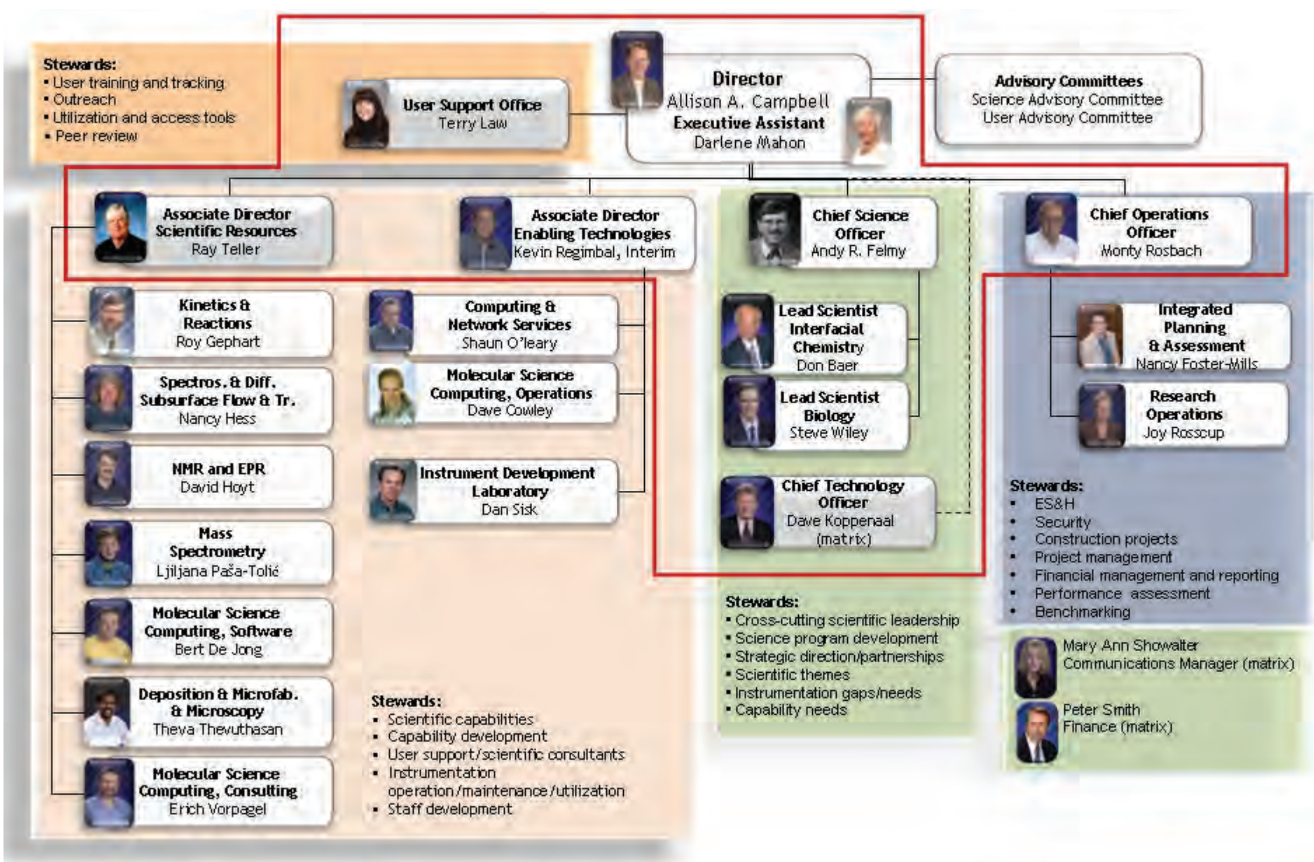


Figure 4-3. EMSL Organizational Structure Including Advisory Committees.

Allison A. Campbell,
EMSL Director

4.2.1 EMSL Director

The EMSL Director leads and manages EMSL, a major organizational component of PNNL, to maximize performance in achievement of EMSL's and PNNL's strategic outcomes while fulfilling commitments to customers and Battelle in research and operations excellence.

Ray Teller
Associate Director for
Scientific Resources

4.2.2 EMSL Associate Directors

EMSL has two Associate Directors: one for enabling technologies and another for scientific resources. The Associate Directors provide direct oversight of EMSL capabilities and staff, and are responsible for working with the EMSL Director to implement EMSL's strategy, security, safety, and user programs. They develop and maintain a highly productive technical resource base within assigned capability areas that is closely aligned with related Laboratory capabilities and with relevant sector and product line strategies.

Kevin Regimbal
Interim Associate Director
for Enabling Technologies

4.2.3 EMSL Chief Science Officer

EMSL's Chief Science Officer develops and implements the science vision for EMSL. This includes science themes and programs that enhance the scientific impact of the EMSL user program. In addition, the Chief Science Officer oversees EMSL's intramural and Laboratory-Directed Research and Development programs.

Andy Felmy
EMSL Chief Science
Officer

4.2.4 EMSL Chief Technology Officer

EMSL's Chief Technology Officer develops and implements a capability and technology vision for EMSL including identification of new technologies needed to enable EMSL science themes and programs. The EMSL Chief Technology Officer also acts as a direct liaison with the Fundamental and Computational Sciences Directorate within PNNL.

Dave Koppenaal
EMSL Chief Technology
Officer

Monty Rosbach
EMSL Chief Operations
Officer

4.2.5 EMSL Chief Operations Officer

The EMSL Chief Operations Officer manages EMSL's business and operational processes. This includes managing EMSL's environment, safety, and health policy and procedures as well as facilitating space and the operational aspects required for staff and users to undertake scientific endeavors.

Terry Law
EMSL User Support Specialist

4.2.6 EMSL User Support Specialist

The EMSL User Support Specialist oversees the user proposal and access process, and is responsible for the operation and maintenance of the management systems used to facilitate access to the EMSL. The specialist supports the EMSL Communications Manager in outreach efforts.

4.2.7 EMSL Capability Stewards

EMSL's Capability Stewards oversee the daily operations of EMSL's user program and capabilities. Examples of their responsibilities include ensuring user proposals are competitively reviewed, technically sound, deliver results, and consistent with the EMSL mission; assigning staff to assist users with research; planning and tracking user projects ensuring they are completed on time and within budget; maintaining safe and efficient facility operations; and working with EMSL management and the Chief Science Officer to define research strategies and capability advancement needs.

4.2.8 Science and Technical Staff

EMSL science and technical staff serve as scientific consultants and work closely with users. Staff members develop and sustain expertise to conduct high-quality research in collaboration with EMSL users. Biosketches for EMSL staff and select users can be found in Appendix A. For curriculum vitae, see Appendix B.

4.3 EMSL advisory committees

The Science Advisory Committee (SAC) and User Advisory Committee are independent bodies charged with providing objective, timely advice to the leadership of EMSL. Both committees report to the EMSL Director. The EMSL operations budget funds both advisory committees and is provided by the EMSL Director. Detailed charters are located in Appendix K; minutes and responses are in Appendix AB.

4.3.1 Science Advisory Committee

The SAC includes distinguished scientists from academia, national laboratories, and research institutions across the United States who provide expertise in EMSL's major capability areas of biology, environmental science, molecular science, and theory. The committee provides direct input to the Director of PNNL. Responsibilities and activities of the SAC include the following:

- Providing advice regarding EMSL's focus on national priorities and science challenges.
- Providing advice regarding the strategy for accomplishing EMSL's vision.
- Assisting EMSL with formulating policies related to scientific output, scientific impact, user access, and other issues, as needed.

- Providing advice regarding potential opportunities for transferring science to applications.
- Performing periodic reviews of scientific impact from the various elements of the EMSL user program.

The nature of the goals and purposes of the SAC requires it to be ongoing and dynamic. The committee meets a minimum of once per year, with members supported to visit individually once within a year. Members serve staggered 4-year terms.

Subcommittees of the SAC may be formed to provide recommendations on particular matters related to committee responsibilities. Ad hoc members external to the SAC may be appointed to ensure the competency necessary to conduct the subcommittee's business.

The current members of the SAC are as follows:

- Len Spicer, Duke University (Chair).
- Mark A. Barteau, University of Delaware.
- Gordon E. Brown, Jr., Stanford University.
- Charles T. Campbell, University of Washington.
- Marvin Cassman, Consultant.
- Gregory Choppin, Florida State University.
- Ian Farnan, Cambridge University.
- Barbara J. Finlayson-Pitts, University of California at Irvine.
- George W. Flynn, Columbia University.
- David J. Galas, Battelle.
- Samuel Kaplan, University of Texas-Houston Medical Center.
- Julia Rice, IBM Almaden Research Center.
- Peter J. Rossky, University of Texas at Austin.
- James M. Tiedje, Michigan State University.
- Mary F. Wheeler, University of Texas at Austin.

4.3.2 User Advisory Committee

The User Advisory Committee is a user-elected independent body of experts from academia, industry, and the national laboratory system that provides objective, timely advice and recommendations to EMSL leadership. The committee serves as the official voice of EMSL's user community in its interactions with EMSL management.

The User Advisory Committee is a user-elected, independent body of experts who advise EMSL management.

The responsibilities of the User Advisory Committee include the following:

- Provide a clear channel for the exchange of information and advice between EMSL users and management.
- Provide a formal vehicle for EMSL users to transmit concerns and recommendations to the EMSL Director.
- Design and oversee the EMSL user meetings.
- Provide advice and recommendations to the EMSL Director on how to facilitate the effective use of EMSL.
- Nominate active users for future membership to the committee.

The following committee members were elected by EMSL users via an online election process held November 2006:

- Theresa L. Windus, Iowa State University (Chair).
- Valérie Copié, Montana State University.
- Scott Fendorf, Stanford University.
- Vicki H. Grassian, University of Iowa.
- Wayne Hess, Pacific Northwest National Laboratory.
- Kerry Hipps, Washington State University.
- Patricia M. Irving, InnovaTek, Inc.
- Anne M. Johansen, Central Washington University.
- Sarah C. Larsen, University of Iowa.
- Martin McIntosh, Fred Hutchinson Cancer Research Center.
- Karl T. Mueller, Pennsylvania State University.
- Lisa Porter, Carnegie Mellon University.
- Paul G. Tratnyek, Oregon Health & Science University.
- Angela K. Wilson, University of North Texas.

The User Advisory Committee meets once a year and additional visits are supported similar to the SAC. Additional meetings of the committee or any subcommittees may be scheduled as needed to provide timely advice in support of optimizing EMSL effectiveness.

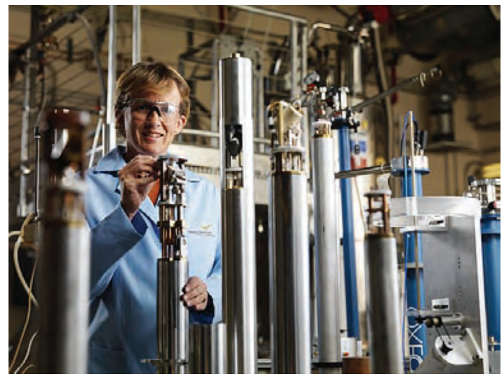
4.4 Governance and assurance

EMSL uses a model for management and assurance, which aligns governance, management, and performance functions within EMSL. The governance function focuses on strategy. Management translates strategic goals into tactical objectives and deploys resources to attain those objectives while managing performance within the limits set by governance. The performance level, where the work is accomplished, is accountable to management for performing work within the established procedures and guidelines, with attention to minimizing risk.

- **Governance – Set Strategic Direction**. Governance, consisting of PNNL and EMSL senior management, with input from the Science and User Advisory Committees and DOE, sets the direction of EMSL, aligns resources with goals, approves operational and business boundaries, and monitors progress.

- **Management – Translate Strategy into Tactics**. Management, which consists of EMSL's Capability Stewards and other managers, translates goals into tactical objectives, deploys resources to achieve the objectives, manages within risk limits, and provides feedback to governance on performance. With direction on strategy, they develop tactical objectives within EMSL's work plans to align resources to goals. After governance approval, management deploys resources to execute business plans and monitors performance, providing regular feedback to governance.

- **Performance – Conduct the Work**. Staff use processes, procedures, and tools to perform day-to-day activities to accomplish tactical objectives, while managing within established operational limits. Performance data and trends relative to the goals and objectives are gathered from this level using self-assessments and are summarized for management and governance to provide information essential for decision-making.



Staff use processes, procedures, and tools to perform day-to-day activities to accomplish tactical objectives, while managing within established operational limits.

Details on performance assessment and business planning are found in Section 10.0.

The following is a nearly completed version of EMSL's Strategic Plan. It has been previously vetted with EMSL's Science Advisory Committee and User Advisory Committee, and is expected to be forwarded to those entities for final review in the near future.

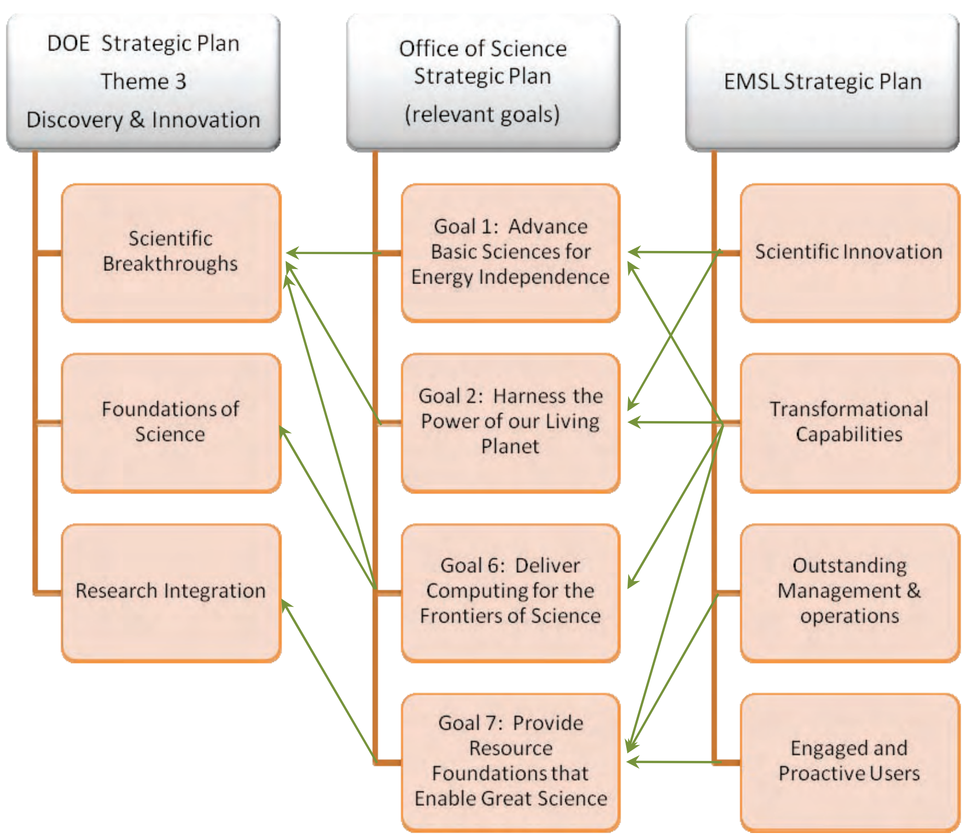
5.0 Strategic Plan

5.1 EMSL's mission

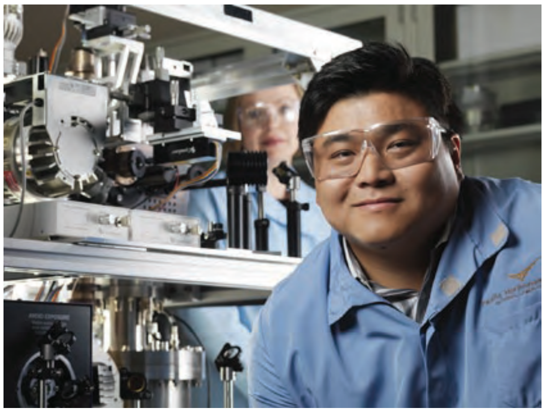
EMSL, a U.S. Department of Energy national scientific user facility located at Pacific Northwest National Laboratory, provides integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation.

5.2 Introduction

This Strategic Plan is EMSL's template for achieving our vision of simultaneous excellence in all aspects of our mission as a national scientific user facility. It reflects our understanding of the long-term stewardship we must work toward to meet the scientific challenges of the Department of Energy and the nation. During the next decade, we will implement the strategies contained in this Plan, working closely with the scientific community, our advisory committees, DOE's Office of Biological and Environmental Research, and other key stakeholders.



This Strategic Plan is fully aligned with the strategic plans of DOE and its Office of Science. We recognize that shifts in science and technology, national priorities, and resources made available through the Federal budget process create planning uncertainties and, ultimately, a highly dynamic planning environment. Accordingly, this Strategic Plan should be viewed as a living document for which we will continually evaluate changing needs and opportunities posed by our stakeholders (i.e., DOE, users, staff, advisory committees), work closely with them to understand and respond to those changes, and align our strategy accordingly.



This Plan is organized around four strategic outcomes 1) Scientific Innovation, 2) Capabilities that Transform Science, 3) Outstanding Management and Operations, and 4) Engaged and Proactive Users. These outcomes provide the framework for the seven critical actions we must take over the next 3 to 5 years:

1. Establishing leadership in EMSL's science themes.
2. Building and deploying transformational capabilities.
3. Integrating computation with experiment.
4. Ensuring that EMSL's workforce meets the scientific challenges of the future.
5. Creating partnerships.
6. Attracting and engaging users in EMSL's long-term strategy.
7. Building a research infrastructure that meets users' emerging scientific needs.

Implementation of these outcomes and actions is grounded in Battelle's management principles of simultaneous excellence in all aspects of management and operations.

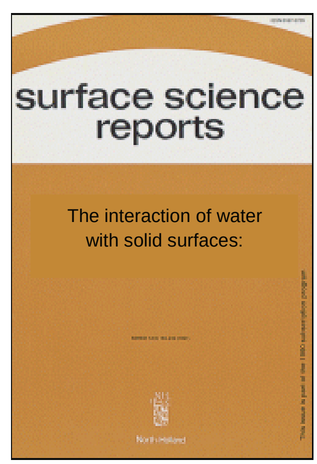
The vision outlined in this Strategic Plan is not an extrapolation of ongoing science but a visionary look towards new opportunities where advances in environmental molecular sciences and the tools that enable these advances can have a significant impact.

Current and developing technologies can be combined in new ways to create a new generation of research tools, and this vision provides a roadmap for the next decade of scientific capabilities that can collectively position EMSL to meet challenges in the environmental molecular sciences.

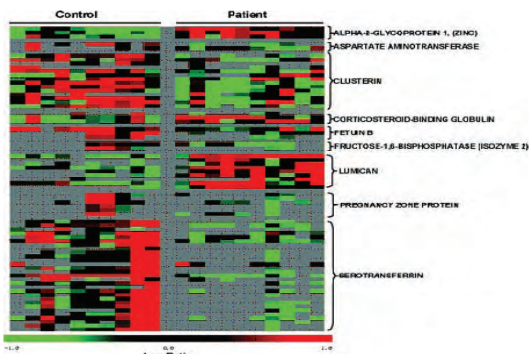
5.3 Our impact

Our vision and strategy for the future is built upon a strong foundation of accomplishment. During the past decade, significant scientific progress has been achieved through development of new capabilities and by focusing combinations of EMSL's state-of-the-art tools and expertise on important scientific challenges. Below are past research highlights that exemplify scientific impact that EMSL has enabled to research important to DOE and the nation.

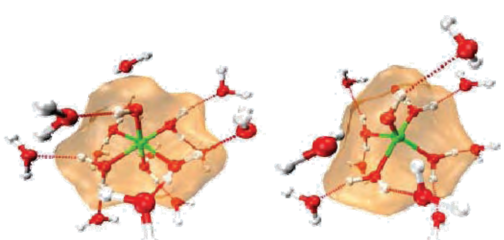
EMSL is a world-leading center for oxide and mineral surface chemistry research. The ability to synthesize unique oxide films and surfaces along with ability to characterize the physical structure and chemical properties has enabled EMSL to make significant contributions in catalysis, photocatalysis and new-generation oxide-based electronic materials as well playing an important role in advancing the understanding of model biogeochemical systems. Both the research and capability development have been recognized by national awards (2002 Federal Laboratory Consortium Technology Transfer Award and 2004 E.W. Muller Award for Outstanding Research in Surface Science). Recent work shows the impact of imaging technologies on our understanding of chemical transformations. Scanning tunneling microscopy measurements of oxygen molecules adsorbing on the surface of rutile [TiO_2 (110)] surface demonstrated that oxygen molecules dissociate only at specific sites (bridging oxygen vacancies) with one O atom healing a vacancy and another O atom bonding at the neighboring titanium site. This observation is of particular interest not only because it is a unique observation of site-specific adsorption, but because TiO_2 is an important catalyst substrate and the base material for photocatalytic destruction of contaminant molecules and the possible production of hydrogen. The research was published in *Journal of Physical Chemistry B* (110:21840-21845).



EMSL is a world leader in unraveling the complex interactions that occur in aqueous systems. Water occurs nearly ubiquitously in environmental systems, and unraveling the molecular-level interactions of ions and contaminants in water (both in solution, at surfaces, and in the atmosphere) is of fundamental importance in environmental molecular science. This unprecedented understanding of aqueous environments requires unique capabilities for studying ion-water clusters in the gas phase. Combining electrospray ionization with laser detachment anion beam photoelectron spectroscopy has enabled the production and spectroscopic characterization of multiply-charged, water solvated, gas-phase cluster ions ubiquitous in aqueous solution but unattainable in the gas phase. Using state-of-the-art molecular-, ion-, and electron-beam instrumentation in EMSL, scientific users have pioneered the use of nanoscale amorphous solid water films to study ion solvation in solution and ice nucleation and crystallization in the upper atmosphere. Water interactions at solid and mineral surfaces are also fundamental to unraveling the chemical behavior of environmental systems; this has been a focus of EMSL research from the beginning. As an example, EMSL user Mike A. Henderson published a comprehensive review of the work in this area which addressed such areas as how water is adsorbed, determining the chemical and electrostatic forces that constitute the adsorbed layer, and how coadsorbates influence these properties of water. Equally important are advances in the theory, modeling, and simulation of the properties of aqueous environments enabled by the world-class EMSL computational resources. Specifically, systematic approaches have been developed to assess the accuracy of various levels of electronic structure theory, and they have been applied to accurately evaluate several solute-solvent and solvent-solvent intermolecular interactions. This approach has paved the way for the development of a new generation of interaction potentials for water-water, ion-water and water-solute systems.



Using EMSL proteomics capabilities, users from the Centers for Disease Control and Pacific Northwest National Laboratory discovered five proteins that could help predict type 1 diabetes with higher sensitivity and specificity than current methods. Research results were published in the *Journal of Proteome Research* [7(2):698-707].

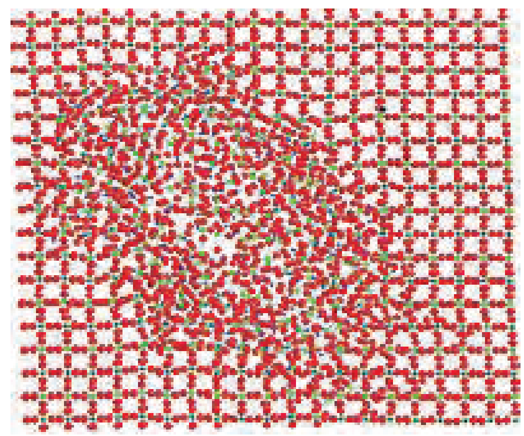


EMSL's high-performance, 11.8-terfaflop supercomputer combined with its premiere computational chemistry software, *NWChem*, allowed a research team from the University of California, Davis; University of Calgary; PNNL; and State University of New York to determine the structure of a five-coordinate aluminum ion in solution. The results were published in *Science* [308(5727):1450-1453].

EMSL's high-throughput proteomics measurement and characterization capabilities are world-leading. Developed using EMSL and programmatic resources, the capabilities are based on customized high-performance liquid chromatography separations coupled with ion trap, Fourier transform ion cyclotron resonance (FT-ICR), time-of-flight (TOF), triple-quadrupole and Orbitrap™ instrumentation, and complemented with comprehensive data interpretation and informatics toolbox. A current throughput of approximately 100 proteome analyses per day can be accommodated, and a database of over 1 million peptides enables comprehensive eukaryotic and prokaryotic protein identification. A particularly strong capability in microbial proteomics has been developed and is being applied to environmental remediation, carbon sequestration, and energy development problems.

EMSL's high-performance computational capabilities and specialized software enable major scientific progress. EMSL scientists lead the development of DOE's premier computational chemistry tool (*NWChem*) to enable researchers to solve scientific questions in areas such as catalysis, solar energy, hydrogen economy, environmental remediation, and biology, while including the complex dynamical behavior of nature in realistic environments. *NWChem* is a leading high-performance computational chemistry software suite that provides researchers with the unique capability to understand complex challenging scientific problems at the molecular level by coupling the power of advanced computational chemistry techniques with existing and rapidly evolving high-performance, massively parallel computing systems. *NWChem* has been recognized with prestigious national awards (R&D 100 and Federal Laboratory Consortium for excellence in technology transfer). Running on EMSL's supercomputing hardware, *NWChem* has enabled the reliable modeling of the thermodynamics cycle of hydrogen release and uptake for chemical boron-nitrogen hydrogen storage compounds, a critical part in the development of environmentally friendly hydrogen-based fuel cells as a power source. It was also used to confirm the discovery of a five-coordinate $Al(H_2O)_4OH^{2+}$ ion as the predominant form in biochemically and geochemically relevant solution environments such as natural bodies of water.

EMSL is a world leader in enabling high-field nuclear magnetic resonance (NMR) to be applied to a wide range of complex systems. EMSL houses a suite of cutting-edge magnetic resonance spectrometers, including a powerful 900-MHz system and the world's only NMR spectrometer and laboratory that are dedicated to the study of solid-phase radiological samples. This unique suite of instruments has contributed broadly to the characterization of biomolecules, surface chemistry, and catalysis research. Special emphasis has been placed on use of high-field capabilities to determine hard-to-examine nuclei such as isotopes of alkaline earth elements, strontium and calcium. These investigations contributed to an improved fundamental understanding of the long-term stability of materials proposed for waste immobilization and this is leading to improved predictive models that support informed decisions on long-term storage of radioactive isotopes. For example, EMSL users from Cambridge University and the Pacific Northwest National Laboratory published a paper in the January 11, 2007, issue of *Nature* that describes the impact of alpha emitters on the crystal structure of zircon. The dedicated radionuclide NMR was instrumental in demonstrating unequivocally that radiation effects rapidly degrade the crystal structure of the mineral.



An improved understanding of how alpha particles decay waste forms is leading to enhanced predictive models that support informed decisions on long-term storage of radioactive isotopes. Results of this research, led by a scientific user from the Cambridge University using EMSL's radiological NMR capabilities, were published in *Nature* [445(7124):190-194].

This Strategic Plan builds on these and past accomplishments of developing transformational capabilities and integrating them to create problem-solving environment for our users. The long-term outcomes of our strategy—scientific innovation, transformational capabilities, outstanding management and operations, and engaged and proactive users—underscore the value we provide to DOE and the nation.

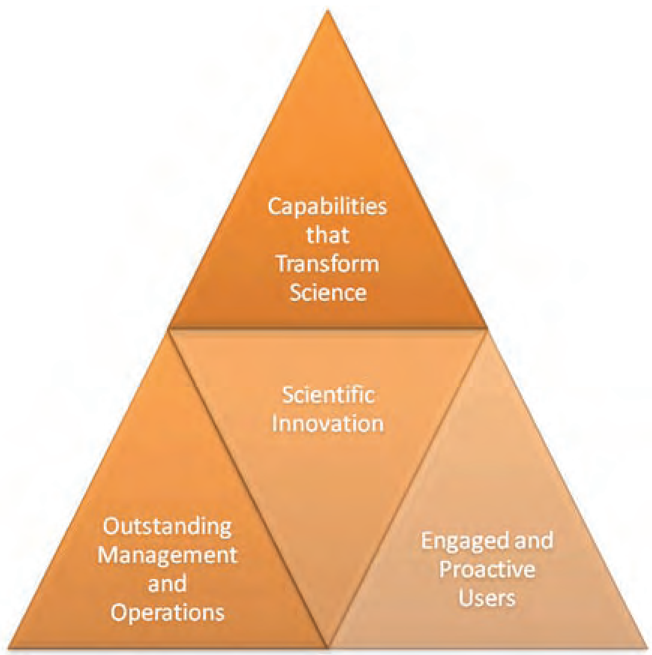
5.4 Our vision

5.4.1 Delivering Scientific Innovation through Integration

Our vision is that EMSL develops and integrates, for use by the scientific community, world-leading capabilities that transform understanding in the environmental molecular sciences and accelerate discoveries relevant to DOE's missions. We will accomplish this through multidisciplinary collaborations between an engaged user community and expert scientists and staff.

Achieving this vision means that EMSL is widely recognized for:

1. ***Developing transformational tools that advance scientific frontiers*** in EMSL's molecular science themes.
2. Adding exponential value by ***integrating science and technology*** across disciplines and scientific capabilities.
3. Empowering a ***distinguished community of users*** that is invested in and advocates the long-term use and success of EMSL.
4. ***Ensuring management excellence*** that propels EMSL into a long-term, upward path of accomplishment and performance.



In achieving this vision, we commit to ***advancing the scientific reputation of EMSL and our users*** by engaging some of best and brightest scientists from around the world who seek out EMSL to accomplish their scientific objectives.

Increased involvement of renowned scientists, high-impact publications, strategic partnerships, and recognition by the scientific community are key metrics for our progress.

5.5 Our strategic outcomes

This Strategic Plan builds on EMSL's strengths in building transformational capabilities and integrating them to create a problem-solving environment for our users. The long-term outcomes of our strategy—scientific innovation, transformational capabilities, outstanding management and operations, and engaged and proactive users—underscore the value we provide to DOE and the nation.

5.5.1 Scientific Innovation:

EMSL will advance fundamental understanding in the environmental molecular sciences and produce accelerated leadership class discoveries for DOE mission-relevant applications.

With more than 2500 user and staff publications in peer-reviewed scientific journals during EMSL's first decade of operation, EMSL is enabling users to make significant contributions to the scientific understanding of the nation's complex energy and environmental problems. In Fiscal Year 2007, EMSL staff and user research appeared in more than 300 articles, including many in prestigious journals such as *Science*, *Nature*, *Proceedings of the National Academy of Science*, and *Journal of the American Chemical Society*.

As we look forward into the next decade of operation, we will establish a world-class research presence in key science themes of importance to DOE and the nation. Advances in understanding aqueous systems and cluster chemistry will enable us to focus on ***atmospheric aerosol chemistry*** and help decrease uncertainties in predicting climate change. Increased knowledge regarding ***biological interactions and dynamics*** and advances in our understanding of oxide materials and ***interfacial science*** will impact both the development of clean and secure energy and environmental cleanup solutions. Predictive knowledge of ***geochemistry/biogeochemistry and subsurface science*** will enable safe and predictive management of legacy and hazardous waste.

5.5.2 Capabilities that Transform Science:

EMSL will develop, integrate and deploy transformational tools that accelerate scientific discovery and innovation; provide a pillar in the nation's scientific infrastructure, and attract and retain the best and brightest scientists as staff and users.

During the past decade, EMSL has established a leadership position in building transformational capabilities in areas such as mass spectrometry based proteomics, magnetic resonance and high-performance computing software.

Moving forward and building upon the past accomplishments, EMSL will, in the next decade, build and deploy new transformational capabilities that will provide researchers with new approaches to view chemical and biological systems—from **single molecules or organisms to complex structures or communities**, from **static to dynamic** processes, from ***ex-situ*** **systems to** ***in-situ*** **observation**. These capabilities are transformational because they transcend the envelope of current ability—they attract the brightest scientific minds in the world and enable discoveries that change the face of science.

Development and integration of these tools requires access to a wider range of resources and capabilities than typically available to individual researchers and research institutions. However, they comprise a set of capabilities appropriate to a national scientific user facility that can equip many extramural scientists to conduct truly unique and transformational research.

"We need TRANSFORMATIONAL discoveries, leading to what I call DISRUPTIVE technologies—technologies that fundamentally change the rules of the game—and that means we need fundamental breakthroughs."
Dr. Raymond Orbach,
Under Secretary for Science,
U.S. Department of Energy

5.5.3 Best-in-Class Management and Operations:

EMSL operations and management systems will be the most effective and efficient in delivering outstanding research; providing a world-class research infrastructure; and supporting a highly productive, world-class staff and user community.

EMSL management is committed to operating the DOE Office of Biological and Environmental Research's national scientific user facility with excellence through strong management, premier facilities, a focused strategy, and consistently communicated policies and plans.

During the past decade, EMSL has built and deployed several management systems that streamline the user proposal and access processes. We have adopted and embedded strong project management principles into our everyday operations, and we have completed the first expansion onto the facility to provide additional raised floor computing space as well as office space for our staff and users.

In the coming years, EMSL will continue to embrace best management practices by improving processes and performance, staff and user engagement, and costs and effort efficiencies. EMSL management will employ a well-structured, integrated management approach with clear roles, responsibilities, and expectations to result in effective line management oversight. EMSL will have a robust system of clear, consistent performance objectives and measurements so that resources are more effectively focused on key objectives and continued improvements are made to meet those objectives.

We will continue to expand and improve our research infrastructure to meet the demands of our users. Our facilities will remain best in class through preventative maintenance efforts. and we will continue to identify future infrastructure needs.

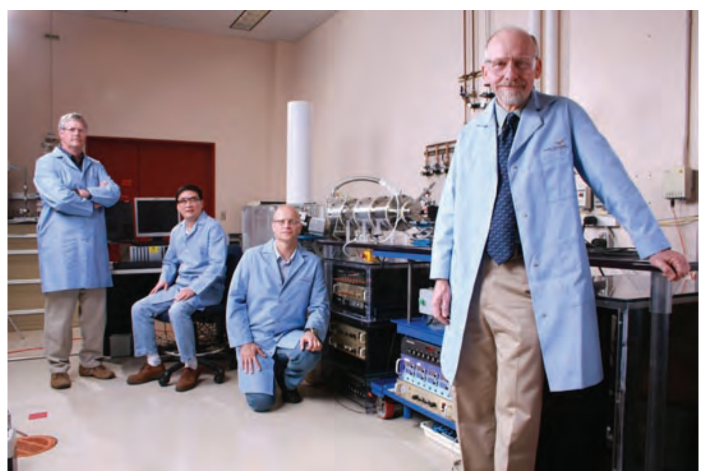
Our environment, health and safety program will remain best in class through active participation in human performance assessments and waste minimization and risk assessment programs.

We will continue to engage our staff through active recruitment of senior leadership and providing staff with the tools that help them to advance their careers.

5.5.4 Highly Engaged and Satisfied User Community:

EMSL's user program will attract the best and brightest scientists who produce scientific discoveries and are engaged in the long-term success of the user program.

EMSL's vision cannot be realized without an engaged, satisfied, and proactive user community, the hallmark of a successful user facility. EMSL's goal is to attract and foster a user community that conducts outstanding research and is actively involved and engaged in EMSL's success. Our goal is to advance the impact of EMSL's scientific accomplishments to the extent that some of the most prestigious scientists from around the world will seek to become users. To that end, we will continue to embrace ideas that build strong user communities. One example is to build upon the EMSL Scientific Grand Challenges that focus multidisciplinary groups of users on challenging scientific problems. The primary purpose of these grand challenges is to answer important scientific questions through a collaborative user-driven approach, using the comprehensive capabilities of EMSL. The scope of the scientific problems to be addressed requires multidisciplinary teaming, and the breadth of a challenge will be of magnitude such that it cannot be addressed at any other existing single facility.



Other approaches for building user engagement include focused workshops and tutorials that bring communities of users together to learn about EMSL capabilities and science themes; use of competitive analysis capabilities to obtain information on top universities where research is conducted that is compatible with EMSL's science themes, and then put into place mechanisms to target the heads of those academic departments with information about EMSL; and identification of one major professional society meeting (e.g., American Chemical Society, American Geophysical Union) per science theme per year where targeted, streamlined outreach efforts—such as a Director's Seminar Series—can be conducted towards relevant technical programs.

5.6 Critical actions

The actions outlined below represent areas where EMSL management will focus effort and resources over the next 3 to 5 years in order to meet our vision and strategic goals. They cross cut and enable all of our strategic outcomes.

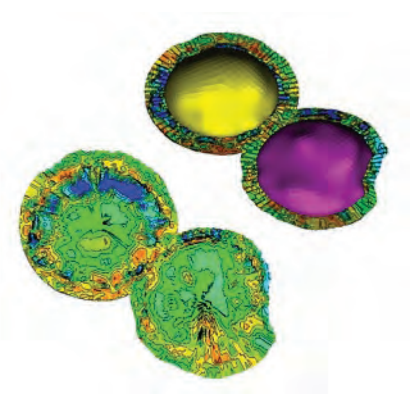
5.6.1 Establish Scientific Leadership in EMSL's Science Themes

EMSL science themes are areas where EMSL can make significant scientific contributions. Current science themes build upon and expand the historical scientific expertise of EMSL. They were evaluated against key criteria including DOE and national relevance, contribution to impactful environmental molecular science, strong national science and technology programs, and the ability to grow a vibrant national user program, and they were selected with broad input and support from the scientific community and EMSL advisory committees. As scientific advances are made, the nature and elements of EMSL's science themes will evolve to reflect both scientific gains and changing societal needs. New areas will be explored and evaluated during annual business planning.

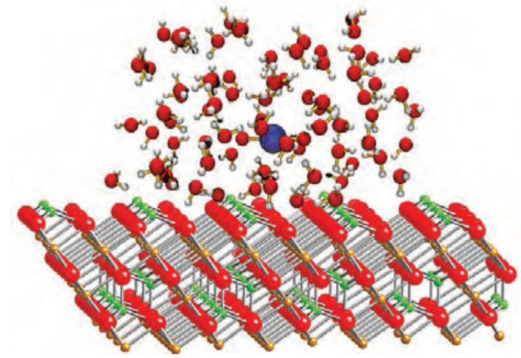
In the next 3 to 5 years, EMSL will establish scientific leadership in its three mature science themes. Measures of success in the area of scientific leadership will include publications in top-tier journals, external reviews, and the ability to attract leading scientists as staff and users.

During the next 5 to 10 years, EMSL will drive scientific progress by creating a cohesive portfolio of user projects under its science themes by issuing annual calls for proposals for user projects that fill gaps in understanding and focus on key scientific questions of importance to DOE and the nation. In doing so, EMSL will make significant scientific contributions in each area as outlined below.

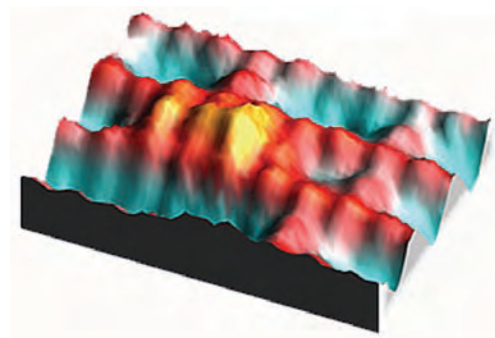
Current Science Themes



The **biological interactions and dynamics** theme emphasizes a systems-level understanding of microbes and microbial communities. The unique biological function, interactions and community dynamics of extremophiles will receive special emphasis. This work will be facilitated by establishing a new capability for culturing and sampling of microbes under precisely controlled conditions and for the isolation and analysis of individual cells and their components. Coupling EMSL's signature strengths in proteomics and metabolomics with the Joint Genome Institute's unique strengths in genomics will provide a breadth of molecular detail never previously achieved. Combining these measurements with high dimensional data management, modeling, and simulation will, in turn, allow for the **first time a predictive understanding of microbial regulatory networks that will enable optimization and manipulation of microbial processes such as CO_2 sequestration**.

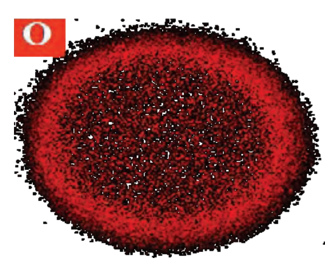


EMSL's **geochemistry/biogeochemistry and subsurface science** theme advances a core strength of EMSL and focuses on one of DOE's singularly important challenges—the cleanup of legacy waste. EMSL's emphasis on molecular-scale understanding of the complex transport and reactive processes taking place in the migration of plumes from nuclear waste sites has the promise for dramatically reducing the costs of cleanup. The understanding of such fundamental processes as proton and electron transfer in complex mineral environments mediated by microbial metabolism is a key scientific challenge. Molecular-level measurements coupled with sophisticated modeling of transport and chemical conversion processes as a function of environmental parameters is our signature approach to solving this problem. To that end EMSL shall, within the next decade, focus user projects in areas that will **improve our ability to predict and modify pollutant transport or transformation in the subsurface**.



The **science of interfacial phenomena** theme exploits signature strengths of EMSL staff and users and focuses on developing an understanding of molecular structure-function relationships at the atomic level that will allow precise control of interfacial activity and selectivity. This science theme will address in a definitive and comprehensive way, for the first time, the effect of nanoscaling on the surface chemistry of well-defined metal oxides. Highly controlled experiments in the growth, characterization, and reactivity of oxide nanodots and continuous films of nanometer thickness will elucidate the effects of quantum-confined and strain-driven electronic structures on the thermal and photochemistries of select materials. The research capabilities and expertise in EMSL will also enable the design of material systems with specialized atomic, electronic, and ionic transport properties. EMSL is an ideal place for this research to be performed because it is a premier oxide laboratory and has provided the foundation for several research areas, including surface chemistry and catalysis. To this end, EMSL will focus user projects on the **development of new understanding that enables the optimization of interfacial properties, such as the control of catalytic activity and longevity**.

Emerging Science Theme



EMSL has also identified an emerging area in **atmospheric aerosol chemistry** that focuses on **establishing a molecular-scale, predictive understanding of the principal chemical and physical processes of aerosol formation, growth, and decay**. Among all the forcing factors in global climate, aerosols stand alone in that the knowledge of their chemical and physical properties are so poorly defined that even the sign of the impact factor is unknown. The greatest uncertainty is the chemistry and physics of organic aerosols, and tracing their life cycle, from molecular to cluster to nanoparticles to many microns, is virtually undefined scientifically. To fully realize this science theme, cohesive and robust science and technology programs are needed within DOE's Office of Biological and Environmental Research and scientific leadership is needed at EMSL. During the next several years, **EMSL will work with BER program managers to identify new science and technology programs that can support user research areas, work to attract scientific leadership to EMSL, and focus user projects around highly focused calls for proposals** to establish a critical mass of user projects, capabilities and expertise that enable a fully mature science theme.

Potential Future Science Themes

As science and technology programs evolve along with the scientific needs of the nation, we will identify potential new areas to focus EMSL resources, including nuclear waste form science, actinide science, and trace detection. During the next several years, EMSL scientific leadership will evaluate the feasibility and potential scientific impact of these areas.

5.6.2 Develop and Deploy Transformational Scientific Capabilities to the Scientific User Community

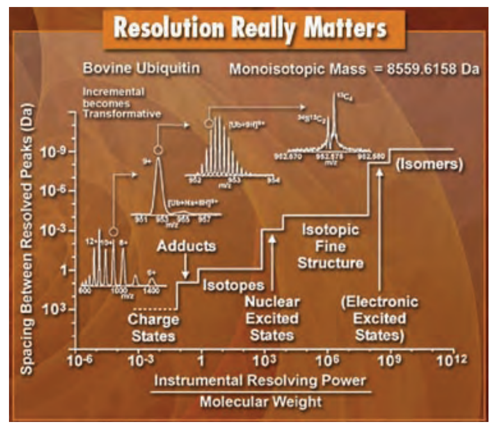
Scientific advancements cannot be made without similar advances in the capabilities used to make discoveries. New tools being developed at EMSL will enable researchers to change how they view chemical and biological systems—from **single molecules to communities of species**, from **static to dynamic processes**, from ***ex-situ* systems to *in-situ* observation**, and will also enable the type of discoveries that truly change the face of science.

Working with users, science advisors, and other scientific leaders, EMSL has identified emerging needs and new scientific tools and resources that will advance scientific discovery in EMSL's science themes. The results of this analysis and a variety of other indicators, including the 2006 National Academies study of advanced research instrumentation and facilities, suggest that there will be fundamental changes in the way science is conducted. These trends and advances define several important technology challenges and opportunities that will be used to focus EMSL capability development activities. These opportunities include tools and techniques for:

1. Moving from Statics to Dynamics in Native Environments.
2. Characterization of Surfaces and Interfaces with Unprecedented Resolution.

3. Design and Synthesis of Increasingly Complex Materials.
4. Predicting Biological Functions from Molecular and Chemical Data.
5. Rapidly Linking Theory with Experiment.
6. Bridging Scales: Bridging the Gap between Molecular and Continuum Understanding.

These challenges, coupled with the directions outlined in the science themes, provide the basis of a vision that will be used to guide capability development in EMSL during the next decade, the details of which are outlined in the EMSL document, “Recapitalizing EMSL: Meeting Future Science and Technology Challenges.” As part of this effort, several major new and exciting development opportunities are envisioned.



1. **Development of the world’s highest-field FT-ICR mass spectrometry system with unprecedented speed and resolution**. Advances in mass spectrometry will bring analytical capabilities for top-down proteomics to a much higher level than is presently possible. Critical information on the proteomic and metabolomic profiles is thought to reside in the minor constituents that are currently below the level of detection of existing mass spectrometers. The challenge is to advance the mass resolution and mass range of mass spectrometry by as much as an order of magnitude while more than doubling the dynamic range (ratio of most abundant to least abundant ions detectable in a given scan) and the sensitivity of ICR analysis. Scientific challenges in the environmental molecular science addressed by this capability involve analyzing the most complex molecules and mixtures imaginable and creating a measurement tool that dramatically extends the range of problems that are amenable to molecular-level investigation.

2. **Integrated capabilities for systems microbiology and extremophile research**. Microbial communities can be considered a network of cells that are controlled by their individual gene and protein regulatory networks. Mapping community function to the properties of their underlying networks requires the growth and sampling of microbes under a wide range of different, and sometimes extreme, conditions. Each sample must then be analyzed using technologies that can reveal the network structure at particular scales (from the community to molecular level). To address this challenging goal, EMSL will develop an integrated capability that will allow the parallel culturing of microbes under a wide range of different controlled conditions coupled with automated and remote controlled capabilities that will allow users

to run long-term experiments remotely. A new generation of flow cytometers and laser dissection equipment will allow the isolation and analysis of individual microbial cells. High-speed microscopes with single-molecule resolution will enable the resolution of cellular structures below the diffraction limit. Multimodal instruments, including a combined NMR and confocal microscope, will reveal the metabolic and gene expression profile of cells within a community. A comprehensive data management system will be developed to link experimental conditions to the compositional analysis of cells and communities. This will enable entirely new computational approaches to be used for the analysis and simulation of microbial function.

3. **Next-generation surface science capabilities**. The need to characterize and then tailor surfaces and interfaces require unique instrumentation in materials synthesis, the ability to probe reaction *in situ* in real time, and new limits of spatial and energy resolution. To address these needs, EMSL will, over the next decade, make substantial investments in the development of:

- A suite of complementary *in situ* and real-time methods to collect high-resolution structural and chemical information, such as can be accomplished using high-resolution transmission electron microscopy with environmental cells
- Combined spectroscopy and microscopy for three-dimensional analysis of structures, including buried interfaces
- A range of unique and state-of-the-art capabilities to advance understanding of complex interfaces and surfaces. New capabilities important in this area include *oxygen plasma-assisted molecular beam epitaxy and high-throughput materials production and analysis.*

4. **Move EMSL's scientific computing to the petascale**. EMSL's high-performance scientific supercomputer is a unique capability tailored to address computational challenges in the environmental molecular sciences. The computational hardware resource science drivers that formed an integral part of the procurement of EMSL's next-generation high performance scientific supercomputer (called Chinook) were derived from EMSL's vision and science themes, solicited white papers, and a technical workshop on scientific computing held at EMSL in December 2004, which were collected in the document "Scientific Challenges: Linking Across Scales."

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

The next-generation supercomputing hardware, Chinook, will consist of tens to hundreds of thousands of processors, a scale that could hardly be envisioned when EMSL's premier computational chemistry code *NWChem* was conceived fifteen years ago. These huge computing resources will enable researchers to tackle scientific problems that are larger and more realistic than ever before, to include more of the complex dynamical behavior of nature, and will allow researchers to ask new and different scientific questions. However, both the changes in scientific needs and computing technology require that we also examine our software capabilities to ensure that *NWChem* and other EMSL-developed software will provide its users with the cutting-edge capabilities they need for next-generation platforms. Bringing *NWChem* to petascale platforms will be a major effort that will require a community of computational chemists, mathematicians, and computer scientists to join forces.

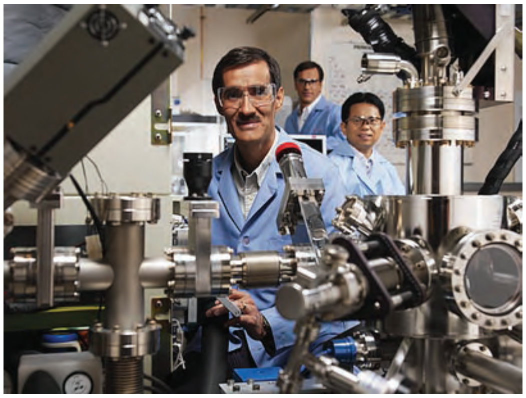
5.6.3 Fully Integrate Scientific Computing and Information Technologies with Experiment to Accelerate Scientific Innovation and Demonstrate the Value of Multidisciplinary Approaches to Science

The 21st century brings a new way in which science is conducted, due, in large part, to the expansion of the internet and new technologies that enable observations of unprecedented quality, resolution and accuracy. At EMSL, we will explore new modes of conducting science that will couple, in near real time, revolutionary new experimental systems with massively parallel supercomputers, digital libraries, and unique visualization environments. These advances will make it possible to accelerate discovery and increase by orders of magnitude the levels of complexity open to exploration and experimentation.

Evolving in parallel with these new capabilities are different ways of working across science disciplines. Increasingly, scientific discovery involves the expertise of individuals from different disciplines, and often from different nations, who work together to address the complexity of today's challenges. The need for multidisciplinary science has made collaboration a centerpiece of the science enterprise. At EMSL, we will demonstrate the value of integrated multidisciplinary science by focusing our user program on the integration of computing and experiment, and through focused calls for proposals and scientific grand challenges.

5.6.4 Ensure EMSL's Workforce Meets the Scientific Challenges of the Future

People are EMSL's most important resource. We are committed to continuing to attract, develop, and retain a diverse workforce of highly regarded staff, which is essential to the long-term health and growth of EMSL. Key to achieving these goals is creating and maintaining a quality work environment



that enables staff to feel valued and to work in a highly productive mode. As we move forward, we must provide the tools, support, and resources that enable staff to develop their careers to the fullest extent possible. We will focus on creating a work environment that enables highly engaged staff to work with passion, to drive innovation, and to move the organization forward toward higher levels of scientific productivity. Key to these actions are active participation in PNNL's Scientist and Engineering Development Program and EMSL Intramural Research Program.

5.6.5 Create Partnerships Across the Department of Energy, National Science Foundation, National Institutes of Health, and Other User Facilities and Targeted Universities

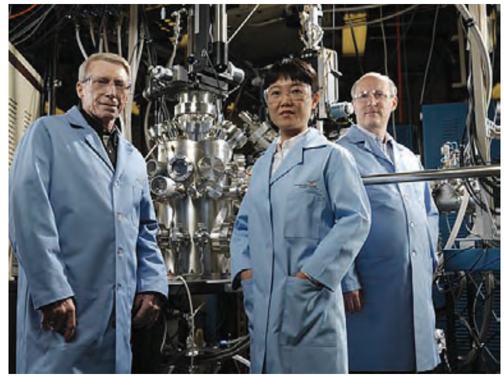
EMSL currently enjoys several partnerships with the NSF, including the NSF-sponsored Environmental Molecular Science Institute and a new PNNL/NSF collaborative program that provides supplemental awards to NSF grantees to support travel for graduate students, postdoctoral fellows, and staff to EMSL. NSF's Integrative Graduate Education and Research Training Grant programs at collaborating universities bring students to EMSL for advanced scientific training, as do traditional grants from other agencies.

In addition, a partnership with NIH's Proteomics Research Resource for Integrative Biology will extend EMSL's base of high-impact users as well as attract students and postdoctoral fellows to EMSL for advanced education and training in molecular science. Finally, strategic partnerships with universities, such as the University of Washington in nanoscience and technology and the Oregon Health Sciences University in applied biosciences, serve to further expand EMSL's user base.

EMSL will build upon these partnerships and develop new collaborations across agencies, organizations and corporations, identifying common goals that can drive scientific and technological innovation. We will work across agencies to identify opportunities for co-investment in new discovery-class tools. We will establish programs that facilitate long-term collaborations between distinguished scientists and young researchers using EMSL.

5.6.6 Attract and Engage Users in EMSL's Long-Term Strategy

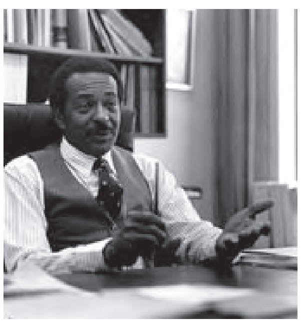
Highly engaged, satisfied users are a hallmark of a successful user facility. EMSL's goal is to attract and foster a user community that is engaged beyond the user's individual research efforts. This will enable us to more effectively involve the user community in EMSL's future directions as well as build advocacy for EMSL and user facilities broadly.



Attracting high-profile scientists as users will enhance EMSL's scientific reputation, increase its visibility, and appeal to the scientific community. Through their research activities and collaborations at EMSL, these high-profile users will help further develop the distinctive scientific areas for which EMSL is known. Additionally, these users will bring to EMSL mentoring and scientific collaboration opportunities for early-career staff and users.

In addition, EMSL needs to continue to foster collaborations with PNNL researchers—PNNL is rich with scientific expertise and technology development abilities. Promoting collaborations among EMSL and PNNL researchers will enable new capability development through joint grant proposals and more efficient use of PNNL-wide resources and intellectual pool—resulting in strengthening both EMSL and PNNL.

Engagement of the user community (both external and internal) in the long-term planning for EMSL is vital to our success. To that end, EMSL has established programs aimed at attracting and engaging its user community.



- **Wiley Research Fellow Program**—recognizes users who make significant contributions to the EMSL user program above and beyond their research involvement.

- **Wiley Distinguished Visiting Scientist Program**—recognizes and encourages distinguished scientists to come to EMSL and make significant contributions to the EMSL user program as well as provide input to and recommendations on the path forward for EMSL.

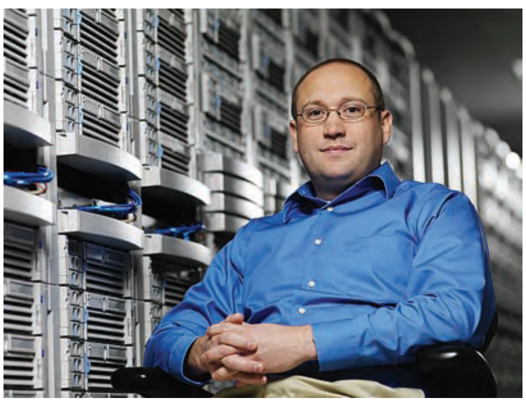
5.6.7 Build a Research Infrastructure that Meets Emerging Scientific Needs

As EMSL moves to build new transformational tools that push the limits of sensitivity and resolution, probe dynamic processes and examine materials in complex native environments, new challenges in infrastructure requirements will emerge. Tight controls on vibration, electromagnetic, and thermal parameters will be required. Networking and cyber requirements will be required to enable the close collaboration of individuals between distant locations. Laboratory environments that allow for the study of radiological materials in native and simulated environments are needed. To address these needs, EMSL has established a long-term vision for future facility enhancements.

Radiological Annex. Access to specialized equipment for the study of radiological materials is in decline nationwide, and a user facility with these capabilities would provide an important resource to scientists throughout the country. In addition, providing training for the next generation of radiochemists and associated nuclear sciences is important to the long-term mission of DOE. Expanded radiochemical capabilities in EMSL would provide these opportunities and allow contribution of high-quality science to areas of importance to DOE's mission. The EMSL Radiological Annex will support enhanced research and radiological actinide capabilities via a complement of unique research capabilities housed in the annex. The annex is planned to be physically separate from the EMSL facility, thus isolating radiological activities, and relying only on the main EMSL facility for support infrastructure such as compressed air, nitrogen, and electrical power. This annex is being proposed at $4.9 million with an expected completion date of FY 2010.

EMSL Quiet Wing. The Quiet Wing will support future capabilities within EMSL that require tight controls on electromagnetic interference, vibration and thermal tolerances. The new Chemical Transmission Electron Microscope, planned for arrival in early FY 2009, will require space of this nature as will future planned investments such as NanoSIMS and other microscopes.

South Electrical Plant. The south electrical plant will support current and future supercomputer capabilities within EMSL. The major need for power and cooling is driven by future computer needs. This $4.9 million building is expected to be constructed by the end of FY 2011 and is being coordinated in conjunction with the PNNL campus electrical infrastructure enhancement planned with the City of Richland.



Computer Room Addition. The computer room addition will support the next-generation supercomputer, High Performance Computing System-4. The future space will lend itself to next-generation technologies of condensed computer arrangements with proper cooling and short-run cable connections, with the existing space used for other computer housing. The expansion is planned for FY 2012 and is also expected to be a $4.9 million project.

EMSL North Addition. Long term, EMSL is looking to expand its footprint to the north to meet emerging demands. More and more environmental specifications around vibration, electromagnetic isolation, temperature, and atmospheric parameters need to be controlled within very tight tolerances. The proposed EMSL North Addition would include construction of two laboratory modules on the north end of the building with an accompanying office pod extending east. This 55,000-square-foot addition is proposed to be initiated in FY 2012, with completion in FY 2014.

5.7 Translating the plan to action

This Strategic Plan guides EMSL's annual planning. The Annual Plan translates EMSL's mission, vision, strategic outcomes and critical actions into tactical actions. Implementation of this Plan is the responsibility of EMSL's Director, Associate Directors, Chief Officers and internal groups responsible for planning and performance. Individual performance appraisals will measure staff accountability and alignment with organizational goals, while annual metrics will track our progress.

5.7.1 Annual Planning Process

This Strategic Plan is EMSL's template for achieving our vision of simultaneous excellence in all aspects of our mission as a national scientific user facility. It provides the foundation for EMSL's annual planning, budget, and performance assessment processes and documents. Through our annual planning process, we solidify the objectives, measures, and targets that will guide our work during the next several years.

5.7.2 Making Investment Decisions

Based on our strategic outcomes, EMSL management identifies key areas for future investment by balancing a variety of concurrent and equally important factors. These areas may reflect emerging opportunities, address pressing challenges, or responding to critical needs. They may require sustained levels of investment over many years, or they may be more narrowly focused and change from year to year. Proposed investments will be evaluated against this matrix of considerations.

Alignment: Alignment with EMSL's mission, vision, and goals. Deciding factors include whether investments lie within the bounds established by the EMSL Strategic Plan, effectively address multiple goals, and do not duplicate the efforts of other institutions.

Impact and Transformation: Promote ideas that are intellectually compelling, innovative and transforming. Deciding factors include the extent to which investments may transform a field of science; are broadly significant or of great interest to DOE; position EMSL at the forefront of an emerging field; contribute to national research and development priorities; or enable scientifically important outcomes.

Budget: Balance investments with funding levels. Deciding factors include whether the proposed level of investment is commensurate with opportunity, level of risk, relevance, and potential impact.

Leveraging Collaborations: Create opportunities for collaboration. Deciding factors include whether investments augment other DOE activities; leverage other community or federal agency investments in research and infrastructure; and broaden participation in EMSL's user program.

Urgency and Readiness: Capture timely opportunities. Deciding factors include whether timing is critical to achieve optimum results, or investment is necessary to maintain long-term stability and progress in critical areas.

5.7.3 Performance and Assurance Management

EMSL uses a model for performance management and assurance, which aligns governance, management, and performance functions within EMSL.

- **Governance – Set Strategic Direction**. Governance, consisting of EMSL senior management, with input from EMSL's advisory committees, PNNL senior management and DOE, sets the direction of EMSL, aligns resources with goals, approves operational and business boundaries, and monitors progress.

- **Management – Translate Strategy into Tactics**. Management translates goals into tactical objectives, deploys resources to achieve the objectives, manages within risk limits, and provides feedback to governance on performance. With direction on strategy, they develop tactical objectives within EMSL's work plans to align resources to goals. After governance approval, management deploys resources to execute business plans and monitors performance, providing regular feedback to governance.

- **Performance – Conduct the Work**. Staff use processes, procedures, and tools to perform day-to-day activities to accomplish tactical objectives, while managing within established operational limits.

Assurance Processes Validate Performance. Governance employs means such as internal audits and assessments, independent oversight, peer reviews, and benchmarking to provide reasonable assurance that goals are being achieved within approved operational boundaries. Self-assessments are used to obtain information on performance, to validate that management systems are performing effectively and efficiently, and to verify that accurate and reliable data are being delivered to decision makers. Assurance is also used to verify that our users are being provided high-quality products and services.

EMSL measures the effectiveness of defined plans and strategies, operations, and overall organization health, and drives improvement through our performance management process. Each fiscal year, EMSL management develops an annual Performance Management and Assessment Plan with associated Dashboard that evaluates and tracks performance against defined goals, objectives, and metrics across EMSL line organizations and management systems. Assessments and evaluations are performed using self, independent, internal, and external assessments, audits, and reviews (including peer review of research results). Outcomes of these processes are used 1) to perform strategy development and management decision making and 2) to identify and enable improvement.

5.7.4 Strategic Timeline and Resource Requirements

Critical Action	As measured by	1-2 YEARS	2-4 YEARS	Steward
Establish scientific leadership in EMSL's science themes	Total and top 10 publications SAC ad hoc reviews	SAC as hoc review of each science theme (1 per year)		Chief Scientist
		Assess Aerosol science theme		
		Deep Dive new Science Themes area		
Develop and deploy transformational scientific capabilities to the scientific user community	New capabilities	FTICR (CD0 in FY09)		Chief Technology Officer
		Make decision on NanoSIMS		
		2nd recapitalization workshop		
		SFG/SHG		
		Build and deploy STORM		Science Lead for Biology
		Build and Deploy SMERF		
		Develop and implement next generation *NWChem* Strategy		AD Enabling Technologies
Integration of computing with experiment	Proposals and publications with integrated capabilities	Call for proposals that focus on integration		User Support Specialist
Create partnerships		MOA with NHFMF		EMSL Director
		Travel funding from NIH for users	Co-funding of next Grand Challenge	
Ensure the scientific leadership meets the challenges of the future	New senior hires Awards and recognition First Authorship	Hire SFG/SHG lead		Associate Directors
		Hire TEM Lead		
			Hire NMR Lead	
Attract and engage users in EMSL's long-term strategy	Distinguished Users	Appoint 6 Wiley Fellows	Appoint 6 Wiley Fellows	EMSL Director
		Award 2 Wiley Visiting Scientist	Award 2 Wiley Visiting Scientist	
Build a research infrastructure that meets emerging scientific needs		Rad Annex		Chief Operations Officer
		Q Wing		
			South Electrical Plant	
			Data center Expansion	

6.0 Science and Research Capabilities

6.1 EMSL's science themes

EMSL plans to increase its scientific impact during a second decade of operation by focusing in specific areas identified as high-priority science themes. These science themes help define and direct development of key capabilities, staffing, and collections of user projects that can have significant impacts on important areas of environmental molecular science that are critical to the U.S. Department of Energy (DOE) and the nation.

Science themes were selected to meet key criteria including relevance to DOE and the nation, impactful environmental molecular science, and the ability to grow a vibrant national user program.

With these factors in mind, EMSL, with input from the scientific community, DOE's Office of Biological and Environmental Research (BER) leadership, and our Science Advisory Committee selected these science themes:

- Biological Interactions and Dynamics.
- Geochemistry/Biogeochemistry and Subsurface Science.
- Science of Interfacial Phenomena (SIP).

Atmospheric Aerosol Chemistry was identified as an emerging theme managed under the SIP science theme. Each of these three mature themes is described briefly in this section.

6.1.1 Biological Interactions and Dynamics Science Theme

Until recently, biology has mostly been a qualitative and descriptive science in which technology has played a relatively minor role. Recent advances driven by whole-genome sequencing and improvements in high-throughput instrumentation, however, have contributed to a rapid transition of the biological paradigm toward understanding biology at a systems level. As a result, biology is evolving from a descriptive to a quantitative and ultimately predictive science where the ability to collect and productively use large amounts of biological data is crucial.

Biology is evolving from a descriptive to a quantitative and ultimately predictive science.

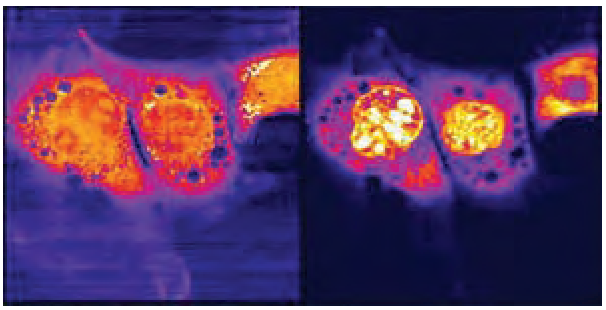
Early work in biology conducted in EMSL was mostly directed toward analyzing the molecular components of organisms. This reductionist approach was driven by early users of the facility as well as by the scientists who developed some of the original EMSL capabilities. The current movement toward systems-level research in biology, however, requires new technologies and approaches. EMSL is situated to develop these capabilities and to make them widely available to the biological community. To help facilitate the transition of biology to a more quantitative science, the Biological Interactions and Dynamics (BID) science theme was created to encourage user proposals in areas aligned with more quantitative and genome-scale science and that could exploit current and future EMSL capabilities. These areas include the following:

- Understanding the protein and metabolite composition of cells as well as the activities and structures of individual proteins or protein complexes.
- Understanding the dynamics of protein composition or localization, and their assembly into multi-protein complexes.
- Investigating properties of biological membranes and the interaction of cells with their environment.

User proposals in these areas are intended to provide the scientific drivers for the development, implementation, and dissemination of technologies needed for the next generation of biological research. For example, our user projects have shown that there is a need to measure and track the temporal and spatial disposition of proteins in cells and to understand how protein complexes give rise to specific activities. An understanding of how multi-protein complexes are assembled is needed for optimizing the response of biological systems (e.g., microbes) in particular environments such as those associated with fuel production or contaminant metabolism. Metabolite profiling is needed to improve our understanding of how cells respond to changes in their environment or energy state.

Much of the research in the BID science theme has been focused on extending current capabilities in high-throughput mass spectrometry and nuclear magnetic resonance spectroscopy (NMR). Enhanced capabilities are also being developed for investigating microbial membranes, such as cryo-transmission electron microscope (TEM), and multimodal and multispectral microscopy. These techniques will generate large amounts of data that will be handled by an integrated data management system. Clearly, integrating multiple types of data to generate a systems-level understanding of biological processes is extremely challenging. However, we have made progress in this area over the last several years and have developed critical capabilities needed for systems biology research.

History in the EMSL: The BID science theme arose from some of the work done to build the earliest capabilities in the EMSL, which were created to understand the physical properties of biological molecules. For example, Steve Colson created a microscopy and laser spectroscopy group that built novel microscopes that were applied to single molecule imaging in biological systems and to understand cell metabolism. They created a Coherent Anti-Stokes Raman Scattering (CARS) microscope that allowed an entirely new way of imaging living biological systems. This design has been incorporated in to multiple commercial instruments. They also created a combined NMR and confocal microscope that won a Discover award for innovative science.



Coherent Anti-Stokes Raman Scattering (CARS) microscope that allowed an entirely new way of imaging living biological systems. CARS image (left) showing concentrations of carbon-hydrogen bonds in live bone marrow stromal cells. Right: fluorescence of stained DNA and RNA stained (right) obtained simultaneously as the CARS image.

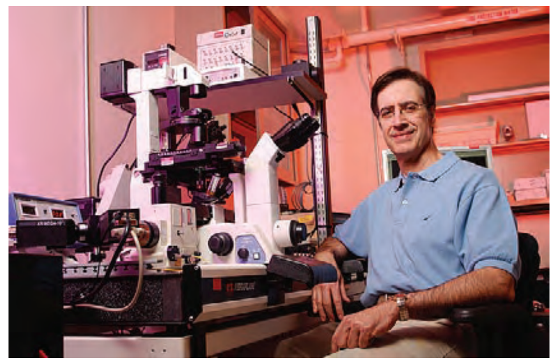
Paul Ellis built a group to apply high-field NMR to elucidate the structure of metalloproteins. Not only did EMSL acquire one of the largest collections of NMR instruments in the world, but also created capabilities to purify proteins as well as characterize and understand different protein structures in both static and dynamic states.

Dick Smith used his expertise in mass spectrometry to build one of the largest protein analysis research groups in the world, focusing on increased measurement sensitivity, resolution, and throughput. This capability has been used to understand the protein expression dynamics of a large number of microbial species and has attracted collaborators and users from around the world.

All of these capabilities were created to understand the physical properties of the molecules of life. The underlying science was driven by the urgent need a decade ago to understand the basic composition of organisms and the molecular properties of cellular constituents. This work was strongly supported by the U.S. Department of Energy (DOE) and other federal agencies, in particular the National Institutes of Health.

The emphasis on the analysis of individual biological constituents started to change with the advent of the Human Genome Project. Genome-based biology was a significant departure from the previous reductionist-driven research in that it emphasized high-throughput data generation and the analysis of the underlying pattern of molecular interactions. DOE was one of the first research agencies to shift its scientific focus toward genomics-driven, systems-scaled research. Its former support for research focused on individual molecules was significantly reduced, requiring a shift in many of the Pacific Northwest National Laboratory (PNNL) programs that provided the underlying science needed to create EMSL capabilities.

In response to the changing national scientific priorities, EMSL has been shifting its research capabilities to accommodate more high-throughput, dynamic, and systems-level research projects. This has been accompanied by a shift in the number of user proposals that are focused on this type of research. Advances in proteomics instrumentation in EMSL have been a primary driver of this research transition, but EMSL is also creating new capabilities in NMR-based metabolomics and imaging to help drive advances in the new field of systems biology.



In response to the changing national scientific priorities, EMSL has been shifting its research capabilities to accommodate more high-throughput, dynamic, and systems-level research projects.

Although we anticipate a significant increase in systems-level research projects over the next several years, EMSL continues to support users who have a more traditional science focus. This demand is expected to decrease as the instrumentation needed for simpler molecular characterizations proliferates in biological laboratories.

6.1.1.1 Specific areas of Biological Interactions and Dynamics science in EMSL

The BID science theme includes research projects that can be roughly associated with four different analytical technologies:

- Mass spectrometry-based proteomics.
- NMR.
- Imaging.
- Computational biology.

We have encouraged users to submit proposal that use multiple technologies and have achieved some success in this area. In particular, EMSL implemented the Membrane Biology Grand Challenge that had the explicit goal of integrating data in genomics, proteomics, imaging, metabolomics, and structural biology to achieve a systems-level understanding of the diurnal cycle of a photosynthetic bacteria. This project, led by Himadri Pakarasi of Washington University in St. Louis, provided the scientific framework for creating both the software and multidisciplinary team needed for systems biology.

Cross-disciplinary work is also facilitated by technology development specifically focused on this task. For example, we have applied both mass spectrometry and NMR to the measurement of metabolites. The combined NMR-confocal microscope allows the simultaneous measurement of gene expression patterns and metabolite concentrations. Bioinformatics software has been written to integrate microarray and proteomics data as a basis for computational modeling. Our increased emphasis on multidisciplinary studies has led to a significant increase in the number of user proposals in the area of systems biology.


Proteomics tools and methods available at EMSL allow detailed characterization of cellular proteins.

Over the last 3 years, there have been 183 publications in the BID science theme, which can be assigned to the following general technology areas:

- Mass spectrometry-based proteomics – 79.
- NMR – 47.
- Imaging – 29.
- Computational Biology – 9.
- Membrane Biology Grand Challenge – 11.

6.1.1.2 Mass spectrometry-based proteomics

Much of the work in proteomics has focused on understanding the protein composition of microbial systems, particularly in comparison to gene expression. This includes research performed in the context of understanding host-pathogen interactions to aid in identifying proteins of likely importance in detecting bacterial pathogens and developing vaccines. The large and rapidly increasing proteomics database at EMSL has become a research resource in its own right.

Proteomics tools and methods available at EMSL also allow detailed visualization and characterization of cellular proteins. The scope of proteomics studies includes the identification of proteins and their abundances, and often other information important for understanding their activity and function such as their localization in the cell, turn-over rates, and modification states. Our ability to study changes in biological systems and describe the variability from large volumes of proteomics data has enabled new insights to be extracted for diverse organisms, and even complex biological systems such as microbial communities in the soil and ocean (see Appendix AD).

Much of the technical developmental work in proteomics has focused on increasing the sensitivity of measurements as well as detecting post-translational modifications. Sensitive measurements are particularly important in measuring the levels of phosphorylated proteins in cells.

Important to the success of this area is the involvement of scientific leaders in the scientific community. Scientific leaders include Dick Smith (PNNL), Desmond Smith (University of California, Los Angeles), Richard Klempke (University of California, San Diego), Mary Lipton (PNNL), Sam Kaplan (University of Texas, Houston), Jay Nelson (Oregon Health and Science University), Tim Donohue (University of Wisconsin), Derek Lovley (University of Massachusetts), Lucy Shapiro (Stanford), Steve Giovanonni (Oregon State University), Roger Brent (Molecular Sciences Institute), Ron Davis (Stanford University), Michael Katze (University of Washington), Maria Pallavicini (University of California, Merced), Ron Tompkins (Massachusetts General Hospital), Mark H. Ginsberg (University of California, San Diego), Lilijana Pasa-Tolic (EMSL), Jim Fredrickson (PNNL), Fred Heffron (Oregon Health and Science University), Karin Rodland (PNNL), Steven Wiley (EMSL), and Tom Squier (PNNL).

Major scientific papers in this research area include the following:

Qian WJ, T Liu, ME Monroe, EF Strittmatter, JM Jacobs, LJ Kangas, K Petritis, DG Camp, and RD Smith. 2005. “Probability-Based Evaluation of Peptide and Protein Identifications from Tandem Mass Spectrometry and SEQUEST Analysis: The Human Proteome.” *Journal of Proteome Research* 4:53-62. (110 citations)

Qian WJ, ME Monroe, T Liu, JM Jacobs, GA Anderson, Y Shen, RJ Moore, DJ Anderson, R Zhang, SE Calvano, SF Lowry, W Xiao, LL Moldawer, RW Davis, RG Tompkins, DG Camp II, and RD Smith. 2005. “Quantitative Proteome Analysis of Human Plasma Following *In Vivo* Lipopolysaccharide Administration Using $^{16}O/^{18}O$ Labeling and the Accurate Mass and Time Tag Approach.” *Molecular & Cellular Proteomics* 4:700-709. (48 citations)

Much of the technical development work in proteomics has focused on increasing the sensitivity of measurements.

Kolker E, AF Picone, MY Galperin, MF Romine, R Higdon, KS Makarova, N Kolker, GA Anderson, X Qiu, KJ Auberry, G Babnigg, AS Beliaev, P Edlefsen, DA Elias, YA Gorby, T Holzman, JA Klappenbach, KAT Konstantinidis, ML Land, MS Lipton, LA McCue, M Monroe, L Pasa-Tolic, G Pinchuk, S Purvine, MH Serres, S Tsapin, BA Zakrajsek, W Zhu, J Zhou, FW Larimer, CE Lawrence, M Riley, FR Collart, JR Yates III, RD Smith, CS Giometti, KH Nealson, JK Fredrickson, and JM Tiedje. 2005. “Global Profiling of *Shewanella oneidensis MR-1:* Expression of Hypothetical Genes and Improved Functional Annotations.” *Proceedings of the National Academy of Science USA* 102:2099-2104. (39 citations)

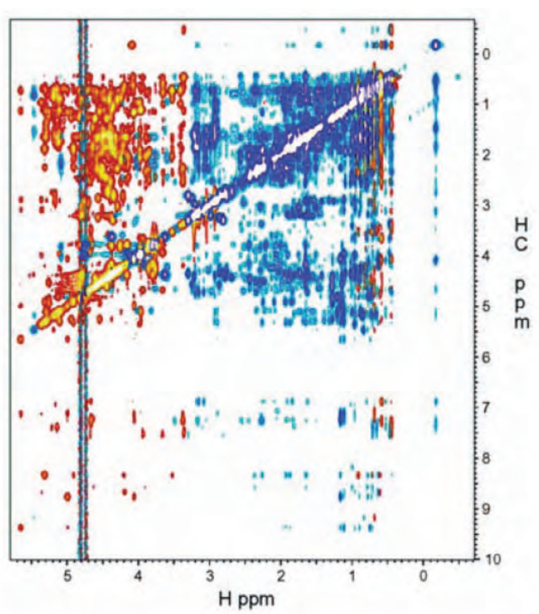
Wang H, WJ Qian, MH Chin, VA Petyuk, RC Barry, T Liu, MA Gritsenko, HM Mottaz, RJ Moore, DG Camp II, AH Khan, DJ Smith, and RD Smith. 2006. “Characterization of the Mouse Brain Proteome Using Global Proteomic Analysis Complemented with Cysteinyl-Peptide Enrichment.” *Journal of Proteome Research* 5:361-369. (35 citations)

Shen Y, J Kim, EF Strittmatter, JM Jacobs, DG Camp II, R Fang, N Tolie, RJ Moore, and RD Smith. 2005 "Characterization of the Human Blood Plasma Proteome." *Proteomics* 5:4034-4045. (33 citations)

Yang F, DL Stenoien, EF Strittmatter, J Wang, L Ding, MS Lipton, ME Monroe, CD Nicora, MA Gristenko, K Tang, R Fang, JN Adkins, DG Camp II, DJ Chen, and RD Smith. 2006. "Phosphoproteome Profiling of Human Skin Fibroblast Cells in Response to Low- and High-Dose Irradiation." *Journal of Proteome Research* 5:1252-1260. (25 citations)

These select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Combined proteomics and genomics analysis of *R. sphaeroides*.
- Comprehensive whole-proteome analysis of *Shewanella* available.
- First use of global proteomics to quantify bacterial proteins isolated from host cells.
- Proteomic characterization of a macaque flu infection model system.
- Proteomic comparison between virulent and avirulent *Burkholderia mallei* strains.
- Researchers utilize proteomics to reveal a core microbial proteome.
- First comprehensive characterization of the whole mouse brain proteome.
- Profile of phosphoproteins involved in cell movement created.
- Probing oxidative stress using intact-protein, high-field mass spectrometry.
- Mass spectrometry identification of endogenously nitrated proteins in mouse brain: Links to neurodegenerative disease.
- Identification of functional pathways associated with clinical tamoxifen-resistance in breast cancer by advanced mass spectrometry.



Two-dimensional projection of a three-dimensional Noesy-^{13}C-HSQC spectrum of unlabeled ubiquitin bound to ^{15}N-^{13}C labeled UbcH5c collected at 900 MHz.

6.1.1.3 NMR

Much of the NMR work at EMSL over the last 3 years has focused on structural studies. The 900-MHz NMR has been particularly useful in allowing larger proteins and complexes to be investigated. Structural work on numerous enzymes was also conducted.

High-field liquid-state NMR has been key for enabling novel approaches for the study of the structures and dynamics of important macromolecular complexes involved in ubiqutin transfer and recognition, cancer etiology and progression, and protein-ribonucleic acid complexes that are fundamental to cell growth and regulation. Further, those systems that have been traditionally excluded from structural studies due to their insolubility or non-crystalline nature are now being investigated using high-field solid-state NMR methods. These systems include amyloid fibrils, nucleocapsid proteins, and large (in excess of 100 kDa) membrane proteins.

Combining theory and structural determinations has been accomplished by the use of two key long-term capability investments at EMSL. The first is implementation of a *NWChem* module that provides *ab initio* quantum mechanical calculations using molecular mechanics constraints. The *NWChem* code was developed at EMSL. The second is the development and implementation of low-temperature solid-state NMR capabilities at high magnetic fields. The latter is designed to allow direct observation of NMR resonances of metals such as zinc and magnesium in metalloproteins that, under ambient conditions, would be arduous if not impossible to accomplish.

Important to the success of this area is the involvement of leaders at PNNL and in the scientific community. These include Paul Ellis (PNNL), Mike Kennedy (Miami University), Rachel Klevit (University of Washington), Valérie Copié (Montana State University), Mike Bowman (University of Alabama), Gabriele Varani (University of Washington), Guy Montelione (Rutgers), Cheryl Arrowsmith (University of Toronto), Patti Liwang (Texas A&M), Chad Rienstra (University of Illinois at Urbana-Champaign), Tatyana Polenova (University of Delaware), Andrew Lipton (PNNL), Paul Majors (PNNL), and David Hoyt (EMSL).

Major scientific papers in this research area include the following:

Hamma T, SL Reichow, G Varani, and AR Ferre-D'Amare. 2005. "The Cbf5-Nop10 Complex Is A Molecular Bracket That Organizes Box H/ACA RNPs." *Nature Structural & Molecular Biology* 12:1101-1107. (36 citations)

Brzovic PS, A Lissounov, DE Christensen, DW Hoyt, and RE Klevit. 2006. "A UbcH5/ubiquitin Noncovalent Complex Is Required for Processive BRCA1-Directed Ubiquitination." *Molecular Cell* 21:873-880. (19 citations)

Powers R, N Mirkovic, S Goldsmith-Fischman, TB Acton, Y Chiang, YJ Huang, L Ma, PK Rajan, JR Cort, MA Kennedy, J Liu, B Rost, B Honig, D Murray, and GT Montelione. 2005. "Solution Structure of *Archaeglobus fulgidis* Peptidyl-tRNA hydrolase (Pth2) Provides Evidence for an Extensive Conserved Family of Pth2 Enzymes in Archea, Bacteria, and Eukaryotes." *Protein Science* 14: 2849-2861. (9 citations)

Ramelot TA, A Yee, JR Cort, A Semesi, CH Arrowsmith, and MA Kennedy. 2007. "NMR Structure and Binding Studies Confirm that PA4608 from *Pseudomonas aeruginosa* Is a PilZ Domain and a c-di-GMP Binding Protein." *Proteins* 66:266-271. (9 citations)

Zhang L, M DeRider, MA McCornack, C Jao, NG Isern, T Ness, R Moyer, and PJ LiWang. 2006. "Solution Structure of the Complex Between Poxvirus-encoded CC Chemokine Inhibitor vCCI and Human MIP-1β." *Proceedings of the National Academy of Science* 103:13985-13990. (5 citations)

Lipton AS, RW Heck, M Valiev, WA De Jong, and PD Ellis. 2008. "A QM/MM Approach to Interpreting ^{67}Zn Solid-State NMR Data in Zinc Proteins." *Journal of the American Chemical Society* 130:6224-6230.

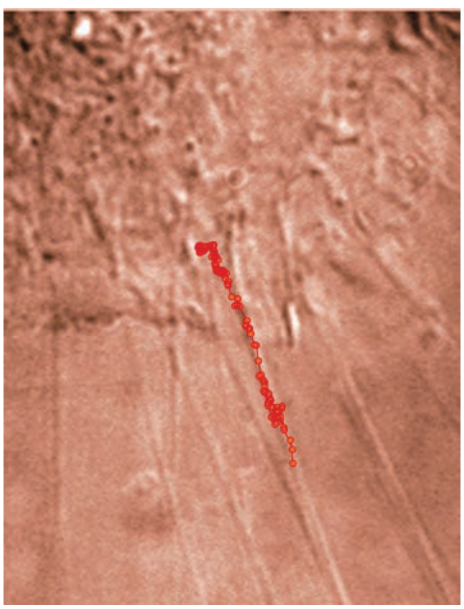
These select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- NMR structural investigations of the breast cancer susceptibility protein, BRCA1.
- Characterization of two potentially universal turn motifs that shape the repeated five-residue fold-crystal structure of a lumenal pentapeptide repeat protein from *Cyanothece* 51142.
- MRI bioreactor aids in understanding the physiology of live cells.
- The synergy between molecular theory and solid-state NMR spectroscopy.

6.1.1.4 Imaging

The activity in the cell imaging group was hampered by the retirement of Steve Colson and the loss of two scientific leaders in EMSL in this area. Nevertheless, the development and application of non-conventional cellular and molecular imaging capabilities have been continued, supporting research in membrane biology, receptor signaling, nanomaterial toxicity, enzymatic reactions, biomimetic processes, and unique fluorescent dyes development, among other areas.

Much of the user activity in cell imaging was in support of the Membrane Biology Grand Challenge. This required analysis of the photosynthetic microbe *Cyanothece* by cryo-EM (cryo-electron microscopy), flow cytometry, and fluorescence microscopy. These techniques were used to follow the changes in expression of multiple proteins during the diurnal cycle and to determine changes in cell structure and position in the cell cycle. The new techniques and experience gained by the EMSL staff in conducting these high-resolution studies have positioned them well for additional investigations. For example, a new sectioning approach for cryo-EM has been developed for studies on *Cynaothece*, which gained the Diatome Award for distinguished work in the field of microscopy, awarded at the Microscopy Society of America meeting in August 2007.



An individual silica nanoparticle, tagged with 1-5 fluorescent molecules, is identified and tracked using time-lapse single-molecule fluorescence imaging, showing the retrograde motion of the particle along the microvillus and revealing the coupling of the particle to the actin filaments across the cell membrane.

Also, a number of studies were done in the area of live cell imaging, especially at the single molecule level. Experience gained in these single-molecule studies was then applied to develop a novel assay for nanoparticle toxicity. The purpose of this work was to advance the understanding of particle solution dynamics in cell culture media as they relate to dosimetry and dose-response, and to the understanding of nanomaterial-cell interactions and pathways. This work was featured on the cover of *Toxicological Sciences*, and highlighted in a special Perspective article (http://pubs.acs.org/cgi-bin/abstract.cgi/ancac3/2007/1/i05/abs/nn700407v.html), as well as in an interview posted at the *ACS Nano* site (http://pubs.acs.org/journals/ancac3/podcasts/index.html (episode 5).

Current leaders at PNNL include Galya Orr and Dehong Hu; current leaders at EMSL include Steven Wiley and Alice Dohnalkova. Additional leaders include Lou Sherman (Purdue), Mark Jones (Oregon State University), Alex Li (Washington State University), Justin Teeguarden (PNNL), Bettye Maddux (Oregon Nanoscience and Microtechnologies Institute/University of Oregon), Robert Tanguay (Oregon State University), Jim Fredrickson (PNNL), Stefano Vicini (Georgetown University), and Cary Lai (Scripps).

Major scientific papers in this research area include the following:

Orr G, D Hu, S Ozcelik, LK Opresko, HS Wiley, and SD Colson. 2005. “Cholesterol Dictates the Freedom of EGF Receptors and HER2 in the Plane of the Membrane.” *Biophysical Journal* 89:1362-1373. (16 citations)

Hendriks BS, G Orr, A Wells, HS Wiley, and DA Lauffenburger. 2005. “Parsing ERK Activation Reveals Quantitatively Equivalent Contributions From Epidermal Growth Factor Receptor and HER2 in Human Mammary Epithelial Cells.” *Journal of Biological Chemistry* 280:6157-6169. (14 citations)

Teeguarden JG, PM Hinderliter, G Orr, BD Thrall, and JG Pounds. 2007. “Particokinetics In Vitro: Dosimetry Considerations for In Vitro Nanoparticle Toxicity Assessments.” *Toxicological Science.* 95:300-312. (13 citations, featured on the journal cover).

Orr G, DJ Panther, JL Phillips, BJ Tarasevich, D Hu, JG Teeguarden, and JG Pounds. 2007. “Submicrometer and Nanoscale Inorganic Particles Exploit the Actin Cachinery to be Propelled Along Microvilli-like Structures into Alveolar Cells.” *ACS Nano.* 1:463-475. (Subject of a special Perspective article and a podcast at the journal’s site.)

These select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Real-time processing and fusion of multiple microscope image streams.
- Particokinetics *in vitro*: Dosimetry considerations for *in vitro* nanoparticle toxicity.

6.1.1.5 Computational biology

This is a growing area of expertise in the BID science theme. The primary aim of computational biology at EMSL is to interpret the large amount of data that can be generated by our high-throughput instrumentation. Much effort has been spent in building the computational infrastructure that will allow this work to be easily accomplished. The most success so far has been in the area of proteomics data management and analysis, but this is being rapidly expanded to additionally focus on integrating genomics and proteomics data.

Researchers at EMSL learned how to modify bioinformatics tools to run efficiently on the EMSL supercomputer.

The Membrane Biology Grand Challenge was the start of a concerted effort by EMSL to develop the expertise in data analysis that can support future directions in systems microbiology. EMSL users have learned how to modify bioinformatics tools to run efficiently on the EMSL supercomputer (e.g., ScalaBLAST) and have developed a data management infrastructure that rapidly integrates microarray and proteomics data sets (Bioinformatics Resources Manager). The plan is to expand the data integration capability rapidly over the next several years to enhance our ability to apply multiple EMSL capabilities to solve complex biological problems in the BID science theme area.

The science leaders who are driving this effort in EMSL include Steven Wiley and Gordon Anderson (EMSL) along with Katrina Waters, Bill Cannon, and Jason McDermott (PNNL).

Major scientific papers in this research area over the last 3 years include the following:

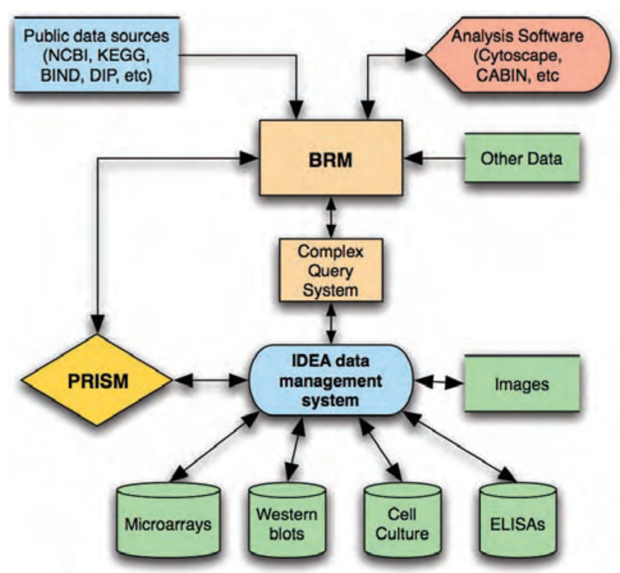
Monroe ME, N Tolic, N Jaitly, JL Shaw, JN Adkins, and RD Smith. 2007. "VIPER: An Advanced Software Package To Support High-Throughput LC-MS Peptide Identification." *Bioinformatics* 23:2021-2023. (8 citations)

Oehmen C and J Nieplocha. 2006. "ScalaBLAST: A Scalable Implementation of BLAST for High-Performance Data-Intensive Bioinformatics Analysis." *IEEE Transactions Parallel Distributed Systems* 17:740-749. (2 citations)

Shah AR, M Singhal, KR Klicker, EG Stephan, HS Wiley, and KM Waters. 2007. "Enabling High-Throughput Data Management for Systems Biology: The Bioinformatics Resource Manager." *Bioinformatics* 23:906-909. (1 citation)

These select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Full collection of more than 1.6 million proteins analyzed using ScalaBLAST.
- High-performance sequence analysis for data-intensive bioinformatics.



Data management infrastructure.

- Systems approach to understanding the molecular mechanism of the light-dark cycles of *Cyanothece*.
- High-throughput visual analytics for biological sciences: Turning data into knowledge.

6.1.1.6 Awards and recognition

Awards and professional recognition indicate the impact of EMSL users within the scientific community. The following list contains a few examples of the awards and recognition for EMSL staff and users in BID over the past 3 years.

Dick Smith

- **Dick Smith** (PNNL) named American Association for the Advancement of Science (AAAS) Fellow, 2006; named to Prestigious 2007 Scientific American 50 List, December 2007; and was elected to a 3-year term on the Council of the Human Proteome Organization.
- **Dave Koppenaal** (PNNL) named AAAS Fellow, 2007.
- **Steven Wiley** (EMSL) appointed to Burroughs Wellcome Fund Advisory Committee.
- **Gerard Parkin** (Columbia University) received the 2008 American Chemical Society Award in Organometallic Chemistry.
- **Sam Kaplan** (University of Texas, Houston), an ISI "Highly Cited Researcher," named AAAS Fellow, 2007.
- **Himadri Pakrasi** (Washington University in St. Louis) installed as a George William and Irene Koechig Freiberg Professor of Biology in Arts and Sciences at the university. Pakrasi received the award established to honor faculty in the field of biology who have demonstrated leadership in research and teaching.

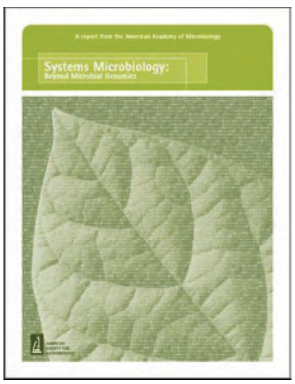
Because many external users do not notify EMSL management of awards and recognition, this information is very incomplete.

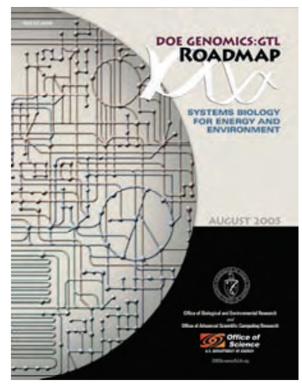
6.1.1.7 Future directions and investments

The transition of biology is driven by the large amounts of molecular data that can be obtained by new high-throughput technologies and by the increasing power of computational analysis tools. The ability to link the physiological behavior of organisms to their molecular properties is crucial for developing a predictive understanding of organisms. This will be the foundation for re-engineering organisms to meet the technological challenges of clean and sustainable energy as well as to minimize the environmental impact of current energy technologies.

The technical challenges that face biology in its transition to a predictive science have been the subject of many workshops and scientific meetings over the last several years. We have relied heavily on the reports from these workshops in the creation of the scientific vision for biology at EMSL. The most important reports that we have used are the following:

- American Academy of Microbiology **Systems Microbiology: Beyond Microbial Genomics Workshop**, December 2004 (http://www.asm.org/academy/index.asp?bid=32329).
- World Technology Evaluation Center report ***Assessment of International Research and Development in Systems Biology*** with the final workshop held at the National Science Foundation, March 2005. Proceedings published by Springer in hardcover, 2007 (http://www.wtec.org/sysbio).
- United States European Union **Infrastructure Needs of Systems Biology Workshop**. May 2007 (http://ec.europa.eu/research/biotechnology/ec-us/docs/us_ec_syst_biology_workshop.pdf).
- DOE Genomics:GTL roadmap ***Systems Biology for Energy and Environment***. August 2005 (http://genomicsgtl.energy.gov/roadmap/index.shtml).





These workshops explored the state of the art in systems biology and the challenges that are being faced by the biological community during the transition to systems biology. Of particular importance has been the identification of technologies and capabilities that would significantly advance progress of this area of research. Those needs that fit within the potential technical capabilities of the EMSL over the next decade were identified as future research areas to explore.

Out of this initial planning phase came the concept of creating an experimental capability to facilitate the integration of the multidimensional quantitative data sets. The configuration of this capability was discussed at the **Systems Microbiology and Extremophile Research Facility Workshop**, March 26, 2008. This workshop was attended by 30 scientists, including prominent microbiologists and systems biologists from around the nation. Unique capabilities in cell growth and analysis were identified as well as important roles that EMSL can play in driving progress in the emerging field of systems microbiology. The implementation of pilot projects in systems microbiology was suggested as a way to most rapidly develop the facility and implementation of a data management system was considered critical.

A major outcome of the workshop was the realization that growing and characterizing living cells under unique and challenging growth conditions required an integrated suite of instruments with automated sampling and computer-controlled monitoring capabilities. Understanding the complexity of multi-cellular systems will also require equipment capable of visualizing processes and molecular structures within living cells. Quantitatively characterizing complex microorganisms and their communities at the molecular level will require a new generation of mass spectrometers of unprecedented speed and resolution. Analyzing multi-protein complexes, post-translational modifications to proteins, and the catalytic mechanisms of protein function will also require improved mass spectrometry and magnetic resonance instrumentation within EMSL.

The interaction of microbes with surfaces is essential for understanding how they function in communities and interact with the environment. Thus, EMSL capabilities in analyzing interfaces and molecular-level structures can be applied to understanding biological systems. However, integrating and making sense of all of these different types of data require conceptual and mathematical frameworks that can link the mechanistic details of biological organisms to their higher-level functions. It also requires the storage of the relevant data in a central repository and the creation of a computational framework for modeling key biological processes. An integrated data management system that provides users with access to all of the data generated at EMSL is essential for enabling systems biology research. The implementation of pilot projects in systems microbiology was suggested as a way to most rapidly develop the facility.

6.1.1.8 Technical challenges

The technical challenges required to address these science challenges occur at different scales of measurement ranging from identifying the microbial community in which the organism exists down to the scale of nanometers in identifying the specific molecular-level structures. **For maximum scientific impact, EMSL must provide a range of capabilities to deal with scale dependence.**

1. The level of the microbial community. **Capabilities need to be developed to grow, identify, and select individual organisms or subsets of organisms from a microbial consortium.** These capabilities should be available within EMSL and allow the ability to vary environmental conditions, observe the microbial community both spatially and temporally, and select specific members of the population for more detailed physiological or molecular-level analysis.

2. The cellular and subcellular level. **Capabilities need to be developed to characterize the architecture of living cells, determine the location of specific proteins or metalloproteins, and isolate individual cellular structures for *ex situ* detailed molecular-level analysis.**

3. The level of characterizing specific molecular-level interactions that occur in biological systems. **Capabilities need to be developed to characterize specific post-translational modifications of proteins, multi-protein complexes and metalloproteins, their three-dimensional structure, and, where applicable, their catalytic mechanisms.** The identification of catalytic mechanisms will require the ability to identify the reactant molecules in real-time along with the associated biological structures.

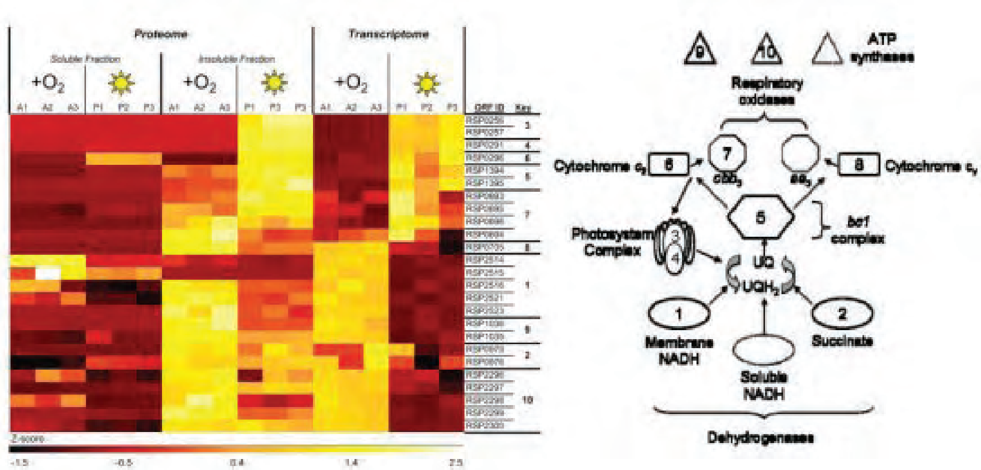
There is also a need to develop the computational infrastructure for the next generation of biological studies. Software systems need to be developed that can facilitate the analysis of the large amount of data that can be collected with advanced instrumentation and which support predictive modeling and exploit the computer resources at EMSL. This software should also exploit the sequence data generated by other facilities, such as the Joint Genome Institute, and broadly enable the understanding of complex, multi-cellular systems. Because interaction data are being gathered on multiple spatial and temporal scales, from the atomic to the community level, computational systems that can link these scale are essential. Data linking, integration, analysis, and access are fundamental requirements for enabling the system-level approach to biology that promises to solve important problems in the next several decades.

Selected BID highlights

Topical Area – Mass Spectrometry-based Proteomics

Combined proteomics and genomics analysis of R. sphaeroides

Work with Sam Kaplan of the University of Houston, which appeared in the *Journal of Microbiological Methods* and the *Journal of Proteome Research*, compared the pattern of gene transcription and protein expression in *R. sphaeroides* during photosynthesis. They performed a global proteomic analysis to compare aerobic and photosynthetic *R. sphaeroides* proteomes. Their results highlighted proteins directly and indirectly associated with the photosynthetic lifestyle of *R. sphaeroides*, and the location of these proteins within cellular fractions, such as the outer membrane and cytoplasm. The accurate mass tag approach, which was developed at EMSL, enabled the identification of a diverse set of proteins, which will help in developing models of photosynthetic behavior.



Heat map (above left) comparison between proteins observed in *R. sphaeroides* aerobic and photosynthetic cultures. Proteins shown in the heat map are involved in energy production for the cell by way of the electron transport pathway (above right). Most of the proteins involved in this pathway were observed in an insoluble protein fraction extracted from each culture during sample preparation. Increasing intensity in the positive range represents abundances that are greater than the mean abundance derived from both culture conditions and sample preparations relative to the standard deviation associated with the mean (Z-score). Decreasing intensity in the negative range represents abundances that are less than the mean abundance relative to the standard deviation. Z-score values for the aerobic and photosynthetic cell cultures also suggest the growth condition in which the protein was observed with the greatest abundance.

A greater understanding of *R. sphaeroides*' photosynthetic behavior is important to applying its unique abilities to, for example, hydrogen production. These studies provide a baseline for future large-scale proteomic studies using PNNL's high-throughput proteomic approach.

Citations: Callister SJ, MA Dominguez, CD Nicora, X Zeng, CL Tavano, S Kaplan, TJ Donohue, RD Smith, and MS Lipton. 2006. "Application of the Accurate Mass and Time Tag Approach to the Proteome Analysis of Sub-cellular Fractions Obtained from *Rhodobacter sphaeroides* 2.4.1 Aerobic and Photosynthetic Cell Cultures." J*ournal of Proteome Research* 5(8):1940-1947.

Callister SJ, CD Nicora, X Zeng, JH Roh, MA Dominguez, CL Tavano, ME Monroe, S Kaplan, TJ Donohue, RD Smith, and MS Lipton. 2006. "Comparison of Aerobic and Photosynthetic *Rhodobacter sphaeroides* 2.4.1 Proteomes." *Journal of Microbiological Methods* 67(3):424-436.

Comprehensive whole-proteome analysis of Shewanella available

Shows potential of mass-spec-based proteomics for improving genome and proteome annotations

Researchers from the University of California, San Diego; the Burnham Institute for Medical Research; and PNNL demonstrated the capability to rapidly and efficiently improve a proteome annotation. Their work highlights the potential for using mass spectrometry-based proteomics to complement genome sequencing and improve both genome and proteome annotations.

Researchers used liquid chromatography-coupled mass spectrometry for proteomic and genomic annotations of *Shewanella oneidensis MR-1.*

The researchers used liquid chromatography-coupled mass spectrometry for proteomic and genomic annotations of the bacterium *Shewanella oneidensis MR-1.* While bacterial genome annotations have improved significantly in recent years, the number of sequenced bacterial genomes is rising sharply, far outpacing scientists' ability to validate the predicted genes, let alone annotate bacterial proteomes. Also, as opposed to annotation processes, techniques—such as determination of post-translational chemical modifications, signal peptides, and proteolytic events—are still in their infancy.

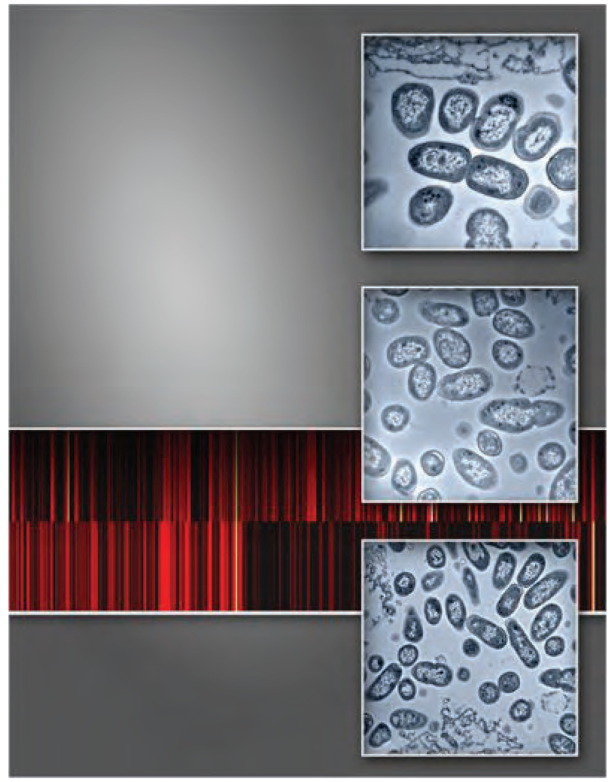
The work is addressing the potential for proteomics measurements as they relate to understanding biological systems important to environmental remediation efforts. The study demonstrates that complementing every genome-sequencing project by a coupled mass spectrometry project would significantly improve both genome annotations at a reasonable cost. It is also one of the most complete proteome analyses ever made available to the scientific community (see http://ober-proteomics.pnl.gov/data/).

Citation: Gupta N, S Tanner, N Jaitly, JN Adkins, MS Lipton, R Edwards, MF Romine, A Osterman, V Bafna, RD Smith, and P Pevzner. 2007. "Whole Proteome Analysis of Post-Translational Modifications: Applications of Mass-Spectrometry for Proteogenomic Annotation." *Genome Research* 17:1362-1377.

First use of global proteomics to quantify bacterial proteins isolated from host cells

Systematic investigation of changes can identify proteins important to detecting bacterial pathogens and developing vaccines

Scientists at PNNL have reported the first systematic investigation using global proteomics to identify changes in the abundance of bacterial proteins associated with macrophage colonization and a new protein that helps the bacterium to survive inside macrophages. Macrophages are large white blood cells, occurring principally in connective tissue and in the bloodstream, which ingest foreign particles and infectious microorganisms. By investigating the changes in *Salmonella* protein abundances during infection by *Salmonella*, the researchers identified a novel protein that is required for *Salmonella* to replicate inside macrophages. These results demonstrate the value of a systematic investigation of bacterial protein changes in identifying proteins of likely importance in detecting bacterial pathogens and developing effective vaccines.



This figure shows the cells of *Salmonella* isolated from macrophages and the results of proteomic analysis of the isolated *Salmonella* cells. Investigation of the changes in *Salmonella* protein abundances during the infection resulted in identification of a novel protein that is required for *Salmonella* to replicate inside macrophages.

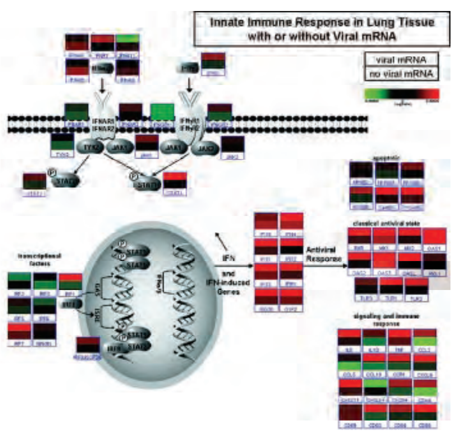
Salmonella enterica serovar Typhimurium is a facultative intracellular pathogen, meaning that it can grow both inside and outside cells. The pathogen can cause gastroenteritis in humans and a lethal infection in mice that lack a macrophage protein called Nramp1. Because the symptoms resemble human typhoid fever, mice infected by the pathogen provide a model system to investigate the development and immunology of typhoid fever in humans.

Citation: Shi L, JN Adkins, JR Coleman, AA Schepmoes, A Dohnalkova, HM Mottaz, AD Norbeck, SO Purvine, NP Manes, HS Smallwood, H Wang, J Forbes, P Gros, S Uzzau, KD Rodland, F Heffron, RD Smith, and TC Squier. 2006. “Proteomic Analysis of *Salmonella enterica* Serovar Typhimurium Isolated from RAW 264.7 Macrophages: Identification of a Novel Protein That Contributes to the Replication of Serovar Typhimurium Inside Macrophages.” *Journal of Biological Chemistry* 281(39):29131-29140.

Proteomic characterization of a macaque flu infection model system

Characterization of a non-human primate model system provides insight into the proteins important in the progression of the flu

Initial proteomic characterization of the macaque flu infection model system used a bottom-up proteomics approach with the isolation of proteins from macaque lung tissue either infected (influenza) or mock-infected, followed by tryptic digestion to peptide form for sequence identification and relative quantitation using liquid chromatography coupled to tandem mass spectrometry analysis. Additionally, a cysteinyl-peptide enrichment step was performed at the peptide level, providing enhanced coverage of the macaque model proteome. The resulting high-quality data set of 14,100 peptides and 3,548 proteins identified in this preliminary study of the macaque model system is, to our knowledge, the first comprehensive proteomic survey performed for this model. Among the proteins detected are many candidates of particular interest based on previous clinical, pathological, and gene expression data, demonstrating the suitability of the non-human primate model for studying influenza virus pathogenesis. These include several well-known interferon-induced proteins as well as other non-cellular mediators of the innate immune response. This new macaque lung protein database creates the foundation for future research efforts aimed at applying comparative quantitative proteomics measurements to longitudinal studies of nonhuman primate models of influenza virus infection.



Innate immune response in lung tissue with or without viral mRNA. This illustrates the significant impact of the presence (top bar) or absence (bottom bar) of influenza viral mRNA on gene expression, even among essentially similarly affected portions of the same lung or among animals that were all infected.

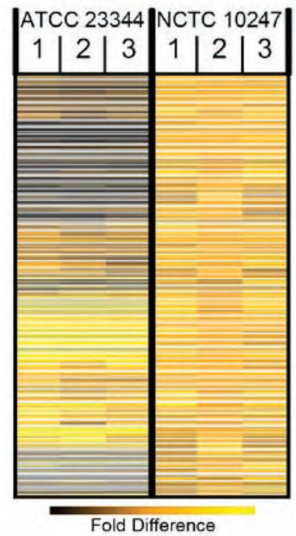
When comparing the differentially identified proteins between uninfected and influenza virus-infected lung tissue samples, consistent with previous observations demonstrating the establishment of an antiviral state in the lungs of influenza virus-infected macaques, we observed an apparent up-regulation of many proteins involved in the innate immune response. These included both interferon-induced proteins and non-cellular mediators of the innate immune response. We believe the findings reported clearly demonstrate the potential of proteomics for assisting in the determination of protein players and pathways affected by influenza virus infection.

Citation: Baas T, CR Baskin, DL Diamond, A García-Sastre, H Bielefeldt-Ohmann, T M Tumpey, MJ Thomas, VS Carter, TH Teal, N Van Hoeven, S Proll, JM Jacobs, ZR Caldwell, MA Gritsenko, RR Hukkanen, DG Camp II, RD Smith, and MG Katze. 2006. “Integrated Molecular Signature of Disease: Analysis of Influenza Virus-Infected Macaques through Functional Genomics and Proteomics.” *Journal of Virology* 80:10813-10828.

Proteomic comparison between virulent and avirulent Burkholderia mallei strains

Quantified 126 that exhibited a twofold abundance difference between the strains

Two species of *Burkholderia* bacteria pose a significant threat to animal and human health. One species, *B. pseudomallei*, causes the disease melliodosis, which affects people throughout Southeast Asia and Australia. The other, *B. mallei*, is primarily an animal pathogen and causes the disease known as glanders. This worldwide disease poses a health threat to cystic fibrosis patients and immunocompromised individuals, and is considered a potential biowarfare agent. While avirulent strains of *B. mallei* do exist, the source of attenuation is not known. Currently, there is no rapid discriminating diagnostic assay, vaccine, or reliable therapy for *B. mallei*; high DNA homology severely limits the ability to distinguish avirulent and virulent strains by standard molecular biology techniques.



Relative abundance data plot for 751 proteins from *B. mallei* global proteome digestion, triplicate analysis. Mass spectrometry intensity values were normalized to ribosomal protein abundances; avirulent strain was used as the baseline comparator. Results show significant differences between the virulent and avirulent strains, which may lead to further discovery or development of clinical biomarkers.

Using a high-throughput liquid chromatography-mass spectrometry-based approach to compare proteins expressed in a virulent strain and the nonvirulent strain, we detected and quantified 751 proteins, 126 of which exhibited a twofold abundance difference between the avirulent and virulent strains. Thirty-one unique proteins were observed in the virulent strain. Of these, three proteins have properties identified as virulence factors in other systems. Additionally, the LPS biosynthesis proteins were fivefold more abundant in the virulent strain. Analysis of the avirulent strain revealed 135 uniquely expressed proteins, 10 percent or more of which have no known function and are ideal targets for further assays.

Although this work has just begun, peptides examined from a global preparation of *Burkholderia* grown *in vitro* have revealed key differences in protein expression between strains of *B. mallei*.

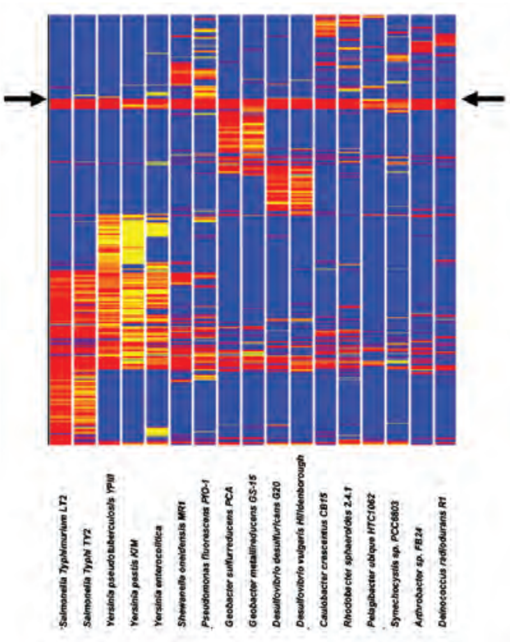
Citations: Hixson KK, JN Adkins, SE Baker, RJ Moore, BA Chromy, RD Smith, SL Mc-Cutchen-Maloney, and MS Lipton. 2006. “Biomarker Candidate Identification in *Yersinia pestis* using Organism-Wide Semiquantitative Proteomics.” *Journal of Proteome Research* 5(11):3008-3017.

Huelseweh B, R Ehricht, and H-J Marschall. 2006. “A Simple and Rapid Protein Array Based Method for the Simultaneous Detection of Biowarfare Agents.” *Proteomics* 6(10):2972-2981.

Rivera-Marrero CA, MA Burroughs, RA Masse, FO Vannberg, DL Leimbach, J Roman, and JJ Murtagh. 1998. “Identification of Genes Differentially Expressed in *Mycobacterium tuberculosis* by Differential Display PCR.” *Microbial Pathology* 25(6):307-316.

Zimmer JS, ME Monroe, WJ Qian, and RD Smith. 2006. “Advances in Proteomics Data Analysis and Display Using an Accurate Mass and Time Tag Approach.” *Mass Spectrometry Review* 25(3):450-482.

Researchers utilize proteomics to reveal a core microbial proteome



The core proteome is revealed for 17 bacteria. Genomic comparisons identified genes common to two or more bacteria (orange) resulting in a core genome of 144 genes. Proteomic measurements were used to verify the existence of these genes as proteins (red) resulting in the identification of a core proteome (arrow).

Diverse bacteria have much in common, right down to the core. Using a peptide database collected at EMSL—six years in the making, comprising approximately 967,000 peptides, and linked to protein and gene data—researchers from PNNL discovered a group of proteins that are shared and commonly expressed by a wide variety of different bacteria.

Called the "core proteome," the ubiquitous nature of this group of proteins suggests that they are fundamental to bacterial life. Knowing what proteins lie outside the core proteome, and thus might be dispensable, offers a new potential strategy for treating infections and creating designer bacteria for alternative energy production and bioremediation.

The researchers analyzed 17 bacteria ranging from the ocean-dwelling *Pelagibacter ubique* to plague-causing *Yersinia pestis*.

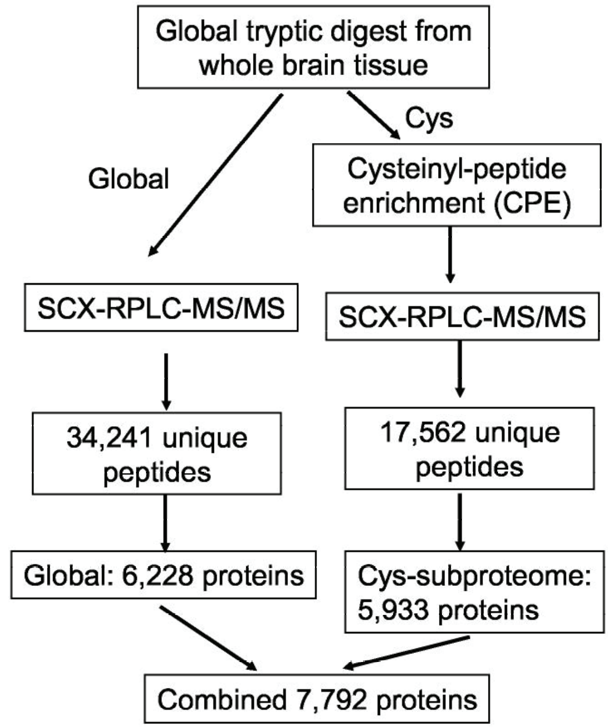
Their study revealed that the core proteome comprised 74 percent of the larger genome sequence-based core genome predictions. The core proteome appears to be responsible for the basal functions of bacteria; more than half is devoted to protein synthesis. Strikingly, about 7 percent of the core proteome is composed of proteins whose function is unknown. Because of the central nature of the core proteome, these proteins need further study. Proteins outside the core proteome are responsible for the lifestyle-specific differences of individual bacterial species.

Citation: Callister SJ, LA McCue, JE Turse, ME Monroe, KJ Auberry, RD Smith, JN Adkins, and MS Lipton. 2008. "Comparative Bacterial Proteomics: Analysis of the Core Genome Concept." *PLoS ONE* 3(2):e1542.

First comprehensive characterization of the whole mouse brain proteome

Scientists from PNNL and the University of California at Los Angeles have completed the first comprehensive characterization of the whole mouse brain proteome and the most comprehensive proteome coverage for the mammalian brain to date.

Most proteomic studies of the mammalian brain have been based on two-dimensional electrophoresis separations coupled with in-gel protein digestion and mass spectrometric identification, but limitations of this approach have prevented extensive coverage of the mouse brain proteome.



A flowchart showing the experimental strategy: preparation of the whole mouse brain using a combination of global tryptic digestion and cysteinyl-peptide enrichment methodology, followed by fractionation and analysis of each fraction, and the peptide/protein identification results from both preparation methods.

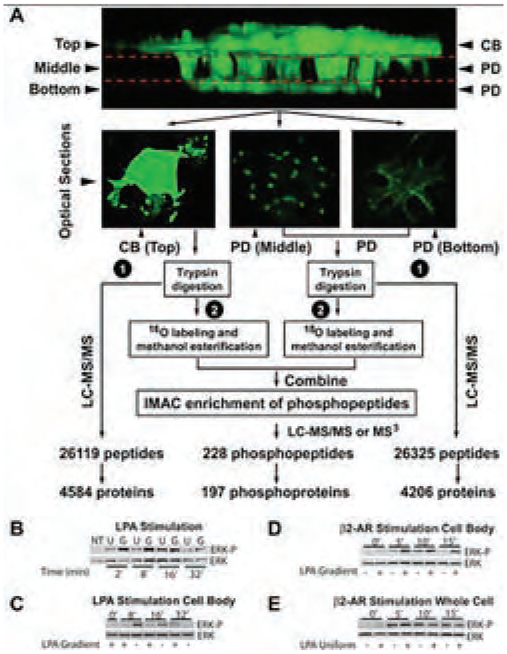
In their study, the team took a global proteomic approach for comprehensive profiling of the brain tissue using liquid chromatography-tandem mass spectrometry (LC-MS/MS) and an extensive protein database for the whole mouse brain. They incorporated a highly efficient cysteinyl-peptide enrichment technique to complement a global enzymatic digestion method, which resulted in significantly increased proteome coverage. Both sample types were analyzed by strong cation exchange fractionation coupled with reversed-phase LC-MS/MS analysis. This extensive analysis identified 48,328 different peptides and 7,792 nonredundant proteins, or ~34 percent of the predicted mouse proteome. The identified proteins provide a broad representation of the mouse proteome with little bias evident.

The mouse brain peptide/protein database generated from this study will be the basis for future quantitative brain proteomic studies using mouse models. The proteomic approach presented here may have broad applications for rapid proteomic analyses of various mouse models of human brain diseases. Ultimately, the researchers hope to achieve a three-dimensional view of the mouse brain proteome and to produce images of specific brain regions.

Citation: Wang H, WJ Qian, MH Chin, VA Petyuk, RC Barry, T Liu, MA Gritsenko, HM Mottaz, RJ Moore, DG Camp II, AH Khan, DJ Smith, and RD Smith. 2006. "Characterization of the Mouse Brain Proteome Using Global Proteomic Analysis Complemented with Cysteinyl-Peptide Enrichment." *Journal of Proteome Research* 5(2):361-369. DOI: 10.1021/pr0503681.

Profile of phosphoproteins involved in cell movement created

Combined proteomics and phosphoproteomics approaches made it possible



Scientists at PNNL and the University of California, San Diego (USCD) created the first comprehensive profile of cell movement. They mapped an extensive network of the signaling proteins controlling cell movement.

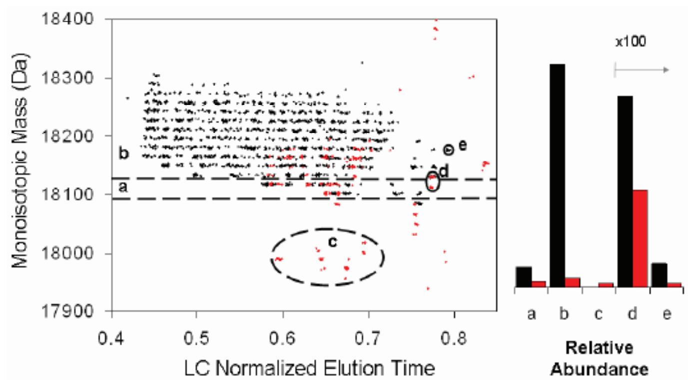
The PNNL team applied global proteome profiling in combination with UCSD-developed phosphoproteomics approaches to understand signal organization in migrating cells. The scientists developed a system that facilitates the separation and isolation of the pseudopodium (PD, or leading part of the cell) and the cell body (CB) compartments of chemotaxing cells for proteomic analysis using microporous filters. This model system recapitulates physiological events associated with chemotaxis, including gradient sensing and pseudopodial protrusion through small openings in the vessel wall during cancer cell metastasis. They mapped the spatial relationship of 3,509 proteins and 225 distinct phosphorylation sites. This revealed networks of signaling proteins that are partitioned into the PD and/or the CB compartments.

This knowledge could lead to a better understanding of cell migration in cancer metastasis and inflammatory disease, which in turn will help in the development of effective treatment methods.

Citation: Wang Y, SJ Ding, W Wang, JM Jacobs, WJ Qian, RJ Moore, F Yang, DG Camp II, RD Smith, and RL Klemke. 2007. “Profiling Signaling Polarity in Chemotactic Cells.” *Proceedings of the National Academy of Sciences* 104(20):8328-8333 doi 10.1073/pnas.0701103104.

Probing oxidative stress using intact-protein, high-field mass spectrometry

Mechanisms that regulate the removal of nitrated and oxidized proteins in cells are critical for preventing a number of diseases (such as diabetes), and reducing the effects of aging. In this work, we used high-resolution liquid chromatography (LC) separations in conjunction with high-mass-measurement accuracy and high-resolution measurements afforded by 12-T Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer at EMSL to probe oxidative stress in calmodulin, which is a signaling protein in macrophages. Importantly, we identified a novel oxidation-dependent lysine cleavage that potentially acts as a biomarker of oxidative stress.



The time vs. mass two-dimensional display (above left) highlights our ability to resolve intact protein masses of individual oxidized CaM species, which are indicators of denitrase activity. CaM species detected prior to (red symbols) and following (black symbols) incubation with cell lysate from activated macrophages: a) CaM & CaMox; b) nYCaMox & 2nYCaMox; c) CaM-Lysine and CaMox-Lysine; d) nYCaM, and e) 2nYCaM. The panel (above right) displays the relative abundance of CaM within each of these five areas. Definitions of the abbreviations follow: CaM, calmodulin; CaMox (nYCaMox), oxidized CaM containing methionine sulfoxides or (and) nTyrs.

Oxidative species not only mediate static and cidal effects on a variety of pathogens, they also nitrate and oxidize host proteins during the immune response. These post-translational modifications (PTMs) to intracellular proteins in various inflammatory states also are implicated in many age-related diseases. In this context, the accumulation of nitrotyrosines in proteins may result from an aberrant repair pathway. Previous work postulated denitrase activity in various tissues based on the loss of immunoreactivity involving antibodies against nitrotyrosine. However, attributing the loss in immunoreactivity to denitration is equivocal, as this effect may be caused by degradation of the nitrated protein, alterations in protein structure that cover the epitope, chemical alteration of the nitrotyrosine, and/or enzymatic denitration. Characterization of the product following denitration and corresponding loss of immunoreactivity requires the use of an analytical tool that can confirm the involvement of specific proteins, thereby ruling out the ambiguous interpretations based on antibody recognition.

We used intact protein reversed-phase LC-FT-ICR mass spectrometry to monitor the time-dependent changes in the nitration of calmodulin (nYCaM) in macrophages following macrophage activation with lipopolysaccharide endotoxin. Tentative identifications of PTMs were assigned by combining tryptic peptide information generated from bottom-up analyses with online collision-induced dissociation tandem mass spectrometry at the intact protein level, which confirmed localization of the nitrated sites. Our results indicate that macrophage activation associated with an oxidative burst stimulates a dramatic reduction in the abundance and diversity of oxidatively modified proteins. More specifically, we established that macrophage repair pathways can repair nitrated tyrosines and oxidized methionines within a signaling protein to their original unmodified states to retain optimal protein function.

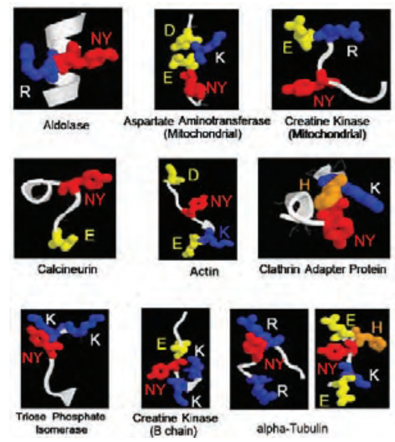
We also identified a modification-dependent C-terminal lysine cleavage that is likely to alter calmodulin function. We propose that the cleaved calmodulin is a useful biomarker of intracellular oxidative stress conditions because of both the oxidation dependence of this lysine cleavage and the stability of the cleavage product. This stability is in contrast to the reversible modifications we observed for nitrotyrosine and methionine sulfoxide. The transient nature of nitrotyrosine and methionine sulfoxide renders these currently used biomarkers inaccurate.

Mass spectrometry identification of endogenously nitrated proteins in mouse brain

Links to neurodegenerative disease

Parkinson's, Alzheimer's, and Lou Gehrig's diseases and other brain disorders are among a growing list of maladies attributed to oxidative stress, which is the cell damage caused during metabolism when oxygen in the body assumes ever more chemically reactive forms. EMSL mass spectrometry capabilities were used to identify proteins sensitive to nitrating conditions *in vivo*, resulting in a data set in which more than half the proteins were indicated in neurodegenerative disorders.

Increased nitrotyrosine modifications of proteins have been documented in multiple pathologies in tissue types linked to oxidative stress, as well as playing a role in the redox regulation of normal metabolism. To identify proteins sensitive to nitrating conditions *in vivo*, a comprehensive proteomic survey of the whole mouse brain using liquid chromatography/liquid chromatography-mass spectroscopy/mass spectroscopy analyses was performed. This effort generated a mammalian brain data set in which 7,792 proteins were identified.



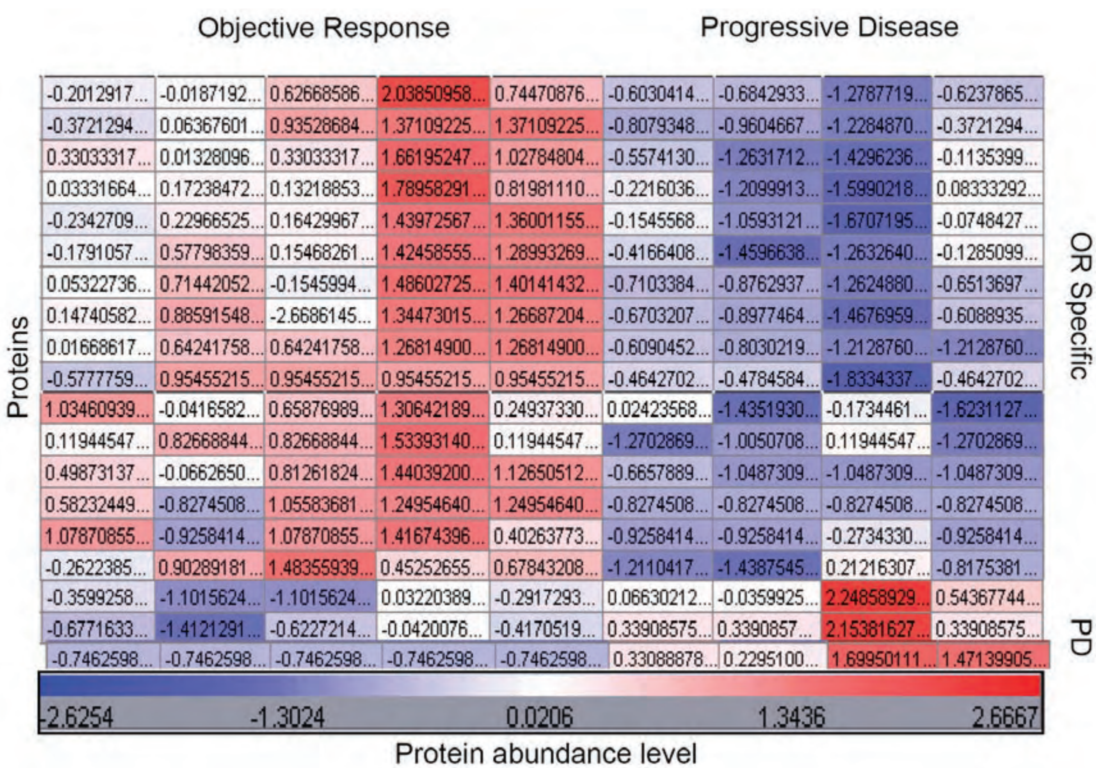
Three-dimensional structures around nitrotyrosines in identified proteins.

This large-scale analysis resulted in the identification of 31 unique nitrotyrosine sites within 29 different proteins. Over half the nitrated proteins identified are involved in Parkinson's disease, Alzheimer's disease, or other neurodegenerative disorders. Similarly, nitrotyrosine immunoblots of whole-brain homogenates show that treatment of mice with 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine, an experimental model of Parkinson's disease, induces increased nitration of the same protein bands observed to be nitrated in brains of untreated animals. Comparing sequences and available high-resolution structures around nitrated tyrosines with those of unmodified sites indicates a preference of nitration *in vivo* for surface-accessible tyrosines in loops, a characteristic consistent with peroxynitrite-induced tyrosine modification. In addition, most sequences contain cysteines or methionines proximal to nitrotyrosines, contrary to suggestions that these amino acid side chains prevent tyrosine nitration. More striking is the presence of a positively charged moiety near the sites of nitration, which is not observed for non-nitrated tyrosines. Together, these observations suggest a predictive tool of functionally important sites of nitration and that cellular nitrating conditions play a role in neurodegenerative changes in the brain. Future studies should extend these proteomic measurements to consider the relationship between protein nitration and specific neurodegenerative diseases as well as tyrosine-kinase-signaling pathways.

Citation: Sacksteder CA, WJ Qian, TV Knyushko, H Wang, MH Chin, G Lacan, WP Melega, DG Camp, RD Smith, DJ Smith, TC Squier, and DJ Bigelow. 2006. "Endogenously Nitrated Proteins in Mouse Brain: Links to Neurodegenerative Disease." *Biochemistry* 45(26):8009-8022.

Identification of functional pathways associated with clinical tamoxifen-resistance in breast cancer by advanced mass spectrometry

A Umar from the Erasmus University Medical Center in Rotterdam, The Netherlands, visited EMSL to characterize functional pathways that lead to clinical resistance to tamoxifen (anti-estrogen) treatment in breast cancer patients. For this study, Dr. Umar used laser microdissected tumor cells from patients that either were or were not responding to tamoxifen treatment. Although laser microdissection has the great advantage of enabling isolation of selected subpopulations of cells, such as tumor cells, and thus overcoming the issue of tissue heterogeneity, only a few thousand cells—amounting to a few hundred nanograms of protein—can be collected per tissue. The ultra-sensitive nanoscale LC-FT-ICR technology developed at EMSL showed excellent proteome coverage and good reproducibility for ~3,000 laser micro-dissected breast carcinoma cells. Umar obtained the protein profiles of 50 different tumor samples and was able to demonstrate proteins specifically expressed in either responding or nonresponding tumors.



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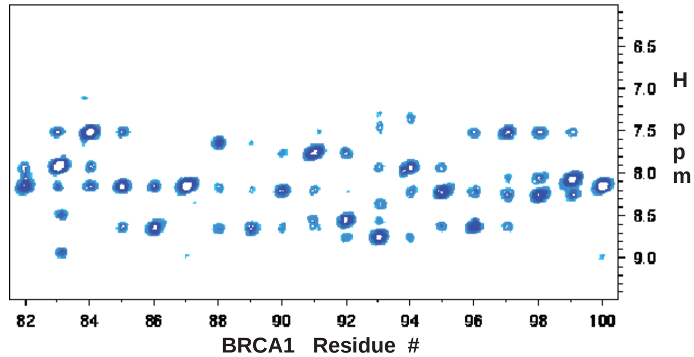
Detail of response-specific protein profile. Hierarchical clustering with z-scores was performed on 1,999 proteins using protein abundance (obtained by averaging measured peptide abundances). The average protein abundance level is represented with a white background color, while the abundance levels above and below the average are represented by red and blue background colors.

Citation: Umar A, TM Luider, JA Foekens, and L Pasa-Tolic. 2007. "NanoLC-FT-ICR MS Improves Proteome Coverage Attainable for Approximately 3000 Laser-Microdissected Breast Carcinoma Cells." *Proteomics* 7:323-329

Topical Area – NMR

NMR structural investigations of the breast cancer susceptibility protein, BRCA1

A study, led by Rachel Klevit of the University of Washington, investigated the breast cancer susceptibility protein, BRCA1. This system provides a unique opportunity for studying protein-protein interactions with NMR because it involves characterizing the structures and interactions among at least four different protein components: BRCA1, BARD1, an E2 (UbcH5c or UbcH7), and ubiquitin (Ub). The molecular weight of the fully assembled complexes approaches 60 kD. In previous years, Dr. Klevit's group had been able to collect a great deal of data on the individual components of this system. However, more recent data collected on EMSL's 600-, 800-, and 900-MHz NMR spectrometers allowed them to develop a model of the complex series of protein-protein interactions that are required to assemble an active BRCA1-dependent ubiqutin-ligase complex.

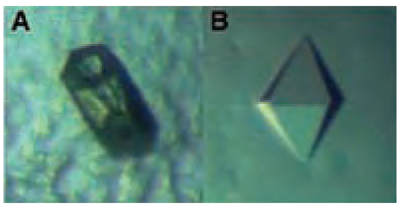


Strip plot from ^{15}N-edited NOESY-HSQC Helix 3 of the N-terminal domain of BRCA1.

Citation: Brzovic P, AV Lissounov, D Christensen, DW Hoyt, and RE Klevit. 2006. "A UbcH5/Ubiquitin Noncovalent Complex is Required for Processive BRCA1-Directed Ubiquitination." *Molecular Cell* 21(6):873-880.

Characterization of two potentially universal turn motifs that shape the repeated five-residue fold-crystal structure of a lumenal pentapeptide repeat protein from Cyanothece 51142

The crystal structure was determined for R*f*r32, which is one of 35 pentapeptide repeat proteins (PRPs) in the diurnal cyanobacterium *Cyanothece*. The structure is dominated by 21 tandem pentapeptide repeats that fold into a right-handed quadrilateral β-helix, or R*f*r-fold. Analysis of the main chain (ϕ, ψ) dihedral orientations for the pentapeptide repeats reveals structural details for the two distinct types of four-residue turns adopted by the pentapeptide repeats in the R*f*r-fold, labeled type-II and type-IV β-turns, that may be universal motifs that shape the R*f*r-fold in all PRPs.



Two different crystal forms of R*f*r32 grown using the hangingdrop, vapor-diffusion method at 6x magnification: A, hollow rods with a hexagonal face and B, bipyrimides.

HB Pakrasi and his colleagues at Washington University (WU) in St. Louis, Missouri, have recently sequenced the genome of the diurnal cyanobacterium *Cyanothece* sp. PCC 51142. One of the interesting features of the genome, as determined by the annotation team led by WU's E Welsh, is the presence of 35 proteins containing tandem pentapeptide repeats. Such PRPs are identified by the presence of at least eight consecutive repeating five-residues (RFR) approximately described by the consensus motif A[D/N]LXX. While such proteins are scattered throughout the genomes of organisms in both the prokaryotic and eukaryotic kingdoms, PRPs are especially abundant in cyanobacteria. The sheer number of PRPs in cyanobacteria coupled with their predicted location in every cellular compartment argues for an important, yet unknown, physiological and biochemical function. To gain biochemical insights into this mystery, we have determined the crystal structure for one of the 35 PRP in *Cyanothece*, R*f*r32, as part of an EMSL Molecular Biology Scientific Grand Challenge project.

R*f*r32 is a 167-residue PRP with an N-terminal, 29-residue signal peptide. As shown in the figure, the protein construct of R*f*r32 lacking the 29-residue signal peptide crystallized in two different forms that yielded identical structures. H Robinson at Brookhaven National Laboratory collected x-ray data at the National Synchrotron Light Source on these crystals that diffracted to a resolution of 2.1 Å.

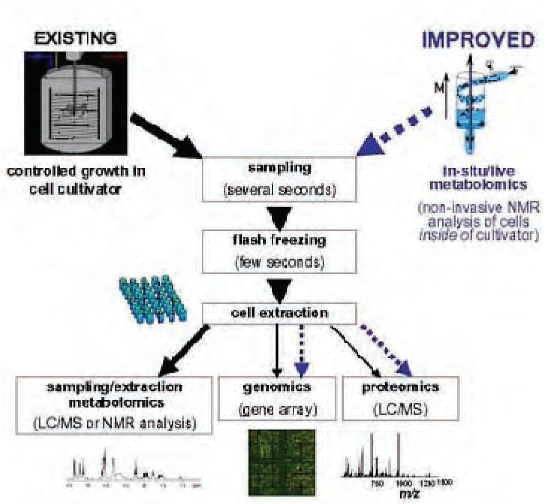
The dominant feature is the novel type of right-handed quadrilateral β-helix, a repeated five-residue fold (R*f*r-fold), adopted by the 21 consecutive pentapeptide repeats. This R*f*r-fold is reminiscent of a square tower with four distinct faces with each pentapeptide repeat occupying one face of the R*f*r-fold. Four consecutive pentapeptide repeats complete a coil that makes a revolution with approximately a 4.8-Å increase every 20 residues. A stylized representation of a complete coil in an R*f*r-fold, which is the higher-order structural unit adopted by four tandem pentapeptide repeats, is shown in the figure. The coils of the tower in R*f*r32 are held together by short stretches of parallel β-sheets (Face 1) and β-bridges (Faces 2-4) (single-residue β-sheets), which are integral to the quadrilateral shape of the R*f*r-fold. There is a regular orientation of the side chains of each pentapeptide repeat. Designating the center residue of each pentapeptide repeat i with the preceding residues labeled i-1 and i-2 and the following residues labeled i+1 and i+2, we observed that the i-2 and I residues all point toward the interior of the tower and pack the middle of the R*f*r-fold. The side chain of the i^{th} residue is predominately a large hydrophobic group (Leu or Phe), while the side chain of the i-2 residue is predominately a small and usually hydrophobic group (Ala > Ser, Thr, and Val). On the other hand, the side chains of the i-1, i+1, and i+2 residues all point away from the interior of the tower and form the exterior, solvent-exposed surface of the R*f*r-fold. Unlike the side chains that are directed to the interior, which are primarily hydrophobic and form regularly stacked columns, the side chains directed to the exterior are typically hydrophilic and do not assume a regular form.

Clearly, two distinct patterns are observed for the five residues constituting each coil on Face 1 and for the five residues constituting each coil on Faces 2, 3, and 4. After thorough analysis of the crystal structures of R*f*r32 and MfpA (from *Mycobacterium tuberculosis*), it became evident that each pentapeptide repeat could be grouped into one of two types of four-residue type II and type IV β-turns. The major differences between the two types of β-turns are the ψ and ϕ torsion angles of the i and i+1 residue results from an ~90° rotation of the peptide unit between these two residues. Because of the repetitive nature of the pentapeptide repeat sequence, we predict that the regular shape of the R*f*r-fold is maintained by these two distinct β-turns and that they may be universal motifs that shape the R*f*r-fold in all pentapeptide repeat proteins.

Citation: Buchko GW, S Ni, H Robinson, EA Welsh, HB Pakrasi, and MA Kennedy. 2006. "Characterization of Two Potentially Universal Turn Motifs that Shape the Repeated Five-Residue Fold-Crystal Structure of a Lumenal Pentapeptide Repeat Protein from *Cyanothece* 51142." *Protein Science* 15(11):2579-2595.

MRI bioreactor aids in understanding the physiology of live cells

Instrument helps scientists to optimize bio-based product processes



Feeding microbes waste and having them convert it into valuable chemicals may sound far fetched, but scientists are closer, thanks to a new technology developed at EMSL. A first-of-its-kind magnetic resonance imaging (MRI) bioreactor provides accurate metabolic information for live cells maintained in a controlled growth environment. Similar to clinical MRI, this *improved* technology uses noninvasive (nuclear) MRI and spectroscopy (MRI/MRS) methods to monitor microbial metabolite concentrations *in the reactor* without removal or processing. This new technology provides a major advantage because metabolite levels can change significantly due to handling. Further, this technology allows for frequent, repeating measurements without diminishing the sample. Finally, it is compatible with high-throughput genomic and proteomic analyses.

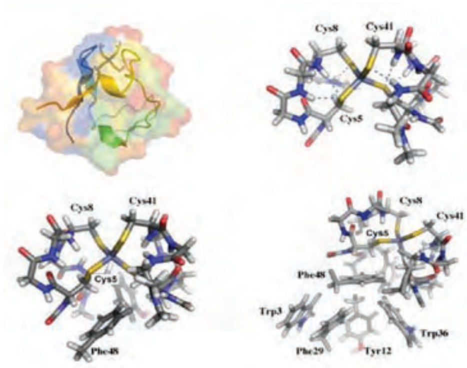
The MRI/MRS bioreactor was used to study metabolites produced by *Eubacterium aggregans*, an anaerobic bacterium of interest for bio-fuel production. The study showed that in addition to known metabolic byproducts, *E. aggregans* produces significant concentrations of lactate, a metabolite not previously reported. This suggests that the activities of its metabolic networks are different from what were predicted based on older experimental techniques.

Citation: Majors PD, JS McLean, and JC Scholten. 2008. “NMR Bioreactor Development for Live In-Situ Microbial Functional Analysis.” *Journal of Magnetic Resonance* 192(1):159-166. Artwork from this article was featured on the cover of the journal.

The synergy between molecular theory and solid-state NMR spectroscopy

Understanding DNA repair proteins important to link environmental impact to biological health effects

Research evaluating the local electronic environment of zinc that affects the structural or chemical function in proteins has been accelerated by the use of two key long-term capability investments at EMSL. The first is implementation of a *NWChem* module that provides *ab initio* quantum mechanical calculations using molecular mechanics (QM/MM) constraints; the *NWChem* code was developed at EMSL. The second is the successful development and implementation of low-temperature solid-state NMR capabilities at high magnetic fields. The latter is designed to allow direct observation of NMR resonances of metals such as zinc and magnesium in metalloproteins which, under ambient conditions, would be arduous if not impossible to accomplish.



Optimized quantum regions of Pf-rubredoxin, a zinc-containing DNA repair protein. Combined QM/MM calculations were performed on Pf-rubredoxin with increasing complexity in the quantum region. The research demonstrated sensitivity of the predicted NMR parameters to not only hydrogen bonding, but lone pair (LP)-π interactions. The research team achieved good agreement between theory and experimental values of both the electric field gradient and anisotropic shielding tensors.

A study employing the converged methodologies discusses how QM/MM methods help elucidate the NMR spectra of zinc in a pivotal type of zinc metalloprotein, in which zinc is coordinated by four cysteines. In this case, the zinc plays an essential structural role.

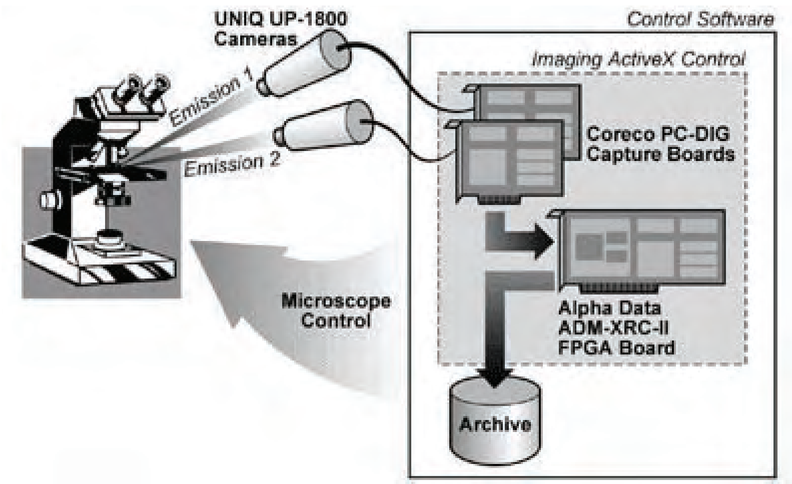
Based on knowledge gained from these investigations, the authors are primed to investigate zinc sites (again fully coordinated by cysteine residues) where one of the cysteines has been activated by the zinc, allowing it to serve as a reactive center in DNA repair.

This powerful combination of theory and experiment will be utilized to probe the means by which coordination geometry differentiates between a structural site and a reactive site, allowing a deeper understanding of DNA repair mechanisms.

Citation: Lipton AS, RW Heck, GR Staeheli, M Valiev, WA De Jong, and PD Ellis. 2008. “A QM/MM Approach to Interpreting Zn-67 Solid-State NMR Data in Zinc Proteins.” *Journal of the American Chemical Society* 130(19):6224-6230.

Topical Area – Imaging

Real-time processing and fusion of multiple microscope image streams



The control system of the dual-camera confocal microscope coordinates image acquisition, processing, and data archiving, as well as instrument control.

How a team of PNNL and Utah State University scientists and programmers overcame problems with a unique microscope developed for obtaining live images and cells and proteins is the topic of a cover story in the October 2005 issue of *Scientific Computing & Instrumentation.* The story, "Pixel Perfect - A Real-Time Image Processing System for Biology," describes how a multi-spectral confocal microscope developed at PNNL works (see figure), and how the instrument's image registration problems were solved by 1) developing a comprehensive, in-house user interface to operate the scope, 2) developing a new kind of calibration procedure, and 3) creating a real-time image "warper" in the instrument hardware.

Citations: Perrine KA, DF Hopkins, BL LaMarche, SE Budge, and MB Sowa. 2005. "Pixel Perfect - A Real-Time Image Processing System for Biology." *Scientific Computing & Instrumentation* September 2005 Issue, pp. 16-20.

Perrine KA BL LaMarche, DF Hopkins, S Budge, LK Opresko, HS Wiley, and MB Sowa. 2007. "High-Speed Method for *In Situ* Multispectral Image Registration." *Microscopy Research Techniques* 70:382-389.

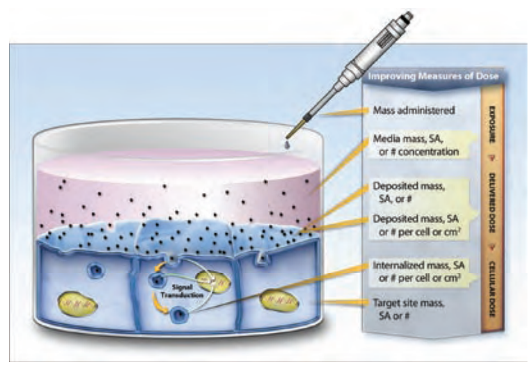
Particokinetics in vitro

Dosimetry considerations for in vitro nanoparticle toxicity

Researchers at PNNL are working to improve the basis for *in vitro* laboratory assessment of nanoparticle toxicity. To understand nanotoxicity, an accurate understanding of the dose to cells is first required. The PNNL team introduced the concept of cellular dose *in vitro* as an important metric. Their results, which appeared as the cover story in the February 2007 issue of *Toxicological Sciences*, included a review of experimental methods for measuring cellular dose *in vitro* and an outline for a computational approach to *in vitro* nanomaterial dosimetry.

Nanoparticles are particles of matter that measure less than 100 nanometers (a nanometer is one-billionth of a meter). They exhibit unique properties that have novel applications in a wide range of industries. However, nanomaterial researchers and manufacturers face an increasing concern from the governmental, environmental, and industrial groups regarding the potential health hazards of nanoparticles. This will be addressed, in part, by providing rapid assessments using high-throughput, *in vitro* cell-based systems.

The factors and processes controlling cellular doses of nanoparticles are different from those for chemicals. In solution, nanoparticles diffuse and settle according to their size and density, unlike chemicals. Varied total amounts of particles with different sizes and densities will therefore reach cells in the bottom of cell culture dishes used in these test systems. Thus, defining dose for nanoparticles in an *in vitro* system is more dynamic and complicated and less comparable across particle types than it is for chemicals. The researchers developed the principles that can be used to understand these processes and their effect on toxicity assessments.



The dose for nanoparticles *in vitro* increases in specificity and relevancy as dose measures move from administered amount to amount delivered to cells or internalized by cells.

Improving the basis for comparative dose-response analysis *in vitro* for nanoparticles by considering kinetics and applying the principle of target tissue dose (cellular dose *in vitro*) will impact research areas such as discovery of fundamental particle characteristics influencing toxicity and uptake, comparative nanoparticle toxicity, and the dynamics of cellular response to nanoparticles.

Citation: Teeguarden JG, PM Hinderliter, G Orr, BD Thrall, and JG Pounds. 2007. "Particokinetics *In Vitro*: Dosimetry Considerations for In Vitro Nanoparticle Toxicity Assessments." *Toxicological Sciences* 95(2):300-312.

Topical Area – Computational Biology

Full collection of more than 1.6 million proteins analyzed using ScalaBLAST

Tool harnesses power of supercomputer for proteomics

ScalaBLAST is a high-throughput sequence analysis engine based on the National Center for Biotechnology Information BLAST distribution. It allows users to harness the power of supercomputers or commodity clusters to accelerate the rate of performing normal BLAST searches against a target database.

One of the key limitations in any sequence analysis pipeline is the need to compare a large collection of proteins from many organisms against itself to detect commonalities between the proteins of different species and within a species. In conjunction with the Joint Genome Institute, current steward of a large collection of microbial genomes, CS Oehmen of PNNL and P Hugenholtz of Lawrence Berkeley National Laboratory used ScalaBLAST to analyze the full collection of more than 1.6 million proteins against itself in less than 13 hours using 1,000 processors of the MPP2 supercomputer.

An additional large search was performed in which each of the 1.6 million microbial protein sequences was compared to the nonredundant list of more than 3 million proteins distributed by the National Center for Biotechnology Information. This step is often performed on genomes as part of a quality control process. For a data set of this size, it is not possible for most BLAST users to analyze the full data set in a tractible time, because for most standalone BLAST installations, a single genome of a few thousand proteins takes many days to process.

ScalaBLAST provides a high-throughput sequence analysis engine that allows users to harness the power of supercomputers to accelerate the rate of performing normal BLAST searches against a target database.

Oehmen and Hugenholtz were able to use ScalaBLAST on MPP2 to process the entire list of 1.6 million proteins against the nonredundant database using 1,500 processors in fewer than 20 hours. This collection of results will be shared with the Joint Genome Institute to be used in conjunction with the microbial genome data as a significant information resource for the worldwide community of biological researchers.

Citation: Oehmen C and J Nieplocha. 2006 “ScalaBLAST: A scalable Implementation of BLAST for High-Performance Data-Intensive Bioinformatics Analysis.” *IEEE Transactions Parallel Distributed Systems* 17:740-749.

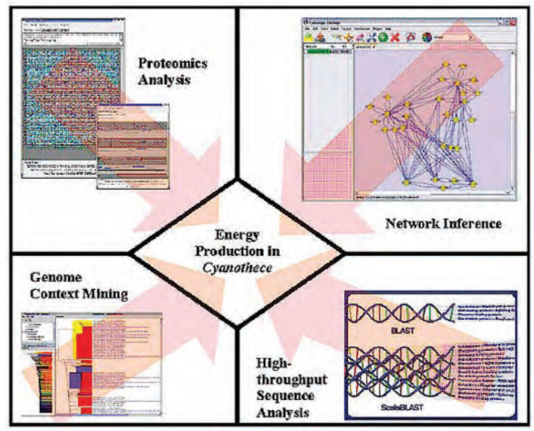
High-performance sequence analysis for data-intensive bioinformatics

Cyanobacteria are organisms that are capable of producing energy through photosynthesis and nitrogen fixation. Because these organisms represent a large fraction of earth's total biomass, their energy-producing processes may be a significant source of information related to renewable energy production and environmental cleanup. To fully understand and use these organisms, we modified genetic analysis tools to quickly analyze them at both the genetic and system levels.

Cyanothece is a relatively unstudied cyanobacterium with unique characteristics, including the ability to produce energy through two separate mechanisms:

- Photosynthesis.
- Nitrogen fixation.

Cyanothece relies on photosynthesis during daylight but "switches" to nitrogen fixation in the absence of light. This behavior might rely on a "diurnal" cycle, meaning the organism "anticipates" nightfall. However, evidence suggests that circadian cycles play a role in *Cyanothece's* "switching" behavior. Circadian cycles are bio-chemically based processes that react to the change from light to dark. Because switching between nitrogen fixation and photosynthesis requires extensive remodeling of the cell's molecular machinery, the switch would be expected to be energetically unfavorable, yet *Cyanothece* is a highly efficient organism.



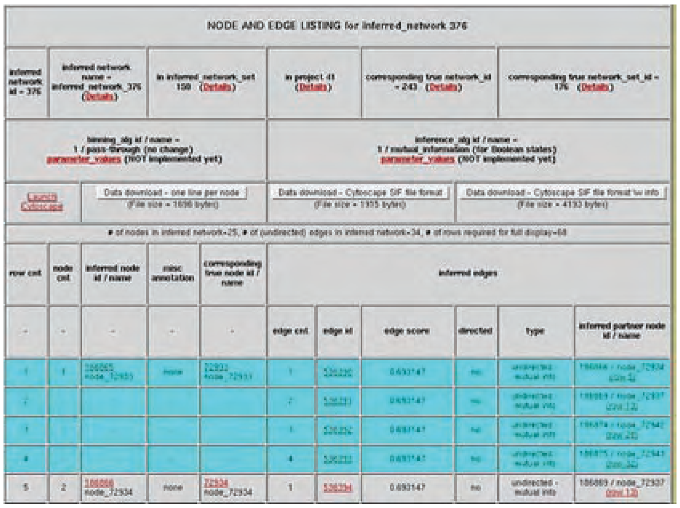
The analysis tools involved in discovery of *Cyanothece's* genetic structure include high-throughput sequence analysis, proteomics analysis, Bayesian network inference, and genome context mining.

To understand how *Cyanothece* is capable of performing such dramatic changes, the team would need to understand the underlying genetic mechanisms and how those mechanisms affect the organism at the system level. Using ScalaBLAST and other computational tools, the team rapidly annotated *Cyanothece's* genome. They performed a gene context analysis using Similarity Box software. This analysis led to the discovery of two proteins involved in nitrogen fixation. These discoveries were confirmed in a proteomics study using PQuad (a proteomics results browser), which indicated the differential presence of key nitrogenase proteins from samples taken at night. SEBINI (a network inference tool) was used to infer the relationship of these proteins to other nitrogenase proteins. The significance of these proteins was confirmed at the system level through clustering analysis tools, including metabolomic, proteomic, and microarray analyses. More significantly, the tools the team modified and made available through this EMSL Grand Challenge project enabled the team to accomplish these analyses in a few minutes. In the past, a similar set of analyses would have taken days.

Citation: Taylor RC, A Shah, C Treatman, and M Blevins. 2006. "SEBINI: Software Environment for BIological Network Inference." *Bioinformatics* 22(21):2706-2708.

Systems approach to understanding the molecular mechanism of the light-dark cycles of Cyanothece

Studying complex biological phenomena at multi-levels of detail requires analyzing different types of data from many sources, including imaging technologies, bio-informatics, transcriptomics, and proteomics. As an ever wider variety of high-throughput methods enter mainstream scientific analyses, handling the complexity and volume of data from these disparate sources requires new algorithms for processing, visualization, and analysis.



The Software Environment for Biological Network Inference (SEBINI) has been created to provide an interactive environment for the deployment and evaluation of algorithms used to reconstruct the structure of biological regulatory and interaction networks.

We present integrative, multi-level analysis of circadian cycling in *Cyanothece* sp. 51142 under the auspices of the EMSL Grand Challenge in Membrane Biology project, which is a multi-institutional collaboration among Washington University in St. Louis, Purdue University, Saint Louis University, the Danforth Center in St. Louis, and PNNL. The focus of the Grand Challenge consortium is to understand how cycling of metabolites, gene expression, and proteins leads to physiological changes in *Cyanothece* during light and dark cycles.

Integration of correlations across transcriptomic, proteomic, and metabolomic data sets is being accomplished with a novel suite of computational tools developed at PNNL. These integrated tools include Similarity Box, an interactive dendogram/clustering tool, PQuad, a proteomics data set viewer, SEBINI, a network inference environment and ScalaBLAST, a high-performance BLAST accelerator. Analyzing this large and complex collection of data sets using novel tools and hardware has made it possible to identify vital molecular components in circadian cycles. Once identified, the goal is to experimentally verify the importance of these components *in vivo.*

Citations: Sofia HJ and GC Nakamura. 2007. "Similarity Box: Visual Analytics for Large Genomic Sets." (submitted to *Bioinformatics*).

Havre SL, M Singhal, DA Payne, and BM Webb-Robertson. 2004. "PQuad: Visualization of Predicted Peptides and Proteins." *Visualization 2004*, IEEE pp. 473-480.

Taylor RC, A Shah, CC Treatman, and ML Blevins. 2006. "SEBINI Software Environment for Biological Network Inference." *Bioinformatics* 22(21):2706-2708.

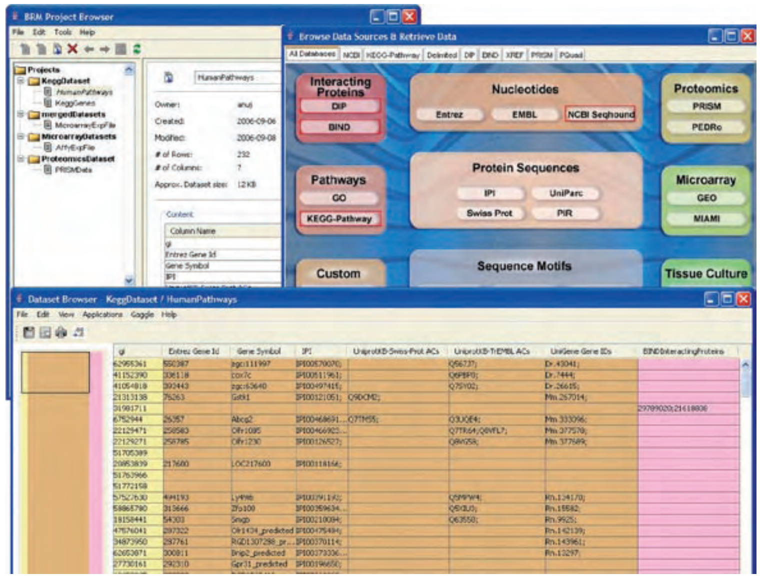
Oehmen CS and J Nieplocha. 2006. "ScalaBLAST: A Scalable Implementation of BLAST for High-Performance Data-Intensive Bioinformatics Analysis." *IEEE Transactions on Parallel and Distributed Systems* 17(8):740-749.

Altschul SF, W Gish, W Miller, EW Myers, and DJ Lipman. 1990. "Basic Local Alignment Search Tool." *Journal of Molecular Biology* 215(3):403-410.

High-throughput visual analytics for biological sciences

Turning data into knowledge

A diverse team of researchers collaborated on an entry for the International Conference for High-Performance Computing, Networking, Storage, and Analysis Analytics Challenge and was named one of the top three finalists. The final competition will take place in November at the SC06 meeting in Tampa, Florida.



The Bioinformatics Resource Manager Client. The Project Browser (top left) displays data sets with metadata information. The Data set Browser (bottom center) tracks provenance of data using colors to distinguish data sources. The data retrieval panels (top right) are used to retrieve data from external data sources.

For the Analytics Challenge, the team demonstrated an end-to-end solution for processing data produced by high-throughput, mass spectrometry-based proteomics. This approach, which allows biological hypotheses to be explored, is based on a tool called the Bioinformatics Resource Manager. The resource manager will interact with high-performance architectures and experimental data sources to provide high-throughput analytics to specific experimental data sets. Peptide identification is achieved by a specially developed, data-intensive version of Polygraph, which has been shown to scale well beyond 1,000 processors.

Visual analytics applications, such as PQuad or Cytoscape, may be used to visualize protein identities in the context of pathways using data from public repositories such as the Kyoto Encyclopedia of Genes and Genomes.

The end result is that a user can go from experimental spectra to pathway data in a single workflow, thereby reducing the time-to-solution wait for analyzing biological data from weeks to minutes.

To view the video included with the PNNL/EMSL entry, go to mms://ims4.pnl.gov/winmedia/2006/BRM/brm.wmv.

Citations: Shah AR, M Singhal, KR Klicker, EG Stephan, HS Wiley, and KM Waters. 2007 "Enabling High-Throughput Data Management for Systems Biology: The Bioinformatics Resource Manager." *Bioinformatics* 23:906-909.

Webb-Robertson BJ, ES Peterson, M Singhal, KR Klicker, CS Oehmen, JN Adkins, and SL Havre. 2007 "PQuad–A Visual Analysis Platform for Proteomic Data Exploration of Microbial Organisms." *Bioinformatics* 23:1705-1707.

6.1.2 Geochemistry, Biogeochemistry, and Subsurface Science Theme

One of the most challenging issues confronting the U.S. Department of Energy (DOE) is the safe and cost-effective management of environmental pollutants and the remediation of hazardous waste sites. DOE is responsible for managing some 40 million cubic meters of contaminated soils and 1.7 trillion gallons of contaminated groundwater. At the Hanford Site in Richland, Washington, alone, DOE invests ~$2 billion a year in cleanup activities related to storing and processing radioactive waste in underground tanks and extensive remediation of soils and groundwater contaminated by past disposal practices and tank waste leaks. These issues are also national problems. For example, across the United States, thousands of Superfund sites exist with various levels and types of contamination such as organics, heavy metals, inorganics, and radionuclides. In the future, the subsurface migration of the byproducts of energy production, including nuclear waste and carbon dioxide, represents one of the most daunting challenges to DOE, and the safe and cost-effective disposal of these byproducts could be a limiting factor in deploying new energy technologies for the nation.

Molecular-level processes, such as aqueous complexation, adsorption to different mineral phases, or microbial reduction of redox active metals, often control the transport and fate of contaminants in the environment. These processes occur in chemically and physically heterogeneous subsurface environments. Understanding the structure, chemistry, and nanoscale geometric properties of mineral/water and microbe/mineral interfaces are critical to a mechanistic understanding of subsurface reactivity and contaminant transport. As a result, molecular-level studies of interfacial geochemistry and biogeochemical reactions have been an active area of research for more than a decade. Unraveling these phenomena at the molecular level and determining their impact on contaminant migration and transformation is a key objective of this science theme.

History in EMSL: As a result of its importance to DOE, subsurface science was, and continues to be, foundational area of EMSL. The focus on subsurface science led to the formation of the Environmental Dynamics and Simulation Group within EMSL, and is now the focus on the Geochemistry, Biogeochemistry, and Subsurface (GB&SS) science theme within EMSL.

Within the broader community, EMSL advances the applications and impact of molecular science.

Within the broader GB&SS community, EMSL advances the applications and impact of molecular science. In this regard, the role and impact of fundamental molecular science studies in GB&SS over the past decade has provided insights in geochemical/biogeochemical reactivity and in utilizing the insights to address field-scale problems in subsurface contamination and transport. This science theme focuses on interfacial molecular geochemistry and biogeochemistry and understanding the fact and transport of chemical and microbial species in the subsurface. There is a special emphasis on the chemistry of radionuclides, especially uranium.

Overall impact of EMSL: For research to unravel both fundamental geochemical/biogeochemical reactivity and field-scale issues requires EMSL support in different aspects of subsurface science, including the following:

- Mineral surface reactivity.
- Biogeochemistry/environmental microbiology.
- Aqueous phase geochemistry.
- Reactive transport modeling/field-scale related research.

The range of capabilities in EMSL allows the facility to support this portfolio of user research and assist in integrating research in these important areas. As an example of the impact of EMSL research in GB&SS, Table 6-1 summarizes the research activities supported by EMSL, the number of publications in each research area since the last EMSL review, and the number of citations of these publications. Several publications in the table included research in different areas. For example, research on microbial mineral reduction could be included in either biogeochemistry/environmental microbiology or mineral surface reactivity. In such cases the decision regarding which area to include the publication was based on the principal area of contribution.

Table 6-1. Research Activities, Publications, and Publication Citations for GB&SS Research Since the 2005 EMSL Operational Review.

Research Area	Research Activities	Publications	Research Citations
Mineral reactivity and surface science	Molecular simulations/characterization of surface reactions, macroscopic mineral reactivity, biogenic mineral formation	90	414
Aqueous complexation, ligand binding, and thermodynamics	Molecular simulation of aqueous reactions, spectroscopic examination of species in solution, overall emphasis on radionuclides	36	121
Reactive transport modeling and field-scale related research	Characterization of field samples, flow and transport laboratory, use of supercomputer for reactive transport modeling	49	91
Biogeochemistry and environmental microbiology	Fundamental studies of microbe surface reactions, proteomics, and microbial community dynamics	32	231
Supporting science	Development of environmental sensors, instrument/technique development for surface characterization, radiation damage in minerals	56	226

6.1.2.1 Mineral surface reactivity

This area of GB&SS includes research in molecular geochemistry of interfacial reactions, macroscopic mineral reactivity studies, and fundamental studies of biogenic mineral formation. There were 90 publications in mineral surface reactivity over the past 3 years with 414 literature citations. Of these publications, 41 studied oxide surface reactions, 20 involved studies of silicate surfaces, and 25 utilized molecular simulation.

The key EMSL staff and resident users include Don Baer, Andy Felmy, Nancy Hess, Ravi Kukkadapu, Kevin Rosso, Zheming Wang, and John Zachara. The following principal investigators (i.e., those not listed as EMSL staff or key resident users) had at least one publication on their user project: Paul Bagus (North Texas), Gerry Gibbs (Virginia Tech), Don Truhlar (University of Minnesota), Sunkyung Choi (University of Arizona), Jim Kirkpatrick (Michigan State University), Bill Casey (University of California, Davis), Shas Mattigod (PNNL), Brent Peyton (Washington State University), Ken Williams (Lawrence Berkeley National Laboratory), Tom Borch (Colorado State University), Jiamin Wan (Lawrence Berkeley National Laboratory), Maciej Gutowski (Heriot-Watt University), David Dixon (University of Alabama), Nancy Ross (Virginia Polytechnic Institute), Eric Pierce (PNNL), Tim Magnuson (Idaho State University), Pete McGrail (PNNL), Dan Gamelin (University of Washington), Karl Mueller (Pennsylvania State University), Geoffrey Bowers (Michigan State University), Edgar Buck (PNNL), Hailiang Dong (Miami University), James Rustad (University of California, Davis), Young Deng (Washington State University), Fumio Ohuchi (University of Washington), Dawn Wellman (PNNL), Lee Penn (University of Minnesota), Mike Hochella Jr. (Virginia Tech), and John Komlos (Princeton University).

The most cited literature publications in this research area are listed here:

Nurmi JT, PG Tratnyek, V Sarathy, DR Baer, JE Amonette, KH Pecher, CM Wang, JC Linehan, DW Matson, R Penn, and MD Driessen. 2005. "Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics." *Environmental Science and Technology* 39(5):1221-1230. (80 citations)

Wan J, TK Tokunaga, E Brodie, Z Wang, Z Zheng, D Herman, TC Hazen, MK Firestone, and SR Sutton. 2005. "Reoxidation of Bioreduced Uranium Under Reducing Conditions." *Environmental Science and Technology* 39(16):6162-6169. (28 citations)

Wang CM, DR Baer, LE Thomas, JE Amonette, J Anthony, Y Qiang, and G Duscher. 2005. "Void Formation during Early Stages of Passivation: Initial Oxidation of Iron Nanoparticles at Room Temperature." *Journal of Applied Physics* 98(9):094308(7). (20 citations)

Kerisit SN, and KM Rosso. 2006. "Computer Simulation of Electron Transfer at Hematite Surfaces." *Geochimica et Cosmochimica Acta* 70(8):1888-1903. (17 citations)

Rustad JR, and AR Felmy. 2005. "The Influence of Edge Sites on the Development of Surface Charge on Goethite Nanoparticles: A Molecular Dynamics Investigation." *Geochimica et Cosmochimica Acta* 69(6):1405-1411. (16 citations)

Sani RK, BM Peyton, A Dohnalkova, and JE Amonette. 2005. "Reoxidation of Reduced Uranium with Iron(III) (Hydr)Oxides under Sulfate-Reducing Conditions." *Environmental Science and Technology* 39(7):2059-2066. (15 citations)

Ilton ES, A Haiduc, CL Cahill, and AR Felmy. 2005. "Mica Surfaces Stabilize Pentavalent Uranium." *Inorganic Chemistry* 44(9):2986-2988. (15 citations).

Four select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Formation of uranium(V) on mineral surfaces.
- Mineral surfaces linked by electrons through the mineral's bulk.
- Re-oxidation of reduced iron and uranium.
- Unraveling the binding of alkaline earth cations.

6.1.2.2 Aqueous complexation/ligand binding thermodynamics

This area of GB&SS includes spectroscopic and molecular simulations of ion solvation, ligand binding, and solution speciation; as well as the use of this information to develop aqueous thermodynamic models. There is a strong emphasis and expertise on radionuclides, especially actinide species.

There were 36 publications in this area of GB&SS supported by EMSL over the past 3 years with 121 literature citations. Molecular simulation contributes to almost all of the publications (30 out of 36). There is a heavy emphasis on the chemistry of radionuclides, especially uranium, with 22 out of 36 publications in this area.

The key EMSL staff and resident users include Eric Bylaska, Herman Cho, Bert DeJong, Andy Felmy, Nancy Hess, Eugene Ilton, Chongxuan Liu, and Zheming Wang.

The following principal investigators had at least one publication on their user project: Barry Bickmore (Brigham Young University), Sam Bryan (PNNL), David Dixon (University of Alabama), Maciej Gutowski (Heriot-Watt University), Lee Penn (University of Minnesota), Dhanpat Rai (PNNL), James Rustad (University of California, Davis), Don Truhlar (University of Minnesota), and John Weare (University of California, San Diego).

The most cited literature publications in this research area are listed here:

Swaddle TW, J Rosenquist, P Yu, EJ Bylaska, WH Casey, and BL Phillips. 2005. "Kinetic Evidence for Five-Coordination in $AlOH_{(aq)}^{2+}$ Ion." *Science* 308(5727):1450-1453. (23 citations)

Gutowski KE, and DA Dixon. 2006. "Predicting the Energy of the Water Exchange Reaction and Free Energy of Solvation for the Uranyl Ion in Aqueous Solution." *Journal of Physical Chemistry A* 110(28):8840-8856. (23 citations)

Groenewold GS, AK Gianotto, KC Cossel, MJ Van Stipdonk, DT Moore, N Polfer, J Oomens, WA De Jong, and L Visscher. 2006. “Vibrational Spectroscopy of Mass-Selected $[UO_2(ligand)_n]^{2+}$ Complexes in the Gas Phase: Comparison with Theory.” *Journal of the American Chemical Society* 128(14):4802-4813. (14 citations)

Three major scientific accomplishments in this research area over the past 3 years are described at the end of this section:

- Molecular simulations of the coordination environment around the uranyl ion.
- Five-coordinate Al(III) in solution.
- Discovery of previously unidentified silica oligomers in solution.

6.1.2.3 Reactive transport modeling and field-scale research

This area of GB&SS includes examination of soils and sediments collected at field sites using laser fluorescence spectroscopy, Mössbauer spectroscopy, nuclear magnetic resonance (NMR) and other methods; solution/groundwater flow and transport studies conducted in EMSL’s flow and transport laboratory; and use of the EMSL supercomputer for simulations of subsurface flow and transport.

There were 49 publications in this area of GB&SS supported by EMSL over the past 3 years with 91 literature citations. Approximately one-half (25) of these publications utilize the flow and transport laboratory on the EMSL supercomputer. The remainder utilize the other molecular-level characterization capabilities in the facility.

The key EMSL staff and resident users include Ravi Kukkadapu, Chongxuan Liu, Paul Majors, Jim McKinley, Mart Oostrom, Zheming Wang, Tom Wietsma, Steve Yabusaki, and John Zachara.

The following principal investigators had at least one publication on their user project: Vanessa Bailey (PNNL), Chin-Hsin Cheng (Cornell University), John Cliff (unknown), Baolin Deng (University of Missouri), Georg Grathoff (Portland State University), Jon Istok (Oregon State University), Johannes Lehmann (Cornell University), Joel Mallard (PNNL), Bruce McNamara (PNNL), Tsuomu Ohno (University of Maine), Dave Rector (PNNL), Wooyong Um (PNNL), Andy Ward (PNNL), Dawn Wellman (PNNL), Charlie Werth (University of Illinois), Kenneth Williams (Lawrence Berkeley National Laboratory), Fred Zhang (PNNL), and Jacob Dane (Auburn University).

The most cited literature publications in this research area are listed here:

Wang Z, JM Zachara, PL Gassman, C Liu, O Qafoku, W Yantasee, and JG Catalano. 2005. “Fluorescence Spectroscopy of U(VI)-Silicates and U(VI)-Contaminated Hanford Sediment.” *Geochimica et Cosmochimica Acta* 69(6):1391-1403. (14 citations)

McKinley JP, JM Zachara, C Liu, SM Heald, BI Prenitzer, and B Kempshall. 2006. "Microscale Controls on the Fate of Contaminant Uranium in the Vadose Zone, Hanford Site, Washington." *Geochimica et Cosmochimica Acta* 70(8):1873-1887. (9 citations)

Ojovan MI, W Lee, A Barinov, IV Startsceva, DH Bacon, BP McGrail, and JD Vienna. 2006. "Corrosion of Low Level Vitrified Radioactive Waste in a Loamy Soil." *Glass Technology* 47(2):48-55. (7 citations)

Serne RJ, W Um, SB Yabusaki, and AT Owen. 2005. "Enhanced Radionuclide Immobilization and Flow Path Modifications by Dissolution and Secondary Precipitates." *Journal of Environmental Quality* 34(4):1404-1414. (5 citations)

The following major scientific accomplishments in this research area over the past 3 years can be found at the end of this section:

- U(VI) contamination at Hanford: The BX-102 overflow event.
- Unraveling pore-scale heterogeneity.
- Migration of carbon tetrachloride in the subsurface at the Hanford Site.

6.1.2.4 Biogeochemistry and environmental microbiology

This area of GB&SS includes fundamental studies of the surface reactions of microbes, microbe biology, proteomics, and microbial community dynamics.

There were 32 publications in this area of GB&SS supported by EMSL over the past 3 years with 231 literature citations.

The key EMSL staff and resident users include Alice Dohnalokova, Jim Fredrickson, Alan Konopka, Ravi Kukkadapu, Paul Majors, Mary Lipton, and John Zachara.

The following principal investigators had at least one publication on their user project: Terry Beveridge (University of Guelph), Haluk Beyenal (Washington State University), William Burgos (Pennsylvania State University), David Cooper (Idaho National Laboratory), Hailiang Dong (Miami University), Carrick Eggleston (University of Wyoming), Peter Lu (Bowling Green State University), Matt Marshall (PNNL), Andy Neal (University of Georgia), Geoffrey Puzon (Washington State University), Eric Roden (University of Wisconsin), and Liang Shi (PNNL).

The most cited literature publications in this research area are listed here:

Ghosal D, MV Omelchenko, E Gaidamakova, V Matrosova, A Vasilenko, A Venkateswaran, M Zhai, HM Kostandarithes, H Brim, KS Makarova, LP Wackett, JK Fredrickson, and MJ Daly. 2005. "How Radiation Kills Cells: Survival of *Deinococcus radiodurans* and *Shewanella oneidensis* Under Oxidative Stress." *FEMS Microbiology Reviews* 29(2):361-375. (31 citations).

Fang R, DA Elias, ME Monroe, Y Shen, M McIntosh, P Wang, CD Goddard, SJ Callister, RJ Moore, YA Gorby, JN Adkins, JK Fredrickson, MS Lipton, and RD Smith. 2006. "Differential Label-free Quantitative Proteomic Analysis of *Shewanella oneidensis* Cultured under Aerobic and Suboxic Conditions by Accurate Mass and Time Tag Approach." *Molecular & Cellular Proteomics* 5(4):714-725. (24 citations)

Shi L, B Chen, Z Wang, DA Elias, M Uljana Mayer, YA Gorby, S Ni, BH Lower, DW Kennedy, DS Wunschel, HM Mottaz, MJ Marshall, EA Hill, AS Beliaev, JM Zachara, JK Fredrickson, and TC Squier. 2006. "Isolation of a High-Affinity Functional Protein Complex between OmcA and MtrC: Two Outer Membrane Decaheme c-type Cytochromes of *Shewanella oneidensis* MR-1." *Journal of Bacteriology* 188(13):4705-4714. (25 citations)

Elias DA, ME Monroe, MJ Marshall, MF Romine, AS Beliaev, JK Fredrickson, GA Anderson, RD Smith, and MS Lipton. 2005. "Global Detection and Characterization of Hypothetical Proteins in *Shewanella oneidensis* MR-1 Using LC-MS Based Proteomics Based Proteomics." *Proteomics* 5(12):3120-3130. (19 citations)

Examples of major scientific accomplishments in this research area over the past 3 years can be found at the end of this section:

- Biogeochemistry Grand Challenge.
- Geophysical imaging of stimulated microbial biomineralization.
- First proteomics study of the microbial community populations in the Sargasso Sea.

6.1.2.5 Supporting science

This area of GB&SS includes the development of environmental sensors for radionuclides and other contaminants, the effects of radiation damage on mineral stability, and instrument/technique development for surface, nano-particle, and protein/metabolite characterization.

Molecular-level studies of interfacial geochemistry and biogeochemical reactions have been an active area of research for more than a decade.

There were 56 publications in this area of GB&SS supported by EMSL over the past 3 years with 226 literature citations.

The key EMSL staff and resident users include Herman Cho, Scott Chambers, Tim Droubay, Zdenek Dohnalek, and Bruce Kay.

The following principal investigators had at least one publication on their user project: Paul Bagus (University of North Texas), Shankar Chellam (University of Houston), Rene Corrales (University of Arizona), Myriam Cotten (Pacific Lutheran University), Ulrike Diebold (Tulane University), Oliver Diwald (Vienna University of Technology), You-Jun Fu (Washington State University), Jay Grate (PNNL), Philip Hugenholtz (Joint

Genome Institute), Mike Kennedy (Miami University), David Kramer (Washington State University), Yuehe Lin (PNNL), Peter Lu (Bowling Green State University), Chuck Peden (PNNL), Lee Penn (University of Minnesota), Wendy Shaw (PNNL), Tom Squier (PNNL), Lai-Sheng Wang (Washington State University/PNNL), Roderick Wasylishen (University of Alberta), William Weber (PNNL), Robert Wind (PNNL), Dave Wunschel (PNNL), Wassana Yantasee (PNNL), and Weiwen Zhang (PNNL).

The most cited literature publications in this research area are listed here:

Lin L, NS Lawrence, S Thongngamdee, J Wang, and Y Lin. 2005. "Catalytic Adsorptive Stripping Determination of Trace Chromium(VI) at Bismuth Film Electrodes." *Talanta* 65(1):144-148. (33 citations)

Chen G, Y Lin, and J Wang. 2006. "Monitoring Environmental Pollutants by Microchip Capillary Electrophoresis with Electrochemical Detection." *Talanta* 68(3):497-503. (22 citations)

Liu G and Y Lin. 2005. "Electrochemical Stripping Analysis of Organophosphate Pesticides and Nerve Agents." *Electrochemistry Communications* 7(4):339-343. (18 citations)

Examples of the major scientific contributions in this research area over the past 3 years are briefly described at the end of this section:

- Luminescence from the trans-dioxotechnetium(V) chromophore.
- NMR technologies developed for biofilm studies.

6.1.2.6 Awards and recognition

The following list contains a few examples of the awards and recognition for EMSL staff and users in GB&SS over the past 3 years.

- **Paul Meakin** (Idaho National Laboratory) won the 2007 Gunnar Randers Research Prize awarded every second year "in the area of physics of condensed matter" and presented by King Harald V of Norway.
- **Don Baer** (EMSL) was the 2007 winner of the EMSL Director's Award for outstanding leadership and scientific contributions.
- **Paul Tratnyek** (Oregon Health and Science University) was a winner of the 2007 Oregon Health and Sciences University Faculty Senate Award.
- **Jim Rustad** (University of California, Davis) was named Chancellor's Fellow at University of California at Davis.
- **Eric Bylaska** (EMSL) was elected to National Energy Research Scientific Computing Center User Group Executive Committee.

- **Andy Felmy** (EMSL) became Chief Scientist for EMSL, and served as a panel lead for the Basic Research Needs in Geosciences Workshop in 2008 and a panel member in the Office of Advanced Scientific Computing Research (OASCR) workshop "Computational Subsurface Sciences" in 2007.
- **David Dixon** (University of Alabama) received the award for Outstanding Computer Based Honors Project Director, University of Alabama, 2006, presented the Charles A. Coulson Lecture at the University of Georgia, 2007, and was a panel lead for the OASCR workshop Computational Subsurface Sciences, in 2007.
- **Tjerk Straatsma** (PNNL) promoted to Laboratory Fellow in 2005 at PNNL and served as a panel member in the OASCR/Oak Ridge National Laboratory Workshop Scientific Impacts and Opportunities in Computing: Geosciences, 2008.
- **Alice Dohnalkova** (EMSL) won the Diatome Award for distinguished scientists in the field of microscopy by the Microscopy Society of America in August 2007.
- **Jim Fredrickson** (PNNL) named 2006 Fellow of the American Association for the Advancement of Science and appointed as Chief Scientist for GTL.
- **Michael Hochella, Jr**. (Virginia Tech) named 2007 Fellow of the American Association for the Advancement of Science.
- **James Amonette** (PNNL) won the 2008 Fitzner/Eberhardt Award for outstanding contributions to science education.
- **John Zachara** (PNNL) named 2006 Fellow of the American Association for the Advancement of Science; won the 2007 E.O. Lawrence Award.


John Zachara (center) received the E.O. Lawrence Award, which honors scientists and engineers at mid-career for exceptional contributions in research and development that support DOE and its missions.

Because many external users do not notify EMSL management of awards and recognition, this information is very incomplete.

6.1.2.7 Future directions and investments

With these accomplishments in mind, the goal is to prepare EMSL to meet future scientific challenges in GB&SS. In this regard, EMSL sponsored a series of workshops beginning in 2006. The first workshop, titled The Environmental Molecular Sciences Laboratory Radiological NMR Spectroscopy Workshop, evaluated future capability needs in radiological science at EMSL, with an emphasis on NMR and electron paramagnetic resonance capabilities.

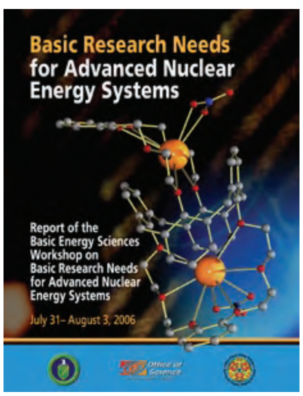
Also in 2006, EMSL sponsored the workshop The Development of New User Research Capabilities in Environmental Molecular Science, which evaluated the future scientific challenges, technology challenges, and investment opportunities in all EMSL science themes including GB&SS. This workshop, which is described in detail in the *Recapitalizing EMSL: Meeting Future Science and Technology Challenges* (see Appendix L), also helped establish the initial investment plan to begin the recapitalization of EMSL as supported by DOE Office of Biological and Environmental Research.

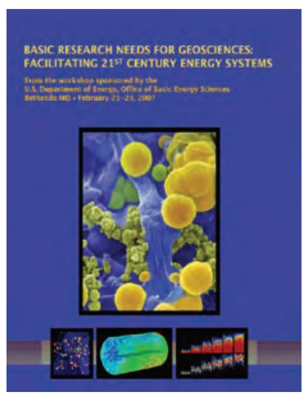
Subsequently, EMSL also supported three other workshops that at least partially addressed scientific opportunities in the area of GB&SS:

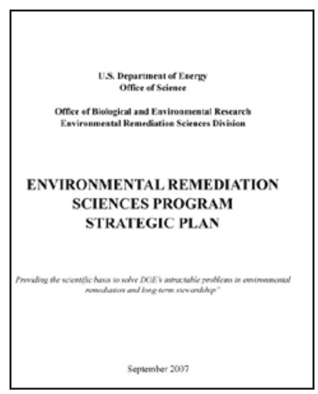
- The *NWChem* Meeting on Science-Driven Petascale Computing and Capability Development, January 25-26, 2007, centered around the status and future direction of *NWChem*

- Science Challenges and Design Concepts for the Next-Generation High-Performance FT-ICR Mass Spectrometer, January 16-17, 2008, which focused on identification of technology and instrumentation impediments in reaching the next generation of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) performance

- The Systems Microbiology and Extremophile Research Facility workshop, March 26, 2008, identified those capabilities needed to build a systems-level understanding of microbes and microbial communities, especially those that can withstand extreme environments.







Several DOE-sponsored reports have provided valuable input and perspective in developing future research challenges in GB&SS.

Several reports have also provided valuable input and perspective (Table 6-2) in the development of future research challenges in GB&SS, including the 2006 Basic Energy Sciences sponsored workshop Basic Research Needs in Advanced Nuclear Energy Systems; the 2007 Basic Energy Science workshop Basic Research Needs in Geosciences: Facilitating 21st Century Energy Systems; and the *Environmental Remediation Sciences Program Strategic Plan*, last published in September 2007. Finally, ongoing discussions with EMSL's Scientific and User Advisory Committees have provided valuable input and perspective in the development of future challenges in GB&SS.

Specific goals and investments: Taken together, EMSL workshops and the reports listed in Table 6-2 represent a thorough look at the future scientific challenges and opportunities as seen by hundreds of

Table 6-2. Examples of Research Defined in Workshops and Planning Documents Where Molecular Science Investigations Can Have a Significant Scientific Impact.

Workshop or Planning Document	Priority Research Directions	Grand Challenges	Crosscutting Research
Basic Research Needs for Geosciences	Mineral-water interface complexity and dynamics	Simulation of multiscale systems for ultra-long times	Microscopic basis of macroscopic complexity
	Nanoparticle and colloid chemistry and physics	Computational thermodynamics of complex fluids and solids	Thermodynamics of the solute-to-solid continuum
	Biogeochemistry in extreme subsurface environments		
Basic Research Needs for Advanced Nuclear Energy Systems	Physics and chemistry of actinide-bearing materials and the f-electron challenge	Developing a first-principles, multiscale description of materials properties in complex materials under extreme conditions	Physics and chemistry at interfaces and confined environments
	Mastering actinide and fission product chemistry under all chemical conditions		Physical and chemical complexity in multi-component systems
Environmental Remediation Sciences Program Strategic Plan (all research priorities)	Determine the dominant electron donors/acceptors fueling microbial metabolic processes under reducing conditions and the dominant pathways for radionuclide/metal and organic transformations and sequestration	Develop and validate predictive transport and remediation models using high-performance computational tools to incorporate long-term biogeochemical reaction kinetics and fluid dynamics and to link multiple processes at different spatial and temporal scales	Experimentally verify coupled fate and transport models through integrated laboratory, intermediate-scale, and long-term field studies

scientists in the field. The challenge for EMSL is to synthesize this extensive list of recommendations, along with a detailed knowledge of current EMSL capabilities, into an action plan for future investments that will enable the needed future scientific investigations. Fortunately, as noted in *Recapitalizing EMSL: Meeting Future Science and Technology Challenges* (see Appendix L), there are certain crosscutting molecular science themes that can form the basis for an investment strategy. These crosscutting themes are as follows:

- Moving from statics to dynamics in native environments.
- Characterization of surfaces and interfaces with unprecedented resolution.
- Design and synthesis of increasingly complex materials.
- Predicting biological functions from molecular and chemical data.

The following text describes the planned investments in each of these themes as well as the scientific challenges that these investments can address. However, these themes cannot address all of the scientific challenges that have been outlined in these planning documents, because some require studies at different scales, may fall outside of these molecular science investment categories, and/or impact several of these categories. These investments will be described at the end of this section.

Moving from statics to dynamics in native environments: This concept means more than just moving from equilibrium property determination to reaction kinetics, although that is an important part. All systems are dynamic, even at equilibrium, so unraveling reaction dynamics is central to unraveling the mechanisms of equilibrium reactions as well as irreversible reactions such as the hysteresis and the effects of aging, which are often observed in adsorption studies on mineral surfaces. The other concept included here is experimental determinations in native environments, which is important in the case of redox sensitive properties and the issues associated with exposure to atmospheric gases and in relating laboratory experiments to field conditions.

These concepts are clearly articulated in many of the research challenges in Table 6-2, including mineral-water interface complexity and dynamics, nanoparticle and colloid chemistry and physics, the microscopic basis of macroscopic complexity, and in the Office of Biological and Environmental Research (BER) priorities of the biogeochemical impacts of reducing conditions.

Examples of the investments we have made or plan to make in this area include the following:

- Micro- x-ray diffraction (XRD) with a contained cell to examine samples without exposure to the atmosphere, and microbial surfaces which cannot be examined by higher energy synchrotron radiation.
- Cryo-transmission electron microscope (TEM) to examine frozen intact microbial surfaces.
- Chemical TEM with an environmental cell which can maintain a gaseous environment for observing the reacting surface (planned purchase).
- Development of NMR probes with circulating reacting gases, which can be extended to high pressure to treat supercritical reactivity (e.g., carbon dioxide sequestration).
- Optical probes for *in situ* reactivity studies including second harmonic generation and sum frequency generation.

Many of the capabilities in the new systems microbiology and extremophile research are also designed to examine living cells in their native environment.

Characterization of surfaces and interfaces with unprecedented resolution: In GB&SS, the concept of "unprecedented resolution" applies to energy resolution (e.g., for determining oxidation states), mass resolution (e.g., for proteomics), and spatial resolution. Striving for this goal is fundamental to molecular science in general and impacts many of the research priorities in Table 6-2 relating to mineral and microbiological reactivity.

Planned specific investments include the following:

- Advanced capabilities in NanoSIMS for simultaneous imaging of elements/isotopes on minerals and soft surfaces at the nanoscale.
- Focused ion beam capability for partitioning and characterizing heterogeneous samples with high spatial resolution.
- Higher brightness (10x) monochromatic x-ray photoelectron spectroscopy for enhanced determination of surface phase composition and oxidation state information.
- Enhanced NMR capabilities for imaging fluid flow in subsurface materials.
- Cryo-solids probe for analysis of low-abundance nuclei.

Planned investments in enhanced NMR capabilities will aid in imaging fluid flow in subsurface materials at the Hanford Site and elsewhere. This will enable researchers to protect the Columbia River, a major water resource in the Pacific Northwest.

- New capabilities in FT-ICR MS for achieving unprecedented mass resolution for microbial proteomics.
- High-energy and -spatial resolution TEM with environmental cell (previously described).

Design and synthesis of increasingly complex materials: The area of material design and synthesis has been a supporting area for GB&SS and includes preparation of oxide surfaces with well-defined molecular properties as well as the development of sensors for environmental applications. As a supporting area, it also can enhance research designed to address many of the scientific areas outlined in Table 6-2.

The major new investment planned for this area is a new oxygen plasma assisted molecular beam epitaxy capability for preparation of oxides surfaces with trace components in specific reactive locations.

Predicting biological functions from molecular and chemical data: This concept area underlies a great deal of biogeochemical and microbial research work supported by BER and the need for capabilities in this area are clearly articulated in the *Environmental Remediation Sciences Program Strategic Plan* (see Table 6-2). However, the need for new research capabilities in biogeochemical and microbial research was also clearly articulated in the Basic Energy Sciences workshop on geosciences, especially with respect to future research challenges in dealing with extreme environments created by the disposal of the byproducts of energy production. Many of these new capabilities were specifically articulated in the two workshop reports: *The Systems Microbiology and Extremophile Research Facility* and *Science*

Challenges and Design Concepts for the Next-Generation High-Performance FT-ICR Mass Spectrometer. These capabilities include growing and characterizing living cells under unique and challenging growth conditions, and unraveling the complexity of multicellular systems, complex microorganisms, and their communities at the molecular level.

New theoretical modeling and computational capabilities: Development of new theoretical approaches and computer models has been important in the EMSL since its inception. Most notable among these activities was the development of *NWChem*, a software package for computational chemistry on high-performance computer systems. The *NWChem* Meeting on Science-Driven Petascale Computing and Capability Development in 2007 outlined capabilities needed in computational chemistry that directly relate to the challenges in GB&SS in Table 6-2 and the experimental investments in EMSL. These new capabilities include improved algorithms and computer code for the following:

- Calculations of dynamics in chemical transformations.
- Modeling of the chemistry of interfaces and the condensed phase.
- Coupling multiple scales.
- Improved incorporation of relativistic effects in modeling the chemical behavior of the heavy elements.

These new computational capabilities are well aligned with the scientific challenges in GB&SS in terms of determining interfacial reactivity and the dynamic properties of mineral surface reactions. Such approaches are also important in guiding the development of new thermodynamic and kinetic models for reactions under extremes of temperature and pressure and for multi-component systems. These research challenges were highlighted in the *Basic Research Needs for Geosciences* (Table 6.1.2-2). The ability to treat these increasingly complex systems computationally, from the molecular level to the nanoscale level or higher, is key to evaluating how molecular information can be transferred and used at higher scales. Bridging the gap between the molecular to continuum scale was identified as a research priority in all of the DOE- and EMSL-sponsored workshops.

The new computational capabilities in EMSL, specifically the supercomputer Chinook, are also utilized for reactive transport calculations that support the BER research priorities outlined in the *Environmental Remediation Sciences Program Strategic Plan*.

Other GB&SS investments: In addition to the crosscutting molecular science investments that impact the science challenges in GB&SS, additional investments in this science theme fall outside of these specific molecular areas. These investments are described in this section.

Development of techniques for microscale reactive transport studies: One of the key scientific challenges identified in Basic Research Needs for Geosciences Workshop was in nanoparticle and colloid chemistry and physics. One important science challenge was in developing a fundamental theory for colloid migration in the subsurface. Developing an improved understanding of the subsurface transport of microbes is also of fundamental importance in the area of bioremediation and environmental microbiology. Although these science challenges will not be solved by any single investment, one of the key recommendations from the 2006 EMSL workshop on new user capabilities was to establish a microscale flow and transport laboratory. EMSL will have the capability to examine the migration of nanoparticles, colloids, and microorganisms in microcells with specially designed geometries and controllable flow and/or growth conditions. Such flow cells have also been used to examine the impact of reactant mixing and precipitate formation on flow and transport under varying reactant concentrations and flow conditions. Resolution of these issues contributes directly to several of the research priorities for BER.

Establishing a radiochemical annex: GB&SS was chosen as one of the founding capabilities in the EMSL principally owing to the proximity of EMSL to the Hanford Site, an area of extensive subsurface radionuclide contamination. This initial ~$250-million investment by the DOE has resulted in significant scientific progress in GB&SS; however, for EMSL to reach its full potential with respect to addressing DOE subsurface contamination issues, it is imperative that many of the molecular science capabilities in EMSL be able to handle radioactive materials.

GB&SS was chosen as a founding capability in EMSL, primarily because of the proximity of EMSL to the Hanford Site, a former plutonium production complex that has released chemicals and radionuclides into the ground.

The need for such radiological capabilities in EMSL has become apparent on several occasions over the past few years. First, the BER Advisory Committee review of EMSL listed the following recommendations relative to the need for radiological capabilities:

- "A capability for the measurement and characterization of radiological samples should be developed" (page 25).
- "The capabilities of the Environmental Spectroscopy and Biogeochemistry Facility would be enhanced by increasing the ability to accept and interrogate samples containing radioisotopes. An on-site radiological annex (or other means to achieve this objective) should be developed" (page 30).
- "Increased ability to perform additional work with radioisotopes and radioactive materials would increase the impact of EMSL research on DOE and national needs" (page 32).

Second, these recommendations were supported by the EMSL Science Advisory Committee recommendation in 2006: "The SAC agreed that incorporation of a radiochemical annex would be a unique and distinctive capability for EMSL as a user facility and would allow work with radioactive tracers not currently permitted within the facilities." Third, a workshop on radiological NMR was held in May 2006, demonstrating the need for such capabilities within the EMSL and the active support of a broad user community.

As currently envisioned, the radiochemical annex would be composed of four laboratories: a Sample Receiving and Analysis Laboratory, an Interfacial Sciences Laboratory, a Biological Sciences and Isotope Tracer Laboratory, and a Magnetic Resonance Laboratory.

The **Sample Receiving and Analysis Laboratory** would house a chemical stockroom, the material balance account of radionuclides, the analytical equipment, the fume hoods, controlled atmosphere chambers, and glove boxes for sample manipulation and safety. The analytical equipment would include the counting instrumentation for alpha, beta, and gamma radiation, and the equipment for analysis of solutions and associated materials.

The **Interfacial Sciences Laboratory** would house the equipment for high-precision surface analysis. This would include the x-ray photoelectron spectroscopy, secondary ion mass spectrometer, scanning probe microscopy equipment, and capabilities for scanning electron microscope and TEM. This specialized instrumentation would be transferred to the EMSL radiochemical annex during the on-going EMSL recapitalization.

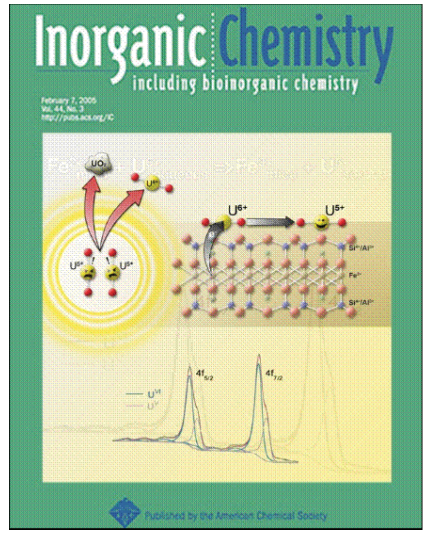
The **Biological Sciences and Isotope Tracer Laboratory** would house the equipment for conducting radiotracer studies including growth chambers, protein- and metabolite-labeling equipment, venting hoods, sample separation setups, and counting and analysis, especially for low energy isotopes.

The **Magnetic Resonance Laboratory** would contain both a high-field (~500 MHz) and a low-field (~100 MHz) NMR. The high-field instrument would bring the benefits of higher sensitivity and greater spectral dispersion. However, most elements of the actinide series have multiple stable oxidation states, with formal charges that imply the metal will have unpaired electrons. For these complexes, low magnetic fields would be preferable to higher fields for NMR measurements.

Selected GB&SS highlights

Topical Area – Mineral Surface Reactivity

Formation of U(V) on mineral surfaces



Although uranium was discovered in 1789, aqueous U(V) was not identified until the 1940s during the Manhattan Project. U(V) in aqueous solution as UO_2^+ has a narrow stability field between pH 2 and 4; outside this pH regime U(V) rapidly disproportionates. The initial findings discounted the possibility of U(V) existing in the environment. EMSL user Eugene Ilton and co-workers discovered that heterogeneous reduction of aqueous U(V) at ferrous mica surfaces produces and preserves U(V), as a sorbed species, over a broad range of solution compositions. The results show that U(V) could play an important, but previously unidentified role in the geochemical cycling of uranium. This research was the cover feature of the May 2005 issue of *Inorganic Chemistry*.

Citation: Ilton ES, A Haiduc, CL Cahill, and AR Felmy. 2005. "Mica Surfaces Stabilize Pentavalent Uranium." *Inorganic Chemistry* 44(9):2986-2988.

Mineral surfaces linked by electrons through the mineral's bulk

Scientists have long known that electrons can travel through some iron oxides when voltage is applied, but they have assumed that electrons stemming from chemical reactions alone won't move spontaneously through the mineral's bulk. That long-standing assumption has caused chemists to treat different faces of a bulk mineral as independent entities that don't communicate with each other. EMSL users Svetlana Yanina and Kevin Rosso reported, for the first time, that the simultaneous dissolution of different faces of a single mineral crystal could drive the growth of a more stable surface and that these growth and dissolution processes were linked by electron conduction through the bulk crystal. These results were published this year in the journal *Science*.

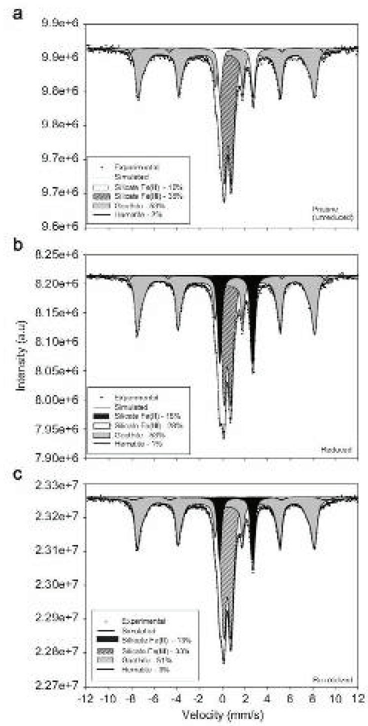
Iron building up into pyramids on one face of an iron (III) oxide crystal sends electrons to another face, which slowly dissolves.

Citation: Yanina SV and KM Rosso. 2008. "Linked Reactivity at Mineral-Water Interfaces through Bulk Crystal Conduction." *Science* 320(5873):218-222.

Re-oxidation of reduced iron and uranium

Effective bio-remediation depends on the durability of bio-reduced sediments to retain contaminants. Sediment containing a mixture of iron-phases, including iron-oxides and iron-silicates, and manganese oxides was bio-reduced in a long-term flow-through column experiment followed by re-oxidation with dissolved oxygen. ^{57}Fe-Mössbauer spectroscopy measurements showed that bio-stimulation resulted in partial reduction (20 percent) of silicate Fe(III) to silicate Fe(II), while the reduction of iron-oxides was negligible. As shown in the figure, the Mössbauer spectra of the re-oxidized sample were similar to that of pristine sediment, showing that the silicate Fe(II) could be re-oxidized. The oxidized manganese was transformed to Mn(II) during bio-reduction but, unlike silicate Fe(II), the Mn(II) was not re-oxidized when exposed to oxygen, indicating a reducing environment relative to manganese is retained in the sediments even after re-oxidation.

This research directly relates to the potential for sediments to re-oxidize uranium, an important and well-cited area of research in EMSL.



Mössbauer spectra (12K) of the (a) pristine sediment, (b) bio-reduced sediment, and (c) re-oxidized sediment.

Citations: Komlos J, RK Kukkadapu, JM Zachara, and PR Jaffé. 2007. "Biostimulation of Iron Reduction and Subsequent Oxidation of Sediment Containing Fe-Silicates and Fe-Oxides: Effect of Redox Cycling of Fe(III) Bioreduction." *Water Research* 41(13):2996-3004.

Wan J, TK Tokunaga, E Brodie, Z Wang, Z Zheng, D Herman, TC Hazen, MK Firestone, and SR Sutton. 2005. "Reoxidation of Bioreduced Uranium Under Reducing Conditions." *Environmental Science and Technology* 39(16):6162-6169.

Sani RK, BM Peyton, A Dohnalkova, and JE Amonette. 2005. "Reoxidation of Reduced Uranium with Iron(III) (Hydr) Oxides under Sulfate-Reducing Conditions." *Environmental Science and Technology* 39(7):2059-2066. (15 citations)

Unraveling the binding of alkaline earth cations

Researchers have shown that the 21.14-T (900-MHz) NMR field strength provides an order-of-magnitude enhancement to the signal-to-noise ratio for ^{87}Sr experiments.

Determining the exact bonding environment of alkaline earth cations (strontium, calcium, and magnesium) in natural materials is important both because isotopes of these cations (e.g., ^{90}Sr) are subsurface contaminants at DOE sites and because they are part of, or form the structural framework of, important natural minerals. Unfortunately, determining the exact binding environment of these cations by traditional approaches–such as x-ray diffraction (XRD)–has been complicated by disorder and stacking faults in the mineral structures, and traditional nuclear magnetic resonance (NMR) spectroscopy has proven difficult as well, because of the low natural abundance of the NMR active nuclei (e.g., ^{25}Mg, ^{87}Sr), the isotopes' low gyromagnetic ratio, and large quadropole moment. Fortunately, researchers at Pennsylvania State University and elsewhere have shown that the 21.14-T (900-MHz) NMR field strength provides an order-of-magnitude enhancement to the signal-to-noise ratio for ^{87}Sr experiments and that quadrupolar Carr Purcell Meiboom Gill analysis and double frequency sweep preparatory scheme results in several-orders-of-magnitude enhancements to the signal-to-noise ratio, thereby permitting the detection of strontium resonances in soil minerals. These developments have led to studies that have unraveled the binding environment of strontium in a variety of soil minerals, including hydroxides, carbonates, micas, and montmorillonites. In addition, use of the 900-MHz NMR has helped define the binding environment of magnesium in hydrotalcites, one of the few natural minerals that can act as anion exchangers. Determining the variations in structure that can result in selective anion exchange properties is important in predicting the potential for subsurface migration of highly mobile anionic constituents. The recent work on hydrotalcites was recognized in the journal *Science*.

Citations: Bowers GM, MC Davis, R Ravella, S Komarneni, and KT Mueller. 2007. "NMR Studies of Heat-Induced Transitions in Structure and Cation Binding Environments in Strontium-Saturated Swelling Mica." *Applied Magnetic Resonance* 32:595-612.

Bowers GM, AS Lipton, and KT Mueller. 2006. "High-Field QCPMG NMR of Strontium Nuclei in Natural Minerals." *Solid State Nuclear Magnetic Resonance* 29(1-3):95-103.

Bowers GM, R Ravella, S Komameni, and KT Mueller. 2006. "NMR Study of Strontium Binding by a Micaceous Material." *Journal of Physical Chemistry B* 110(14):7159-7164.

Chorover J, SK Choi, P Rotenberg, RJ Serne, N Rivera, C Strepka, A Thompson, KT Mueller, and PA O'Day. 2008. "Silicon Control of Strontium and Cesium Partitioning in Hydroxide-Weathered Sediments." *Geochimica et Cosmochimica Acta* 72(8):2024-2047.

Crosson GS, SK Choi, J Chorover, MK Amistadi, PA O'Day, and KT Mueller. 2006. "Solid-State NMR Identification and Quantification of Newly Formed Aluminosilicate Phases in Weathered Kaolinite Systems." *Journal of Physical Chemistry B* 110(2):723-732.

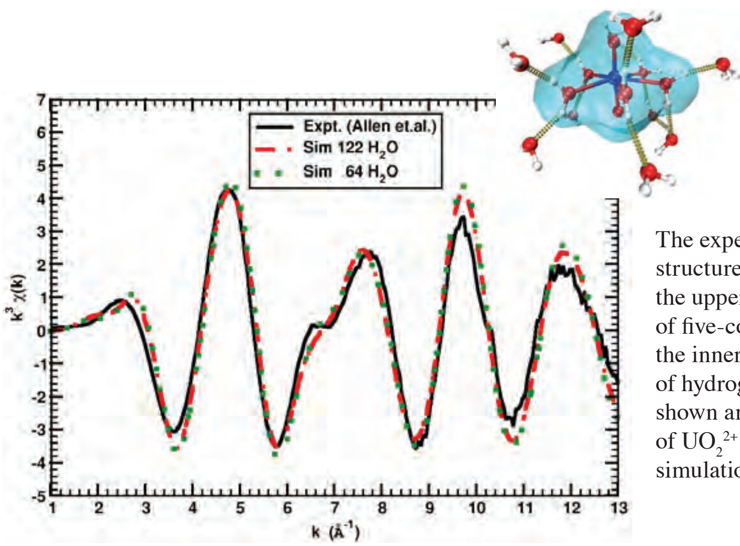
Sideris PJ, UG Nielsen, Z Gan, and C.P. Grey. 2008. "Mg/Al Ordering in Layered Double Hydroxides Revealed by Multinuclear NMR Spectroscopy." *Science* 321:113-117.

Topical Area – Aqueous Complexation/Ligand Binding Thermodynamics

Molecular simulations of the coordination environment around the uranyl ion

A major challenge to the DOE mission to clean up releases of legacy waste containing radionuclides is that the fate, transport, and transformation of radionuclides in the subsurface and across key groundwater-surface water interfaces is not well understood. In the dynamic realm of solution-phase radionuclide coordination chemistry, the formation and stability of complexes is controlled by coordination, geometry, oxidation state, and cooperative effects between different ligands. Probing these aspects provides fundamental insight that is leading to an understanding of the effect of electronic structure and bonding preferences that could eventually be exploited to manipulate radionuclide behavior.

Results from first-principles Car-Parrinello Molecular Dynamics, done with EMSL's *NWChem* software and supercomputing resources, show that the UO_2^{2+} ion is five-fold coordinated. The results are in excellent agreement with experimental information obtained from extended x-ray absorption fine structure experiments (see figure).



The experimental and simulated extended x-ray absorption fine structure spectra of UO_2^{2+} in water are in perfect agreement. In the upper right corner, a snapshot of the two inner solvation shells of five-coordinate UO_2^{2+} are shown. The blue surface identifies the inner-coordination spheres and golden lines show the array of hydrogen bonds that are formed in the structure. The results shown are from NWChem Car-Parrinello Molecular Dynamics of UO_2^{2+} and 122 H_2O molecules in a cubic cell (29 Å) with a simulation time for 10 ps.

The simulations provide unique insights into the behavior of water molecules around the UO_2^{2+} ion not been seen in previous calculations. In addition to the 10 water molecules hydrogen bonding with the 5 water molecules bonded to the uranium atom, on average about 4 water molecules form bonds with the UO_2^{2+} oxygen atoms. These water molecules rapidly exchange, in contrast to the first and second shell waters around in the equatorial plane around the uranium. This research was published in the *Journal of Chemical Physics.*

An even more basic need is to obtain a fundamental understanding of the interaction, complex formation, and oxidation behavior of radionuclides in the presence of multiple ligands. Researchers from Idaho National Laboratory and Wichita State University are using infrared multiple photon dissociation experiments to probe the competitive formation and reactivity of $UO_2^{2+/1+}$-ligand complexes in the gas-phase, controlling the type of ligands, number of ligands, and oxidation state of the uranyl.

Collaborating with EMSL staff members NWChem density functional calculations and EMSL's super-computer have been employed to obtain a complete understanding and interpretation of the measured infrared spectra and non-intuitive photo-fragmentation pathways. This collaborative research has resulted in more than seven publications in high-ranking journals, including the *Journal of the American Chemical Society* and *ChemPhysChem*.

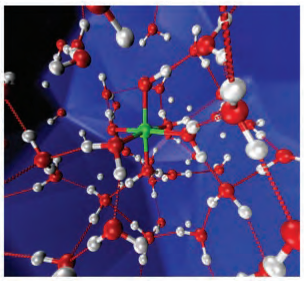
Citations: Nichols P, EJ Bylaska, GK Schenter, and WA de Jong. 2008. “Equatorial and Apical Solvent Shells of the UO_2^{2+} Ion.” *Journal of Chemical Physics* 128:124507.

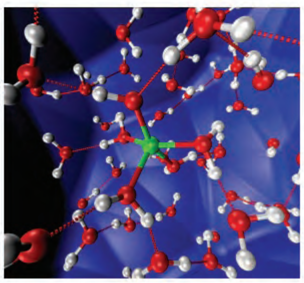
Groenewold GS, MJ Van Stipdonk, WA de Jong, J Oomens, GL Gresham, ME McIlwain, D Gao, B Siboulet, L Visscher, M Kullman, N Polfer, and IA Infante. 2008. “Infrared Spectroscopy of Dioxouranium (V) Complexes with Solvent Molecules: Effect of Reduction.” *ChemPhysChem* 9:1278.

Groenewold GS, AK Gianotto, KC Cossel, MJ Van Stipdonk, DT Moore, N Polfer, J Oomens, WA de Jong, and L Visscher. 2006. “Vibrational Spectroscopy of Mass Selected $[UO_2(\text{ligand})_n]^{2+}$ Complexes in the Gas Phase: Comparison with Theory.” *Journal of the American Chemical Society* 128:4802.

Five-coordinate Al(III) in solution

Trivalent aluminum ions are important in natural bodies of water, but the structure of their coordination shell is a complex unsolved problem. In strong acid (pH < 3.0), Al^{3+} exists almost entirely as the octahedral $Al(H_2O)_6^{3+}$ ion, whereas in basic conditions (pH > 7), a tetrahedral $Al(OH)_4^-$ structure prevails. In the biochemically and geochemically critical pH range of 4.3 to 7.0, the ion structures are less clear. Other hydrolytic species, such as $AlOH(aq)^{2+}$, exist and are traditionally assumed to be hexacoordinate. The results show, however, that the kinetics of proton and water exchange on aqueous Al^{3+}, coupled with newly developed Car-Parrinello simulations (part of *NWChem*), support a five-coordinate $Al(H_2O)_4OH^{2+}$ ion as the predominant form of $AlOH(aq)^{2+}$ under ambient conditions. This result contrasts Al^{3+} with other trivalent metal aqua ions, for which there is no evidence for stable penta-coordinate hydrolysis products.





The kinetics of proton- and water exchange on aqueous Al^{3+}, coupled with simulations, support a five-coordinate $Al(H_2O)_4OH^{2+}$ ion as the predominant form of $AlOH_{(aq)}^{2+}$ under ambient conditions.

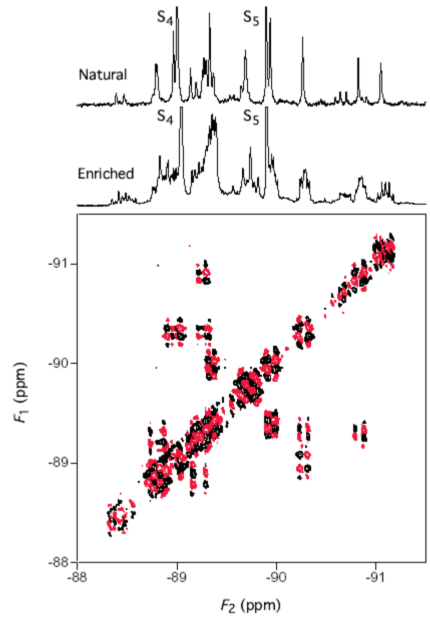
In addition to their importance in natural waters, the transition of tetrahedral aluminate ion ($Al(OH)_4^-$) to octahedral coordination in solid phases, such as gibbsite, is extremely slow kinetically. Unraveling the molecular mechanisms responsible for this slow conversion of aluminate to solid-phase precipitates is one of the, if not the, most important scientific challenge facing the Hanford Site in operating the $12 billion Waste Treatment Plant, because the high temperature, highly basic waste-leaching solution contains high concentrations of aluminate that must be removed without precipitating within the transfer lines in the plant or in the different radionuclide separation processes. Identification of the structure of five-fold coordination complexes could be a key to unraveling the mechanisms of this tetrahedral to octahedral transition. The results of this research were published in the journal *Science*.

Citation: Swaddle TW, J Rosenqvist, P Yu, E Bylaska, BL Phillips, and WH Casey. 2005. "Kinetic Evidence for Five-Coordination in $AlOH(aq)^{2+}$ Ion." *Science* 308(5727):1450-1453.

Discovery of previously unidentified silica oligomers in solution

Silica solution species can be important complexants for radionuclides, especially tetravalent actinides, in the subsurface under basic conditions associated with leaking tank wastes. Establishing a fundamental understanding of all of the silica species present in solute ion allows better predictions of the fate and transport of contaminants in the environment. Unfortunately, a plethora of polymerized silica species can exist under basic conditions and these species must be identified to determine possible radionuclide-silica complexes in solution.

In 2006, evidence for nine new solution-state silicate oligomers was discovered at EMSL using ^{29}Si NMR homonuclear correlation experiments of ^{29}Si-enriched samples. The proposed assignments are validated by comparisons of experimental and simulated cross-peaks obtained with high-digital resolution. The internuclear connectivity indicated by the NMR data suggests that several of these oligomers can have multiple stereoisomers, including conformers and/or diastereomers. The stabilities of these oligomers and their possible stereoisomers have been investigated by electronic structure calculations.



(Bottom) Two-dimensional ^{29}Si DQF–COSY spectrum of bicyclic hexamer, (top) comparison of one-dimensional ^{29}Si spectra natural and enriched abundance spectra.

Experimentally, the significant advancement made in this study was the use of a double-quantum filter in collection of the two-dimensional ^{29}Si COSY (COrrelation SpectroscopY) measurements of isotopically enriched silicate solutions. This was essential to suppress the intense dispersive diagonal peaks of singlet lines, which obscure several cross-peaks and autocorrelation multiplets near the diagonal in the nonfiltered experiment.

Computationally, analysis of the correlation experiments shows that the newly detected oligomers contain only a small number of chemically inequivalent silicon sites, in most cases three or less, and confirm that several oligomers have several stereoisomers that are stable energy minima, and thus are satisfactory structures. The chirality of certain silicon sites greatly expands the spectrum of geometries that a silicate network can have, both in solution-state species and in solid lattices. These diastereomers will have different NMR parameters, chemical properties, and structures, which suggest greater attention will be needed in future experimental and theoretical studies in the specification of silicate structures with the potential for configurational and conformational isomerism.

Citation: Cho H, AR Felmy, R Craciun, JP Keenum, N Shah, and DA Dixon. 2006. “Solution State Structure Determination of Silicate Oligomers by ^{29}Si NMR Spectroscopy and Molecular Modeling.” *Journal of the American Chemical Society* 128(7):2324-2335.

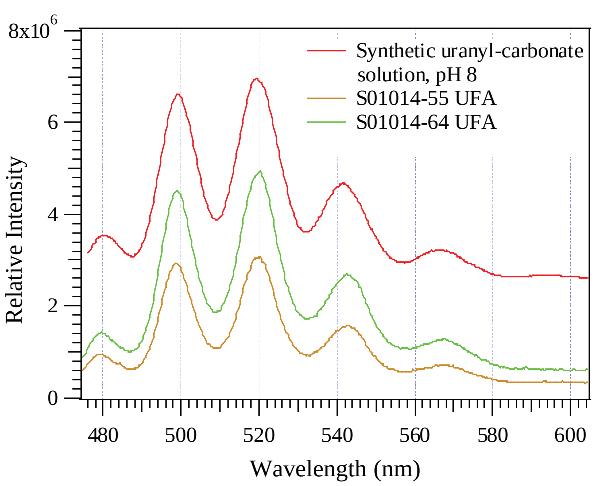
Topical Area – Reactive Transport Modeling and Field-Scale Research

U(VI) contamination at Hanford: The BX-102 overflow event

Plumes of uranium(VI) exist in Hanford Site groundwater and their number is growing as residuals of waste stream discharges move through the vadose zone. As an example, an estimated 91,600 gallons of $BiPO_4$ metal waste solution containing ~7 to 8 metric tons of uranium(VI) was discharged to the vadose zone as a result of the overfilling of tank BX-102, the largest recorded single release of U(VI) to the subsurface at the Site.

In 2001, a borehole was drilled through the metal waste plume proximate to tank BX-102 to provide information on the depth distribution and inventory of uranium and technetium from the incident in 1951. Examination of the distribution of uranium solids by electron microprobe and x-ray absorption spectroscopy (performed at the Advanced Photon Source) showed the abundant presence of uranium microcrystallites within fractures in silicate sediment clasts.

Research in EMSL has focused on characterization of the chemical form of these microcrytallines, primarily by fluorescence spectroscopic measurements on the uranium(VI)-contaminated sediments and groundwaters at both liquid helium and liquid nitrogen temperature.



Fluorescence emission spectra at 5.2 K of Hanford Site vadose zone porewaters beneath tank BX-102. $\lambda_{\varepsilon\xi}$ = 415 nm.

The well-resolved vibronic peaks in the fluorescence spectra of the four sediment samples suggested that the major fluorescence species was a crystalline uranyl mineral phase. Such a conclusion was consistent with the x-ray microprobe analyses. A comparison of the uranium(VI) fluorescence spectra in the sediments with those of known uranium(VI) in the mineral specimens indicated that the uranyl mineral in the sediments was most probably a uranyl phosphate (phosphuranylite or meta-autunite, specifically) or a uranyl silicate (soddyite, uranophane, or boltwoodite).

The porewaters from both 299-E33-45 sediments -55 and -64 showed fluorescence spectra that were almost identical to those of uranyl bis- and tris-carbonate complexes at pH 8, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. These uranium species are apparently migrating through the vadose zone.

Further studies examined the potential for microbial reduction of the sodium boldwoodite phase and the impact of calcium on the reduction reaction using both laser fluorescence and transmission electron microscopy capabilities in EMSL. In addition, the diffusivities in the granitic grain fractures were also examined by nuclear magnetic resonance pulse gradient spin echo measurements in EMSL. All of these studies were important in developing a sodium boldwoodite dissolution and intragrain diffusion model for predicting the U(VI) migration near tank BX-102.

Citations: Liu C, B-H Jeon, JM Zachara, and Z Wang. 2007. "Influence of Calcium on Microbial Reduction of Solid Phase U(VI)." *Biotechnology and Bioengineering* 97(6):1415-1422.

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Liu C, JM Zachara, W Yantasee, PD Majors, and JP McKinley. 2006. "Microscopic Reactive Diffusion of Uranium in the Contaminated Sediments at Hanford, United States." *Water Resources Research* 42:w12420.

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Unraveling pore-scale heterogeneity

While there is general agreement that pore-scale heterogeneity plays an important role in subsurface reaction and flow/transport processes, characterization efforts have typically focused on sediment properties on the scale of architectural elements while essentially neglecting fine-scale heterogeneity. Consequently, there is a lack of consensus on which microscopic geometrical properties are needed to predict the macroscopic transport properties required for field-scale model predictions.

Resolution of the effects of multi-scale heterogeneity on subsurface transport requires large simulations, typically ~105 to 107 grid cells. Progress in this research is dependent on a variety of computer simulation tools, most of which have been developed for use on massively parallel computers, such as EMSL's supercomputer.

Ward and coworkers made use of a Lattice-Boltzmann model and digital representations of porous media with different degrees of heterogeneity and particle aspect ratios. The Lattice-Boltzmann flow simulation method can efficiently use massively parallel computers to resolve the effects of complex boundaries.

This work has led to the development of new constitutive theory for describing saturation-dependent anisotropy for porous media. The new theory has been incorporated into the PNNL STOMP (Subsurface Transport Over Multiple Phases) computer model and is already being used for the evaluation of remedial options for a variety of waste management areas at the Hanford Site and within the DOE complex.

Citations: Stewart ML, AL Ward, and DR Rector. 2006. "A Study of Pore Geometry Effects on Anisotropy in Hydraulic Permeability Using the Lattice-Boltzmann Method." *Advances in Water Resources* 29(9):1328-1340.

Ward AL, ZF Zhang, and GW Gee. 2006. "Upscaling Unsaturated Hydraulic Parameters for Flow Through Heterogeneous Anisotropic Sediments." *Advances in Water Resources* 29(2):268-280.

Migration of carbon tetrachloride in the subsurface at the Hanford Site

Plutonium recovery near the center of DOE's Hanford Site in southeastern Washington State resulted in organic and aqueous wastes that were disposed of at several cribs, tile fields, and French drains. The organic wastes consisted of carbon tetrachloride (CT) mixed with lard oil, tributyl phosphate, and dibutyl butyl phosphonate. The major disposal facilities received a total of about 13,400,000 L of liquid waste containing up to 900,000 kg of CT. The majority of the CT entered the subsurface as an organic liquid.

In recent years, two major remediation technologies have been applied to remove CT from the vadose zone and groundwater at Hanford. Since 1991, about 78,000 kg of CT was removed using a soil-vapor extraction system in the vadose zone. In addition, a pump-and-treat system for the unconfined aquifer removed 9,700 kg of CT from groundwater since 1994.

Carbon tetrachloride infiltration and redistribution in Hanford sediments. The carbon tetrachloride in the unsaturated zone was later removed using soil vapor extraction.

Over the years, several conceptual models and modified versions have been proposed to explain the behavior of CT mixtures in the subsurface of the Hanford 200 West Area and the limited and decreasing yields of the soil vapor extraction and pump-and-treat systems. Research in the EMSL has focused on improving the understanding how CT has migrated through the subsurface and how the remediation technologies affected the CT source zones. Most of this research was done through experimentation in the Subsurface Flow and Transport Laboratory and simulations on the supercomputer.

An update of the CT conceptual model contains components developed with support from EMSL research. For instance, a theory was developed for pore-scale displacement physics of non-miscible fluids, leading to the formation of residual CT in the vadose zone. This theory was implemented into the STOMP simulator and successfully tested against detailed intermediate-scale experiments. A picture of one the experiments, showing the infiltration and redistribution behavior of CT in Hanford sediment, has been included.

In related work, a novel approach tying CT saturations to interfacial areas was developed. The data sets to test and verify the new theory were developed in the EMSL. Experimental data from EMSL flow cell experiments was then used to demonstrate the relation between mass-flux reduction in groundwater and poorly accessible CT sources, likely to be the case at the Hanford Site.

Both the experimental and theoretical studies related to CT residual saturation formation, the relationship between CT saturation and interfacial area, and mass flux of dissolved CT into groundwater, have led to improved understanding of the CT behavior at the Hanford Site. The implementation of the experimentally tested theories into the STOMP simulator have yielded detailed simulations that have supported soil vapor extraction remediation decisions.

Citations: Brusseau ML, E DiFilippo, JC Marble, and M Oostrom. 2008. "Mass-Removal and Mass-flux-reduction Behavior for Source Zones with Hydraulically Poorly-accessible Immiscible Liquid." *Chemosphere* 8:1511-1521.

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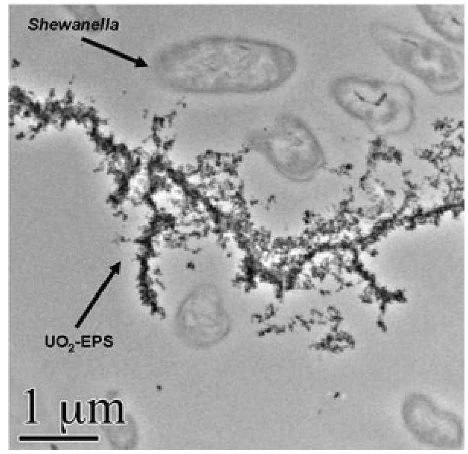
Topical Area – Biogeochemistry and Environmental Microbiology

Biogeochemistry Grand Challenge

A Biogeochemistry Grand Challenge, led by PNNL scientists John Zachara and Jim Fredrickson, and involving 28 investigators from PNNL, Virginia Tech, UAE Norwich, the University of Guelph, Stanford University, Whitworth College, University of Wyoming, University of California, Georgia Tech, and University of Milwaukee studied how organisms exchange energy and electron flux with mineral matter in soils, sediments, and subsurface materials.

A multidisciplinary approach was developed for the grand challenge to evaluate the hypothesis that the outer membrane cytochromes (OMCs) MtrC (locus tag SO1778) and OmcA (SO1779) in the dissimilatory metal-reducing organism *Shewanella oneidensis* MR-1 transfer electrons to iron and manganese oxide mineral substrates. The approach involves a combination of *in vitro* and *in vivo* biologic and biogeochemical experiments and computational analyses that, when integrated, provide a conceptual model of the electron transfer process. The *in vitro* studies involve the purification and characterization of proteins and protein complexes and determination of structural and electrochemical properties by redox titration, thin-film voltammetry, and electron paramagnetic spectroscopy. Experiments with purified proteins include binding experiments and force measurements to establish mineral-protein interactions and kinetic studies to determine electron transfer rates as well as evaluation of the effect of metal ion structural environment on electron transfer rate. *In vivo* experiments complement the *in vitro* studies by establishing the phenotype of specific mutants, probing the location of the OMCs with respect to the cell-mineral interfacial environment, determine architectural features of the interface including distances, functional groups, and biomolecules involved, and the binding forces between proteins and minerals, and the attachment of whole cells to reactive minerals, the kinetics of electron transfer, and the resulting biotransformation products. Numeric experiments and modeling are probing the influence of mineral surface defects, free energy, and electron diffusion within the oxide; and heme orientation, approach distance, and redox potential effects on electron transfer from cytochrome groups to Fe(III) oxide surfaces. The resulting conceptual model was evaluated by integrating and comparing various experimental, i.e., *in vitro* and *in vivo* electron transfer kinetics, and theoretical results.



Research under EMSL's biogeochemistry grand challenge to investigate the mechanisms of bacterial extracellular electron transfer to metals and radionuclides revealed that c-type cytochromes—novel redox proteins located on the cell surface—facilitate electron transfer of contaminants such as uranium. The result is the formation of the mineral uraninite, which is relatively immobile in the environment. The research was featured in *PLoS Biology* [4(8):1324-1333].

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Wigginton NS, KM Rosso, BH Lower, L Shi, and MF Hochella Jr. 2007. "Electron Tunneling Properties of Outer Membrane Decaheme Cytochromes from *Shewanella oneidensis*." *Geochimica et Cosmochimica Acta* 71(3):543-555.

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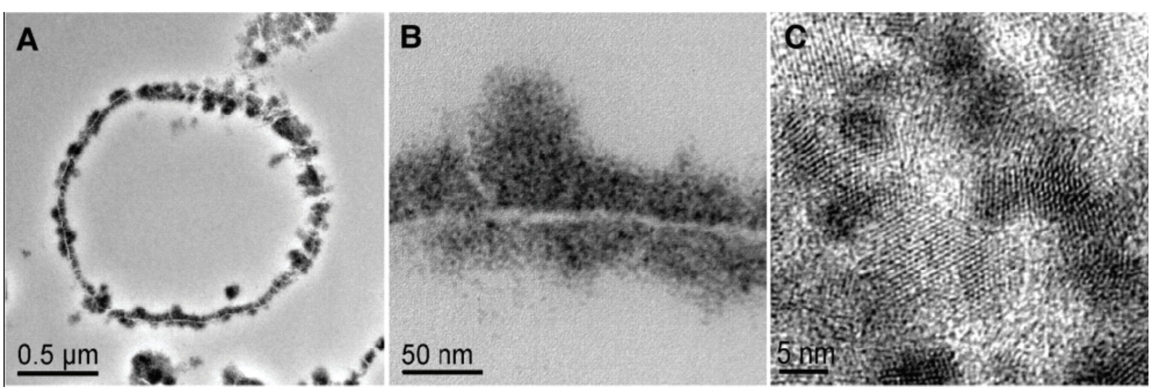
Geophysical imaging of stimulated microbial biomineralization

High-resolution geophysical techniques have proven extremely useful at the field scale for estimating hydrogeological properties and providing information about subsurface environments. In this study, the sensitivity of two geophysical techniques, complex resistivity and acoustic wave propagation, was tested on the products of microbial biomineralization. The primary objective was to follow the reaction dynamics of a column-scale biostimulation experiment using conventional biogeochemical and mineralogical measurements, as well as noninvasive geophysical techniques. Specifically, the hypothesis that metal sequestration via microbe-induced sulfide precipitation creates physical property changes that directly alter the response of geophysical signals was tested. The temporal response of such signals against concomitant changes in fluid chemistry and microbial biomass was tested to investigate if the geophysical responses are sensitive to the products of biomineralization. The geophysical responses were validated using electron microscopy techniques.

Sulfate-reducing bacterium *Desulfovibrio vulgaris* was used for monitoring of microbe-induced sphalerite (ZnS) and mackinawite (FeS) precipitation within saturated sand-packed columns. Acoustic wave measurements and saturated hydraulic conductivity measurement were done during the duration of the experiment. Columns were terminated after 78 days and analyzed for concentration of sediment-affixed metal sulfides and microbial biomass. Transmission and scanning electron microscopy were used for characterizing microbe-mineral associations and the crystal size and aggregation state, and they documented significant spatial variability in the abundance and distribution of cells and their associated mineral products. Transmission electron microscopy-based analysis of the precipitates revealed them to be a mixture of ZnS and FeS, with an average crystal size of 3 nm (see figure). Scanning electron microscopy revealed grain coatings consisting of dense accumulations of sulfide-encrusted microbes.



(A and B) Cross-sectional transmission electron microscopy images of a single *D. vulgaris* cell with membrane-bound ZnS and FeS precipitates. (C) High-resolution transmission electron microscopy revealed the nanocrystalline character of the precipitates with a typical particle size of 3 to 5 nm.

The spatiotemporal changes in complex resistivity and acoustic wave propagation were resolved from variations in the electric charge-carrying capacity and elastic moduli of precipitates and pore fluids. The changes persisted over time and were confined exclusively to those regions where metals were sequestered in insoluble precipitates. Temporal changes in the geophysical signals appear to offer insight into the aggregation state of the sulfides and may be indicative of pore-scale crystal growth and aging, with such a result having implications for the fate and transport of microbe-induced precipitates. Our laboratory results are relevant to the larger spatial scales of the natural environment where methods currently used for field-scale geophysical monitoring may be used in an analogous fashion. These results show the potential of using complex resistivity and acoustic wave techniques for remotely monitoring regions of contaminant sequestration via biomineralization and for evaluating the overall long-term stability of such precipitates.

Citation: Williams KH, D Ntarlagiannis, LD Slater, A Dohnalkova, SS Hubbard, and JF Banfield. 2005. "Geophysical Imaging of Stimulated Microbial Biomineralization." *Environmental Science and Technology* 39(19):7592-7600.

First proteomics study of the microbial community populations in the Sargasso Sea

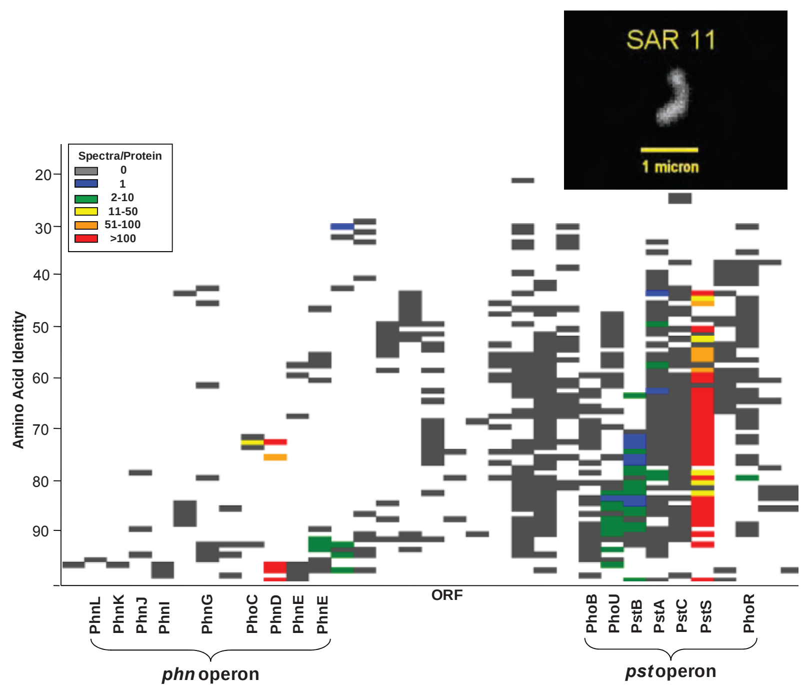
Community genome sequences (metagenome) can at best provide insights into potential functionality of a microbial community. Proteomics is a stable characterization tool for microbial functionality in ecological studies due to the relatively rapid turnover of mRNA and the relative stability of the protein complement. Proteins are functional bio-indicators that point to

- Specific biogeochemical processes
  - Periplasmic or outer membrane cytochromes.
  - Cellulases and other extracytoplasmic macromolecular hydrolases.
  - Hydrogenases.
  - Nitrogen or sulfur reductases.
- Processes that are induced or repressed as a consequence of specific resource limitations in nature, or due to a specific environmental perturbation.

Additionally, analysis of protein catalysts (with an eventual link to enzymatic activities and metabolic flux analysis) can provide the most direct analysis of microbial functionality in natural ecosystems.

Our ability to study changes in biological systems and describe the variability from large volumes of proteomics data has enabled new insights into diverse organisms and even complex biological systems, such as microbial communities in the soil and ocean.

Metaprotemic analysis of naturally occurring microbial communities from the Bermuda Atlantic Time Series Station revealed that the cells express abundant transport proteins to maximize nutrient uptake activity relative to the total energy expended by the cell. To address the challenge of using a mass spectrometric based proteomics approach without the advantage of a fully sequenced genome, the research team used



A large proportion of the detected peptides were unique to either SAR11, *Prochlorococcus*, or *Synechococcus*. Operons highly expressed by seawater bacteria at the Bermuda Atlantic Time Series Station included multiple variants of the same gene/protein. Periplasmic transporters were the most highly detected subunits, but the ATPase and permease subunits and regulatory proteins were also frequently observed.

BLASTp (on EMSL's supercomputer) to find protein sequences within the sequence reads available from Craig Venter's ocean voyages that aligned well with annotated sequences from two of the most dominant oceanic bacteria clades: SAR11 and *Synechococcus*.

Initial findings indicate that the dominant survival mechanisms of these organisms involve active transport of dissolved nutrients into the cells from the surrounding waters. Understanding the response of transporter production to seasonal changes and variances in atmospheric carbon supply will provide insight into the global carbon cycling and could help to address global warming.

This work is a pioneering effort to investigate the protein expression of a community of marine bacteria and reveal the mechanisms by which this community interacts with its environment and contribute to biogeochemical cycles.

Citation: Sowell SM, LJ Wilhelm, AD Norbeck, MS Lipton, CD Nicora, DF Barofsky, CA Carlson, RD Smith, and SJ Giovanonni. "Transport Functions Dominate the SAR11 Metaproteome at Low Nutrient Extremes in the Sargasso Sea." *International Society for Microbial Ecology (ISME) Journal*, In Press.

Topical Area – Supporting Science

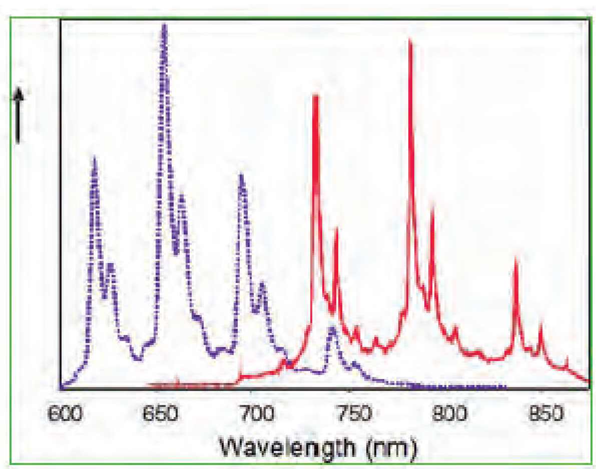
Luminescence from the trans-dioxotechnetium(V) chromophore

Subsurface contamination by technetium is of concern because of the extremely long life of its most common isotope, ^{99}Tc, and the fast migration in soils exhibited by its most common chemical form, pertechnetate. This research contributes to the potential to develop an electrochemical-fluorescence-based sensor to detect technetium in contaminated groundwater at the Hanford Site and elsewhere. A sensor would provide onsite monitoring, either by immersion in subsurface water for continuous monitoring or for immediate analysis of collected samples. The device would combine electrochemistry, spectroscopy, and selective partitioning capabilities, the combination of which substantially improves selectivity.

Funded by DOE's Environmental Management Science Program, this research features a collaboration among researchers from the University of Cincinnati, University of Wyoming, and PNNL. The work involves the spectroelectrochemical detection of pertechnetate in the vadose zone.

The team measured the luminescence and excited-state lifetime properties of a newly discovered Tc(V) chromophore using EMSL's Liquid Helium Line Narrowing Laser-Induced Time-Resolved Fluorescence System. Their research led to the discovery of the first luminescence from trans-dioxo-technetium(V) complexes. The room- and low-temperature luminescence studies of trans-$[TcO_2(L)_4]^+$ (L = pyridine or picoline) and trans-$[TcO_2(CN)_4]^{3-}$ opens a new chapter in technetium chemistry, both in a fundamental and practical sense. The low-temperature luminescence spectrum (see figure) for $[TcO_2(pic)_4](BPh_4)$, with $[ReO_2(pic)_4](BPh_4)$ shown as an overlay spectrum, clearly shows a lower-energy (~180-200 cm^{-1}) vibronic progression for analogous rhenium and technetium complexes. This important development allows the researchers to develop a theoretical model that can be used to predict the optical behavior of technetium complexes in general.

This discovery also provides the first opportunity to directly compare fundamental luminescence properties of second- and third-row d2 metal-oxo congeners. The analytical applications of the TcO_2 chromophore offer promise for design of dual-mode complexes that can correlate luminescence and radioimaging properties into a single agent. For the project's purposes, luminescent Tc(V) complexes are a significant advance in the team's design of a spectroelectrochemical sensor for detection of pertechnetate in the environment.



Low-temperature (8 K) luminescence spectra of microcrystalline $[ReO_2(pic)_4](BPh_4)$ (blue) and $[TcO_2(pic)_4](BPh_4)$ (red). Spectra are not normalized for excitation intensity differences.

Citation: Del Negro AS, Z Wang, CJ Seliskar, W Heineman, BP Sullivan, SE Hightower, TL Hubler, and SA Bryan. 2005. "Luminescence from the Trans-Dioxotechnetium(V) Chromophore." *Journal of the American Chemical Society* 127(43):14978-14979.

NMR technologies developed for biofilm studies

Biofilms are microbial communities that are attached to solid surfaces and to one another in an excreted polymer matrix. They are found in or on nearly every natural environment including humans, where they influence many environmental and health-related processes. The researchers have adapted a hybrid optical and NMR microscope to provide detailed metabolic information for biofilms grown on microscope slides maintained under controlled growth conditions.

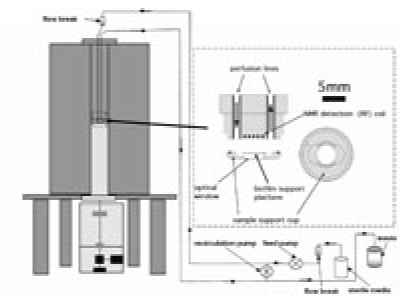


Illustration of the recirculation/dilution flow loop system for NMR microscopy of *in situ* biofilms. The inset shows an exploded view of the perfusable cell culture sample chamber containing a glass cover slip that serves as a biofilm growth surface at the measurement location.

Developments include a perfused microscope sample chamber integrated into a flowing growth reactor, its integration with NMR microscopy hardware, and localized ^{1}H NMR techniques to image biofilm growth and to measure the concentrations of hydrogen-containing metabolites (growth substrates and metabolic byproducts) and a NMR spectroscopic-imaging method to map biofilm metabolism as a function of biofilm depth with 22-micron resolution. Microbe metabolism and phenotype vary rapidly with depth in biofilms—this is responsible for biofilm properties such as the ability to induce surface corrosion and their resistance to anti-microbial agents. *Ex situ* biofilm cultivation was employed, which yielded improved sample properties (uniform biofilm thickness and robust attachment to the glass microscope slide surface) suitable for depth-resolved measurements, and provided improved growth-environment control.

Citations: Majors PD, JS Mclean, JK Fredrickson, and RA Wind. 2005. "NMR Methods for In-Situ Biofilm Metabolism Studies: Spatial and Temporal Resolved Measurements." *Water Science and Technology* 52(7):7-12.

McLean JS, O Ona, and PD Majors. 2008. "Correlated Biofilm Imaging, Transport and Metabolism Measurements via Combined Nuclear Magnetic Resonance and Confocal Microscopy." *The ISME Journal* 2(2):121-131.

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6.1.3 Science of Interfacial Phenomena Science Theme

Interfaces control many chemical and physical properties of natural and engineered materials critical to environmental- and energy-related research and technologies important to the mission of the U.S. Department of Energy (DOE) and to society in general. The importance of interfaces has been highlighted in DOE workshops covering topics including geosciences, solid-state lighting, solar energy, and advanced nuclear energy systems.

Covers from a few of the DOE workshops that highlight the importance of interfacial science.

Tailored or designed surfaces and interfaces are important as model systems for detailed study of processes that occur on natural heterogeneous materials in the environment and for developing materials with new properties for energy production, catalysis, or other uses.

The behaviors of complex heterogeneous materials in the environment may never be fully understood without model systems that allow specific aspects of that complexity to be examined in detail. Likewise, material systems with interfaces optimized with specific properties are essential for the technologies needed for a secure environment and a stable energy future. Understanding these often complex interfaces requires methods to characterize naturally complex materials and minerals found in the environment and to understand increasingly complex materials designed and synthesized to have a desired functionality.

The Science of Interfacial Phenomena (SIP) science theme is focused on understanding and gaining control of structure-function relationships at the atomic level to allow the design of new energy technologies and to understand the behaviors of natural systems. Topics of major emphasis in this science theme include the following:

- Catalytic structure-function relationships to allow precise control of catalytic activity and selectivity.
- Gaining critical knowledge of photocatalysis and photochemistry.
- Design material systems with specialized charge and mass transport properties.

The science and technological issues that need to be addressed to achieve these goals complement and to some degree naturally intersect those of the other science themes. The ability to characterize surfaces and small particles also provides a natural pathway for addressing issues of atmospheric aerosol chemistry. Developing technologies that rely on improved understanding and control of molecular-level structural, dynamic, and transport properties of interfaces include the following:

- New generations of selective catalysts.
- Thin-film solar cells.

- Solid-state lighting.
- Hydrogen production and storage.
- Solid-oxide fuel cells.
- Chemical sensors and radiation detectors.
- Materials for next-generation nuclear reactors.

6.1.3.1 Specific areas of interfacial science in EMSL

Interfacial science was identified as critical during the foundation of EMSL; it was also recognized that significant scientific impact would be best achieved by focusing efforts in specific areas. The 1990 Environmental Materials and Interfaces Workshop, part of a series held to define the scope and capabilities of EMSL, highlighted specific aspects of interfacial science important to EMSL. These areas included the following:

- Advancing the understanding of oxide and mineral surface chemistry.
- Characterizing natural and model materials with state-of-the-art tools.
- Linking theory and experiment.
- Understanding the mineral/water interface.

These topical areas formed the core scientific focus of the initial interfacial studies in EMSL as well as a method for focusing development of capabilities.

The initial focus of interfacial science in EMSL has provided a foundation for a significant amount of research. The initial focus areas included the following:

- Mineral and oxide surface chemistry including:
  - Synthesis of model oxide and mineral films and surfaces for environmental and catalysis studies.
  - Interaction of oxide surfaces with small molecules.
  - Comprehensive characterization of oxide films and surfaces.
- Catalysis
  - Understanding fundamentals of reactions and mechanisms.
  - Development of new robust catalyst materials.
- Waste processing and tank chemistry
  - Fundamental science associated with waste forms.
  - Chemistry of tank constituents.
- Sensors
  - Materials development for chemical and biological sensors.
  - Sensor testing and characterization.

New and expanding areas of SIP: As EMSL evolved, some areas have diminished or disappeared. Other areas have expanded, and new areas have appeared. Analysis of the publications of EMSL users since 2005 shows that

- Waste processing and tank chemistry have significantly decreased.
- Several areas increased in importance and new areas developed including:
  - Photocatalysis (new).
  - Electronic and magnetic properties of oxides (new).
  - Doping and defects on surface, interface, and other properties (new).
  - Development of new energy-related materials (increased).
  - Synthesis and characterization of micro- and nano-particles (including aerosols) (increased).

Developing an emerging science theme – Interfacial and particle analysis related to atmospheric aerosol chemistry: The development of specialized abilities to characterize the overall and surface composition and chemistry of individual particles (or small collections of particles) has led to increased interface and particle analysis activities related to atmospheric aerosol chemistry. Several EMSL users have identified aerosol chemistry as an area that should be of growing scientific importance and impact to understanding local pollution, aspects of climate change, and health effects. This developing area has a range of analysis needs and capability requirements that overlap with other aspects of SIP, but also move it in new directions.

EMSL considers atmospheric aerosol chemistry to be an emerging science theme. We are working with DOE as well as current and potential users to identify areas of expansion and to develop the scientific vision and tools that would position EMSL to have a high impact in this area. We are working to develop this area so that it reaches a critical size and the role and scientific vision for EMSL in this area can be established.

Role and impact of interfacial studies in EMSL: Based on the number of science theme proposals submitted in SIP starting in 2006 and an analysis of all EMSL publications, interfacial topics have the highest level of user activity in EMSL (Figure 6-1). Even when excluding topics that directly tie to atmospheric aerosol research, the number of user proposals submitted on SIP is larger than those of the other science themes. SIP proposals are highly multi-instrument oriented with approximately 75 percent of these SIP proposals requesting use of more than one instrument. Approximately 60 percent of the SIP science theme user proposals are led by principal investigators outside of PNNL.

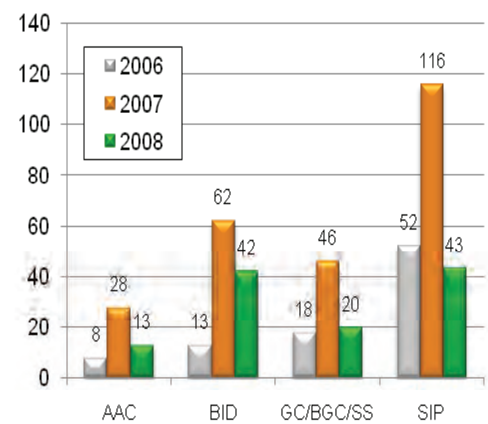
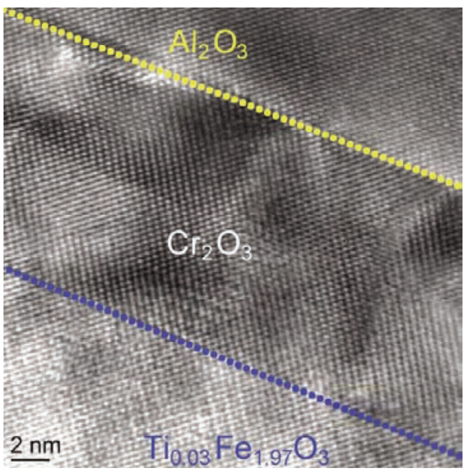


Figure 6-1. User Proposals by Area for the 2006, 2007, and 2008 Science Theme Calls. AAC = Atmospheric Aerosol Chemistry; BID = Biological Interactions and Dynamics, GC/BGC/SS = Geochemistry, Biogeochemistry, and Subsurface Science.

EMSL use publications have been analyzed to determine areas of significant impact. All user publications starting from 2005 were examined (some 1250 papers) and were counted if they contributed to the science identified in a science theme. In this analysis, a paper might be counted in more than one theme. Approximately 650 of the 1250 papers could be classified as significantly related to SIP. To get a picture of where these EMSL user paper were making contributions, SIP related papers were categorized into major groupings related to science or technology. If several papers covered similar or related topics, these subgroups are identified and the number of relevant papers listed.

To provide a sense of the research activities in these areas, descriptions are provided along with identification of the scientific leadership and example publications. Publication counts for these areas can be found in Table 6-3. Selected highlights that have been prepared over the last 3 years that fit into these areas are listed and can be found at the end of the section.

6.1.3.2 Oxide films, oxide surface chemistry, and oxide catalysis



This high-resolution image shows an example of the high-quality oxide films that can be grown in EMSL using the oxygen plasma assisted molecular beam epitaxy.

Oxide and mineral surface chemistry and oxide thin film properties are major areas of EMSL user activity. Methods for the synthesis and characterization of oxide films and surfaces provide an important foundation for much of this research. Although many oxides are being studied, EMSL remains strong on studies involving TiO_2.

Important to the success of this area is the involvement of leaders in the scientific community. Leaders include Professors Charles Campbell (catalysis and surface chemistry, University of Washington), D. Wayne Goodman (catalysis and surface chemistry, Texas A&M), David Dixon (theory, University of Alabama), Dan Gamelin (magnetism and materials synthesis, University of Washington), and the late J. Mike White (catalysis and surface chemistry, University of Texas).

Six PNNL Laboratory Fellows participate in this area: Scott Chambers (oxide film synthesis), Mike Henderson (oxide surface chemistry and photochemistry), Chuck Peden (catalysis), Michel Dupuis (theory), Bruce Kay (physical chemistry), and Don Baer (interfacial properties, EMSL staff). Other key contributors are Kevin Rosso (PNNL), Zdenek Dohnalek (PNNL), Janos Szanyi (PNNL), Igor Lyubinetsky (EMSL), and Eric Bylaska (EMSL).

Major scientific papers in this research area include the following:

Kaspar TC, SM Heald, CM Wang, JD Bryan, T Droubay, V Shutthanandan, S Thevuthasan, DE McCready, AJ Kellock, DR Gamelin, and SA Chambers. 2005. "Negligible Magnetism in Excellent Structural Quality Cr_xTi_1-xO_2 Anatase: Contrast with High-TC Ferromagnetism in Structurally Defective Cr_xTi_1-xO_2." *Physical Review Letters* 95:217203. (47 citations)

Table 6-3. Subcategories of EMSL SIP Papers.

Research Area	Publications
Oxide films, oxide surface chemistry, and oxide catalysis	190
Oxide surface chemistry/photochemistry	40
Oxide catalysis	24
Oxide magnetism and electronic properties	More than 60
Oxide nanostructures	15
Oxide geochemistry (many of these papers will likely also be counted in the biogeochemistry science theme)	25
Catalysis	140
Oxides catalysis	24
Theory/calculation	17
Transportation	10
Oxide surface chemistry	34
Bioreactors/micro-reactors	16
Water/hydration/oxide or Particle/Water Interface	40
Water and solvation	30
Oxide water interface	10
Synthesis, Characterization, and Properties	75
Self assembly (including soft landing)	20
Ion irradiation based nano synthesis	5
Functional nanomaterials (mostly sensor)	30
Energy and the Environment	55
Hydrogen storage	18
Fuel cells (mostly solid oxide)	10
Biofuels	16 (many catalysis related)
Environmental and contamination removal	10
Defects and Radiation	60
Radiation oxides	16
Defects and nanostructure stability	20
Clusters and Nanostructured Materials	115
Synthesis of nanoparticles and functional nanomaterials (with emphasis in sensors)	50
Properties of nanostructure materials or nano-sized objects including the role of defects	12
Physical and chemical properties of clusters	45
Environmental Particles and Aerosol Chemistry	70
Aerosol characterization and reactivity	34
Field-scale measurements and climate modeling	10
Supporting research	25
Sensors	120
Biosensors	45
Carbon nanotube based	25
Functional surface films	30

Many of the numbers in this table are appoximate.

Punnoose A, J Hays, A Thurber, MH Engelhard, RK Kukkadapu, C Wang, V Shutthanandan, and S Thevuthasan. 2005. "Development of High-temperature Ferromagnetism in SnO_2 and Paramagnetism in SnO by Fe Doping." *Physical Review B* 72:054402. (28 citations)

Henderson MA. 2005. "Photooxidation of Acetone on TiO_2(110): Conversion to Acetate via Methyl Radical Ejection." *Journal of Physical Chemistry B* 109(24):12062-12070. (16 citations)

Tait SL, Z Dohnalek, CT Campbell, and BD Kay. 2005. "n-Alkanes on MgO(100). I. Coverage-dependent Desorption Kinetics of n-butane." *Journal of Chemical Physics* 122:164707. (17 citations)

The following select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Oxygen Atoms Display Novel Behavior on Common Catalyst.
- Hopping Hydrogen.

6.1.3.3 Catalysis

Both fundamental and applied catalysis research, often related to oxide surfaces, has been a long-standing component of EMSL. Approximately 140 publications were associated with catalysis. This included publications on oxide catalysis and oxide surface chemistry.

The PNNL Institute for Interfacial Catalysis (IIC) is a major user of EMSL and helps engage academic and industrial catalysis leaders from around the world as EMSL users (http://iic.pnl.gov/). Many of the academic researchers interested in fundamental research also contribute in the area of oxide surface chemistry. Major users outside of PNNL include Charlie Campbell (University of Washington), D Wayne Goodman (Texas A&M), David Dixon (University of Alabama), and Mark Bussell (Western Washington University). From PNNL, leaders include Chuck Peden (acting director of IIC), Yong Wang, Mike Henderson, Conrad Zhang, and Janos Szanyi.

Standing beneath a powerful superconducting magnet, EMSL's David W. Hoyt adjusts a sample probe for NMR analysis.

Major scientific papers in this research area include the following:

Szanyi J, JH Kwak, DH Kim, SD Burton, and CHF Peden. 2005. "NO_2 Adsorption on BaO/Al_2O_3: The Nature of Nitrate Species." *Journal of Physical Chemistry B* 109:27-29. (33 citations)

Campbell CT and CHF Peden. 2005. "Chemistry – Oxygen Vacancies and Catalysis on Ceria Surfaces." *Science* 309:713-714. (18 citations)

Sawhill SJ, KA Layman, DR Van Wyk, MH Engelhard, C Wang, and ME Bussell. 2005. "Thiophene Hydrodesulfurization Over Nickel Phosphide Catalysts: Effect of The Precursor Composition and Support." *Journal of Catalysis* 231:300-313. (23 citations)

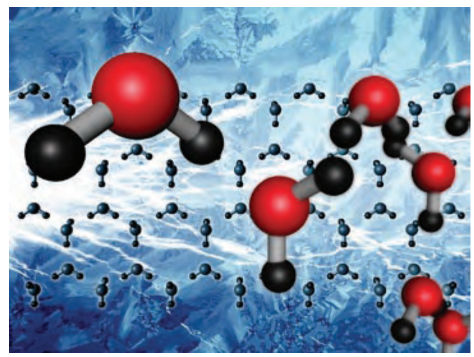
Select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Institute for Interfacial Catalysis (portions of *C&E News* article).
- 900-MHz NMR enables novel catalysis studies.
- Constant Flow: Novel probes that revolutionize *in situ* nuclear magnetic resonance investigations of catalysts and reaction intermediates.

6.1.3.4 Water/hydration/oxide or particle/water interface

Water is the most relevant environmental and biological fluid, and the water-solid interface is critical to geochemistry, atmospheric aerosols chemistry, sensors, and biological processes (human and biofuels). Water-related work in EMSL involves modeling of water structure, theoretical development of models of water structure, experimental work on model systems (amorphous water/ice), and theoretical and experimental measurements of the solid/liquid interface. Theory related to water has a long history in EMSL as do studies of the mineral/water interface.

Water-related work in EMSL involves developing and applying theoretical models of water structure and the water surface interface. Science leaders in the theory and modeling area include Sotiris Xantheas (PNNL), Bruce Garrett (PNNL), Greg Schenter (PNNL), David Dixon (University of Alabama), Eric Bylaska (EMSL), Jim Rustad (University of California at Davis), Rene Corrales (University of Arizona), and Andy Felmy (EMSL).



Researchers found that ice generated voltages as large as that in the battery in your TV's remote control at temperatures between 30°K and 150°K.

There are also experimental studies of model water systems, led by Bruce Kay (PNNL), Jim Cowin (PNNL), Greg Kimmel (PNNL), and experimental measurements of the solid/liquid interface. Leaders include Kevin Rosso (PNNL), Don Baer (EMSL), Eugene Ilton (PNNL), and Mike Henderson (PNNL). Hydrations studies are experimental and theoretical, and leaders include Lai-Sheng Wang (Washington State University/PNNL) and many of the theoreticians examining water, as noted.

Major scientific papers in this research area include the following:

Kimmel GA, NG Petrik, Z Dohnalek, and BD Kay. 2005. "Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer." *Physical Review Letters* 95(16):166102. (33 citations)

Zhang Z, O Bondarchuk, BD Kay, JM White, and Z Dohnalek. 2006. "Imaging Water Dissociation on TiO_2(110): Evidence for Inequivalent Geminate OH Groups." *Journal of Physical Chemistry B* 110(43):21840-21845. (16 citations)

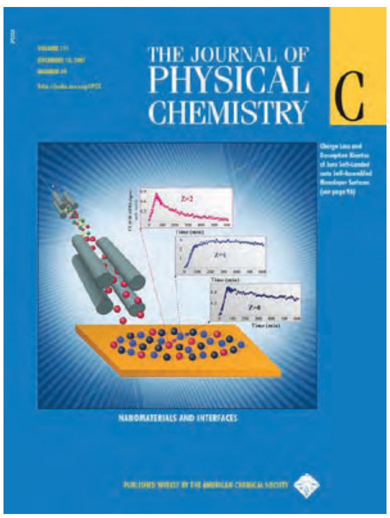
Wang H, RC Bell, MJ Iedema, GK Schenter, K Wu, and JP Cowin. 2008. “Pyroelectricity of Water Ice.” *Journal of the American Chemical Society* 112(20):6379-9389.

Valiev M, JR Rustad, JH Weare, and EJ Bylaska. 2007. “Structure and Dynamics of the Hydration Shells of the Al^{3+} Ion.” *Journal of Chemical Physics* 126(10):Art.no.104505. (1 citation)

A select scientific accomplishment in this research area over the past 3 years is highlighted at the end of this section:

- One molecule at a time: New model deciphers the hydrogen bonding network in different water environments.

6.1.3.5 Synthesis, characterization, and properties



The soft landing of large molecules on a surface provides a unique way to make functional surfaces using large molecules.
[*J. Phys. Chem. C*, 2007, 111:18220.]

Creating films, particles, and surfaces with engineered properties is an essential component of many different user activities in EMSL including catalyst, sensor, environmental remediation, and energy systems research. Therefore, synthesis and characterization activities permeate most of the areas of the SIP science theme, including the growth of high-quality model single crystal oxide films for the surface chemistry, catalysis, and magnetic properties noted in Section 6.1.3.2. This topic highlights the many papers that focus on other types of synthesis methods along with characterization, even though many point directly toward the specific intended applications. There are ~75 synthesis-focused papers (not primarily tied to growth of oxide thin films or surfaces).

Although many different groups are involved in synthesis and synthesis-related capabilities in EMSL, the areas of high activity often link to research of PNNL or EMSL scientists. Key contributors are Julia Laskin (PNNL), Bruce Kay (PNNL), Zdenek Dohnalek (PNNL), S Thevuthasan (EMSL), V Shutthanandan (EMSL), Greg Exarhos (PNNL), and Alex Punnoose (Boise State University).

Major scientific papers in this research area include the following:

Wang Y and G Cao. 2006. “Synthesis and Enhanced Intercalation Properties of Nanostructured Vanadium Oxides.” *Chemistry of Materials* 18:2787. (25 citations)

Shin Y, CM Wang, and GJ Exarhos. 2005. “Synthesis of SiC Ceramics by the Carbothermal Reduction of Mineralized Wood with Silica.” *Advanced Materials* 17(1):73-77. (25 citations)

Hays J, A Punnoose, R Baldner, MH Engelhard, J Peloquin, and KM Reddy. 2005. “Relationship Between the Structural and Magnetic Properties of Co-doped SnO_2 Nanoparticles.” *Physical Review B* 72:075203. (24 citations)

Fryxell GE. 2006. “The Synthesis of Functional Mesoporous Materials.” *Inorganic Chemistry Communications* 9(11):1141-1150. (7 citations)

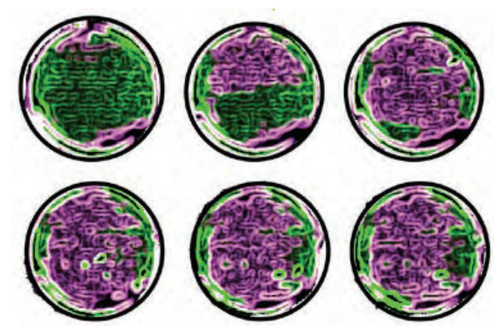
Wang CM, Y Zhang, V Shutthanandan, DR Baer, WJ Weber, LE Thomas, S Thevuthasan, and G Duscher. 2005. “Self-assembling of Nanocavities in TiO_2 Dispersed with Au Nanoclusters.” *Physical Review B, Condensed Matter* 72(24):245421, 1-5. (2 citations)

Select scientific accomplishments in this research area over the past 3 years is highlighted at the end of this section:

- Research on soft landings glides onto cover of top physics journal.
- Reactive ballistic deposition of porous TiO_2 films: Growth and characterization.

6.1.3.6 *Energy and the environment*

The design of materials with specific surface and interfacial behaviors relevant to clean energy production and storage or environmental remediation is a growing user activity in EMSL. A significant applied development program for solid oxide fuel cells has some fundamental aspects and characterization efforts that link to EMSL. Many researchers in areas of environmental contamination use EMSL interfacial tools to address specific questions.



Magnetic resonance imaging slices of a polymer layer in an operating fuel cell provide an example of a real-time real-environments imaging capability. These images show dynamic movement of the dehydration layer (purple) and spatial water distribution (green).

The scientific leaders in this area include Tom Autrey (hydrogen storage, PNNL), Glen Fryxell (contamination removal, PNNL), Theva Thevuthasan (material synthesis, EMSL), Larry Pederson (PNNL), Dave King (PNNL), Prabhakar Singh (PNNL), and Subhash Singhal (PNNL). Catalysis studies related to biofuels are associated with the IIC.

Major scientific papers in this research area, which has seen ~55 papers published in the last 3 years, include the following:

Lin Y, X Cui, C Yen, and CM Wai. 2005. “Platinum/Carbon Nanotube Nanocomposite Synthesized in Supercritical Fluid as Electrocatalysts for Low-Temperature Fuel Cells.” *Journal of Physical Chemistry B* 109(30):14410-14415. (57 citations)

Gutowska A, L Li, Y Shin, CM Wang, XS Li, JC Linehan, R Scott Smith, BD Kay, BA Schmid, WJ Shaw, MS Gutowski, and T Autrey. 2005. "Nano-Scaffold Mediates Hydrogen Release and Reactivity of Ammonia Borane." *Angewandte Chemie International Edition* 44(23):3578-3582. (54 citations)

Fryxell GE, Y Lin, SK Fiskum, JC Birnbaum, H Wu, S Kelly, and KM Kemner. 2005. "Actinide Sequestration Using Self-Assembled Monolayers on Mesoporous Supports." *Environmental Science and Technology* 39(5):1324-1331. (24 citations)

Kim J, HF Jia, and P Wang. 2006. "Challenges in Biocatalysis for Enzyme-based Biofuel Cells." *Biotechnology Advances* 24:296-308. (28 citations)

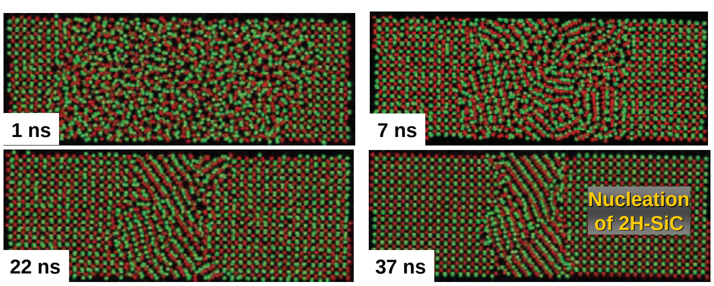
Minard KR, VV Vishwanathan, PD Majors, LQ Wang, and PC Rieke. 2006. "Magnetic Resonance Imaging (MRI) of PEM Dehydration and Gas Manifold Flooding During Continuous Fuel Cell Operation." *Journal of Power Sources* 161(2):856-863. (7 citations)

Select scientific accomplishments in this area over the past 3 years are highlighted at the end of this section:

- Probing reaction pathways using *in situ* ^{1}H NMR spectroscopy.
- Conductivity of oriented samaria-doped ceria thin films grown by oxygen-plasma-assisted molecular beam epitaxy.

6.1.3.7 Defects and radiation

Defects at surfaces, interfaces, and within materials or films play a major role in determining the physical and chemical properties of materials and materials interfaces. Defects were not an initial focus within EMSL and were not initially considered as an obvious part of interfacial science. As user activity expanded in this area, the importance of defects in catalysis and photocatalysis, the need for mass and charge transport across interfaces for solid-state lighting and photovoltaics, and the role of defects in the structures of nano-sized objects demonstrate that defects and related processes are an increasingly important component of interfacial science. Defect-related interfaces are present even when considering the generation of healing of amorphous regions in a material or defect generation and migration due to radiation. As with many user activities in EMSL, this area has a high focus on linking theory, computation, and experiment.



Molecular dynamics simulation of recrystallization in 3C-SiC at 2000K. The closer linking of theory and experiment is an increasing component of many EMSL user projects.

The leading scientific user in this area is PNNL Fellow William Weber who attracts users and collaborators from around the world. Users include Professor Rod Ewing (University of Michigan) and Ian

Farnan (Cambridge University). Other contributors are Yanwen Zhang (EMSL), Fei Gao (PNNL), Ram Devanathan (PNNL), S Theva Thevuthasan (EMSL), and V Shutthanandan (EMSL).

Major scientific papers in this research area include the following:

Farnan I, H Cho, and WJ Weber. 2007. “Quantification of Actinide alpha-Radiation Damage in Minerals and Ceramics.” *Nature* 445:190-193. (9 citations)

Bylaska EJ, K Tsemekhman, and F Gao. 2006. “New Development of Self-Interaction Corrected DFT for Extended Systems Applied to the Calculation of Native Defects in 3C-SiC.” *Physica Scripta* T124:86-90. (6 citations)

Zhang Y, WJ Weber, V Shutthanandan, and S Thevuthasan. 2006. “Non-linear Damage Accumulation in Au-irradiated $SrTiO_3$.” *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 251(1):127-132. (5 citations)

Devanathan R, LR Corrales, WJ Weber, A Chartier, and C Meis. 2006. “Molecular Dynamics Simulation of Energetic Uranium Recoil Damage in Zircon.” *Molecular Simulation* 32(12-13):1069-1077. (2 citations)

Select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Radiation degrades nuclear waste-containing materials faster than expected.
- Ceramic, heal thyself.

6.1.3.8 Clusters and nanostructured materials

The physical and chemical properties of clusters, nanoparticles, and other nanostructured materials have become increasingly important in fundamental studies and as the basis for various applications. As has been widely noted, interfaces and surfaces play major roles in determining the properties of these materials. Many EMSL user activities are associated with the synthesis and characterization of clusters or nanostructured materials.

Leading users contributing in this area include Professor Lai Sheng Wang (Washington State University/PNNL) and PNNL staff members Marvin Warner, Yuehe Lin, and Jay Grate.

Major scientific papers in this research area include the following:

Bulusu S, X Li, LS Wang, and X Zeng. 2006. “Evidence of Hollow Golden Cages.” *Proceedings of the National Academy of Sciences of the United States of America* 103(22):8326-8330. (46 citations)

Nurmi JT, PG Tratnyek, V Sarathy, DR Baer, JE Amonette, KH Pecher, CM Wang, JC Linehan, DW Matson, R Penn, and MD Driessen. 2005. "Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics." *Environmental Science and Technology* 39(5):1221-1230. (80 citations)

Ji M, X Gu, X Li, X Gong, J Li, and LS Wang. 2005. "Experimental and Theoretical Investigation of the Electronic and Geometrical Structures of the Special Au30 Cluster." *Angewandte Chemie International Edition* 44(43):7119-7123. (23 citations)

Boggavarapu K, S Bulusu, HJ Zhai, S Yoo, LS Wang, and X Zeng. 2005. "Planar-to-Tubular Structural Transition in Boron Clusters: B20 as the Embryo of Single-Walled Boron Nanotubes." *Proceedings of the National Academy of Sciences of the United States of America* 102(4):961-964. (29 citations)

The following select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Buckyballs make room for gilded cages.
- EMSL capabilities instrumental in nanoparticle size study.

6.1.3.9 Environmental particles and aerosol chemistry (emerging science theme)

Second-generation Single Particle Laser Ablation Time-of-Flight mass spectrometer (SPLAT II) collecting data on an aircraft over Alaska during a 2008 field research campaign. As part of the campaign, SPLAT II measured the characteristics of aerosol particles in the atmosphere that contribute to climate change.

Increasingly, it is recognized that the chemistry and surface reactivity of these types of particles can have a significant impact on environmental processes. In many ways, environmental and atmospheric particles have much in common with clusters and nanoparticles. Some of the same methods are highly useful to characterize them. EMSL user activities in this area include studies of physical and chemical properties of particles, using unique EMSL analytical tools and capabilities. In some cases, instruments that are normally applied to study model aerosols in the laboratory are transported to the field for application of naturally formed aerosols.

The scientific leaders in aerosol science and atmospheric chemistry include Professor Vicki Grassian (University of Iowa), Professor Barbara Finlayson-Pitts (University of California, Irvine), Professor Sergey A. Nizkorodov (University of California, Irvine), Professor Mario J. Molina (University of California, San Diego), Professor Hai Wang (University of Southern California), and Professor Kimberly A. Prather (University of California, San Diego); Mary K. Gilles (Lawrence Berkeley National Laboratory), Professor G. Barney Ellison (Colorado State University). These experts are teaming with PNNL and EMSL staff including Julia Laskin, Alex Laskin, M. Liz Alexander, Alla Zelenyuk, and Mario Molina to make progress on this topic. Important work on theoretical modeling has been led by David Dixon (University of Alabama) while V Shutthanandan, Dan Gaspar, Chongmin Wang, Scott Lea, Paul Gassman, Matt Newburn, Jim Cowin, and Martin Iedema (all PNNL) have made contributions to laboratory studies.

Researchers showed that large population centers, such as Mexico City, do not accelerate the formation of climate-changing aerosols.

Major scientific papers in this research area include the following:

Laskin A, MJ Iedema, A Ichkovich, ER Graber, I Taraniuk, and Y Rudich. 2005. "Direct Observation of Completely Processed Calcium Carbonate Particles in Polluted Atmospheric Environment." *Faraday Discussions* 130:453-468. (30 citations)

Zelenyuk AN, Y Cai, and D Imre. 2006. "From Agglomerates of Spheres to Irregularly Shaped Particles: Determination of Dynamic Shape Factors from Measurements of Mobility and Vacuum Aerodynamic Diameters." *Aerosol Science and Technology* 40(3):197-217. (22 citations)

Laskin A, TW Wietsma, BJ Krueger, and VH Grassian. 2005. "Heterogeneous Chemistry of Individual Mineral Dust Particles with Nitric Acid. A Combined CCSEM/EDX, ESEM and ICP-MS Study." *Journal of Geophysical Research. D. (Atmospheres)* 110(D10):D10208. (20 citations)

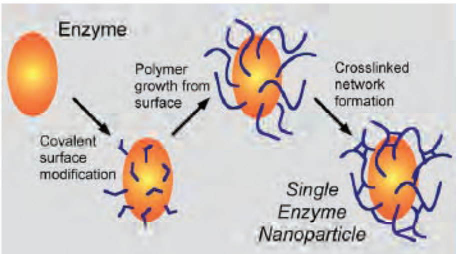
Laskin A, JP Cowin, and MJ Iedema. 2006. "Analysis of Individual Environmental Particles Using Modern Methods of Electron Microscopy and X-Ray Microanalysis." *Journal of Electron Spectroscopy and Related Phenomena* 150(2-3):260-274. (14 citations)

Johnson KS, BM Zuberi, L Molina, MJ Molina, MJ Iedema, JP Cowin, DJ Gaspar, CM Wang, and A Laskin. 2005. "Processing of Soot in an Urban Environment: Case Study from the Mexico City Metropolitan Area." *Atmospheric Chemistry and Physics* 5:3033-3043. (23 citations)

Select scientific accomplishments in this research area over the past 3 years are highlighted at the end of this section:

- Experimental studies of heterogeneous gas-to-particle reactions using novel particle-on-substrate stagnation flow reactor approach.
- Chemical speciation of sulfur in marine particles.
- Application of methods of high-resolution mass spectrometry to study chemistry of secondary organic aerosol.
- A new mechanism for ozonolysis of unsaturated organics on solids: Phosphocholines on NaCl as a model for sea salt particles.

6.1.3.10 Sensors



Synthesis approach for creating single enzyme nanoparticles, which have potential applications as biosensors and as biocatalysts [*Chem. Eng. Sci., 2006,* 61:1017].

The development of highly selective materials for new types of sensors for environmental monitoring, process control, and other applications has been part of EMSL since the foundation. The surfaces and interfaces of these materials and sensor systems are carefully designed to achieve selective properties and to optimize the collection of highly specific information.

The scientific leaders in this area include PNNL staff Jay Grate, Yuehe Lin, and Marvin Warner who have laboratories in EMSL. Leaders in this field also include Professor JB Kim (Korea) and PNNL staff members Shane Addleman and Glen Fryxell.

Major scientific papers in this research area include the following:

Kim J, JW Grate, and P Wang. 2006. "Nanostructures for Enzyme Stabilization." *Chemical Engineering Science* 61:1017-1026. (40 citations)

Lin YH, W Yantasee, and J Wang. 2005. "Carbon Nanotubes (CNTs) for the Development of Electrochemical Biosensors." *Frontiers in Bioscience* 10:492-505. (37 citations)

Liu G, and YH Lin. 2006. "Amperometric Glucose Biosensor Based on Self-Assembling Glucose Oxidase on Carbon Nanotubes." *Electrochemistry Communications* 8(2):251-256. (33 citations)

A major scientific accomplishments in this research area over the past 3 years is highlighted at the end of this section:

- A biosensor layered like lasagna.

6.1.3.11 Awards and recognition

Awards and professional recognition indicate the impact of EMSL users within the scientific community. EMSL users are highly involved in professional societies: are organizing symposia and being recognized by their societies. The following list contains a few awards and recognition for EMSL staff and users in SIP over the past 3 years.

- **William Weber** (PNNL) elected into the inaugural class of Materials Research Society Fellow, American Association for the Advancement of Science (AAAS) Fellow, and serves as principal editor and editorial board member for *Journal of Materials Research* and on the editorial board for *Nuclear Instruments and Methods in Physics Research.*

- **Bruce Kay** (PNNL) elected AAAS Fellow and AVS Fellow.
- **Greg Exharos** (PNNL) elected President of AVS, AAAS Fellow, serves as editor of *Vacuum* and was Chair of Publication Committee for the *Journal of Vacuum Science and Technology* (2003-2007).
- **Michel Dupuis** (PNNL) elected American Physical Society Fellow.
- **Scott Chambers** (PNNL) elected AVS Fellow.
- **Chuck Peden** (PNNL) elected AVS Fellow, serves as Chair Catalysis Division of American Chemical Society, and serves on the editorial board of *Journal of Vacuum Science and Technology*.
- **Mike Henderson** (PNNL) elected AVS Fellow.
- **Don Baer** (EMSL) elected AVS Fellow, serves as review editor and on the editorial board for *Surface and Interface Analysis*, associate editor for *Journal of Vacuum Science and Technology* (1988-1990), and is on the editorial board and an associate editor for *Surface Science Spectra*.
- **Yuehe Lin** (PNNL) serves as the North American editor of the *Journal of Nanoscience and Nanotechnology*, associate editor of *Advanced Science Letters*, and on the editorial boards for *Nanomedicine* and *NanoBiotechnology*.

Fung Ou

- **Mark Engelhard** (EMSL) serves as Chair of Publication Committee for *Journal of Vacuum Science and Technology* (2007-current) and associate editor of *Surface Science Spectra*.
- **Janos Szanyi** (PNNL) serves on the editorial board of *Catalysis Letters*.
- **Fung Ou** (Rice University) won the 2007 Nanoscience Foresight Award and the 2008 AVS Student Award.
- **Yanwen Zhang** (EMSL) received the Presidential Early Career Award for Scientist and Engineers (PECASE) for 2005.
- **Julia Laskin** (PNNL) received PECASE for 2006, American Society for Mass Spectrometry Biemann Medal in 2008.
- **Jean Futrell** received the American Chemical Society FH Field and JL Franklin Award for Outstanding Achievement in Mass Spectrometry.
- **Dick Smith** (Montana State University) named AVS Fellow. Smith, a professor of physics, has been a user of EMSL since the facility opened—in fact, he served on the review team for the accelerator.
- **Satyanarayana Kuchibhatla** (University of Central Florida) received an AVS Graduate Research Award for 2007.

Julia Laskin

Lai-Sheng Wang

- **Lai-Sheng Wang** (Washington State University and PNNL) received Humboldt Research Award for his lifetime achievements in nanoscience.
- **Ajay S. Karakoti** (University of Central Florida) will receive AVS student awards at the AVS meeting October 2008 in Boston.
- **Sudipta Seal** (University of Central Florida) elected to the 2008 Class of Fellows by the ASM International Board of Trustees.

Because many external users do not notify EMSL management of awards and recognition, this information is very incomplete.

6.1.3.12 Future directions and investments

We are adding and planning new capabilities in EMSL that will enable research for the next decade based on knowledge of major user activities and instrument activity, information from users and our Science and User Advisory Committees, and examination of DOE needs and possible future program plans, which provide funding for many of our users. In addition, workshops for DOE, National Academy of Sciences, and others help us gather input. The scientific and capability development directions important for interfacial science in EMSL and the directions they indicate are remarkably clear, consistent, and technically challenging.

Based on assessment workshops and other sources of information, the EMSL strategic plan states:

> *EMSL will in the next decade, **develop new understanding that enable the optimization of interfacial properties, such as the control of catalytic activity and longevity for environmental and energy applications**.*

The science challenges to be addressed in SIP were summarized in the EMSL Development of New User Research Capabilities in Environmental Molecular Science Workshop report as follows:

- *Expanding our understanding and ability to rationally design, synthesize, and characterize complex surfaces, films, and interfaces.* One focus of this area is to enhance our ability to deal with complex materials, structures, and environments. Manipulating complex materials and the related interfaces will allow the creation of films/materials with designed properties related to sensor, detector, catalysis, and energy needs.

- *Understanding and controlling the dynamic properties of surfaces and interfaces.* We are just beginning to understand the truly dynamic nature of surface and interface structures that will have major impacts on the nature and presence of defects and reaction sites. These dynamic effects may be more apparent for organic materials or biomaterials, but also apply to “static” inorganic surfaces and interfaces. This time and environment dependence adds new opportunities for understanding and controlling structure-function relationships at surfaces and interfaces of many types. These dynamic effects will influence our understanding of chemical reactivity for catalysis, photocatalysis, and bioactive materials. They also have significant implications for processes involving mass and charge transport necessary for detectors, sensors, fuel cells and photovoltaics, as well as offering new approaches to control reaction processes.

These themes, as well as capability development needs to be described, are similar to the topics identified in many different DOE workshops. Interfaces and surfaces play important roles in the priority research directions identified in DOE workshops. Several common themes and capability needs are identified in many of these workshops including the following:

DOE Workshops Highlighting Surface or Interface Science

- *Basic Research Needs for Materials under Extreme Environments*
- *Basic Research Needs: Catalysis and Energy*
- *Future Science Needs and Opportunities for Electron Scattering: Next Generation Instrumentation and Beyond*
- *Basic Research Needs for Electrical Energy Storage*
- *Basic Research Needs for Geosciences: Facilitating 21st Century Energy System*
- *Basic Research Needs for Advanced Nuclear Energy Systems*
- *Basic Research Needs for Solid-State Lighting*
- *Nanoscience Research for Energy Needs*
- *Theory and Modeling in Nanoscience*

- The increasing need to understand surface and interfaces in natural or operating environments or conditions. This *in situ* capability was highlighted in catalysis and energy, electron scattering, geosciences, and energy storage workshops.

- Growing understanding that the dynamics of surfaces and interfaces play a major role in their properties. The importance of interfacial dynamics and charge transport across interfaces was noted in extreme environments, energy storage, solid-state lighting, and nanoscience and energy workshops.

- Closer coupling of theory and experiment was highlighted in catalysis, theory, and modeling in nanoscience workshops.

- Designing interfaces for specific functional properties and lifetime. Interface design was highlighted in advanced nuclear systems, catalysis and energy, and nanoscience and energy workshops.

A 2006 report from the National Academy of Sciences, *Advanced Research Instrumentation and Facilities*, also raises issues relevant to instrumentation in a major user facility such as EMSL. They note that

> "In recent years, the nature of S&E research has changed dramatically, as have the instruments that support and advance this research. In addition to many other factors, the rise in interdisciplinary research, with its focus on large-scale problems that require a variety of techniques, demands more advanced instrumentation. As a result,
>
> - The need for particular instruments has broadened, crossing scientific and engineering disciplines.

- Instruments that were once of interest only to specialists are required by a wide array of scientists to solve critical research problems.

- Researchers have become increasingly dependent on advanced instruments that require highly specialized knowledge and training for their proper use and greatest effectiveness."

Identification of crosscutting capability development themes in EMSL: In the 2006 EMSL New Research Capabilities for Users Workshop, areas of technical challenge specifically for interfacial science were raised. However, many of these areas strongly resonated with the issues identified in several different ways by groups focused on other science themes. The general challenges indicate areas where techniques and capability developments are important to scientific progress and capabilities for our user community. These overlapping or crosscutting areas included the following:

- ***In-situ/operando*/real-time probes**: The ability to measure chemical and structural characteristics of surfaces and nanostructured materials as a function of environment and time is critical for understanding the dynamical and transient behaviors of materials and interfaces relevant for a more advanced understanding of structure-property relationships. Capability developments that facilitate *in situ* capabilities should be emphasized.

- **High-resolution and interfacial analysis tools**: Information must be obtained about the structure, composition, and chemical properties of specific sites and small areas. To do this, the following abilities are considered important:

  - Probe atomic and molecular structure and composition of solid/solid; solid/liquid; and solid/gas interfaces.
  - Combine spectroscopy and microscopy.
  - Provide high-resolution tools for engineering natural materials.

- **Sample synthesis and preparation capabilities**: Important needs include the synthesis of complex (composition and morphology) oxide interfaces, films, and surfaces as well as developing methods to observe and control growth processes in real time, including in solution. Preparing and handling samples to retain desired properties is an increasingly important challenge. The integration of precision calorimetric tools with nanostructure synthesis can provide the experimental basis for testing in-detail theoretical model accuracy.

- **Experiment-theory links – New level of verified theory for interfaces and nanostructures**: Although fundamental theoretical tools can contribute to our understanding of molecular structures with increasingly large numbers of atoms and complexity, it is still difficult to experimentally validate theoretical predictions. Although it is possible to verify calculated structures, kinetic and energetics provide a more critical test of accuracy. An important goal is to be able to calculate energetics with the accuracy needed for chemical predictions.

The following list summarizes many of the needs identified from the variety of sources and identifies an agenda for capability development for interfaces (closely mapping to the crosscutting themes above):

- **Make it**. Design and synthesis of increasingly complex materials and interfaces.
- **Characterize it**. New generation high-resolution (energy and spatial) analysis tools and integrated imaging.
- **Real-time measurements in real conditions**. *In-situ*/operando/real-time probes to measure a variety of properties.
- **(Near) real-time data processing** and analysis, nearly immediate results alter the nature and productivity of what can be done. This couples to rapid linking of theory and experiment.
- **Closer coupling** of modeling with design, synthesis, characterization, and properties.

The EMSL Development of New User Research Capabilities in Environmental Molecular Science Workshop included working groups in the areas of **interfacial phenomena** and **atmospheric aerosol chemistry**. Although many of the science issues for future research clearly differed between the two groups, many of the technology and specific capability needs overlapped significantly. Overlapping discussion included the following: importance of optical and other real-time *in situ* methods, a need to study particle nucleation and growth, the need for high-resolution and three-dimensional analysis. Thus, many of the capabilities planned for biogeochemistry and interfacial science will impact aerosol work. An aerosol chamber for detailed chemical analysis of aerosols during nucleation and growth in different environments is listed as an example of a capability being explored primarily for this developing science theme.

Examples of specific near-term and longer-term investments: *Recapitalizing EMSL: Meeting Future Science and Technology Challenges* and the capital acquisition plan provide an overview and timeframe of some capital equipment plans for EMSL. In this section, a few development efforts and major equipment purchases are provided as examples of how specific issues are being addressed.

Design and synthesis of increasingly complex materials – next generation complex oxide synthesis system: Oxygen plasma assisted molecular beam epitaxy had been a major capability in EMSL for award-winning research in catalysis, geochemistry and biogeochemistry, photochemistry, and spintronic materials. Major development is needed for precise control of atomic fluxes to allow the synthesis of complex films with well-controlled quantities of dopants and trace components.

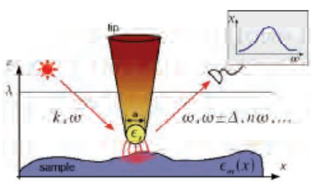
The technology needed for this level of control is just being developed. The major challenge for the development of this new instrument is the control of deposition flux to a degree not currently possible with existing technologies. To this end, the PNNL Laboratory Fellow Scott Chambers is working with other groups and vendors to develop a next-generation method for monitoring and controlling the flux of minor species so that there will be unprecedented control for dopant levels in complex oxides.

Characterization of surfaces and interfaces with unprecedented resolution: Because no one instrument or capability provides the range of information needed in this area, this need will be addressed by adding new equipment and linking instruments and analysis.

In FY 2008, EMSL added a dual beam scanning electron microscope/focused ion beam (FIB/SEM) to the microscopy suite. This instrument is helping meet these resolution needs in the following ways:

- The combination of ion milling and electron imaging allows three-dimensional analyses of natural and synthesized materials. This approach is being used to map interfaces and pores in a natural mineral system.

- Selection and extraction of specific regions of a model or engineered or natural material for detailed analysis. This capability has been used to examine the phase changes in specific regions of fuel cells to understand aging and prepare selected area samples for transmission electron microscope (TEM) or even Auger analysis.

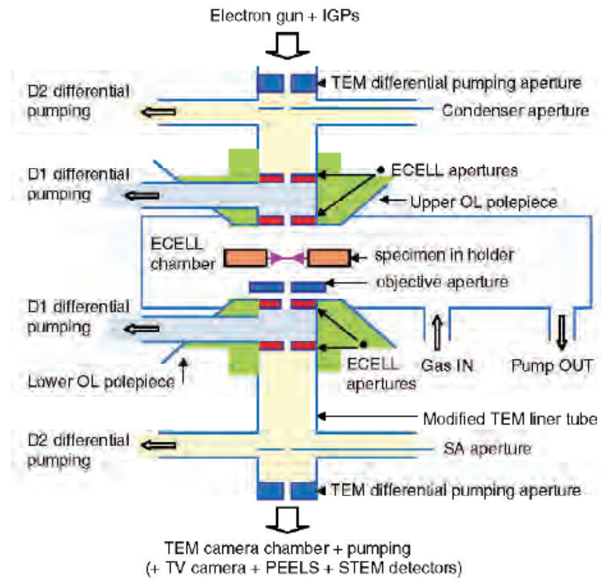


General concept of scattering-type near-field optical microscopy (*s*-SNOM) for spectroscopic nano-imaging.

New capabilities are planned to combine scanning probe microscopy (SPM) and optical measurements to enable high-resolution chemical and morphological analysis of surfaces. Professor Markus Raschke of the University of Washington has been using the EMSL FIB/SEM capabilities to design scanning transmission microscope (STM) tips with specific shapes to optimize the electric field for field enhanced optical measurements. He has worked with EMSL staff to prepare a partner proposal that would meet one of the objectives for future years. Although this general concept is not new, Professor Raschke has significantly advanced the technology and has the knowledge to work with EMSL to create a robust, high-quality tool that will be a significant addition to EMSL.

Other high-resolution capabilities planned or under consideration include NanoSIMS, TEM, and a SPM-based single site chemistry system. The NanoSIMS had the distinction of being a specific instrument recommended by the study groups for each science theme at the EMSL capability workshop. Although a single site chemistry capability was recommended by workshop participants, the details and approach were not. A team of experts began by determining what would enable a truly advanced instrument to be available for EMSL and drafted a concept paper, which includes the use of low-temperature scanning probe technology, hyperthermal molecular beam capability (such as currently used by Bruce Kay and Zdenek Dohnalek in EMSL), and a high-pressure cell for catalytic studies. This approach builds on capabilities and approaches in use in EMSL and combines them in new ways to propose next-generation capabilities.

Moving from statics to dynamics in native environments: Several types of capabilities are being included in EMSL to conduct an expanded range of experiments in increasingly realistic conditions and/or under dynamic conditions. A microbeam x-ray diffraction system has been installed and is being used to examine samples without air exposure and to follow some reactions and phase transformations as they occur.



Schematic drawing of TEM with internal environmental cell.

EMSL is procuring an aberration corrected TEM (Chemical TEM) designed for conducting measurements in gas and liquid environments. This is a DOE major item of equipment and money for this instrument became available in February 2008. This TEM is expected to include an electron monochrometer and an image corrector. These capabilities will allow details of the microstructure, defects sites, and catalyst chemistry to be examined at temperatures as high as 1000°C at pressures up to 20 Torr and enable high-resolution electron energy loss data to be collected that will enable distinguishing the chemical states of transition metals. We also plan to take advantage of the developing microtechnology of TEM probes to produce liquid cells.

In situ TEM measurements are becoming increasingly important in many areas. Chongmin Wang is developing a TEM probe on which a model of a lithium battery can be constructed so that the phase changes and degradation processes can be studied.

Schematic diagram of microtechnology-based liquid cell attached to a TEM probe.

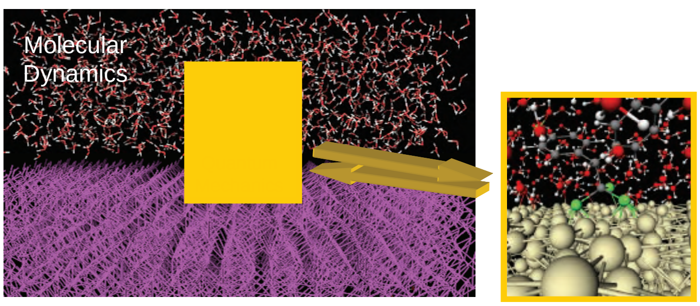
The importance of detailed *in situ* real-time study of particle nucleation and growth was highlighted in interfacial (related to nanoparticles) and atmospheric aerosol chemistry in the 2006 EMSL workshop on capabilities in molecular sciences. A white paper on a system for nucleation and growth of aerosols, with plans for detailed examination of aerosol chemistry and the impact of environmental changes and contaminants, is being developed.

Other capabilities in development or planned with *in situ* focus include new optical methods (including Raman, infrared, and non-linear optical capabilities in appropriate environmental chambers), and novel probes for NMR (version 1 now being tested).

Rapidly linking theory with experiment: Two current development projects deal with linking theory and experiment: one dealing with faster and improved data analysis, and the second, the ability to apply fundamental chemistry codes to surfaces.

We are developing a way to provide **near real-time data analysis** of x-ray photoelectron spectroscopy (XPS) data. We expect that the approach can be extended to other systems. Users place a high demand on our XPS capability for several reasons. Our capability uses best practices. We have considerable expertise in system operation and analysis. Most of the experiments conducted are not routine in one or more ways that may involve experimental design, sample handling, or data analysis.

We have concluded that it is possible to use approaches developed by Professor James Castle (University of Surrey) and others to both improve the routine data analysis conducted and to enable many of these analyses to be computed and reported almost as quickly as the data is collected. At the moment, data may be analyzed hours or days after the experiment. By having a routine rapid analysis that contains more information, users will get needed information much more rapidly, and it may be possible to end or redirect experiments as they are being done.



Conceptual image showing a hybrid *ab initio* molecular dynamics calculation of an organic molecule with a solid surface covered with liquid water. The method combines bond making or breaking in the quantum mechanics level (inset) with the affect of the solid and liquid parts treated with molecular mechanics methods. Advanced versions of this approach have been implemented into *NWChem* and can be used to study reactions in liquids or at surfaces.

The rigorous chemical calculations that have been done using the EMSL ***NWChem*** codes are being extended to be more applicable to **surfaces and interfaces**. Modeling the chemistry in the condensed phase and at complex interfaces requires the use of methods that scale effectively with the system size, and the development of approaches that enable the coupling of scales ranging from atoms to macroscopic systems. Current developments in *NWChem* are focused on the coupling of high-accuracy quantum chemical methods and *ab initio* dynamics methods with molecular mechanics and continuum methods to describe chemical processes on extended systems. In addition, work is underway to improve parallel performance to enable researchers to study larger complex interfaces using EMSL's supercomputer.

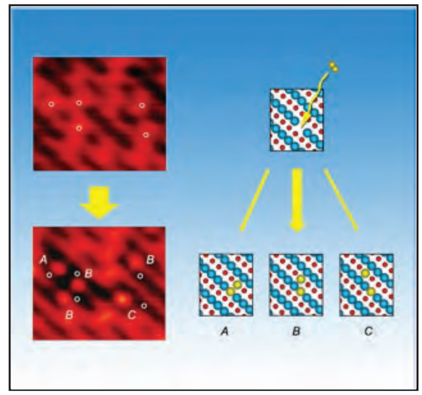
Selected SIP highlights

These highlights have been selected from a variety of sources, both internal and external to EMSL and Pacific Northwest National Laboratory (PNNL).

Topical Area – Oxide Films, Oxide Surface Chemistry, and Oxide Catalysis

A focus on oxide surface and film chemistry has been a major part of the history of EMSL and is a major area of EMSL user activity.

Oxygen atoms display novel behavior on common catalyst



Migration of "hot" oxygen atoms on the surface of a catalyst was featured on February 2008 cover of *The Journal of Physical Chemistry C.*

Like waltzing dancers, the two atoms of an oxygen molecule usually behave identically when they separate on the surface of a catalyst. However, new research from EMSL reveals that on a particular catalyst, the oxygen atoms act like a couple dancing the tango: one oxygen atom plants itself while the other shimmies away, probably with energy partially stolen from the stationary one.

Scientists from EMSL and PNNL discovered this unanticipated behavior while studying how oxygen interacts with reduced titanium oxide, a popular catalyst and a model oxide. Their research began with a slice of titanium oxide crystal, oriented so that titanium and oxygen atoms line up on the surface in alternating strips, forming titanium troughs between oxygen rows. By heating the sample, the team created surface imperfections or spots where an oxygen atom vacated its row. Using scanning tunneling microscopy, the researchers found that molecular oxygen only broke apart when it encountered a vacancy.

The team also expected one of the atoms to make the vacancy its home, and the second to situate itself right next to its former partner. Instead, the scientists found that the mobile oxygen atom, called a "hot" atom, moved one or two crystal lattice spaces away. Among all events the team observed, more than three quarters of the hot atoms hopped one or two spaces away before becoming mired on the surface.

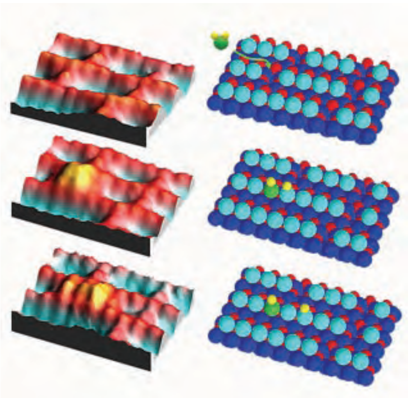
The team postulated that the hot atom may get the energy to move from the rearrangement of the bonds within the oxygen molecule and between the oxygen atom and titanium surface. The calculated energy from these sources was about two to three times that needed to get an immobilized oxygen unstuck. "This finding may be important in surface reactivity. We don't know yet," EMSL's Igor Lyubinetsky, lead investigator, says.

The chemical event could, for example, be affected by the extra energy the oxygen atom possesses. The effect might also play into whether surface oxygen atoms interfere with the chemistry between the catalyst and other chemicals. In any event, the result will keep chemists tangoing with new questions for a long time.

Citation: Du Y, Z Dohnalek, and I Lyubinetsky. 2008. "Transient Mobility of Oxygen Adatoms upon O_2 Dissociation on Reduced TiO_2(110)." *Journal of Physical Chemistry C* 10.1021/jp077677u.

Hopping hydrogen

Researchers at PNNL and the University of Texas at Austin discovered that a single hydrogen atom will not remain stationary after it splits from a water molecule on the surface of the catalyst rutile titanium oxide. The hydrogen atom hopscotches across the oxygen atoms that stud the surface of the catalyst, while the hydrogen on what is left from water remains fixed, suggesting that the electronic structure of this popular catalyst is not entirely as it seems.



A scanning tunneling microscope (left) shows the atoms on the catalyst's surface before (top), during and after (bottom) water adsorption. The red ridges represent oxygen atoms; the light blue valleys, titanium atoms. The yellow ridges represent hydrogen atoms that have split from the water molecule. On the right is a model showing water splitting.

By understanding how water's atoms behave on this catalyst's surface, scientists and engineers may be able to develop more efficient solar cells, corrosion-resistant materials, and technologies that split water to generate hydrogen gas, which is a possible alternative fuel for everything from heating homes to powering automobiles.

Citation: Zhang Z, O Bondarchuk, BD Kay, JM White, and Z Dohnalek. 2006. "Imaging Water Dissociation on TiO_2(110): Evidence for Inequivalent Geminate OH Groups." *The Journal of Physical Chemistry, Part B* 110:21840-21845.

Topical Area – Catalysis

Both fundamental and applied catalysis research, sometimes related to oxide surfaces, has been a long-standing component of EMSL scientific activities.

Institute for Interfacial Catalysis

[*Sections excerpted from the article "National lab leverages its assets and diverse expertise for basic and applied research" published in the November 19, 2007, edition of C&E News*.]

Pacific Northwest National Laboratory hasn't deliberately kept its catalysis prowess a secret. It just kind of turned out that way. But these days the lab is on a mission to spread the word about its highly successful catalysis programs.

Tucked away in southeastern Washington in the quiet town of Richland, PNNL has been the site of focused efforts in catalysis research for decades. "Catalysis goes back a long way here," says Charles H. F. (Chuck) Peden, interim director of the lab's Institute for Interfacial Catalysis (IIC). "We've had major programs in applied catalysis since the 1970s," he says. "They were big efforts but almost unknown outside of the lab."

The lab's strength in catalytic chemistry wasn't kept under wraps for reasons of national security or to prevent leaks of sensitive information. Rather, as Peden explains, in the early days, catalysis researchers at PNNL were focused on applied projects that simply didn't lend themselves to going to scientific meetings and conferences and reporting on the results. "Plenty of reports describing that work were written for the Department of Energy," Peden insists, "but the catalysis world hardly heard about any of it."

Nonetheless, word that PNNL is a good place to study catalysis got around, and the lab managed to build research groups with expertise in several areas. Among those are fundamental catalysis science and the use of a variety of computational and experimental tools and techniques including surface spectroscopy. Also included are automobile emissions cleanup, biomass conversion, and catalytic microreactor development. The microreactor technology has been commercialized by Ohio-based Velocys, which markets the energy-efficient and space-saving chemical reactors to companies in the energy and chemicals sectors.

Turning Over On A Dime. Developed at PNNL, this catalytic microreactor converts methanol into CO and H_2 for use in mini fuel cells or elsewhere and includes vaporizers, steam reformers, and combustors.

In Peden's view, one of the key factors that helped raise the lab's profile was the success of the EMSL at PNNL. EMSL is a large national user facility at which a host of experimental and computational resources is available to the public—on a peer-reviewed proposal basis—for studying a broad range of molecular science topics, many of which are essential to catalysis. The Richland laboratory was a natural venue for EMSL because molecular sciences have been a strong suit of PNNL since day one.

Forty years ago, the lab was established to address the nuclear chemistry and chemical engineering research needs that stemmed from production of plutonium at the adjacent DOE Hanford Site, says Douglas Ray, PNNL associate laboratory director for fundamental and computational sciences. Today, only about 15 percent of PNNL's operations are devoted to chemical separations of radioactive materials and related topics, he says. Yet PNNL remains firmly rooted in the molecular sciences.

"One of the features that distinguishes PNNL from the other DOE national labs is the focus on chemistry and chemical engineering," Ray stresses. In contrast, physics dominates the scientific disciplines at the other DOE labs. Among PNNL's scientists and engineers, some 40 percent were trained in the molecular sciences, including chemistry, chemical engineering, biochemistry, geochemistry, and related areas, Ray notes. Peden adds that the lab's strength in catalysis, an interdisciplinary molecular science, "follows naturally from that chemistry foundation."

An area of concentrated catalysis research at PNNL is biomass conversion. Senior scientist Conrad Zhang, staff scientist Johnathan E. Holladay, postdoctoral associate Haibo Zhao, and their coworkers take advantage of high-throughput-screening methods to optimize reaction conditions and to find effective catalysts that convert sugars and other biomass derivatives into 5-hydroxymethylfurfural, a valuable chemical intermediate.

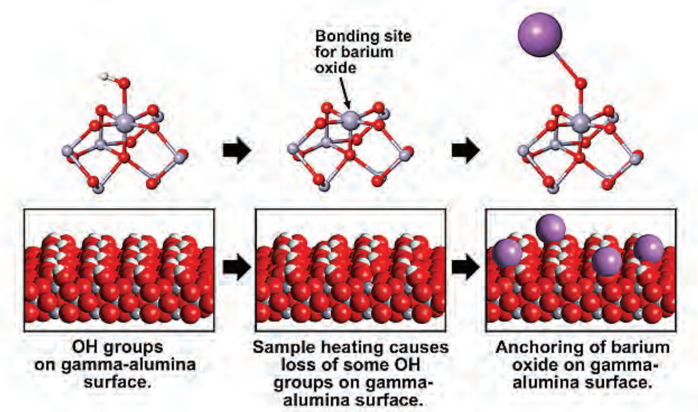
Numerous other high-end instruments in EMSL and in other PNNL laboratories stand ready to reveal subtle details of catalyst properties. In one such example, Peden and coworkers determined via ultrahigh magnetic field NMR methods that previously unobserved penta-coordinated Al^{3+} ions are hot spots for catalyst nucleation on γ-alumina (*J. Catal.* 2007, 251, 189) [See next highlight]. That material is widely used as a catalyst support in petroleum refining and automotive emissions control applications.

900-MHz NMR enables novel catalysis studies

The ability to tailor catalysts one atom at a time is a step closer to reality, in part, because of the 900-MHz NMR spectrometer at EMSL. Researchers from the Institute for Interfacial Catalysis (IIC) at PNNL have used the 900-MHz NMR to generate the highest resolution spectra ever obtained of a common catalyst support and observed, for the first time, how the support interacts with a catalyst at the atomic scale.

To really understand catalysts, they must be studied in molecular and atomic detail. Peering closely, the IIC team, led by PNNL's Chuck Peden, characterized a model system of the common γ-alumina support, γ-Al_2O_3, and the catalyst, barium oxide (BaO). γ-alumina materials serve as a support material for many catalysts, including BaO. Because BaO absorbs nitrogen oxides (NO_x)—a family of vehicle emissions products—the model system is a promising combination for emissions control.

Despite the importance of γ-alumina materials, technology has previously not allowed detailed studies of them. Peden said, "The chemical properties of γ-alumina compounds are such that using traditional surface structure techniques to study them is not feasible. EMSL's 900-MHz NMR allowed us to perform studies not possible before."

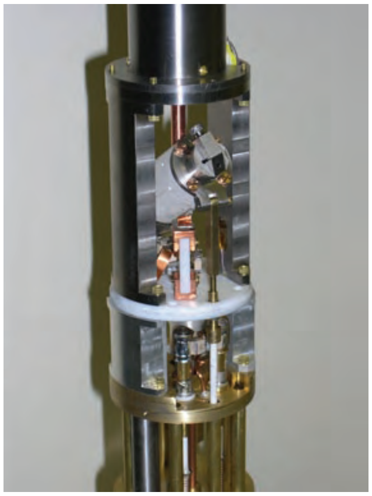


Using the 900-MHz NMR, Peden and his team obtained the highest resolution NMR spectrum of γ-Al_2O_3 known to date. They also observed, for the first time, where and how a catalytically active phase (BaO) interacts with the surface of an aluminum oxide as the catalyst is being synthesized. The team's data suggest that five-fold coordinated Al^{3+} ions form a nucleation site on the surface of γ-Al_2O_3 on which BaO molecules collect. In fact, changes in the NMR spectra obtained using varying levels of BaO showed a nearly mole-per-mole correlation between the penta-coordinated Al^{3+} ions consumed and catalyst deposited.

Peden presented his findings at the AVS 54th International Symposium in Seattle. In future studies, the team will examine the interaction of γ-Al_2O_3 with other metal and metal-oxide particles of catalytic interest to determine if penta-coordinated Al^{3+} ions are nucleation sites for other catalysts.

Citation: Kwak JH, JZ Hu, DH Kim, J Szanyi, and CHF Peden. 2007. "Penta-Coordinated Al^{3+} Ions as Preferential Nucleation Sites for BaO on γ-Al_2O_3: An Ultra-High-Magnetic Field ^{27}Al MAS NMR Study." *Journal of Catalysis* 251:189-194.

Constant flow: Novel probes that revolutionize in situ NMR investigations of catalysts and reaction intermediates



CF-MAS probe used to study *in situ* catalytic reactions at temperatures up to 400°C.

Leveraging the experience gained in designing and building the discrete magic angle turning probe series, we have built a new 9.5-mm, 400°C, constant-flow, magic-angle-spinning (CF-MAS) probe to study *in situ* catalytic reactions. This probe, designed to operate while the rotor spins at several kHz, will permit NMR studies of steady-state flow of gaseous reactants over a catalyst bed at temperatures up to 400°C. The CF-MAS probe will be used initially to study the carbonylation of dimethyl ether to methyl acetate on mordenite. The ability to use NMR spectroscopy to examine reactants, intermediates, catalysts, and products under normal reaction conditions will greatly expand our knowledge of catalytic processes.

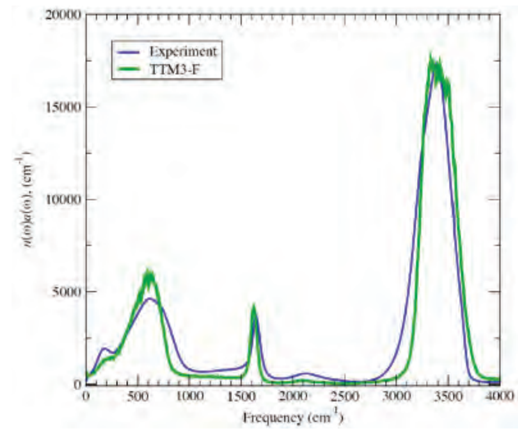
This probe had been developed as part of the EMSL capability and staff development effort. It has been built and tested, and the first catalysis experiments are in progress. Patent submitted.

Topical Area -- Water/hydration/oxide or Particle/Water Interface

One molecule at a time

New model deciphers the hydrogen bonding network in different water environments

The infrared spectra of liquid water obtained by experimentation map closely to results from the new computational model.



The infrared spectra of liquid water obtained by experimentation map closely to results from the new computational model.

A new, improved computational model that describes the structure and dynamics of water molecules in both small assemblies and the liquid has been developed at PNNL by Sotiris Xantheas and George Fanourgakis. Known as TTM3-F, the new model represents a significant improvement over currently available ones by providing a better description of the interactions and the spectroscopic signatures of water molecules in different environments.

Understanding water at the molecular level is essential to advancing frontiers in such areas as aqueous chemistry, hydrogen generation and storage, and the transport of contaminants in surface and subsurface environments.

“Until now, no model could as fully describe the vibrations of water molecules, from a single water molecule and small water clusters, to liquid water, ice and clathrate hydrates,” Xantheas said.

The scientists used the results of high-level electronic structure calculations on water clusters performed previously at two institutions to frame the new model. The results came from EMSL and the National Energy Research Scientific Computer Center at Lawrence Berkeley National Laboratory.

To model the vibrational spectra, the researchers incorporated the novel idea that interaction with the surrounding water molecules makes the dipole moment (the location of a molecule’s positive or negative charge) of a single water molecule in a condensed phase environment qualitatively and quantitatively different than the corresponding dipole moment in the gas phase. Inclusion of this information in TTM3-F enabled better alignment with the observed infrared spectra.

The team then tested the new model by measuring the average structure and other thermodynamic and transport properties of liquid water. The close agreement of the results of the simulation with the experimental ones validated the model’s effectiveness.

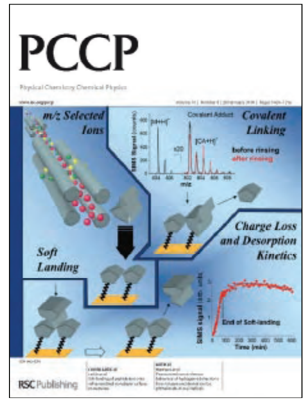
The researchers are enhancing TTM3-F to include the interactions of water with positive or negative ions of lithium, sodium, fluorine, chlorine and other elements, as well as to further study the structure and spectroscopic features of aqueous interfaces. Recipient of a reintegration grant from the European Union, Fanourgakis is now with the Institute for Electronic Structure and Laser at the University of Crete, Greece, and continues to participate in the water model collaboration.

Citation: Fanourgakis GS and SS Xantheas. 2008. "Development of Transferable Interaction Potentials for Water. V. Extension of the Flexible, Polarizable, Thole-Type Model Potential (TTM3-F, v. 3.0) to Describe the Vibrational Spectra of Water Clusters and Liquid Water." *Journal of Chemical Physics* 128:074506.

Topical Area – Synthesis, Characterization, and Properties

The design, synthesis, and characterization of particles, films, interfaces, and surfaces for specific properties are important components of EMSL. The synthesis and characterization activities permeate most of the activity areas of the SIP science theme, including the growth of oxide films for the surface chemistry, catalysis, and magnetic properties research.

Research on soft landings glides onto cover of top physics journal



EMSL users, Julia Laskin, Omar Hadjar, and Peng Wang, show that the complex science of softly depositing small proteins on a surface is both beautiful and informative. The images they provided for an invited review article on the current understanding of soft-landing phenomena grace the cover of the February 28, 2008, issue of *Physical Chemistry Chemical Physics*. The accompanying article has been rated number 7 by the Institute of Scientific Information for its impact in atomic, chemical, and molecular physics.

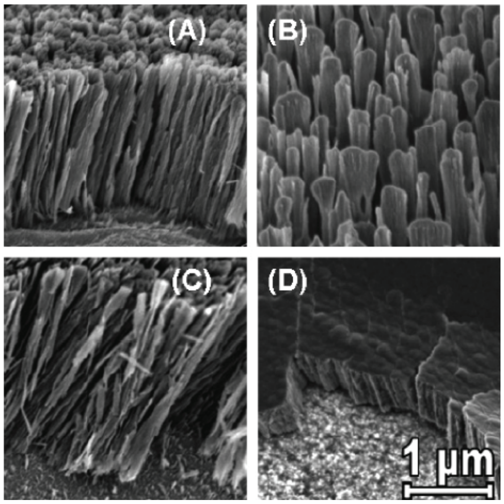
The soft-landing experiments use mass spectrometry as a separation technique for preparing novel materials and exploring reactivity at interfaces. Soft landing of low-energy complex ions provides a convenient and flexible platform for tailoring properties of substrates and opens new opportunities for preparing extremely pure, uniform layers of molecules on surfaces that could lead to better sensors and new biomaterials.

Further, studies of depositing biomolecules on substrates will also help to obtain a molecular-level understanding of the interactions of peptides and proteins with hydrophobic and hydrophilic surfaces. This research is relevant to transporting biomolecules through membranes in organisms and determining binding energies between biomolecules and model surfaces in the absence of solvents.

Citation: Laskin J, P Wang, and O Hadjar. 2008. “Soft-Landing of Peptide Ions onto Self-Assembled Monolayer Surfaces: An Overview.” *Physical Chemistry Chemical Physics* 10:1079-1090. DOI: 10.1039/b712710c.

Image reproduced by permission from Julia Laskin, Omar Hadjar, and Peng Wang and the Royal Society of Chemistry from Laskin J, P Wang, and O Hadjar. 2008. “Soft-Landing of Peptide Ions onto Self-Assembled Monolayer Surfaces: An Overview.” *Physical Chemistry Chemical Physics* 10(8):1069-1216.

Reactive ballistic deposition of porous TiO_2 films: Growth and characterization



SEM images of TiO_2 films deposited via RBD. (A) Top and (B) side views of a film grown at 300K and at a deposition angle of 85°. (C) Side view of a film grown at 100K and 85°, (similar in appearance to the film grown at 300K). (D) Side view of a film grown at 300K and at 70°.

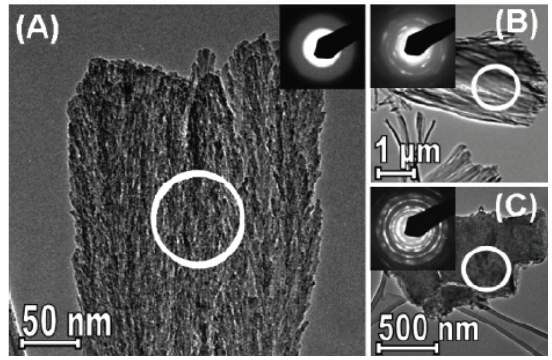
Titania (TiO_2) is widely used as a catalyst and may provide a pathway for the use of solar radiation as a viable source of clean energy. This work describes a method to create nanoporous TiO_2 films with a combination of high surface area and thermal stability that could serve as supports for applications in heterogeneous catalysis.

As a material, TiO_2 has attracted much attention because of its uses in a wide range of applications such as heterogeneous catalysts, gas sensors, photocatalysts, optical coatings, and pigments. Correspondingly, it is the most studied metal oxide in surface science. Recently, there has been great interest in the growth and chemical characterization of metal-oxide-supported metal particles and thin films as model systems for industrial catalytic systems. These films are of interest from the aspect of fundamental chemistry as well as for the study of surfaces that better emulate those employed in industrial catalytic systems.

This study explored high-surface-area, porous TiO_2 thin films that were grown using reactive ballistic deposition (RBD) and glancing angle deposition techniques. Prior work showed that these techniques can produce highly porous, high-surface-area metals, metal oxides, and other materials. The techniques are based on a simple shadowing model. At glancing angles, random height differences that arise during the initial film growth can block incoming flux essentially creating shadows that result in void regions in the shadowed region. If surface and/or bulk diffusion are slow compared to the incident flux (i.e., if the molecules "hit and stick"), then the voids remain unfilled. Continued deposition results in porous films with filamentous columnar morphologies. Varying degrees of film porosity can be achieved by varying the deposition angle and substrate temperature.

The figure shows scanning electron microscopy (SEM) images for a 750-ML thick TiO_2 film deposited 85° from substrate normal and at a sample temperature of 300K. The images confirm that the film consists of an array of separated filaments that grow toward the physical vapor deposition source. Image C shows a film deposited at 85° and 100K; the image of this film appears to be very similar to the film grown at 300K (images A and B). The images indicate that an increase in temperature from 100 to 300K does not increase the mobility of ad-atoms enough to affect the morphology of the film. Image D shows a film deposited at 70° and 300K. Decreasing the deposition angle from 85° to 70° has a dramatic effect on film structure as seen in image D. On this length scale, a film deposited at 70° appears dense, but films deposited at this angle actually prove to have the greatest surface area as was confirmed using nitrogen adsorption.

Transmission electron microscopy (TEM) analysis of filaments scraped from a tantalum plate and placed on amorphous carbon grids was performed. The filaments grown at both 100 and 300K reveal nanoscale features within the filaments when viewed under high magnification (image A). Selected area diffraction of individual filaments indicates that the filaments are predominantly amorphous; however, in some cases, randomly oriented groups of filaments display the well-defined diffraction patterns seen in images B and C. D-spacing values extracted from these selected area diffraction patterns are indicative of the rutile phase.



TEM images of TiO_2 films accompanied by insets with SAD. (A) A single amorphous filament from a film deposited at 85° and 300K. (B) A cluster of filaments from the same film as (A) displaying a SAC pattern corresponding to polycrystalline rutile TiO_2. (C) A portion of a film grown at 70° and 300K with a high degree of crystallinity.

This work confirms that nanoporous, high-surface-area TiO_2 films can be synthesized by reactive ballistic deposition of titanium metal in under oxygen ambient conditions. The SEM and TEM results show that the films consist of arrays of separated filaments. The surface area and the distribution of binding site energies of the films were measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption of nitrogen. We found that TiO_2 films deposited at 50K and 70° display the greatest specific surface area (100 m^2/g). In addition, the films retain greater than 70 percent of their original surface area after annealing to 600K. The combination of high surface area and thermal stability suggests that these films could serve as supports for applications in heterogeneous catalysis.

Citation: Flaherty DW, Z Dohnálek, A Dohnálkova, BW Arey, DE McCready, N Ponnusamy, CB Mullins, and BD Kay. 2007. “Reactive Ballistic Deposition of Porous TiO_2 Films: Growth and Characterization.” *Journal of Physical Chemistry C* 111:4765-4773.

Topical Area – Energy and the Environment

The design of materials with specific surface and interfacial behaviors relevant to clean energy production or environmental remediation is a growing user activity in EMSL.

Probing reaction pathways using in situ ^{1}H NMR spectroscopy

In collaboration with Professor Leon Shaw's group from the University of Connecticut, researchers from PNNL used *in situ* variable temperature ^{1}H NMR spectroscopy to observe the products produced during controlled conditions. The results gave direct evidence of the two-step reaction pathway for evolution of H_2 in the dehydrogenation reaction:

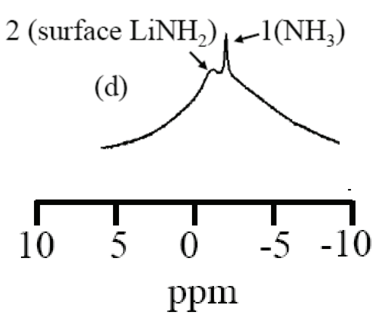
$$LiNH_2 + LiH = Li_2NH + H_2 \tag{1}$$

This Li-N-H system, first reported by Chen et al., has been extensively investigated as potential hydrogen storage material. It was shown that decomposition is rapid in the order of 25 milliseconds, and several studies have hinted that a two-step mechanism existed (see equations 2 and 3).

$$LiNH_2 = 1/2Li_2NH + 1/2NH_3 \tag{2}$$

$$1/2NH_3 + 1/2LiH = 1/2\ LiNH_2 + 1/2H_2 \tag{3}$$

Results from this *in-situ* experiment at EMSL resulted in definitive direct evidence for the two-step mechanism.



^{1}H spectrum of $LiNH_2$ power acquired at 30°C, which highlights the molecules attributed to surface $LiNH_2$ and the NH_3 released at 30°C.

During the variable temperature *in-situ* NMR experiment performed on a powder sample of $LiNH_2$ that was prepared using high-energy ball milling, three separate peaks were identified in the subsequent ^{1}H spectra (see figure). These peaks verified the existence of bulk $LiNH_2$, surface $LiNH_2$, and gaseous NH_3. All assignments were assisted by understanding the connection of line width to molecular motion. In particular, fast motion on the NMR time scale leads to narrow lines and rigid slow motion to wide lines.

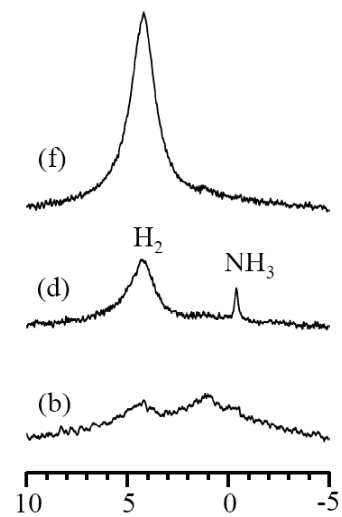
Changing the temperature conditions shows that NH_3 was released slowly at 30°C and the speed of ammonia release significantly increased at temperatures above 75°C.

The variable temperature *in situ* NMR experiments (see figure) on a powder sample consisting of a mixture of $LiNH_2$ + LiH that was mechanically activated via high-energy ball milling reveals the observation of NH_3, indicating that reaction (3) is not very fast until temperatures above 150°C are reached and that the minimum temperature required activating reaction (2) is lower than the temperature required to activate reaction (3). The appearance of the NH_3 peak (d, in the figure) and the disappearance of the NH_3 peak (f, in the figure) clearly confirm the two elementary reaction steps (i.e., NH_3 is generated first by $LiNH_2$ [see Equation (2)] and then NH_3 reacts with LiH to release H_2 [Equation (3)]).

The *in situ* techniques developed here serve to illustrate the potential application of a relatively simple approach that will enable the real-time observation of mechanistic data and performance evaluation in future hydrogen storage material studies.

Citations: Chen P, Z Xiong, J Luo, J Lin, and KL Tan. 2002. "Interaction of Hydrogen with Metal Nitrides and Imides." *Nature* 420(6913):302-304.

Hu JZ, JH Kwak, Z Yang, W Osborn, T Markmaitree, and LL Shaw. 2008. "Probing the Reaction pathway of Dehydrogenation of the $LiNH_2$ + LiH Mixture using *in situ* ^{1}H NMR Spectroscopy." *Journal of Power Sources* 181(1):116-119.



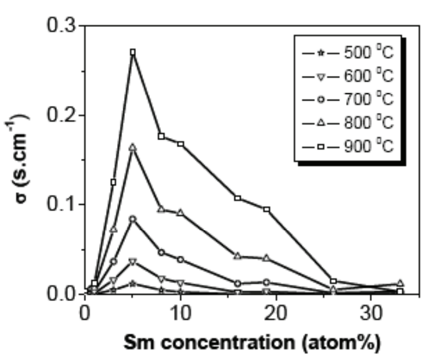
Representative *in situ* ^{1}H NMR spectra of the $LiNH_2$ + LiH samples. Spectrum (f) was acquired then the temperature was ramped from 150°C to 180°C (no NH_3 peak observed). Trace Spectrum (d) was acquired when the temperature was ramped from approximately 40°C to 150°C. Both the NH_3 product from Equation 2 and the H_2 product from Equation 3 are observed. Spectrum (b) was acquired at room temperature.

Conductivity of oriented samaria-doped ceria thin films grown by oxygen plasma assisted molecular beam epitaxy

Because of global demands for increased energy resources and sustainable and renewable alternative energy, technologies such as solid-oxide fuel cells (SOFCs) are becoming the significant focus of researchers across the globe. In an effort to make this technology economically and practically viable for everyday use, it is of paramount importance for researchers to understand the fundamental aspects that control the performance of an SOFC. The heart of the SOFC is the electrolyte material that transports oxygen ions from cathode to anode. High-quality, epitaxial thin films of doped cerium oxide (a potential material for SOFC electrolytes at low and intermediate temperatures) are an excellent resource that allows researchers to explore the fundamental mechanisms that control the ionic conduction in SOFC electrolytes.

Use of conventional powder-processed pellets with porosity and grain boundaries makes analysis more complicated. Oxygen plasma assisted molecular beam epitaxy capabilities housed at EMSL have allowed researchers to synthesize high-quality epitaxial thin films with controlled dopant levels and thickness.

Among the various materials used for low- and intermediate temperature SOFC electrolyte application, samaria (Sm_2O_3, samarium oxide) doped ceria (CeO_2, cerium oxide) (SDC) is expected to be the best possible material. Hence, high-quality epitaxial SDC films were grown on sapphire (0001) substrates.



The conductivity of $Ce_{1-x}Sm_xO_2$*Δ films as a function of samaria concentration for the temperature range of 500 to 900°C.

The grown films were characterized using various *in situ* and *ex situ* techniques to understand their structure, crystalline quality, elemental distribution, and chemical composition (oxidation states of the cations). After establishing the optimum growth conditions, films with various amounts of dopant concentrations were grown (1 to 33 atom% samaria). Electrochemical impedance measurements were carried on these films using a four-probe van der Pauw method. The conductivity data obtained from these measurements were analyzed as a function of temperature and dopant concentration. Some of the salient features from this work are

- Ceria films with more than 10 atom% samaria were found to show polycrystalline features, while the films with less than 10 atom% samaria were found to be epitaxial, highly oriented films.
- Rutherford backscattering spectrometry and x-ray and electron diffraction measurements confirmed the high-quality, epitaxial nature of the films.
- 5 atom% samaria doping was found as an optimum concentration to obtain maximum conductance among various compositions.

- The reduction in the conductivity in films with high dopant concentration is attributed to the polycrystalline nature of the films. In the polycrystalline films, grain boundaries may act as scattering centers for the oxygen ions, hence the observed decrease in the overall conductivity.

- The higher ionic conduction at lower temperatures in the highly oriented SDC films is attributed to the alignment of oxygen vacancies (generated to retain the electrical neutrality of the ceria [$Ce^{4+}O^{2-}$] crystal when doped with Sm^{3+}). The aligned oxygen vacancies help efficiently transport oxygen ions across the electrolyte from cathode to anode.

Various ongoing user research programs at EMSL are focused on exploring the finer details behind these observations and are aimed at developing a comprehensive understanding of the fundamental mechanisms that control the performance of nanoscale doped-oxide materials as potential SOFC electrolyte materials.

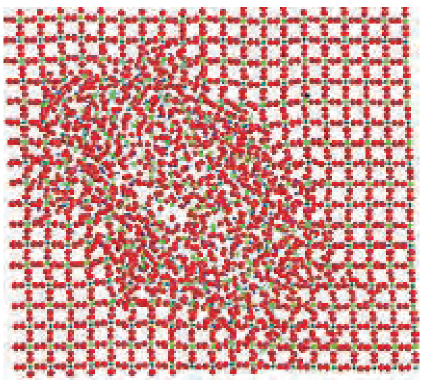
Citation: Yu ZQ, SV Kuchibhatla, LV Saraf, OA Marina, CM Wang, MH Engelhard, V Shutthanandan, P Nachimuthu, and S Thevuthasan. 2008. "Conductivity of Oriented Samaria-Doped Ceria Thin Films Grown by Oxygen-Plasma-Assisted Molecular Beam Epitaxy." *Electrochemical and Solid State Letters* 11(5):B76-B78.

Topical Area – Defects and Radiation

It has become increasingly clear that defects at surfaces, interfaces, and within materials or films play a major role in determining the physical and chemical properties of materials and materials interfaces.

Radiation degrades nuclear waste-containing materials faster than expected

New method enlists NMR spectroscopy to test durability of mineral-based waste forms. Minerals intended to entrap nuclear waste for hundreds of thousands of years may be susceptible to structural breakdown within 1,400 years, a team from the University of Cambridge and PNNL reported in the January 11 issue of *Nature*.



An improved understanding of how alpha particles decay waste forms is leading to enhanced predictive models that support informed decisions on long-term storage of radioactive isotopes. Results of this research, led by a scientific user from the Cambridge University using EMSL's radiological NMR capabilities, were published in *Nature* [445(7124):190-194].

The new study used NMR to show that the effects of radiation from plutonium incorporated into the mineral zircon rapidly degrades the mineral's crystal structure.

This could lead to swelling, loss of physical strength, and possible cracking of the mineral as soon as 210 years, well before the radioactivity had decayed to safe levels, said lead author and Cambridge earth scientist Ian Farnan.

According to current thinking, highly radioactive substances could be rendered less mobile by combining them, before disposal, with glass or with a synthetic mineral at a very high temperature to form a crystal.

However, the crystal structure can only hold the radioactive elements for so long. Inside the crystal radioactive decay occurs, and tiny atomic fragments called alpha particles shoot away from the decaying nucleus, which recoils like a rifle, with both types repeatedly blasting the structure until it breaks down.

This may increase the likelihood for radioactive materials to leak, although co-author William J. Weber, a fellow at PNNL, who made the samples used in the study, cautioned that this work did not address leakage, and researchers detected no cracking. Weber noted that the "amorphous," or structurally degraded, natural radiation-containing zircon can remain intact for millions of years and is one of the most durable materials on earth.

Some earth and materials scientists believe it is possible to create a structure that rebuilds itself after these "alpha events" so that it can contain the radioactive elements for much longer. The tests developed by the Cambridge and PNNL team would enable scientists to screen different mineral and synthetic forms for durability.

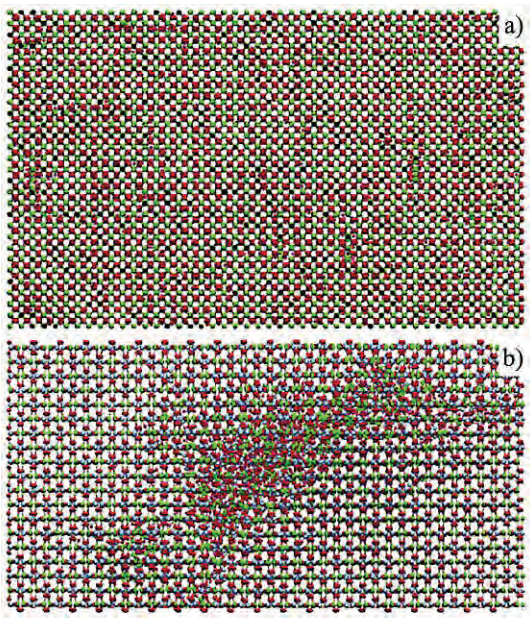
As well as making the storage of the waste safer, new storage methods guided by the NMR technique could offer significant savings for nations facing disposal of large amounts of radioactive material.

Countries including the United States, Britain, France, Germany, and Japan are all considering burying their nuclear waste stockpiles hundreds of meters beneath the earth's surface. Doing so necessitates selection of a site with sufficiently stringent geological features to withstand any potential leakage at a cost of billions of dollars. For example, there is an ongoing debate over the safety of the Yucca Mountain nuclear waste repository site in Nevada. A figure published in *Science* in 2005 put that project's cost at $57 billion.

Citation: Farnan I, HM Cho, and WJ Weber. 2007. "Quantification of Actinide Alpha-Radiation Damage in Minerals and Ceramics." *Nature* 445:190-193.

Ceramic, heal thyself

A new computer simulation has revealed a self-healing behavior in a common ceramic that may lead to development of radiation-resistant materials for nuclear power plants and waste storage.



Simulation shows how defect-engineered zirconia repairs radiation-induced damage in yttria-stabilized zirconia. (Top), the defects produced by radiation are few and far between, having less impact on the properties of the material. (Bottom), in zircon, the defects are clustered, which could compromise the material's integrity.

Researchers at PNNL found that the restless movement of oxygen atoms heals radiation-induced damage in the engineered ceramic yttria-stabilized zirconia.

Scientists Ram Devanathan and Bill Weber modeled how well that ceramic and other materials stand up to radiation. "If you want a material to withstand radiation over millennia, you can't expect it to just sit there and take it. There must be a mechanism for self-healing," said Devanathan.

"This research raises the possibility of engineering mobile defects in ceramics to enhance radiation tolerance," Weber said. He noted that materials capable of handling high-radiation doses also "could improve the durability of key equipment and reduce the costs of replacements."

The researchers approached their investigation in three steps. First, they analyzed yttria-stabilized zirconia, a compound of yttrium and zirconium oxides that contains random structural defects called "vacancies." The defects occur because yttrium has a smaller electrical charge than zirconium. To correct the charge imbalance, zirconia gives up oxygen atoms. But, the loss of these oxygen atoms leaves empty oxygen sites. The remaining oxygen atoms constantly jump in and out of those sites.

"It is like a classroom full of fidgety kids," said Devanathan. "When the teacher turns her back, the kids constantly jump into empty chairs, leaving their own chairs vacant until another kid leaps into the seat."

Next, the scientists simulated an atom undergoing alpha decay. An alpha particle shoots out of the atomic nucleus with such force that the remainder of the atom recoils in the opposite direction. The recoiling atom can cause significant damage to surrounding atomic structures.

Finally, the researchers used data analysis algorithms developed at PNNL to look for atoms knocked out of place. The results showed that displaced oxygen atoms in the yttria-stabilized zirconia "found seats" in the pre-existing vacancies throughout the ceramic.

Although the self-healing activity does not completely repair the material, the defects are less apt to cause problems because they are spread out. This characteristic indicates that yttria-stabilized zirconia, which is used today in such items as solid oxide fuel cells and oxygen sensors, might be suitable for nuclear applications.

The researchers also simulated the impact of radiation on zircon, a ceramic that is a candidate for immobilizing high-level nuclear waste. The simulation defects clustered together in simulations of zircon, changing the properties of the material. “Clustered defects are much more difficult to repair than isolated defects,” Devanathan said.

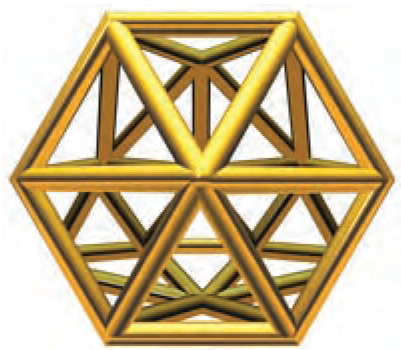
The scientists now are refining the simulations and applying them to other materials.

Citation: Devanathan R and WJ Weber. 2008. “Dynamic Annealing of Defects in Irradiated Zirconia-Based Ceramics.” *Journal of Materials Research* 23(3):593-597.

Topical Area – Clusters and Nanostructured Materials

The physical and chemical properties of clusters, nanoparticles, and other nanostructured materials have become increasingly important both in fundamental studies and as the basis for a variety of important applications. As has been widely noted, interfaces and surfaces play major or dominate roles in determining the properties of these materials. Many EMSL user activities are associated with the synthesis and characterization of clusters or nanostructured materials.

Buckyballs make room for gilded cages



Schematic drawing of a hollow 16-atom gold cluster. Much of the cluster work involves close coupling of experimental measurements understood through theoretical modeling.

Scientists have uncovered a class of gold atom clusters that are the first known metallic hollow equivalents of the famous hollow carbon fullerenes known as buckyballs.

The fullerene is made up of a sphere of 60 carbon (C) atoms; gold (Au) requires many fewer—16, 17 and 18 atoms, in triangular configurations more gem-like than soccer ball. At more than 6 angstroms across, or roughly a ten-millionth the size of this comma, they are nonetheless roomy enough to cage a smaller atom.

"This is the first time that a hollow cage made of metal has been experimentally proved," said Lai-Sheng Wang, the paper's lead corresponding author.

Wang is an affiliate senior chief scientist at PNNL and professor of physics at Washington State University. The experiments were buttressed and the clusters' geometry deciphered from theoretical calculations led by Professor Xiao Cheng Zeng of the University of Nebraska and co-corresponding author.

Wang, who worked in the Richard Smalley lab that gave the world buckyballs, is part of a large cluster of researchers who have spent much of the past decade attempting to find the fullerene's kin in metal. But their search has proved difficult because of metal clusters' tendency to compact or flatten.

Experiments at EMSL elicited the photoelectron spectra of clusters smaller than Au-32, which had been theorized as the gold-cage analog to C-60 but ruled out by Wang's group in an experiment that showed it as being a compact clump.

They instead turned their attention to clusters smaller than 20 atoms, which earlier work by Wang's group showed were three dimensional—a golden pyramid, no less—but larger than 13 atoms, known to be flat. The spectra and calculations showed that clusters of 15 atoms or fewer remained flat but that all but one possible configuration of 16, 17, and 18 atoms open in the middle. At 19 atoms, the spaces fill in again to form a near-pyramid.

"Au-16 is beautiful and can be viewed as the smallest golden cage," Wang said. He pictures it as having "removed the four corner atoms from our Au-20 pyramid and then letting the remaining atoms relax a little," and thus opening up space in its center.

It and its larger neighbors are stable at room temperature and are known as "free-standing" cages—unattached to a surface or any other body, in a vacuum. "When deposited on a surface, the cluster may interact with the surface and the structure may change."

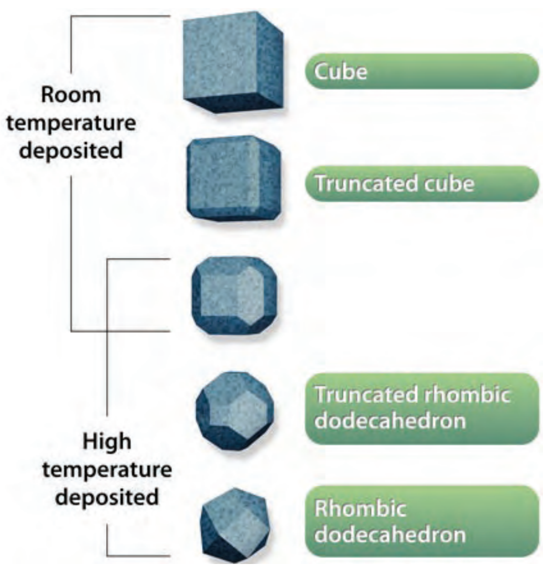
Wang and his co-workers suspect "that many different kinds of atoms can be trapped inside" these hollow clusters, a process called "doping."

"These doped cages may very well survive on surfaces," suggesting a method for influencing physical and chemical properties at smaller-than-nano scales, "depending on the dopants."

Wang's group has not yet attempted to imprison a foreign atom in the hollow Au cages, but they plan to try.

Citation: Bulusu S, X Li, LS Wang, and X Zeng. 2006. "Evidence of Hollow Golden Cages." *Proceedings of the National Academy of Sciences of the United States of America* 103(22):8326-8330. (46 citations)

EMSL capabilities instrumental in nanoparticle size study



EMSL capabilities such as transmission electron microscopy were instrumental in studying nanoparticles created at room temperature. The particle size dependent properties can be valuable in applications such as drug delivery and remediation.

A research team from the EMSL, PNNL, and University of Idaho has used room-temperature methods, instead of traditional high temperature methods, to create metallic-iron nanoparticles with varying shapes. Oxide and metallic iron nanoparticles with size-dependent properties could be valuable for applications such as medical imaging, drug delivery, information storage, and groundwater remediation.

The research, featured on the cover of the June 25, 2007, issue of *Nanotechnology*, involved formation of the particles using a sputter-gas-aggregation method at room temperature in labs at the University of Idaho. The particles were then delivered to EMSL and analyzed using transmission electron microscopy, electron diffraction, and Wulff shape construction.

The room-temperature-deposited nanoparticles were found to have three distinct structures: 1) a simple six-sided cube, a shape not seen in high-temperature formations; 2) a truncated cube, which looks like a cube with each of the edges shaved off; and 3) a rounded shape composed of 12 hexagons and 6 squares, a shape researchers have seen when particles are formed at higher temperatures.

"These new shapes expose high-energy surfaces to the environment," said EMSL Lead Scientist for Interfacial Chemistry, Don Baer, who is co-author of the paper. Particles created at high-temperature expose low-energy surfaces. The high-energy surfaces change the reactivity and magnetism of the particles.

The results, combined with those already reported, suggest that by using a low-temperature process, the synthesis parameters can be altered to select particle shape with the possibility of optimizing particles for specific chemical or magnetic properties. The researchers are now working to produce enough particles in specific shapes so that they can examine the particles' magnetic and chemical properties.

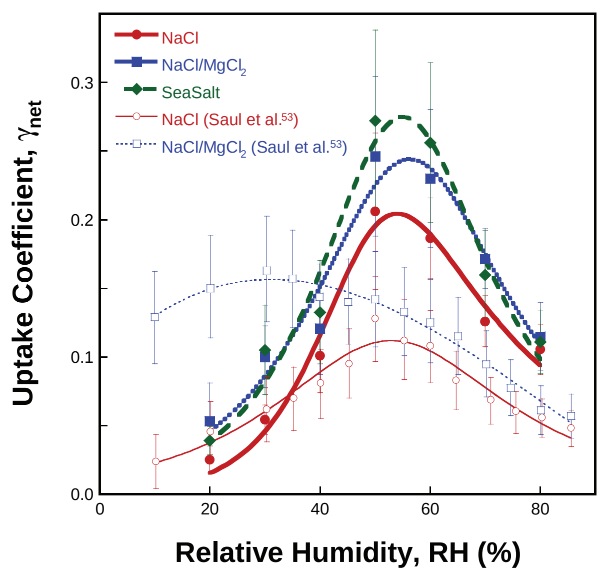
Citation: Wang CM, DR Baer, JE Amonette, MH Engelhard, Y Qiang, and J Antony. 2007. "Morphology and Oxide Shell Structure of Iron Nanoparticles Grown by Sputter-Gas-Aggregation." *Nanotechnology* 18:255603 (7pp).

Topical Area – Environmental Particles and Aerosol Chemistry

In many ways aerosols and particulates have much in common with clusters and nanoparticles. Some of the same methods are highly useful to characterize them. However, several EMSL users believe that the surface chemistry and surface reactivity of these types of particles can have a significant impact on atmospheric processes including global warming and the distribution of atmospheric pollution. EMSL user activities in this general area include laboratory studies of aerosol and particulate properties and use of unique EMSL characterization tools on field-scale studies. In some cases, instruments that are normally applied to the study of model aerosols in the lab are transported to the field for application of naturally formed aerosols.

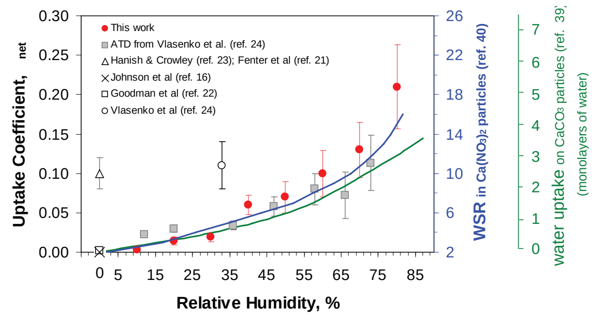
Experimental studies of heterogeneous gas-to-particle reactions using novel particle-on-substrate stagnation flow reactor approach

A novel Particle-on-Substrate Stagnation Flow Reactor (PS-SFR) experimental approach has been developed by staff and users of EMSL, to study the kinetics of heterogeneous, gas-to-sea salt particle reactions. In this new approach, substrate-deposited particles are exposed to reactive gases, followed by chemical analysis of the particles, using advanced instrumentation in EMSL. The reactor design and flow parameters were guided by computational fluid dynamics performed by the University of Southern California team members to ensure the diffusion flux was uniform for all particles undergoing reaction. The experimental protocol and data interpretation were successfully implemented in laboratory studies focused on heterogeneous gas-to-particle reactions relevant the atmospheric chemistry of sea salt and mineral dust. A complementary combination of the reported results with previously published single particle mass spectrometry data was essential to understanding uptake kinetics over a wide range of particle sizes and experimental conditions. The developed experimental approach offers options for multi-instrumental analyses of particle samples and therefore can be applicable to a wide variety of reactions of interest not only for the atmospheric chemistry community but also for the surface science and catalysis communities.



Values of uptake coefficient as a function of relative humidity for HNO_3 reaction with NaCl, mixture of NaCl/$MgCl_2$ and sea salt particles (Liu et al. 2007).

Heterogeneous reactions between nitric acid and aerosol particles, such as sea salt and carbonates present in mineral dust, serve as major sinks for gaseous metric acid and nitrogen oxides, which impacts the overall chemical balance of the troposphere. Results from our studies using PS-SFR approach show that NaCl and $CaCO_3$ have a similar reactive HNO_3 uptake at RH<40% but exhibits a very different humidity dependence. The uptake of HNO_3 onto NaCl was found to increase with the decreasing RH and peak around a relative humidity of 55%, and then below the efflorescence relative humidity (~45% RH) the uptake coefficient decreases rapidly (see figure on previous page). While uptake of HNO_3 onto $CaCO_3$ was found to increase monotonically with an increase in relative humidity due to hygroscopic growth of the reaction product $Ca(NO_3)_2$ (see next figure). As a result, if $CaCO_3$ and NaCl aerosol particles are present in the same HNO_3 polluted air mass, both heterogeneous reaction channels could occur. They may take place equivalently or competitively depending on specific conditions. Sea salt and mineral dust particles are the largest components, by mass, of global aerosol burden and contribute substantially to atmospheric chemistry, air quality and climate change issues.



Experimentally determined uptake coefficient as a function of the relative humidity for HNO_3 reaction with $CaCO_3$ particles (Liu et al. 2008).

The developed approach is expected to be applicable to a variety of reactions of interest not only for the atmospheric research community but also for the surface science and catalysis communities.

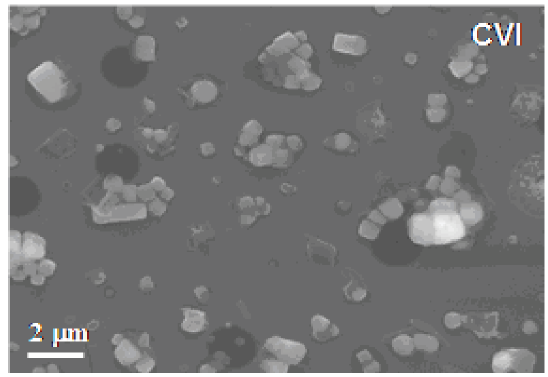
Citations: Liu Y, JP Cain, H Wang, and A Laskin. 2007. "Kinetic Study of Heterogeneous Reaction of Deliquesced NaCl Particles with Gaseous HNO_3 Using Particle-on-Substrate Stagnation Flow Reactor Approach." *Journal of Physical Chemistry A* 111:10026.

Liu Y, ER Gibson, JP Cain, H Wang, VH Grassian, and A Laskin. 2008. "Kinetics of Heterogeneous Reaction of $CaCO_3$ Particles with Gaseous HNO_3 over a Wide Range of Humidity." *Journal of Physical Chemistry A* 112:1561.

Chemical speciation of sulfur in marine particles

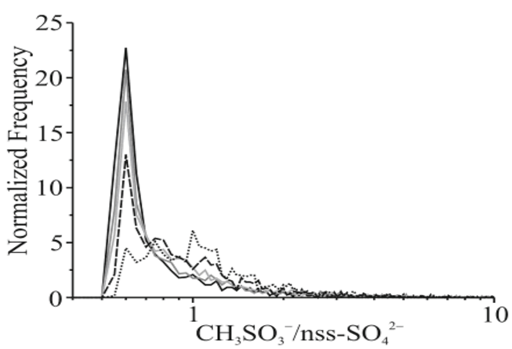
Detailed chemical speciation of field collected particles from the marine boundary layer over the California current was performed using a combination of complementary microanalysis techniques. On the basis of composition, morphology, and chemical bonding information, two externally mixed, distinct classes of sulfur-containing particles were identified: chemically modified (aged) sea salt particles and secondary formed sulfate particles. The results indicate substantial heterogeneous replacement of chloride by methanesulfonate ($CH_3SO_3^-$) and non-sea-salt sulfate (nss-SO_4^{2-}) in sea-salt particles with characteristic ratios of nss-S/Na > 0.10 and $CH_3SO_3^-$/nss-SO_4^{2-} > 0.6.

A research team of EMSL staff and users and presented the first observations of both $CH_3SO_3^-$ and SO_4^{2-} sulfur compounds in marine aerosol, identified on a single particle basis. Both time-of-flight secondary ionization mass spectrometry (TOF-SIMS) and scanning transmission x-ray microscopy with near-edge x-ray absorption fine structure spectroscopy (STXM/NEXAFS) techniques indicate an external mixture consisting primarily of two particle classes; mixed sea salt/$CH_3SO_3^-$/SO_4^{2-} and sulfur-rich particles of mixed H_2SO_4/$(NH_4)_2SO_4$ composition (see figure on right). Unambiguous, qualitative speciation of sulfur containing compounds and quantitative assessment of the $CH_3SO_3^-$/nss-SO_4^{2-} ratios have been facilitated using combined data sets from three techniques: computer controlled scanning electron microscopy with energy dispersed analysis of x-rays (CCSEM/EDX), quantitative assessment of elemental composition of individual particles; TOF-SIMS, qualitative molecular speciation of sulfur-containing compounds in individual particles; and STXM/NEXAFS, quantitative assessment of different forms of sulfur within individual particles. The data provided by these techniques offer a rich set of qualitative and quantitative information that is of primary importance to atmospheric chemistry processes in the marine boundary layer involving sea salt and marine sulfate particles.



SEM image of marine particles. Sea salt particles are larger, irregularly shaped supermicron particles with NaCl cubic crystal cores. Ammonium sulfate particles are spherical submicron particles (Hopkins et al. 2008).

For the first time, size-dependent nss-S/Na and $CH_3SO_3^-$/nss-SO_4^{2-} ratios are reported for marine particles. Characteristic ratios of nss-S/Na > 0.10 are reported for sea salt particles, with higher values observed for smaller particles, indicating more extensive formation of sulfur-containing salts. Characteristic ratios of $CH_3SO_3^-$/nss-SO_4^{2-} > 0.60 are reported for sea salt particles of all sizes, with higher values for large particles (see figure on left). This indicates that $CH_3SO_3^-$ salts are likely the dominant form of nss-sulfur in large particles while nss-SO_4^{2-} is more common in smaller



Distribution of $CH_3SO_3^-$ to nss-SO_4^{2-} ratio present in particles with diameter in the range 0.31 – 0.5, 0.5 – 0.79, 0.79 – 1.26, 1.26 – 2 and > 2 µm (black, dark grey, light grey, dashed and dotted lines, respectively). (Hopkins et al. 2008).

particles. In the past, much attention has been given to the hygroscopic and optical properties of sea salt aerosol and the corresponding mixed sea salt/sulfate particles that can be formed as a result of the $DMS \rightarrow SO_2 \rightarrow H_2SO_4$ reaction sequence that is assumed to dominate in the mid-latitude marine boundary layer. However, our analysis of field-collected sea salt particles presented in the manuscript indicate that DMS conversion to MSA can result in $CH_3SO_3^-$/nss-$SO_4^{2-} > 0.60$ and nss-S/Na > 0.1 ratios, as were observed under specific conditions of the coastal area north of San Francisco. These findings indicate that modeling of the marine boundary layer aerosols and cloud formation processes require extensive data on the hygroscopic and CCN properties of mixed sea salt/$CH_3SO_3^-/SO_4^{2-}$ and perhaps other organo-sulfur particles. These data are fairly scarce and require future research.

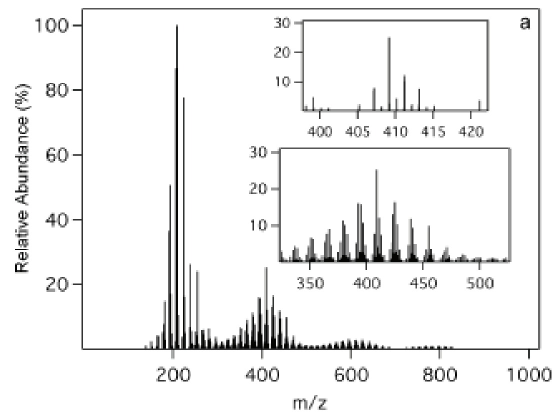
Citation: Hopkins RJ, Y Desyaterik, AV Tivanski, RA Zaveri, CM Berkowitz, T Tyliszczak, MK Gilles, and A Laskin. 2008. "Chemical Speciation of Sulfur in Marine Cloud Droplets and Particles: Analysis of Individual Particles from the Marine Boundary Layer Over the California Current." *Journal of Geophysical Research* 113:D04209.

Application of methods of high-resolution mass spectrometry to study chemistry of secondary organic aerosol

Methods of high-resolution mass spectrometry have been applied to study chemical composition of secondary organic aerosol (SOA) formed from the ozone-initiated oxidation of limonene. A significantly more complex SOA composition than that predicted by previously reported mechanisms was discovered. A possible reaction mechanism for the formation of the first generation SOA molecular components has been presented.

High-resolution mass spectrometric characterization of SOA particles formed from the ozone-induced oxidation of limonene revealed that the chemical composition of these particles is significantly more complex than that predicted by the basic Criegee mechanism of alkene ozonolysis. The mass spectra reveal ~1500 condensed products of oxidation as illustrated in the figure.

This work convincingly demonstrated that in order to account for the very large number of poly-functional species that exist in SOA in both monomeric and polymeric form, one has to include rich chemistry involving alkylperoxy and alkoxy radicals formed from the decomposition of carbonyl oxide intermediates.



Representative positive ESI mass spectra of SOA particles extracted in acetonitrile. The data include peaks with >0.5% abundance relative to the largest peak in the spectrum. (Walser et al. 2008).

The authors described a minimal set of reactions required to produce a distribution of limonene ozonation products that is consistent with mass-spectrometric observations. Even with a fairly restrictive set of reaction rules, inclusion of alkylperoxy and alkoxy chemistry in limonene ozonation produces some 1000 products with 140 unique m/z values in the monomeric mass range (m/z <300). The discussed mechanism includes known isomerization and addition reactions of the carbonyl oxide intermediates generated during the ozonation of limonene. In addition, it includes isomerization and decomposition pathways for alkoxy radicals resulting from unimolecular decomposition of carbonyl oxides that have been disregarded by previous studies. The isomerization reactions yield numerous products with a progressively increasing number of alcohol and carbonyl groups, whereas C–C bond scission reactions in alkoxy radicals shorten the carbon chain. Together these reactions yield a large number of isomeric products with broadly distributed masses. A qualitative agreement is found between the number and degree of oxidation of the predicted and measured reaction products in the monomer product range.

The large number of isomeric products produced in the oxidation of just one terpene shows how challenging it will be to obtain detailed characterization of molecular composition of ambient SOA particles that typically result from oxidation of multiple precursors. The ultimate goal of research on chemical mechanisms of SOA formation is to find out which reactions out of the infinite number of possibilities actually take place, and which are likely to be insignificant. It is expected that for such complex systems the answer to this question will come from coupling mass spectrometry and information theory, and this work can be viewed as the first step in that direction.

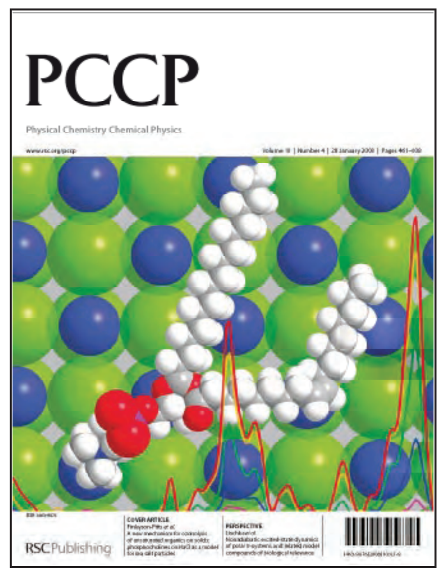
Citation: Walser ML, Y Desyaterik, J Laskin, A Laskin and SA Nizkorodov. 2008. "High-Resolution Mass Spectrometric Analysis of Secondary Organic Aerosol Produced by Ozonation of Limonene." *Physical Chemistry Chemical Physics* 10:109.

A new mechanism for ozonolysis of unsaturated organics on solids: Phosphocholines on NaCl as a model for sea salt particles

Sea salt particles are a major contributor to the global aerosol burden. They are formed by wave action, which carries along organic material with the sea salt. A major source of this organic layer is the decomposition of marine organisms, which have biomembranes that are a mixture of lipids, hydrophobic proteins, and carbohydrates. Phospholipids and fatty acids are common products of biomembrane disintegration. Previous work has indicated that fatty acid lipids in sea salt particles can be enhanced by factors of $(5\text{-}9)\times10^4$ compared to ocean surface water. An organic coating on sea salt particles is expected to modify the chemical and physical properties of the particles.

Distinguished EMSL user Barbara Finlayson-Pitts (University of California, Irvine) collaborated with EMSL researcher Scott Lea to determine the effect of ozone and ultraviolet light exposure on phospholipid-coated salt crystals using Fourier-transform infrared spectrometry, matrix-assisted laser desorption/ionization mass spectrometry, and Auger electron spectroscopy. They found a new mechanism for the ozonolysis of unsaturated organics on aerosols that may increase the understanding of chemistry, photochemistry, and toxicity of these aerosols in dry, polluted environments.

They reported on the oxidation of an unsaturated phospholipid, 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (OPPC), adsorbed on NaCl as a model for lipids on sea salt. The primary ozonide formed in the reaction has a sufficiently long lifetime that it can react with other species such as O_3 or H_2O. The reaction of OPPC/NaCl with ozone was studied in a flow apparatus equipped with a Fourier-transform infrared spectrometer (DRIFTS). O_3 and relative humidity were controlled and measured in these experiments. In some experiments, the reacted mixture was photolyzed using a high-pressure xenon arc lamp to probe for photochemically active products.



Model of OPPC adsorbed onto NaCl with corresponding DRIFTS spectra upon exposure to ozone superimposed.

Their experiments showed that the ozone-alkene chemistry on solids is quite different from that in the gas phase or in solution. In particular, the primary ozonide formed on addition of O_3 to the double bond is sufficiently stable, with a lifetime of ~100 ms that it can undergo further reactions with O_3 and with water vapor. The ozone reaction with OPPC is sufficiently fast that a lifetime of only 15 minutes is expected in the atmosphere at 100 ppb O_3. Even at typical concentrations of O_3 in remote regions, the OPPC lifetime will still only be on the order of an hour. It is clear from the data that the reaction with H_2O will under most circumstances be the major removal path for the primary ozonide (POZ) in the atmosphere.

There may be situations where formation of the secondary ozonide (SOZ) ring represents a significant part of the reaction. For example, consider polluted, dry areas such as Mexico City with O_3 peaks of ~400 ppb.

Under dry conditions with a relative humidity of ~20 percent, the lifetime of the POZ ring is about 90 ms for reaction with O_3 and 5 ms for reaction with H_2O. While hydrolysis still dominates the removal of POZ, some SOZ would be formed. The health effects of SOZ are not known. However, given that it is an oxidant and that the organic side chains will increase its solubility in lipids and cell membranes, it has the potential to negatively impact health. This work was featured on the cover of *Physical Chemistry Chemical Physics* in January 2008.

Citation: Karagulian F, AS Lea, and BJ Finlayson-Pitts. 2008. “A New Mechanism for Ozonolysis of Unsaturated Organics on Solids: Phosphocholines on NaCl as a Model for Sea Salt Particles.” *Physical Chemistry Chemical Physics* 10(4):528-541.

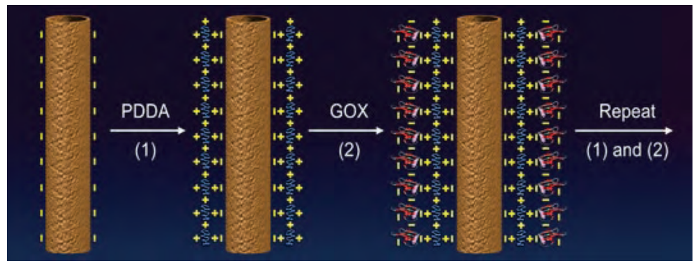
Topical Area – Sensors

The control of surface chemical interactions at interfaces and the transport of charge or mass across them are often central to the design and operation of sensors. The development of highly selective materials for new types of sensors for environmental monitoring, process control, and other applications has been part of EMSL since the user facility began operations. The surfaces and interfaces of these materials and sensor systems are carefully designed to achieve selective properties and to optimize the collection of highly specific information.

A biosensor layered like lasagna

In a mixing of pasta metaphors, PNNL scientists have used electrostatic attraction to layer reactive biological molecules lasagna-like around spaghetti-like carbon nanotubes.

The technique enables enzymes, with the help of a long, noodle-like polymer molecule, to self assemble layer-by-layer on a single carbon nanotube.



A polymer, here labeled PDDA, clings to a carbon nanotube of opposite charge, and an enzyme, GOX, does the same with the polymer. The steps can be repeated to build up a biosensor's layers, enzyme count and sensitivity.

Lin and co-author Guodong Liu coaxed electrostatic clinginess in a polymer and an oppositely charged protein-enzyme, in this case glucose oxidase, which reacts in the presence of blood sugar. The catalyzed products from the reaction ping the carbon nanotube; if the tube is connected to an electrode, the tube will carry a signal that corresponds precisely with the amount of glucose detected. The first polymer binds to the carbon nanotube. Enzymes are attracted to the polymer, leaving an outer layer for the next polymer of opposite charge to cling to, and so on.

An individual strand coated with one to six layers ranges from 30 nanometers to about 50 nanometers thick. "Each polymer layers is porous," Lin said. "This allows the glucose to diffuse in and come into contact with the enzymes."

"The polymers trap the enzymes in place," Liu said. "You can go up to five or six layers to improve the sensitivity of the detector, but after that, the more enzyme layers inhibit diffusion of the glucose."

"Now that the glucose enzyme biosensor has passed the test," Lin said, "it should be possible to build a similar sensor using other enzymes that react specifically with other biological chemicals, environmental pollutants or even microbes and their toxic byproducts." In February 2008 issue of *Analytical Chemistry*, Lin and colleagues also reported, the use of a similar technique to construct sensors for nerve agents.

Citation: Liu G and Y Lin. 2006. "Carbon Nanotube-templated Assembly of Protein." *Journal of Nanoscience and Nanotechnology* 6(4):948-953.

6.2 EMSL's research capabilities

EMSL has clustered laboratory space around similar instrument capabilities. This enables users to more quickly identify capabilities of interest while also streamlining management and operational support for those capabilities. EMSL's research instruments are clustered into eight capability groupings:

- Deposition and Microfabrication (Section 6.2.1)
- Kinetics and Reactions (Section 6.2.2)
- Molecular Science Computing (Section 6.2.3)
- Mass Spectrometry (Section 6.2.4)
- Microscopy (Section 6.2.5)
- NMR and EPR (Section 6.2.6)
- Spectroscopy and Diffraction (6.2.7)
- Subsurface Flow and Transport (6.2.8)
- Instrument Development Laboratory (6.2.9)
- Computing and Networking Services (Section 6.2.10)

Researchers from around the world are encouraged to use EMSL's unique capabilities in combination with each other with an emphasis on merging computational and experimental instruments. The layout of these capabilities within EMSL and a discussion of laboratory operations are found in Section 9.0.

6.2.1 Deposition and Microfabrication

EMSL offers sophisticated deposition and microfabrication tools for creating functional surfaces, nanomaterials, and thin films with specific properties. Users apply these methods to design and create materials (or materials systems) with specific surface, bulk, and/or interfacial properties for energy and environmental applications. Applications and resources include the following.

Catalysis, surface chemistry, and other functional surfaces: Growing ideal and designed or altered surfaces optimized for specific functions provides a foundation for both fundamental and application oriented studies related to catalysis and other areas where understanding surface chemistry is important.

Model systems for geochemistry and biogeochemistry: Growing oxide and mineral films with varying structure and complexity provides model materials for understanding natural processes such as solution-mineral interactions and biogeochemical interfaces.

Materials with optimized or designed properties: Film growth and ion implantation methods provide the basis for creating materials with specific properties. The ability to carefully dope oxide films provides materials that are useful for understanding and controlling photocatalytic reactions and the development of oxides with ferromagnetic properties at and above room temperature. Photochemical processes are relevant to clean energy production and environmental cleanup while magnetic oxides can enable future spintronic-based electronic devices.

Chemical and biological sensing: Film and surface layer deposition and modification, micro- and nano-lithography, and solution synthesis capabilities provide tools to create functional sensing materials and materials systems.

6.2.1.1 Capabilities supporting deposition

Oxygen plasma assisted molecular beam epitaxy system: Research using EMSL's molecular beam epitaxy (MBE) deposition system centers around the synthesis and characterization of novel oxide, ceramic, and mineral materials as single-crystal, epitaxial films. Such materials are of interest in scientific and technological fields including semiconducting oxides, magnetic oxides, optics, thermal and photocatalysis, and geochemistry. This system consists of a custom MBE chamber, designed in EMSL, with an electron cyclotron resonance plasma gas source, four electron-beam evaporation solid sources, three effusion cell solid sources, and *in situ* optical (atomic absorption) and reflection high-energy electron diffraction probes for real-time monitoring of the metal fluxes and surface structure and morphology, respectively.

EMSL's Molecular Beam Epitaxy System

The MBE deposition system is equipped with two additional chambers. The first chamber is outfitted with x-ray and ultraviolet photoemission spectroscopy as well as x-ray photoelectron diffraction and low energy electron diffraction capabilities. These techniques allow researchers to measure detailed compositional and electronic/geometric structural properties of epitaxial films, surfaces, and interfaces. The second chamber is designed for *in situ* photochemistry studies. This chamber is equipped with a gas doser, mass spectrometer, and a mercury arc-lamp light source. These chambers are connected by a 21-foot-long transfer system that allows samples to be moved from one system to other using ultrahigh vacuum capabilities.

Molecular beam epitaxy-II: A smaller scale dual-chamber ultrahigh vacuum system equipped with an electron cyclotron resonance oxygen plasma source with three effusion cells, two e-beam evaporation cells, and *in-situ* reflection high energy electron diffraction capability is utilized for research related to the fundamentals of solid oxide fuel cell research and understanding fundamental optical properties and band tailoring of CuO based system. The second chamber has the ability to analyze the chemical state of the elements using XPS as well as x-ray photoelectron diffraction.

Pulsed laser deposition system: This system is engineered for epitaxial growth of oxide, ceramic, or synthetic mineral thin films. The system is composed of the following:

- Electro-polished stainless steel chamber pumped via a turbo molecular pump and backed by a rotary scroll dry pump.
- Excimer laser (krf) for excitation at 248 nm.
- Three standard mass flow control units for precise and reproducible process gas during deposition.
- Electron cyclotron resonance plasma gas source.
- Reflection high-energy electron diffraction for real-time monitoring of the surface structure and morphology.
- Continuous compositional spread control system for combinatorial synthesis using up to three different targets.

The system is capable of growing uniform, multilayer, or compositionally spread combinatorial complex-oxide thin films with abrupt interfaces. Pulsed laser deposition is uniquely well suited to excel in the growth of thin epitaxial films with complex multi-component stoichiometry.

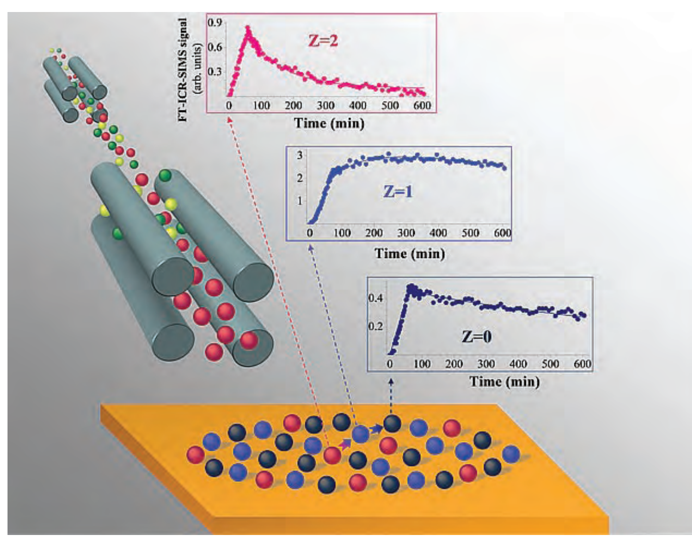
Reactive ballistic deposition: The combination of reactive ballistic deposition and glancing angle deposition can produce highly porous, high-surface-area metals, metal oxides, and other materials. The techniques are based on a simple shadowing model. At glancing angles, random height differences that arise during the initial film growth can block incoming flux, essentially creating shadows that result in void regions in the shadowed region. If surface and/or bulk diffusion are slow compared to the incident flux (i.e., if the molecules "hit and stick"), the voids remain unfilled. Continued deposition results in porous films with filamentous columnar morphologies. Varying degrees of film porosity can be achieved by varying the deposition angle and substrate temperature.

Metallorganic chemical vapor deposition system: This system is capable of growing uniform (both thickness and composition) oxide thin films with abrupt interfaces. The system contains a rotating disk reactor, two metallorganic source delivery systems (bubbler vapor phase and direct liquid-source injection), and the potential of using an oxygen microwave plasma unit.

Mass-selected ion deposition system: Electrospray source: A new capability, the mass-selected ion deposition system includes the following:

- High-transmission electrospray ion source.
- Quadrupole mass filter.
- Bending quadrupole that deflects the ion beam and prevents neutral molecules originating in the ion source from impacting the surface.
- Ultrahigh vacuum chamber for ion deposition by soft landing.
- Vacuum-lock system for introducing surfaces into the ultrahigh vacuum chamber without breaking vacuum.

The design allows users to control soft-landing energies (0-500 eV) and spot sizes from around 5 mm to 1 mm in diameter. Phosphorus screen detector is used to monitor the spot size prior to ion deposition. This capability is used for controlled highly specific deposition of complex ions on surfaces, covalent immobilization of mass-selected ions on a variety of surfaces, and preparation of novel catalysts using soft-landing of mass-selected ions.



EMSL users are performing soft-landing experiments using mass spectrometry as a separation technique that allows them to prepare novel materials and explore reactivity at interfaces. A convenient and flexible approach for tailoring properties of substrates, soft-landing of complex ions opens new opportunities for preparing extremely pure, uniform layers of molecules on surfaces that could lead to better sensors and new biomaterials.

High-energy ion beam synthesis of nano-structures: The accelerator laboratory at EMSL offers the capabilities to synthesize highly epitaxial nanoparticles and nanofibers underneath the surface of the material. Depth, composition, and size distribution can be controlled by selecting appropriate energy of the ions, ion species and annealing temperature, or additional energy deposition by selected ion irradiation. Embedded nanostructures have potential applications in catalysis, thermoelectric, and photonic applications.

Spin coating and other wet chemical reaction capabilities: Various nanostructures and thin films relevant to energy and environmental applications are synthesized using these capabilities. Two specialized spin coaters are used to support user activities related to deposition of polymers, organic thin films, and oxide based sol-gel synthesized films.

Langmuir-Blodgett thin film deposition: Langmuir-Blodgett thin film deposition capability in a clean room is mainly used to support user activities related to self-assembled monolayer depositions of organic thin films. This thin film deposition technique is based upon usage of water or hexane non-miscible single monolayer followed by computer controlled dip coating of substrate to achieve single monolayer growth. The addition of a new lithium-ion deposition capability for battery applications is also expected to be installed in the clean room in FY 2009.

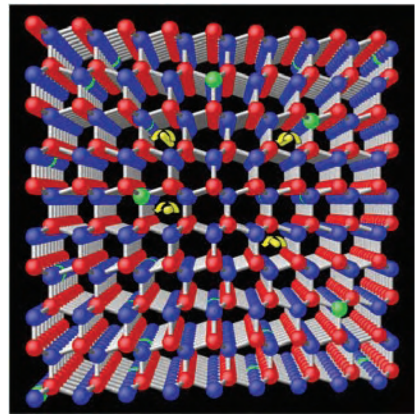
Vacuum evaporators and sputter deposition systems: Vacuum evaporation, portable tabletop sputter deposition, and carbon coating capabilities across the laboratories are heavily used to support user activities in deposition of conducting layers for microscopy applications and deposition of gold, copper, and chromium for usage in various stages of micro-/nano-fabrication.

6.2.1.2 Capabilities supporting microfabrication

Focused ion beam: The FEI Helios Nanolab dual-beam focused ion beam/scanning electron microscopy (FIB/SEM) provides rapid and selected region preparation of samples for transmission electron microscopy (TEM) and other spectrometers; three-dimensional analyses of nanoscale materials and other small objects; and the capability for nanoscale lithography. This instrument allows specimens prepared by FIB micromachining to be manipulated for scanning TEM imaging, electron backscatter diffraction, energy dispersive analysis by x-rays, or fabrication purposes such as welding to a TEM sample grid without breaking the vacuum within the instrument. The system is equipped with two deposition sources to achieve carbon and platinum controlled depositions at the nanoscale. The FIB/SEM also has Nabity nanolithography system useful for large-scale transfer of ion beam etched or deposited nanostructures.

Clean room: Microfabrication equipment in the clean room provides a significant research and development capability in the areas of microstructures, microsensors, and microanalytical systems. Unlike highly automated industrial production equipment, the microfabrication equipment in EMSL has multipurpose functionality. The equipment supports microprocessing activities that include thin film deposition, thermal treatments, microphotolithography, chemical etching, inspection and characterization, bonding and packaging, and test and measurements.

6.2.1.3 Unique capabilities



Researchers are using depositing tools developed at EMSL to grow and understand the properties of magnetically doped oxides. These oxides may allow electron spin to supplement electron charge in computing and signal processing.

The **oxygen plasma assisted MBE** at EMSL is a world-class resource for the synthesis of high-quality, well-oriented model oxide single crystal films with well-defined interfaces that can be used in many different areas. A groundbreaking focus on the surface and interfacial properties of oxides and oxide-based materials has been part of EMSL since the initial conception of the facility. This unique capability has supported the foundation to current research in spintronics, catalysis, photocatalysis and photochemistry, radiation damage of oxides and ceramics, nanoparticle chemistry, and properties of aerosol, mineral and bio-mineral interfaces.

With unique, newly developed **mass-selected ion deposition** capability, EMSL users are performing soft-landing experiments using mass spectrometry as a separation technique. This allows the users to prepare novel materials and explore reactivity at the interfaces. This capability provides a convenient and flexible approach for tailoring properties of substrates and soft-landing of complex ions that opens new opportunities for preparing extremely pure, uniform layers of molecules on surfaces.

The **FIB/SEM** opens up a new area of research in nanofabrication and three-dimensional reconstruction of structures using a combination of electron backscattering and energy dispersive x-ray analysis along with the rapid sample preparation for TEM without breaking the vacuum within the instrument. The samples prepared using FIB are planned to be analyzed by several surface and bulk sensitive electron, ion and x-ray based capabilities including Auger electron spectroscopy, x-ray photoelectron spectroscopy, secondary ion mass spectrometry, and TEM.

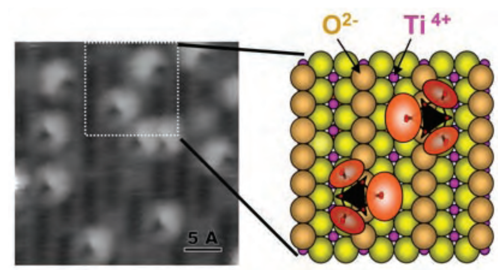
6.2.1.4 Future capabilities

The next generation of the MBE system with precise control of growth rates is planned as a part of recapitalization plan. Capability development is expected to start in FY 2009. This will dramatically enhance the capability with much needed control of the composition of thin films.

6.2.2 Kinetics and Reactions

EMSL offers state-of-the-art *in-situ* high-pressure and -temperature kinetics and reaction capabilities integrated with modeling to develop a fundamental molecular-level understanding to control catalytic reactivity and selectivity in designing materials and interfaces with improved energy efficiencies and tailored characteristics. Applications and resources include the following items.

Catalysis: Developing reaction mechanisms associated with controlled catalytic and photocatalytic oxidation and reduction reactions, testing catalyst efficiency, measuring reaction rates, and determining the structure and composition of catalyst surfaces under reaction conditions as well as obtaining information about the concentration of reaction intermediates.



Monodispersed $(WO_3)_3$ clusters on $TiO_2(110)$ were characterized using scanning tunneling microscopy.

Molecule surface interactions: Understanding the energetics and kinetics of molecule-surface interactions with an emphasis on processes occurring on metal oxide surfaces using surface science capabilities with unprecedented spatial and energy resolutions and correlating these results with those from high-pressure and -temperature studies of realistic materials.

Amorphous solid water films and interfaces: Developing a fundamental molecular-level understanding of surfaces of water, water-ice, and water-mineral interfaces through thermal and electron stimulated reactions and ion deposition.

Dynamic processes in real time: Providing specialized *in-situ* experimental capabilities to understand the complex reaction dynamics during chemical transformations, interfacial electron transfer processes, protein-protein interactions, and molecular interactions at the single molecule level.

Ion-surface interactions: Developing molecular-level understanding of interactions of complex ions and molecules with surfaces with an emphasis on understanding the reaction kinetics and dynamics of activating and dissociating complex molecular ions. Studying the kinetics of charge transfer and desorption of complex molecules following ion soft-landing. Developing new approaches for selective modification of substrates using beams of mass-selected hyperthermal ions.

6.2.2.1 Capability details

Ultrahigh vacuum (UHV) surface science capabilities with high-pressure and -temperature side chambers: The model UHV catalysis system is capable of measuring gas/solid reaction rates under realistic, high-pressure (1 atm) conditions using model, low-surface area solid samples. To date, it has been primarily used to measure the kinetics of gas-phase reactions over model heterogeneous catalysts. With research microreactors, such as chemical reaction test stand and RXM-100, or any other catalyst testing and characterization machine studies of realistic catalyst materials, reaction rates can be measured as a function of temperature and varying reagent partial pressures.

Besides studies of thermal catalyzed reactions, researchers have used this equipment to study the mechanisms of room-temperature photocatalyzed reactions over model semiconductor oxide catalysts such as TiO_2. The instrument is capable of performing a number of surface science spectroscopic measurements of the structure and composition of the catalyst surfaces without exposing the samples to air. These *in-situ* and *ex-situ* spectroscopic methods are performed before, during, and after atmospheric pressure kinetic measurements to provide a fairly complete picture of the chemical state of a reactive surface. Notably, they provide information about the concentration of reaction intermediates, the oxidation state(s) of the constituents of the surface, and the structure of the active surface sites.

Molecular beam reaction kinetics instrumentation: This capability consists of three state-of-the-art molecular beam-scattering machines. These UHV machines have a base pressure below 2×10^{-10} Torr in the scattering chambers and are equipped with a suite of *in-situ* surface analytical tools. These tools include the following:

- Auger electron spectroscopy (AES).
- Temperature programmed desorption (TPD).
- Sputter ion gun.
- Low energy electron diffraction.
- X-ray photoelectron spectroscopy (XPS).
- Fourier transform infrared.
- Quadrupole mass spectrometer.

Instruments ICS-I and ICS-II are both equipped with three co-planar molecular beam lines while the third instrument (BSK) has two co-planar beam lines. In all of the instruments, each beam can be independently controlled and operated as a continuous or pulsed effusive or supersonic beam. Instruments ICS-I and ICS-II are also equipped with evaporation sources for nanoscale refractory film synthesis. The molecular beams instruments are ideally suited for investigating the heterogeneous chemical properties on a variety of novel nanoscale films. Modulated molecular beam techniques enable users to determine the adsorption, diffusion, sequestration, reaction, and desorption kinetics in real time. The dynamics and kinetic processes occurring in the nanoscale films are probed using variety of experimental techniques including TPD, atomic beam surface scattering, Auger, and XPS. Elucidation of these processes will further the understanding of solvation and reactions in multi-phase, multi-component solutions and in determining reaction mechanisms on ice, metal, and oxide substrates.

UHV surface chemistry instrumentation: EMSL's UHV surface chemistry high-resolution electron energy loss spectroscopy (HREELS) is designed to study the molecular-level chemistry of adsorbates on metal oxide surfaces. This system is equipped with spectroscopic tools that follow changes in adsorbate chemistry, including HREELS, secondary ion mass spectrometry, and ultraviolet photoemission and (electronic) electron energy loss spectroscopy. This system also contains an ion gun for sample cleaning, and an Auger electron spectrometer and low-energy electron diffraction system for characterizing sample surface composition and structure, respectively. Electron-stimulated and TPD studies are routinely performed using this system. During TPD studies, the researcher can obtain typical information such as quantity and nature (intact or dissociated molecule) of an adsorbed gas. In addition, the user can also estimate the sticking coefficient and activation energy for desorption and/or reaction of the adsorbed molecule.

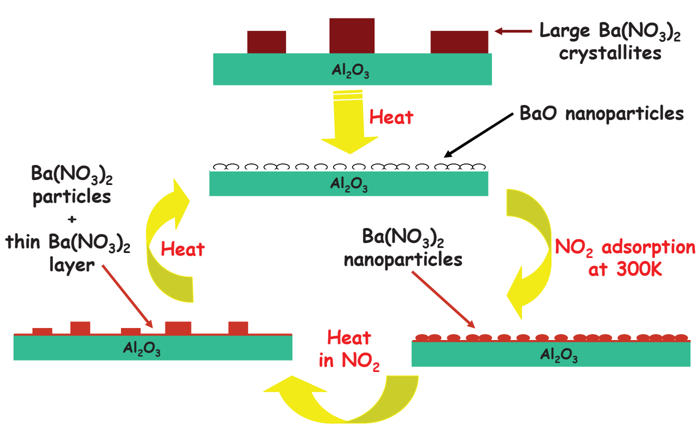
Non-thermal reactions at surfaces and interfaces, and in thin molecular films: Two UHV systems are equipped for fundamental investigations of thermal and non-thermal reactions at surface and interfaces, and in thin molecular films. Each instrument has a low-temperature crystostat (T_{min} ~ 20 K), quadrupole mass spectrometer, sophisticated temperature control, tuneable low-energy electron gun, molecular beam dosing line, and automated data acquisition system. In addition, one system has a FTIR spectrometer for the *in-situ* analysis of reaction intermediates and products. The systems are configured for electron-stimulated desorption and TPD experiments on well-characterized surfaces and thin molecular films.

Quantum XPS spectrometer with catalysis side chamber: The Quantum XPS spectrometer is unique in that this system is attached to a side chamber where the reactions can take place at high pressures and elevated temperatures. The side chamber mainly consists of

1. Furnace where the temperature can go up to 1000°C while the pressure can be in the range of 10^{-9} – 760 Torr (1 atm) under steady gas flow of interest.

2. High-pressure chamber where the pressure can go up to 2 atm while the temperature can be in range of room temperature to 800°C.

Typical gases used in these reaction chambers include CO, CO_2, H_2, O, He, N_2, and H_2O. The sample transfer system allows the samples to be moved between these reaction chambers and XPS analysis chamber under UHV conditions so that sample surfaces can be preserved after reactions for the analysis. The main XPS system uses a focused monochromatic Al Kα x-ray beam that can be varied in size from 10 μm to approximately 200 μm. The beam can be rastered over relatively large areas (about 0.5 mm^2) to generate elemental maps of a surface or used with a sputter source to depth profile. Images of the x-ray generated electrons can also be acquired.



This schematic shows the changes associated with the new NO_x storage-reduction catalysts composed of platinum and barium oxide supported on aluminum oxide.

Micro x-ray diffractometer: The instrument at non-ambient conditions is used to investigate the dynamic processes needed to investigate *in situ*, in particular, the structural and phase changes in the material under the reaction conditions. In the micro system at EMSL, an environmental cell can be easily incorporated with appropriate gas manifold and heating (up to 600°C) systems. The diffractometer is a new generation rotating anode with micro-focus optics, automated x-y stage, and a curved image plate detector. With specialized optics and collimators, the highest spatial resolution of 10 microns can be obtained.

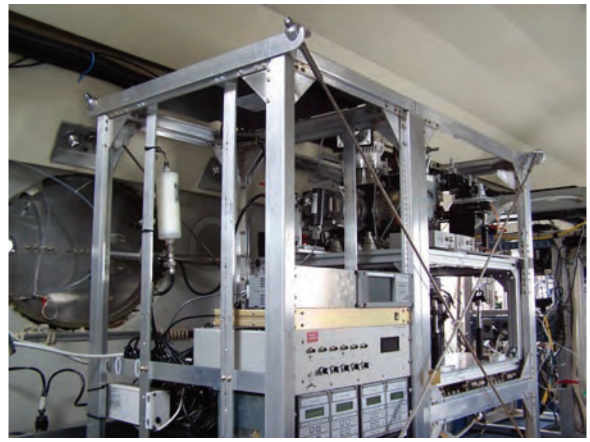
Mass-selected ion-deposition system: This system, a new instrument constructed at EMSL, includes the following:

- High-transmission electrospray ion source.
- Quadrupole mass filter.
- Bending quadrupole that deflects the ion beam and prevents neutral molecules originating in the ion source from impacting the surface.
- UHV chamber for ion deposition by soft landing.
- Vacuum-lock system for introducing surfaces into the UHV chamber without breaking vacuum.

Its design allows users to control soft landing energies (0-500 eV) and spot sizes from around 5 mm down to 1 mm in diameter.

6-Tesla Fourier transform ion cyclotron resonance mass spectrometer: This Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer is a unique instrument specially configured for studying the kinetics and dynamics of surface-induced dissociation of complex ions. The instrument is equipped with a high-transmission electrospray ionization source and an intermediate-pressure matrix-assisted laser desorption ionization source for efficient ionization of large molecules followed by three quadrupoles for ion focusing, mass selection, and storage. Ions are transferred to the ICR cell by a series of electrostatic lenses and impacted orthogonally on a surface. The surface-induced dissociation surface is introduced to the rear trapping plate of the ICR cell using a probe vacuum-lock system. The instrument is also equipped with a Cs^+ ion gun that enables real-time *in-situ* secondary ion mass spectrometry characterization of surfaces during ion soft-landing experiments for studying charge loss and desorption kinetics following ion deposition.

Electrospray ionization source – photoelectron spectroscopy: This instrument couples an electrospray ionization source to a magnetic-bottle time-of-flight photoelectron spectrometer. It was developed to investigate multiply charged anions and solution-phase species in the gas phase. An electrospray ion source produces multiply charged anions. Ion-trap-time-of-flight mass spectrometry is used to analyze the formed anions. Size- and charge-selected photo detachment photoelectron spectroscopy is used to obtain information about the stability and electronic structure of the anions and their microscopic solvation. Anionic species important in organic, inorganic, and biochemistry as well as in solid materials and catalysis are being investigated.



Researchers have used SPLAT II in the field.

Second-generation Single Particle Laser Ablation Time-of-Flight Mass Spectrometer: Known as SPLAT II, this ultra-sensitive, high-precision instrument allows multidimensional characterization of individual aerosol particles. It allows users to study the fundamental processes that govern the chemistry and physics of particles on the nano- and micro-scales. Multidimensional particle characterization directly maps the relationships between particle size, composition, shape, morphology, and particle chemistry, its electronic structure, hygroscopic properties, etc. SPLAT II characterizes individual particles in the size range from 50 nm to 3 µm with a sampling rate of up to 100 particles per second. It detects and characterizes at least 1 particle per second, when the concentration of particles that are 125 nm or bigger are as low as 1 particle per cm^3. SPLAT II simultaneously measures *in-situ* and in real-time individual particle size, internal composition, density, effective density, shape, morphology, fractal dimension, and hygroscopicity. SPLAT II's high sampling rate yields temporal resolution that permits characterization of quickly changing samples, for example, fast chemical reactions, and its high sensitivity allows characterization of particles with low number concentrations. Its versatility allows characterization of any particle type, including volatile and non-volatile fractions of internally mixed aerosol particles commonly encountered in the atmosphere and engine exhaust.

6.2.2.2 Unique capabilities

EMSL researchers use a combination of experimental studies of collisional activation and dissociation of complex molecules in the 6-Tesla FT-ICR mass spectrometer. Preparatory mass spectrometry using soft-landing of mass-selected ions on surfaces enables highly specific modification of surfaces, preparation of novel materials, and molecular-level understanding of interactions of biomolecules with hydrophilic and hydrophobic surfaces in living systems.

SPLAT II allows users to study the fundamental processes that govern the chemistry and physics of particles on the nano- and micro-scales. Applications for the instrument include, but are not limited to, climate, air pollution, human health, bioterrorism, and emerging nanotechnologies. Portability is a hallmark of SPLAT II. It is the first field-deployable instrument that provides information in real time on individual particles down to 50 nm in diameter. It is also the first field instrument operated in an infrared-ultraviolet mode, thereby enabling the collection of reproducible and quantitative particle mass spectra.

6.2.3 Molecular Science Computing

EMSL supports a wide range of computational activities, including computational molecular chemistry, simulations of large biomolecules and materials, and reactive chemical transport modeling. The Molecular Science Computing (MSC) capability provides high-performance computing hardware, high-performance computing software, and highly skilled personnel.

6.2.3.1 Current key capabilities

Key MSC capabilities include a combination of production computing hardware, software capabilities, and visualization tools to support scientific research. The hardware includes the Hewlett-Packard Linux-based supercomputer named Chinook. The supercomputer is connected to EMSL's data storage system, NWfs, as well as to the Graphics and Visualization Laboratory via a high-speed network, allowing all of the systems to work together on large-scale scientific applications. Software tools are also available. In addition, EMSL offers workstations and peripherals for data analysis, visualization, training, and software development or testing. Also available are a video editing/mixing system, HDTV camera, multimedia workstations, and a Linux Cluster.

6.2.3.2 Critical instruments

The following are the critically important components of the MSC capability:

The MPP2 will be replaced by Chinook in autumn 2008.

Chinook: The High-Performance Computing System-3 (HPCS-3) has a resource balance similar to MPP2, EMSL's former supercomputer. Chinook will provide EMSL users' supercomputer needs for the next 4 years. Once fully provisioned, Chinook will provide 2,310 nodes; 4,620 2.2-GHz Quad-core AMD processors; 1.33 petabytes local disk; and 36.96-terabytes RAM. It will have a theoretical peak performance of 163 teraflops compared to MPP2's 11.9 teraflops. The shared global file system will have 250 terabytes of disk space.

NWfs: This EMSL archive system uses clusters of low-cost commodity disks to provide fault-tolerant, scalable, long-term storage. Such large-capacity archive systems usually rely on tape for mass storage, but NWfs distinguishes itself by having all data instantly accessible on disk-based storage. NWfs has a capacity of 800 terabytes and the ability to grow as needed to over a petabyte.

6.2.3.3 Available capabilities

Molecular Science Software Suite (MS^3): This is a comprehensive, integrated set of tools that enables scientists to understand complex chemical systems at the molecular level. MS^3 couples the power of advanced computational chemistry techniques with existing and rapidly evolving high-performance massively parallel computing systems with extensible problem-solving capabilities. The suite consists of the Northwest Computational Chemistry Software (*NWChem*), the Extensible Computational Chemistry Environment (Ecce), and the Global Array Toolkit. These three components are briefly described below.

- ***NWChem*** provides an highly scalable, parallel computational chemistry methods to tackle large, complex questions. The software includes highly accurate correlated methods, density functional theory (DFT), plane-wave DFT with Car-Parrinello dynamics, and classical molecular dynamics enabling scientists to model a wide range of molecular properties. These methods combine, for example, to perform mixed quantum-mechanics and molecular-mechanics simulations for accurate simulations of large systems.

- ***Ecce*** provides a domain-encompassing, problem-solving environment for computational chemistry. This software enables EMSL users to easily set up, run, and analyze the results of computational chemistry studies. Ecce is built on top of a web-based data management and inter-application messaging server framework. Running jobs through remote communications, like secure shell, and a batch queue management system allows transparent access to high-performance compute resources from users' desktop workstations. Ecce features a simple installation procedure and extensive online help.

- ***Global Array Toolkit*** includes high-performance computing libraries and tools for applied parallel computing focused on inter-processor communications through the aggregate remote memory copy interface, high-performance input/output through the Parallel I/O tools, and programming models for hierarchical memory systems through the Global Arrays and Memory Allocator libraries. The toolkit is the basis for the scalable parallel framework of *NWChem* and its development is driven by needs of such real scientific application codes on the high-end parallel systems. Development has been supported by EMSL operations and by the DOE Center for Programming Models for Scalable Parallel Computing.

Resources have been developed to facilitate user support and training. These resources include MS^3 websites with user and reference manuals, download information, release notes, frequently asked questions, a list of known bugs, tutorials, and benchmark information; web-based context-sensitive help available from within the software; and a mailing list where users can post support-related questions and get answers from experienced users or the *NWChem* developers.

This software is used by many of the Computationally Intensive Research and EMSL science theme projects and has been distributed to over 2,000 sites worldwide.

High-Performance Software Team: This team has the primary responsibility for developing and supporting MS^3, which includes the following:

- Proactively developing new and scalable software capabilities directly supporting the experimental capabilities at EMSL.
- Developing new software capabilities directly supporting specific EMSL users.
- Developing new high-performance versions of the software and new high-performance algorithms.
- Maintaining and continually refreshing the underlying software architecture in support of new hardware and software technology and standards.
- User support and consulting.
- Conducting training and user workshops.

The team focuses on developing next-generation molecular modeling software, in support of EMSL's science drivers and experimental capabilities, that can run on evolving massively parallel computer technologies. The team is composed of computational chemists and computer scientists (with external collaborations to mathematicians) who work together.

MSC Consulting Team: This group provides a diverse set of services for all users of the MSC computers and Graphics and Visualization Laboratory. With expertise in computational chemistry, biochemistry, bioinformatics, mathematics, and algorithm development in addition to computational science, the team

- Provides general consulting support for scientific software packages.
- Assists users in porting, optimizing, and running code on the MSC computers.
- Conducts training and user workshops.
- Manages all research projects run on the MSC equipment.
- Works closely with the high-performance software team and the operations team.
- Provides basic video production services.

MSC Operations Team: This group operates, maintains, and advances the capabilities of the MSC scientific computing hardware. They are responsible for the operation and implementation of the production supercomputers in the MSC and have developed system management, monitoring, allocation management, and scheduling capabilities. The primary focus is on providing high-quality, reliable production computing cycles and storage capabilities in the MSC to support very large parallel calculations for computationally intensive research.

The Graphics and Visualization Laboratory provides production graphics and visualization equipment for the analysis and display of complex data sets from experiments and computer simulations.

Graphics and Visualization Laboratory: This laboratory provides production graphics and visualization equipment for the analysis and display of complex data sets from both experiments and computer simulations. The real-time digital video capture capability from the graphics compute servers allows fast, yet high-quality, video production. Users can generate presentation media in any form, from video (including all international video standards) to web-based animations.

The Graphics and Visualization Laboratory provides access to scanners, printers, a poster-sized plotter, and various workstations. An overhead projector can display video feed from one of several computers including a portable laptop. Large molecules can be displayed in three dimensions using special liquid-crystal glasses. It has been used for both training and group meetings.

6.2.3.4 Future directions

Computers are subject to continuous improvement. This drives both the need to keep computer hardware up-to-date as well as look to the future for more efficient parallel scientific software. The MSC staff organize workshops with experts in their research fields for future hardware and software needs. To meet these challenges, the following is planned for the MSC capability.

The Chinook supercomputer will allow scientists to study complex scientific problems with larger and more realistic models and get answers faster by scaling computational models to larger numbers of processors. The system is being delivered and tested in two phases. The first phase has started. The second phase is expected to be fully operational in the autumn of 2008. It will replace the current supercomputer, which went online early in 2003.

The *NWChem* meeting, *NWChem* Meeting on Science Driven Petascale Computing and Capability Development at EMSL, was held at EMSL in 2007. The report is available online at http://www.emsl.pnl.gov/docs/nwchem/nwchem.html. It outlines the capability development path for the software. *NWChem*'s development strategy is focused on providing new and essential scientific capabilities to EMSL users and enabling innovative and integrated research at EMSL, while effectively utilizing the latest computing technology on supercomputers that are hundreds of teraflops and tens of thousands of processors in size. Scientific capability areas that will be developed in *NWChem* are aligned with EMSL's science themes. As such, the development strategy for the next 5 years will be two-fold:

- Enable *NWChem* to push the scientific envelope by scaling the software to petaflop architectures. An improved software architecture that can effectively utilize the hardware advances and tens to hundreds of thousands of processors anticipated in the next 10 years will be designed and developed.

- Develop new and essential capabilities that enable research to answer scientific questions in the areas of
  - Kinetics and dynamics of chemical transformations.
  - Chemistry at interfaces and in the condensed phase.
  - Molecular dynamics, spanning longer time regimes.

These two development areas are not independent of each other, as new capabilities often involve new types of algorithms that may be able to exploit the petascale architectures in different ways than the traditional quantum chemistry and molecular dynamics methodologies. In addition, EMSL intends to bring *NWChem* into the open-source software community to enable the software to become a real community code supported by a broad group of developers. Software quality control will maintained through a developers' consortium.

6.2.4 Mass Spectrometry

EMSL's mass spectrometry capabilities enable high-throughput, high-resolution analysis of complex mixtures. These resources are applied to a broad range of scientific problems from proteomics studies with applications such as human health and environmental remediation to aerosol particle characterization and fundamental studies of ion-surface collisions and preparatory mass spectrometry using ion soft-landing.

Proteomics resources and research: EMSL contains proteomics capabilities including instruments and sophisticated bioinformatics methods. This unique and specialized high-throughput capability enables both hypothesis- and discovery-driven research across essentially every area of biological research.

Cutting-edge proteomics tools and methods available at EMSL facilitate advanced global proteomics research and allow detailed visualization and characterization of cellular proteins. The scope of proteomics studies includes identification of proteins and their abundance, and often discovery of other information important for understanding their activity and function (e.g., their position in the cell, turnover rates, and modification states). The ability to study changes in biological systems and describe the variability from large volumes of proteomics data has enabled new insights to be extracted for diverse organisms, and even complex biological systems such as microbial communities in the soil and ocean.

Aerosol particle characterization resources and research: Unique mass spectrometry tools enable EMSL users to characterize environmentally relevant aerosols with high specificity and resolution. Scientists use these tools to study fast chemical reactions, characterize particles with low number concentrations, detect and characterize the chemical structure of organic compounds in aerosols and cloud water samples, and characterize in detail the chemical composition and transformation of particulate matter collected on substrates using novel atmospheric pressure surface ionization techniques.

Ion-surface-collision resources and research: EMSL has a number of mass spectrometers specially configured for studying fundamental aspects of activation, dissociation, and deposition (soft-landing) of complex molecular ions following collision with specially prepared surfaces. Preparatory mass spectrometry using soft-landing of mass selected ions on surfaces enables highly specific modification of surfaces, preparation of novel materials, and facilitates molecular-level understanding of interactions of biomolecules with hydrophilic and hydrophobic surfaces in living systems.

6.2.4.1 Capability detail

Proteomics Capabilities

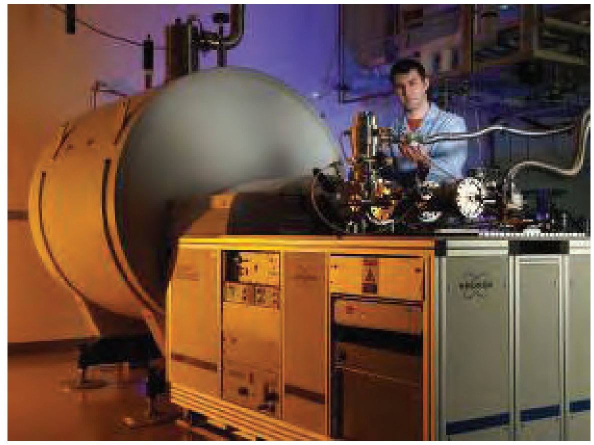
- Fourier-transform (FT) mass spectrometers, including 7-T, 9.4-T, 11.5-T, and 12-T FT ion cyclotron resonance (FT-ICR) spectrometers, a 7-T linear ion trap FT (LTQ-FT) spectrometer, and three LTQ-Orbitraps spectrometers.

- Five ion trap spectrometers and five linear ion trap spectrometers (one with electron transfer dissociation capabilities).

- Two triple-quadrupole mass spectrometers.

- Four time-of-flight (TOF) mass spectrometers.

- Seventeen custom high-performance liquid chromatography (HPLC) systems, three Agilent capillary HPLC systems, and a Dionex nano-HPLC system. The linear ion trap mass spectrometers, LTQ-Orbitraps, LTQ-FT, 11.5-T and 9.4-T FT-ICR spectrometers are seamlessly integrated with the automated HPLC systems for unattended, around-the-clock operation.



This 12-T FT-ICR provides detailed proteome characterization when coupled online to capillary liquid chromatography. This instrument is a centerpiece for the analysis of intact proteins.

Aerosol Capabilities

- LTQ-Orbitrap.
- Field-deployable, second-generation, single-particle, laser-ablation, TOF mass spectrometer (SPLAT II).
- Proton transfer reaction mass spectrometer.
- High-resolution TOF aerosol mass spectrometer.

Ion-Surface Collision Study Capabilities

- 6-T FT-ICR spectrometer configured for studying ion-surface interactions.
- Ion deposition instrument for preparation of novel materials using ion soft-landing.
- TOF secondary ion mass spectrometer (TOF-SIMS).

6.2.4.2 Available capabilities

Proteomics Capabilities

- ***12-T FTICR mass spectrometer***: This system delivers sub-ppm mass accuracy, high resolving power, wide bandwidth detection, high dynamic range, and data-dependent tandem mass spectrometry (MS/MS) for detailed proteome characterization when coupled online to capillary liquid chromatography. The original ion optics were upgraded to include an ion funnel and additional quadrupole stages for enhanced ion transmission. A conventional q-q front end adds a facile and efficient precursor ion selection capability and dissociation for on-the-fly, data-dependent collisionally induced or electron capture dissociation analyses. This instrument is a centerpiece for the analysis of intact proteins.

- ***11.5-T wide-bore FTICR mass spectrometer***: This home-built instrument incorporates an ion funnel interface, ion transfer and storage quadrupoles, and a capacitively coupled cylindrical open-ended ICR cell. This instrument exploits a very-low-noise, radio frequency-shielded environment, and in addition to a ultra-high mass measurement accuracy and mass resolving power, it provides ultra-high sensitivity and dynamic range. It is currently used for automated high-throughput capillary liquid chromatography (LC)-FT-ICR proteome analyses.

- ***9.4-T FTICR mass spectrometer***: This instrument is a 150-mm-bore, actively shielded Bruker Daltonics Apex III. The original ion source was replaced with a custom source. The custom source incorporates an ion funnel, DREAMS technology, and automatic gain control. These modifications permit maximum use of the spectrometer's capabilities by maintaining the optimum number of ions in the ICR cell throughout a liquid chromatography separation and by increasing dynamic range of measurements by ejection of highly abundant ions.

- ***7-T ThermoFinnigan LTQ-FT mass spectrometer***: This instrument is a fusion of the linear ion trap and FT-ICR mass spectrometers. The two modes can be operated separately or together, thus offering unique flexibility.

- ***Three ThermoFinnigan LTQ-Orbitraps***: These instruments are a fusion of the linear ion trap-type mass spectrometer with a new Orbitrap mass analyzer that combines the MS/MS-based fragmentation of the linear ion trap with stable high sensitivity, resolution, and mass accuracy of the Orbitrap component.

- ***Agilent LC-electrospray ionization-TOF mass spectrometer***: This instrument incorporates an orthogonal-axis, TOF mass spectrometer. Its fast data acquisition speed (~100 ms), high resolution (~10,000), and mass measurement accuracy (<3 ppm) make it a good platform for high-throughput, accurate mass analysis. The unique detector design, which employs analog-to-digital converter technology, also significantly broadens the dynamic range of the instrument, making it suitable for quantitative proteome analyses.

- ***Two ESI-ion mobility spectrometer-TOF mass spectrometers***: These instruments incorporate an ion mobility spectrometer (IMS) with an Agilent orthogonal TOF mass spectrometer. With the inherent high speed of gas-phase separation in IMS and the well-designed interface between ion mobility spectrometer and TOF mass spectrometer using PNNL's ion funnel technology, these instruments can perform proteomic sample analysis with extremely high-throughput rates and sensitivity.

- ***Micromass Q-TOF Ultima mass spectrometer***: This quadrupole TOF spectrometer has an ESI source and combines the simplicity of a quadrupole spectrometer, the high ion conductance of a hexapole collision cell, and the ultra-high efficiency of an orthogonal acceleration TOF mass analyzer to achieve simultaneous detection of ions across the full mass range. The TOF analyzer provides for 10,000 resolution and W-OPTICS for a maximum resolution of 17,500 with an upper m/z range of 20,000. This instrument was modified with an electrodynamic ion funnel to improve sensitivity.

- ***Five ThermoFinnigan LTQ mass spectrometers***: These instruments use a linear ion trap that increases sensitivity significantly over previous (LCQ) ion trap mass spectrometers. These instruments are set up and run in production mode. In addition, one instrument has electron transfer dissociation capabilities.

- ***ThermoFinnigan and Sciex triple quadrupole mass spectrometers***: Two research-grade triple quadrupole instruments are available, and are used primarily for sample analysis and further technology and method development activities in regard to multiple-reaction-monitoring studies for targeted proteomic analysis.

- ***HPLC systems***: A signature EMSL proteomics capability is the coupling of capillary separations (liquid chromatography and capillary electrophoresis) to mass spectrometers. Unique capabilities include the in-house-developed, high-pressure HPLC systems (operational up to 20,000 psi) for nanoscale protein and peptide separations and ultra-low-level LC-MS analyses of proteolytic digests along with unique systems automation and integration capabilities

Aerosol Capabilities

- ***Thermo's LTQ Orbitrap™ for environmental research***: This instrument enables fast, sensitive, and reliable detection and identification of compounds in complex mixtures. The instrument is well suited for analysis of ions with m/z in the range 0-2000 Da with mass resolution of up to 100,000 at 400 Da.

- ***SPLAT II***: This is the first field-deployable instrument for characterizing individual particles down to 50 nm in diameter. It is the first instrument operated in the field in an infrared-ultraviolet mode. SPLAT II's applications include but are not limited to climate, air pollution, human health, bioterrorism, and emerging nanotechnologies.

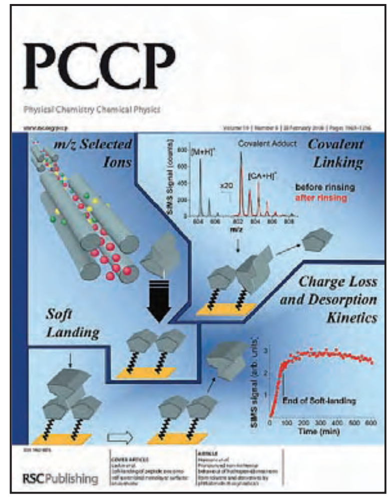
- ***Proton transfer reaction mass spectrometer***: This spectrometer uses chemical ionization mass spectrometry for real-time, online quantification of volatile organic compounds in the air. The instrument provides extremely fast response time (~a second), and detection limits in the range of 50-300 parts per trillion by volume. The instrument is built into an aerospace-grade rack and has been flown on a research aircraft to assess urban air pollution.

- ***High-resolution TOF aerosol mass spectrometer***: This instrument is the last generation of Aerodyne, Inc. instruments capable of providing quantitative size and chemical mass loading information in real-time for non-refractory sub-micron aerosol particles.

Capabilities for Studying Ion-Surface Collisions

- ***6-T FT-ICR mass spectrometer***: This in-house designed and constructed spectrometer uses surface-induced dissociation, for activation and dissociation of large molecules, for studying the energetics and mechanisms of dissociation of protonated peptides, peptide radical cations, organometallic complexes, and non-covalent complexes. This instrument also supports ion-surface collisions and soft-landing studies.

- ***Mass-selected ion deposition instrument***: This in-house designed and constructed instrument incorporates a high-transmission electrospray ion source, quadrupole mass filter, bending quadrupole, an ultrahigh vacuum chamber for ion deposition by soft landing, and a vacuum-lock system for introducing surfaces into the ultrahigh vacuum chamber. The instrument is used for controlled highly specific deposition of complex ions on surfaces, covalent immobilization of mass-selected ions on surfaces and preparation of novel catalysts.

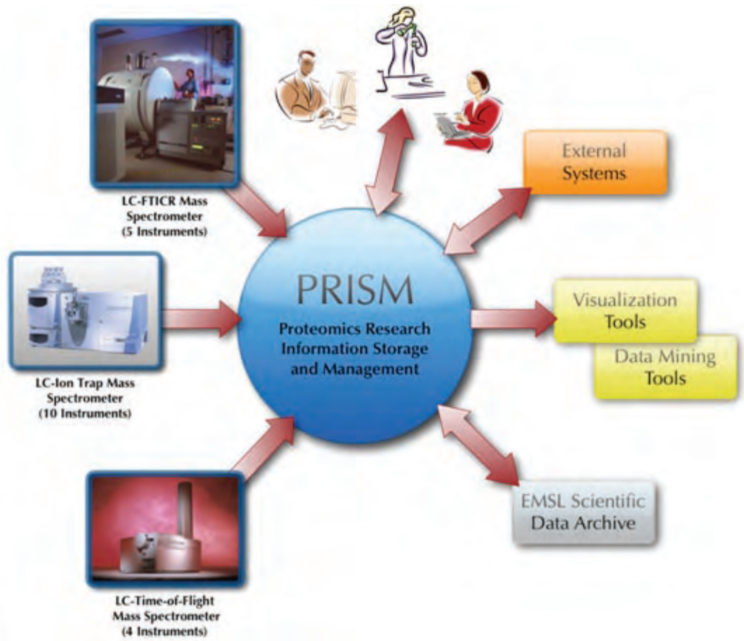


Soft landing research conducted at EMSL was featured on the February 28, 2008, cover of *Physical Chemistry Chemical Physics.*

- ***TOF secondary ion mass spectrometer***: This ultrahigh vacuum surface analytical system is designed to examine surface structure, composition, and chemical state by means of secondary ion detection during ion sputtering. The instrument is furnished with a C_{60} ion gun, a liquid metal ion gun with Au or Bi sources, and a Cs^+/O_2^+ sputter ion gun with emission current stabilizers. The capabilities include surface spectroscopy with high sensitivity and mass resolution, surface imaging with high lateral resolution, depth profiling with high depth resolution, and three-dimensional analysis. The ability to provide cluster ions, such as Bi_n^+ and C_{60}^+, will enable EMSL users to obtain substantial improvements in detection yields, especially in biological materials. The C_{60} ion gun can provide ultimate high mass sensitivity, superior imaging, and a powerful organic sputter depth profiling capability with C_{60}^+ or C_{60}^{2+} ions. This new instrumentation provides flexibility to image with minimal shadowing on samples with high surface topography as well as the highest commercially available mass resolution performance. The system is equipped with a side chamber with limited processing and analytical capabilities.

6.2.4.3 Future directions

Proteomics capabilities: Significant new platform developments in the “technology pipeline” are planned to be introduced over the next 3 to 5 years. This will augment existing MS-based platforms by providing new types of measurements, as well as a large increase in measurement throughput. Among the new platform developments are ion mobility separation techniques that not only greatly decrease analysis times, but also allow new approaches to studying biomolecules. A key capability development area for the EMSL is “top-down proteomics” and associated tools to detect (combinatorially) post-translationally modified proteins (e.g., glycosylation, lipid modifications, phosphorylation, and methylation). The ultimate goal is a high-throughput capability for intact-protein proteomics analogous to the existing “bottom-up,” high-throughput capability based on detecting peptides.



The PRISM (Proteomics Research Formation Storage and Management), data management, and workflow automation system enables high-throughput proteomics research. In addition to managing terabytes of raw data PRISM automates complex analysis pipelines and transforms raw mass spectra into useful biological knowledge.

Aerosol capabilities: Recent innovations in mass spectrometry provide the ability to record mass spectra on substrates, in a controlled environment, without sample preparation by creating ions outside the mass spectrometer. These include desorption electrospray ionization; direct analysis in real time method; desorption atmospheric pressure chemical ionization; and electrospray-assisted laser desorption/ionization. EMSL is interested in applications of these techniques for analysis of aerosol samples collected in laboratory and field studies. Combinations of novel atmospheric pressure surface ionization techniques for *in situ* chemical analysis of surfaces with high-resolution mass spectrometry will enable detailed characterization of particulate matter collected on substrates that is not possible using current techniques.

Ion-surface collision capabilities: The tools developed in EMSL will be used to investigate the rates of proton transfer and electron transfer processes in model systems mimicking metalloproteins, studying the energetics and dynamics of dissociation of non-covalent complexes, exploring the effect of the charge and the radical on fragmentation of peptide ions, and understanding the soft-landing phenomena that provide foundation for preparative mass spectrometry.

6.2.5 Microscopy

EMSL offers sophisticated electron microscopes, scanning probe microscopes, optical microscopes, and other microscopic tools for characterization of surfaces, nanomaterials, biological tissues and molecules, bio-geo interface, materials related to environment and energy, geochemical materials, and thin films with unprecedented spatial and energy resolution. Some of these instruments are equipped with specialized *in-situ* experimental capabilities to understand the complex reaction dynamics during chemical transformations, interfacial electron transfer processes, protein-protein interactions, and molecular interactions at the single molecule level. Users apply these capabilities to characterize different samples in conjunction with other synthesis and characterization capabilities available at EMSL. Applications and resources include the following.

Imaging: Many of the microscopy tools offer nanoscale and sub-nanoscale resolution in imaging of a wide variety of sample types, allowing users to study chemical processes such as reaction mechanisms and interfacial electron transfer in organic thin film devices, nanostructures, geological samples, and biological samples such as protein and bimolecular structures on a surface. In most cases, these capabilities offer topographical and chemical information on a variety of materials, imaging down to individual atoms on a surface.

Tomography and cryogenic imaging: A transmission electron microscope (TEM) equipped with tomography capability allows users to obtain image series for three-dimensional reconstruction of biological and polymer samples at the temperature range of -180ºC to room temperature. A microscope equipped with hardware and software for computer-controlled scanning electron microscopy energy-dispersive x-ray analysis (SEM/EDX) allows users to obtain detailed knowledge about the particle-type composition of non-volatile samples of atmospheric particles.

Particle analysis: Characterization of the particulate matter can be performed using conventional methods of SEM and TEM, emphasizing the internal structure of individual particles; investigating hygroscopic behavior of particles, and making automated measurements of size, aspect ratio, and elemental composition for a large number of individual particles, allowing users to obtain detailed knowledge about the particle-type composition over statistically relevant number of particles using computer control.

Dynamic processes in real time: Specialized *in-situ* experimental capabilities are available to understand the complex reaction dynamics during chemical transformations, interfacial electron transfer processes, protein-protein interactions, and molecular interactions at single molecule level.

Chemical composition analyses: Associated with the electron microscopy capability is a range of chemical composition analyses capabilities based on electron excited photon emission and electron energy loss spectroscopy in TEM. This allows users to learn the chemical composition of the materials while observing the structure.

Site-specific microscopy and three-dimensional topographic and chemical imaging: Contrary to the general imaging of surface structure, a dual beam focused ion beam/scanning electron microscope with a combination of focused ion and electron beams enables imaging and chemical composition analysis layer by layer (depth information) for a specific site, therefore providing three-dimensional topographic structure and chemical composition. This is especially powerful for sampling of less proportional of materials in a buried matrix or mixed in a massive matrix.

Imaging at near real environment: This capability allows imaging and chemical composition of the materials at certain partial pressures so that the materials can be imaged without use of the high vacuum normally required for the general microscope.

6.2.5.1 Current capabilities

High-Resolution TEM: The JEOL 2010 high-resolution TEM is capable of a point-to-point resolution of 0.194 nm. The instrument is typically used to image metals, ceramics, minerals, nanostructured materials, and biological materials and tissues at atomic-bond–length resolution. Scientists use this instrument for research related to spintronics, environmental issues, geophysics and geochemistry, atmospheric issues, biology, and catalysis.

Cryo-TEM: The FEI Tecnai T-12 cryo-TEM complements EMSL's electron microscopy suite and JEOL 2010 analytical high-resolution TEM. The capabilities of the T-12 cryo-TEM include the following:

- Two axes (± 70 degrees) high-tilt stage that allows image tilt series to be obtained for three-dimensional reconstruction using electron tomography with a computer back-projection capability to view slice-by-slice virtual sectioning.

- Cryostage for observing samples in a frozen-hydrated state.

The T-12 cryo-TEM is primarily devoted to biological samples involving morphological and immuno-cyto chemistry studies, but it also supports imaging of samples such as soft materials and polymers. EMSL's T-12 cryo-TEM and associated sample preparation suite, including Vitrobot and ultracryo-microtome, provides outstanding structure preservation through rapid freezing of cells and tissues.

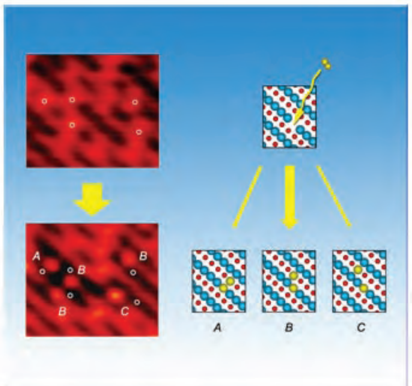
Dual Focused Ion Beam (FIB)/SEM: The FIB/SEM combines two high-resolution microscopy tools that jointly enable nanoscale measurements and the unique preparation of samples and materials for other uses. This instrument provides rapid and selected region preparation of samples for TEM and other spectroscopies; three-dimensional analyses of nanoscale materials and other small objects; and the capability for nanoscale lithography. Functionally, the instrument includes computer-controlled ion-beam micromachining based on a liquid-metal ion source and high-resolution SEM imaging based on a field-emission-gun electron source. Energy-dispersive x-ray spectroscopy (EDX) and electron backscattering diffractions systems including all necessary hardware and software for quantitative and qualitative analyses are incorporated to allow phase identifications.

Environmental scanning electron microscope: EMSL's field-emission environmental SEM (FEI Model XL30) is a state-of-the-art instrument in which samples can be examined using a field-emission source electron beam both in standard (high-vacuum) SEM and environmental (wet) modes of operation. Samples can be examined with 10 to 15 Torr of gas remaining in the chamber. Almost any sample of suitable size can be examined using this microscope without the use of additional specimen preparation procedures, which may introduce various artifacts. The microscope is equipped with secondary electron detector, solid-state backscattered and transmitted electron detectors, several different gaseous secondary electron detectors, and an EDX spectrometer. The EDX spectrometer (EDAX Model 136-10) is outfitted with a Si(Li) detector with an active area of 30 mm^2 and an ATW2 window that allows x-ray detection from elements higher than beryllium (Z>4). The instrument is also equipped with hardware and software for computer-controlled SEM/EDX analysis of particles and sample inclusions.

Single molecule microscopes: Designed in EMSL, the single-molecule optical microscope allows study of complex reaction dynamics such as enzymatic reactions, protein-protein interactions, and interfacial electron transfer process. It is designed and adapted specifically for single-molecule spectroscopy experiments. This instrument contains an inverted optical microscope, continuous-wave and pulsed lasers, optics, spectrometers, and ultrasensitive photon detectors. The single-molecule fluorescence/patch clamp microscope is equipped with the combination of high-sensitivity fluorescence imaging and simultaneous physiological measurements to identify real-time molecular interactions and conformational changes of cell-membrane receptors and their functional consequences. This system is one of the few worldwide that provides the sensitivity needed to quantify molecular interactions at the level of a single molecule or a few molecules simultaneously with the functional outcome of these interactions. The system consists of a wide-field microscope and a set of lasers coupled to a high-sensitivity charge-coupled device camera, combined with a patch-clamp amplifier for single-channel and whole-cell recording.

Photoemission electron microscope: This instrument can image nanoscale surface structures (spatial resolution of approximately 8 nm) by imaging electron emissions induced by ultraviolet and laser light sources. EMSL's photoemission electron microscope (PEEM), from the manufacturer, Elmitec, uses inherently low-aberration magnetic lens elements. A complementary suite of ultrafast lasers serve as a source for studying femtosecond dynamical processes. The PEEM is applied to surface science studies of individual nanostructures and catalytic sites on specially designed metal, semi-conducting, and metal oxide substrates.

Atomic force microscope/scanning tunneling microscope: EMSL offers air, liquid and ultrahigh vacuum (UHV) atomic force microscopes (AFMs)/scanning tunneling microscopes (STMs) to characterize materials in atomic resolution. The Digital Instrument Nanoscope IIIa multimode scanning probe microscope is primarily used to obtain topographical information on nanostructures, nanodevices, and quantum dots; thin films; geological and geochemical samples; protein and bimolecular structures at surfaces; and samples undergoing electrochemical and corrosion processes. The resolution ranges from the submicron-length scale (nanoscale) to the atomic level. The instrument can operate in air and liquid environments and in modes including contact, tapping, frictional force, phase/frequency, magnetic/electrostatic force, tunneling, and capacitance.



An oxygen molecule (yellow, top right) splits when encountering a vacancy on a titanium oxide surface. One atom fills the vacancy and the other can move a couple spaces away (bottom right).

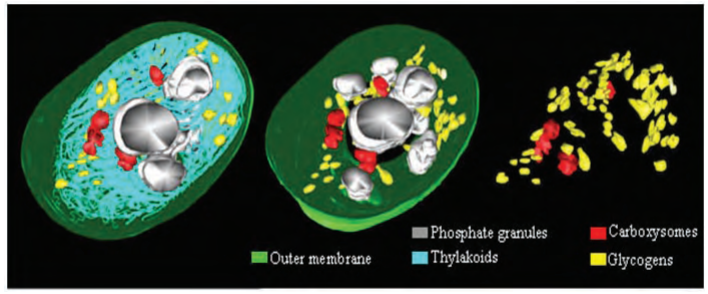
Bio AFM: EMSL's Digital Instruments BioScope™ AFM combines optical and AFM techniques used to examine heterophase processes on mineral surfaces and to image biological systems, such as bacterial colonies, on minerals and other substrates. The BioScope AFM allows samples to be examined in fluids or air with little or no sample preparation. Its optics provide an effective magnification range of 25 to 10,000,000 times and can be used simultaneously with bright-field, fluorescence, and confocal techniques. The microscope supports all major AFM-imaging techniques and modes, including contact and intermittent contact (Tapping Mode™) atomic force, lateral force, force modulation, phase, and lift. The system's NanoScope IV controller enables high-speed data capture of high-pixel–density images (up to 4096 data points per scan line), which makes possible characterization of surface interactions at timescales previously inaccessible to the scanning probe microscope.

UHV AFM/STMs: These surface science tools include multiple complementary probes of surface phenomena. These systems include a pair of interlocked UHV chambers: scanning probe chamber and sample preparation/characterization chamber with surface science capabilities. All systems are equipped with *in-situ* gas delivery under the STM tip to allow atomically resolved studies of chemical reactions at various temperatures. Additionally, one of the systems is equipped with means to expose the samples to ultraviolet light in the analysis position for site-specific photochemistry studies. X-ray photoelectron spectroscopy and the oxygen plasma sputter cleaning capabilities in the sample preparation chamber help to establish a clean surface with chemical state information of the elements for AFM/STM measurements.

6.2.5.2 Unique capabilities

In general, the TEMs are unique capabilities for material characterization. A high-resolution microscope is extensively used for imaging and electron energy loss spectroscopic studies of inorganic materials. The cryo-TEM is customized to accommodate its users' demands within the fast-growing field of biological imaging at the nano-structural level. Coupled with electron tomography capabilities, three-dimensional reconstruction of an object that was acquired from a series of two-dimensional projections using TEM can be achieved.

The other unique capability is the FIB/SEM. This is a new capability, and it opens up a whole new area of research in dimensional reconstruction of structures using a combination of electron backscattering and energy dispersive x-ray analysis. This capability offers a cryostage for investigation of soft materials, in particular, dynamic cellular processes.



Using TEM tomography, EMSL users reconstructed a three-dimensional image of a Cyanothece cell.

UHV AFM and STM capabilities are designed to investigate single site chemistry. These variable temperature capabilities consist of specialized instrumentations, and these capabilities comprise multiple complementary probes of surface phenomena.

6.2.5.3 Future capabilities

A new generation high-resolution TEM with a configuration optimized (and customized) to enable microscopy and other measurements under chemically interesting conditions is being planned as a major new capability for EMSL. This instrument will be designed to allow microscopy, spectroscopy, and some chemical measurements relevant to catalytic and geochemical studies of importance to energy and environmental applications. The microscope will be fitted with a differentially pumped environmental cell and a gas-handling system for chemical studies. Chemical studies with liquids are also anticipated and if necessary these will be accommodated using specialized sample holders. The environmental cell will be designed with apertures and differential pumping so that the microscope can handle high pressure and temperature around the specimen.

To answer questions about the interfacial and defect control of catalytic reactions and the chemical nature of nanoparticles, the microscope will be equipped with an electron beam with low energy spread and high-resolution electron energy loss detector. This will allow detailed chemical information to be obtained with an energy resolution of about 0.2 eV in electron energy-loss spectroscopy. It is anticipated that a monochromator needs to be incorporated with the microscope to achieve this energy resolution. To obtain important information about the role of interface and particle structure on chemical reactivity, the microscope will need to have a point-to-point resolution better than 0.1 nm. It is anticipated that the microscope will need to have an aberration corrector for the image (Cs-image corrector).

EMSL is building a **stochastic optical reconstruction microscope** for imaging of fluorescent biological materials. This new technology will have a resolving power more than 10 times better than conventional optical microscopy. The equipment has been ordered, and work is progressing. Work is also proceeding on improving the fluorescent probes necessary for the process and developing automation software. The system should be operational in January 2009 and be ready for users in spring or summer of 2009.

6.2.6 NMR and EPR

Researchers use EMSL's nuclear magnetic resonance spectroscopy (NMR) and electron paramagnetic resonance spectroscopy (EPR) capabilities to study molecular systems important to biology, environmental remediation, and sustainability as well as other areas of interest to the U.S. Department of Energy and the nation.

EMSL staff members develop a variety of probes and techniques to complement the NMRs available to users.

EMSL houses NMR instruments with frequencies up to 900 MHz, as well as an EPR. EMSL staff members are active in developing a variety of probes and techniques to complement the state-of-the-art magnets. NMR capabilities at EMSL are widely used in the following research areas:

- **Interfacial and *in situ* chemistry**: Solid-state NMR techniques are available for low-gamma nuclei detection and a full range of magic-angle spinning methodologies to study catalytic, advanced material, geochemical, and biological systems in their near-native state and in real time. Dynamics and relaxation experiments allow for distinguishing surfaces from bulk species at higher fields.

- **Interfacial and *in situ* biology**: NMR resources are available for structural biology investigations to determine the structure of large molecular assemblies and to monitor their changes in response to environmental influences. In addition, EMSL offers tools for functional "omics" research, including metabolomics, and a bio-magic angle spinning (BioMAS)/900-MHz NMR system to explore biological membrane proteins in the solid state.

- **Environmental chemistry**: A unique NMR system is available for radiological studies. Users can perform magic-angle spinning of highly radioactive samples with a novel triple-containment rotor. These tools allow users to apply NMR techniques to the study of radioactive waste processing and storage.

- **Metallocomplexes**: Studies of transition metal complexes relevant to biological, environmental, and catalysis systems are emphasized. BioMAS and low-temperature probes can be used to determine conformational changes in membrane protein complexes involving metal clusters as followed by solid-state NMR and by pulsed EPR.

6.2.6.1 Capability detail

The following list describes each of EMSL's NMR and EPR instruments. Section 6.2.6.2 contains further details about the primary NMR and EPR tools available to EMSL users.

- Twelve NMRs, ranging from 85 MHz to 900 MHz (magnetic fields from 2 to 21.1 Tesla), with capabilities for high-field liquid-state, solid-state, and micro-imaging techniques.

- One pulsed EPR spectrometer for probing metal centers in biological and materials systems.
- NMR with radiological capabilities.
- NMR with metabolomics capabilities to study microbial systems and biofluids.
- Extreme-temperature probes, including high-temperature probes to study catalysts in their near-native states and low-temperature probes to study metallo-protein chemistry and structure.
- Novel BioMAS/900-MHz system for bio-solid studies with particular focus on developing methodology for membrane proteins.
- 500-MHz NMR imaging spectrometer, used alone and integrated with confocal optical fluorescence microscopy, allows methods including mapping of biological systems with spectroscopy and diffusion.
- 2-T horizontal wide-bore (300 mm) system used with custom-built hyperpolarized gas imaging enhancement technology for observing air-water exchange in samples ranging from fuel cells to lung tissue.
- Virtual NMR tools for remote access to spectrometer systems.

6.2.6.2 Available capabilities

NMR: 900 MHz (21.1 T). The NMR has a wide range of custom-built probes for studying difficult-to-observe metal systems in the environmental clays and minerals, catalytic materials, and biological contexts. Probes are available for high-resolution solution-state dynamics and structure characterization of biomolecular complexes and a one-of-a-kind Bio-MAS probe for membrane protein observation in the solid-state. Future user needs will be filled with FAST-MAS probe technology, Constant Flow probe systems, and probes capable of more extreme temperatures and pressures than current technology.

Researchers prepare samples for 1 of EMSL's 12 NMRs with capabilities for high-field liquid-state, solid-state, and micro-imaging techniques.

NMR: 800 MHz (18.8 T) Varian Inova. This NMR has extreme low-temperature probes for metallo bio-system observation. This is the highest field EMSL system with a liquid HCN cryoprobe to study bio-complexes in solution state for highly sensitive applications.

NMR: 750 MHz NB (17.6 T) Varian Inova. This NMR is a high-field resource for protein structure determination. It is also used, with custom-built probes, for solid-state observation of lithium and boron in hydrogen storage materials.

NMR: 600 MHz NB Varian LC-NMR System - Metabolomics Cryoprobe. This is an automated and separation technology paired with NMR for metabolomic studies of extracts from microbial cell systems, tissues, and biofluids.

NMR: 600 MHz NB Varian Inova - Cryoprobe. This is a high-sensitivity workhorse system for structure and dynamics determinations of proteins.

NMR: 600 MHz NB Varian Inova. This NMR is used for structure determination of proteins. The broadband probe technology is used for direct observation for multiple frequencies between ^{15}N, ^{13}C, and ^{31}P.

NMR: 500 MHz WB Varian (solids). This unique *in situ* constant flow, magic-angle spin, solid-state probe technology is used for observation of reactions. Extreme low-temperature probes are used for metallo-system observation in biological and materials contexts. High-temperature probes are used for catalytic materials systems.

NMR: 500 MHz WB Bruker Advance - Imaging. This system provides the highest field magnetic resonance imaging resource. The bioreactor technology provides chemostat control of cell growth paired with direct NMR measurement. Unique confocal laser-scanning optical/magnetic resonance microscopy technology allows integrated study of cellular systems.

NMR: 500 MHz NB CMX for Liquids and Solids. A general purpose liquids and solids resource is set for some "walk-up" time, scheduled on a weekly basis. The system has one of two known liquid-state probes capable of extremely low frequency NMR tuning range (^{103}Rh-^{15}N). The NMR can be used with low-level "sealed source" radiological liquid-state samples.

NMR: 300 MHz WB Tecmag Discovery (radioactive samples). This system is a unique resource for solid-state NMR of radionuclide-containing samples. System also has liquid-state capabilities.

NMR: 300 MHz WB CMX for Solids and Liquids. This popular system is used for a wide variety of solid-state applications. Many solid-state NMR probe technologies are developed first on this system. The unique slow-MAS probe technology and the rarely found "DRAWS" probe are used on this NMR to study biological systems in the solid-state.

NMR: 2-T Horizontal Bore Varian Unity Plus (Imaging). This system is used with custom-built hyper-polarized gas imaging enhancement technology for observing air-water exchange in samples ranging from fuel cells to lung tissue.

EPR Pulsed, ENDOR/ELDOR. (Pulsed: X-Band, CW: X and Q-band). This system is used for probing metal centers in biological and materials systems.

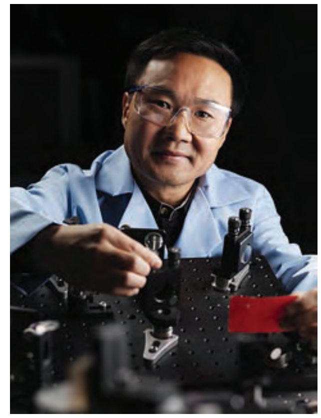
6.2.6.3 Future directions

In the past, this capability was involved with advancing a very diverse group of user projects. In the future, EMSL will focus expertise and custom-built tools on advancing knowledge of metallo systems in increasingly complex and natural contexts (e.g., environmental, biological, and advanced inorganic media). This focused work will be accomplished by combining *in situ* and dynamic magnetic resonance measurement of experimental parameters and pairing these data with computational simulation and modeling to help maximize scientific value. These actions will also involve the following:

- Developing, building, and obtaining advanced probe technology at higher and multiple fields (FAST-MAS probes, Constant Flow probes, probes capable studying systems at more extreme temperatures and pressures).
- Updating console technology for the highest demand instruments.
- Working towards strategic replacement of some lower field systems with state-of-the-art high-field magnet systems.

6.2.7 Spectroscopy and Diffraction

A suite of spectroscopy and diffraction instruments in EMSL allows users to study solid-, liquid-, and gas-phase sample structure and composition at molecular-level resolution. Ideal for integrated studies, the results of spectrometer and diffractometer investigations are easily coupled with EMSL's computational and modeling capabilities, allowing users to apply a multi-faceted research approach for experimental data interpretation and to gain a fundamental understanding of scientific problems.



A suite of spectroscopy and diffraction instruments in EMSL allow users to study solid-, liquid-, and gas-phase sample structure and composition at molecular-level resolution.

At EMSL, a wide range of spectroscopy and diffraction instruments are applied to sample studies for a variety of research applications. These techniques include electron, fluorescence, infrared, ion/molecular beam, Mössbauer and Raman spectrometers, and electron and x-ray diffraction. Some of these techniques are standalone, whereas others can be intrinsically linked to complementary capabilities such as electron backscatter diffraction, found as part of the electron microscope capability. Other spectroscopy and diffraction techniques are situated together to form an integrated suite of capabilities.

6.2.7.1 Capability details

Electron spectroscopy: Achieving nanoscale spatial resolution, EMSL users can study the elemental composition, structural properties, and chemical state of materials with applications to thin films, nanomaterials, catalysis, biological and environmental sciences, corrosion, and atmospheric aerosols. Photoelectron spectrometers interfaced with specialized side chambers for catalysis and photochemistry studies are available in the Surface Analysis Suite along with the Auger electron spectrometer. Various electron microscopes with energy-dispersive x-ray spectroscopy (EDX), electron energy loss spectroscopy, and electron backscatter diffraction capabilities are available in the Electron Microscopy Suite. A high-resolution electron energy loss spectrometer is interfaced with surface science capabilities and temperature program desorption to investigate molecular-level chemistry of adsorbates on metal oxide surfaces.

Fluorescence spectroscopy: EMSL's fluorescence spectroscopy tools include specialized pulsed and continuous wave lasers and detectors over a spectral range spanning the infrared to the ultraviolet. These integrated systems have been applied to identify and characterize the fluorescence spectra and lifetime of novel uranium mineral phases at the Hanford Site, a former plutonium production complex in southeastern Washington State.

Infrared spectroscopy: Fourier transform infrared spectrometers enable the study of various mineral-chemistry topics as well as sorbate binding mechanisms at mineral, biotic, and organic interfaces. The modular design of the spectrometers in this laboratory enables rapid changing of detector and beam-splitter combinations so that researchers can readily change from the visible to the near-, mid-, or far-infrared wavelength ranges. A vacuum bench equipped with a helium-cooled bolometer and step-scanning capabilities is optimized for far-infrared measurements as well as time-resolved spectroscopy. A nitrogen-purged system equipped with a microscope and temperature-controlled mapping stage (-200 to 600°C) allows spatially resolved infrared measurements at the 60-µm level. A variety of cells are available for analyzing gas, liquid, solid, and slurry samples using a variety of techniques. Raman vibrational analyses can be obtained using the Fourier transform-Raman module and Raman confocal microscope.

Ion/molecular beam spectroscopy: Ideal for the study of complex materials, beam capabilities are applied to analyses of thin films and interfaces, studies of radiation effects in solids, ion beam synthesis of nanostructures, and atmospheric aerosol characterization. Ion accelerator system is equipped with gas and sputter ion sources, a 3.0-MV electrostatic tandem ion accelerator, three beam lines, and end stations used for materials modification and analysis using millimeter- to micrometer-size ion beams. In addition, secondary ion beam based capabilities are also available for highly sensitive trace elemental quantification and depth profiling.

Mössbauer spectroscopy: EMSL users can apply versatile and highly sensitive Mössbauer capabilities to obtain information about the valence state, coordination number, and crystal field strengths of iron in a wide range of samples, such as iron oxides in soils and sediments, catalysts, and iron-doped glasses. Five Mössbauer spectroscopy systems with both velocity transducers and transducers for conversion-electron Mössbauer spectroscopy as well as applied field and sources for ^{57}Fe and ^{151}Eu studies are available.

Raman spectroscopy: The Raman spectrometer is high-resolution, modular triple spectrometer that can be operated in high-resolution or high-throughput modes, with both bulk sample and confocal microscopic capability. This instrument has a high degree of flexibility for bulk solid and liquid samples and as well as confocal microscopy for spatially resolved analysis. As a triple spectrometer in subtractive mode with high-density gratings, it can collect Raman spectra to within 5 cm^{-1} of the exciting line with a resolution of 0.3 cm^{-1}. In triple additive mode, the resolution increases to 0.10 cm^{-1}. Detection in these configurations is provided by a 800 x 2000 pixel, back-thinned, liquid nitrogen cooled Charge Coupled Device detector. The confocal microscope is equipped with multiple long working distance objectives and has line-scanning capability, which rasters the focused laser beam across the sample. The microscope is also outfitted with a Linkam THMS600 stage for temperature-dependent Raman measurements between 100K and 898 K ± 0.1K. Excitation for Raman spectra is currently provided by a 100 mW, 532 nm CW diode laser and a 30 mW, 632 nm HeNe laser.

X-ray diffractometers: General purpose and specialized systems, including single-crystal and microbeam capabilities, allow phase analysis of polycrystalline samples and powder specimens, analysis of epitaxial thin films, protein structure determination, and studies of problematic small inorganic molecules. Multiple x-ray diffraction instruments are available with sealed tube, rotating copper or chromium anodes; microfocus capability; variable temperature capability; as well as charge-coupled device and image plate detection.

6.2.7.2 Unique instruments

High-resolution FTIR: The infrared spectroscopy laboratory in EMSL has two research-grade Fourier transform spectrometers available for collaborative use. Both Bruker spectrometers can be used for molecular spectroscopy line position studies or intensity and line-broadening studies and have maximum resolution of 0.0015- to 0.0013-cm^{-1} and can cover the 10- to 45,000-cm^{-1} range (far-infrared to ultraviolet). The spectrometer is equipped with several gas sample cells: a 20-cm gas cell with temperature control over -60°C to 80°C, 40-m and 200-m white cells (room temperature), and a cw slit-jet molecular beam for recording spectra of supersonically cooled molecular spectra (rotational temperature down to 15K).

Time resolved laser induced fluorescence spectroscopy (TRLIFS): This spectroscopy is ideally suited for studying ions and molecules that, upon optical excitation, display fluorescence or phosphorescence lifetimes on the order of nanoseconds or longer. It is commonly used to evaluate the speciation, oxidation state, equilibrium distribution, structure, and bonding of lanthanides, actinides, and transition metal ions. TRLIFS samples may be prepared as solutions, solids, solid suspensions, or as sorbates at solid and sediment surfaces. Applications of TRLIFS include characterizing environmental contaminants, nanoparticles, aromatics and their derivatives, optical materials commonly used in the telecommunication industry, specialty glasses, as well as illumination devices and optical sensors.

Micro-focus x-ray powder diffraction with curved image plate detection: EMSL's microbeam diffractometer is a Rigaku rotating anode with micro-focus optics, automated x-y stage, and a curved image plate detector. Both copper and chromium anodes are available for use. The use of chromium x-rays is especially advantageous when analyzing iron-rich samples. With specialized optics and collimators, the highest spatial resolution is 10 microns, unfocused 70 microns. Two-dimensional detectors, such as curved image plate detectors, allow collection of a larger section of the Ewald sphere. This has many advantages including decreased data collection time required for the same signal-to-noise ratio.

6.2.7.3 Capability development

Applied field Mössbauer spectroscopy: Mössbauer spectroscopy is used to characterize both the oxidation state of iron and distribution of iron between different site symmetries in a material due to the electronic spins of the iron *d*-electrons. The effect of an applied magnetic field on iron in a sample depends on its intrinsic magnetic character (e.g., diamagnetic, paramagnetic, ferromagnetic). Because of this effect, it is possible to resolve peaks that otherwise overlie each other at zero-field. By adjusting the temperature of the sample and magnitude of the applied field, it is possible to completely characterize the iron chemistry of the sample. For example, using an applied field, it is possible to distinguish between Fe(II) and Fe(III) in octahedral sites in magnetite. As a result, it is possible to characterize non-stoichiometric magnetite, as the result of incomplete reduction processes, and is difficult to characterize by other techniques.

Second harmonic generation spectroscopy (SHG): With recent improvements in laser technology, stable powerful lasers necessary for SHG and sum frequency generation (SFG) are available and much easier to maintain and use. As a result, interest in SHG and SFG has resurfaced. SHG/SFG provides unparalleled sensitivity to *in-situ* surface speciation because of the symmetry relationships required for non-linear optical response. Second harmonic generation and sum frequency generation capabilities for probing interfacial reactions *in situ* are being developed (available autumn 2008).

6.2.8 Subsurface Flow and Transport

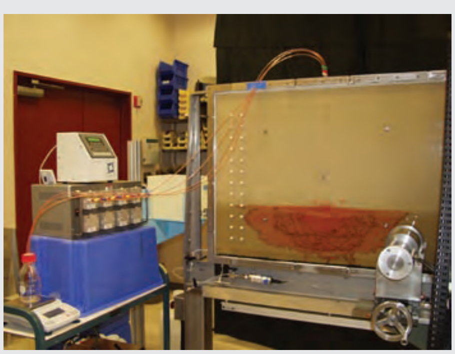
EMSL users can employ subsurface flow and transport capabilities to focus on the application of fundamental physical chemistry concepts to the study of chemical reactions in heterogeneous natural material, with an emphasis on soil and subsurface systems.

EMSL's approach to subsurface flow and transport studies is holistic, integrating flow cells, analytical tools, and predictive modeling capabilities to study the fate and transport of environmental contaminants, including metals, radionuclides, and chemicals.

Various flow cells are available to EMSL users, including column, batch, radial, wedge, and rectangular flow cells as well as microfluidics instrumentation. Flow cells are used in coordination with high-precision, high-sensitivity analytical tools to generate data about sample characteristics by detecting the presence of, for example, carbon, trace metals, ions, nonvolatile compounds, and thermally labile chemicals. EMSL users have the benefit of designing experiments using the predictive subsurface flow and transport simulator, known as STOMP or Subsurface Transport Over Multiple Phases. Data derived from experiments using EMSL's subsurface flow and transport capabilities are used to further refine STOMP.

Historically, a majority of the research has been focused on the transport and fate of non-aqueous phase liquid contaminants such as carbon tetrachloride and trichloroethylene where consideration of transport in both the liquid and vapor phase is important. Other multiple phase fluid flow problems investigated include the dispersive insertion of zero-valent iron and polymer injection to remediate heterogeneous sediments with variable permeability. Recently, the sequestration of cationic, anionic, and radioactive contaminants has been studied as well as novel subsurface remediation strategies including injection of air blankets and desiccation of contaminated sediments.

The results of subsurface flow and transport research have provided the basis for multiple field-scale remediation projects at the Hanford Site, other DOE sites, and aboard. Typically, users come to EMSL with a specific question and work with resident staff to design an experimental approach including the dimension, boundary conditions, and sampling requirements for their intermediate flow experiment. Sometimes,



Dr. Cor Hofstee, an EMSL user from the Netherlands, conducted research at the Subsurface Flow and Transport Laboratory to help locate a spill of light non-aqueous phase liquid (LNAPL) at a site in the Netherlands. LNAPL spilled from a storage tank to the water table and floated on the water table for some time. Then, the water table was raised, and the LNAPL did not rise with the water. Instead, it was trapped below the new water table because of the liquid's high viscosity. At the site, the drillers could not find the LNAPL; based on the experiments conducted at EMSL, the drillers went deeper and found the entrapped LNAPL at ~1-2 meters below the new water table.

the study is the flow and dispersion of a contaminant over times appropriate for testing new remediation strategies on a specific contaminant or sedimentary condition. A numerical simulation of the experiment is conducted before the construction of the actual flow cell. This is to ensure appropriate sedimentary materials, flow rates, etc., are selected and to determine sampling intervals and locations suitable for the data collected. If an existing flow cell is not available, a custom flow cell is constructed onsite to the users' specifications. Users are onsite typically during the design and construction phase and receive data at their home institutions as the experiment progresses. At the conclusion of the experiment, results are compared to the simulation and knowledge gaps are identified.

The experimental migration of fluid is monitored using the dual gamma system as well as through chemical analysis of either the vapor phase in the unsaturated or fluid phase in the saturated zone. Unique and important subsurface environments can be implemented in the flow cells such as the vadose-saturated zone boundary or groundwater flow. Radial flow cells are designed to mimic flow paths around an injection or extraction well.

6.2.8.1 Key capabilities

The following are the key capabilities in the Subsurface Flow and Transport Laboratory:

- Column, batch, radial, and rectangular flow cells.
- Precision, automated pumps to control flow rates.
- Dual energy gamma radiation system, IHCA, multistep, and k-S-P.
- Analytical tools including ion and liquid chromatographs, inductively coupled plasma mass spectrometry, and carbon analysis tools.

6.2.8.2 Unique instruments

Customized flow cells and sampling geometries are designed for each experimental campaign using numerical simulation programs and then fabricated using equipment in EMSL's Machine Shop and Instrument Development Laboratory.

Hydraulic properties measurements: To predict the fate and transport of a contaminant, researchers have to understand the hydraulic properties of sediments. EMSL users have developed three new tools to improve the quality of measurements of hydraulic conductivity and fluid retention properties. These tools include hydraulic conductivity, multistep, and long-column test cells.

6.2.8.3 Capability development

Microfluidics capability with advanced digital imaging capability to monitor flow and transport phenomena such as two-phase mixing and microbial growth kinetics: This new capability would serve to bridge the gap between the laboratory-scale flow capabilities available in the Subsurface Flow and Transport Laboratory and the spectroscopic and modeling efforts on the molecular scale at interfaces that dominate research in EMSL. Flow experiments in intricately patterned wafers are conducted using fluorescent imaging to monitor mixing of various chemical and biochemical reactants. These experiments involve use of two-dimensional flow cells less than 1 cm long and allow researchers to investigate how mixing occurs with ion-milled pillars of different diameter, shape, and packing density. These experiments could be extended so that the silicon surface itself is functionalized.

6.2.9 Instrument Development Laboratory

The Instrument Development Laboratory (IDL) designs, builds, and deploys advanced hardware and custom application software in support of experimental research in EMSL. Representing diverse expertise, IDL staff support EMSL users by providing a variety of design and fabrication services for hardware and software, custom-engineered solutions to research problems, and experience in the interface and control of commercial instrumentation. IDL staff are skilled in the rapid integration of commercial and custom hardware/software packages to suit the exact specifications of specific research projects.

IDL's capabilities and related skills are as follows:

- Electrical Engineering
  - Design from circuits to systems.
  - Custom electronics and instrumentation.
  - Embedded systems.
  - Robotics.
- Software Development
  - Image processing and pattern analysis.
  - Laboratory automation.
  - Remote operation.
  - Data acquisition.
  - Large-scale data management.
- Instrument Fabrication
  - Circuit boards.
  - Component integration.
  - Custom enclosures.

IDL and its staff members provide a variety of technical support to EMSL staff and users.

The IDL has a fully equipped electronics and fabrication shop for EMSL users. The shop includes a fully stocked parts supply, electronic components and small hardware, test and measurement equipment available for checkout, and assistance during business hours. For immediate hardware assistance, customers access the IDL electronics laboratory and receive assistance from any IDL staff member. For work that is limited in scope and not time-consuming, there usually is no charge for services. For larger projects, customers schedule time with an IDL staff member, who assists in defining the work to be done and begins the process of designing solutions.

IDL staff specialize in custom software design, development, and support, including data acquisition, laboratory automation, component integration, data analysis and visualization, data management and archiving, and embedded systems. Using a modular code design model as their basis, IDL staff can develop software in a number of languages, tools, and scripts (e.g., Visual Basic .NET, C# .NET, Java, C, C++, .National Instrument's Labview, and Microsoft SQL Server). In addition, software developers are skilled in instrument control strategies, including General Purpose Interface Bus, serial (RS-232), universal serial bus (USB), infrared, Transmission Control Protocol/Internet Protocol, analog and digital I/O, and high-speed event counting and timing.

The IDL website at http://www.emsl.pnl.gov/capabilities/idl/ provides a full description of IDL capabilities, team highlights, and recent projects.

6.2.9.1 Future directions

The IDL will continue to play an integral role in the EMSL recapitalization effort. The IDL is positioned to develop, customize, and integrate the new instruments and methods proposed and devised by EMSL scientists as part of recapitalization. To that end, the IDL has the mission to foster awareness of candidate technologies and seek out opportunities for their implementation as science enablers. With IDL expertise providing the path from concept to application, the integration of theory and experiment can be realized.

Some technologies with the potential to create significant impacts in environmental molecular science are detailed below. These technologies may offer increases in speed or signal-to-noise ratio, facilitate automated measurement analysis, or make new measurements feasible. Continuing communication of these capabilities to EMSL staff and users remains an important component of IDL's strategy to maximize its impact on the EMSL recapitalization effort.

- **Instrument automation** continues to evolve as software tools improve and network bandwidth increases. Automated instrument control can provide huge efficiency increases, freeing up EMSL staff and user time to analyze data, write up results, or perform other research activities. New capabilities are being developed in multiple programming languages, while legacy applications are being upgraded to work within modern frameworks.

- **Remote instrument control** offers the possibility of making EMSL capabilities available to users remotely, minimizing travel cost and time, and maximizing impact to the user community. During FY 2007, the IDL took another significant step in this direction by drafting a detailed proposal describing an EMSL-wide laboratory automation infrastructure that includes remote control and monitoring of experiments. IDL is still perfecting this concept and exploring funding options. Further strides will be made in areas such as multi-threaded data flow and asynchronous device communications

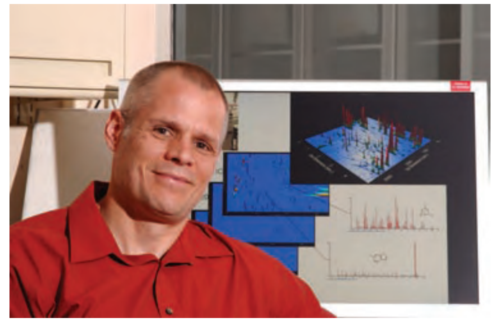
- **Field programmable gate array (FPGA) technology** is being exploited in a new field known as reconfigurable computing which can provide performance gains of several orders of magnitude with select algorithms. This dramatic improvement is clearly applicable to supercomputers and needs to be fully exploited. This effort must include FPGA architecture investigation, inter-FPGA communication, algorithm design and implementation, and testing and validation. The second-generation Single Particle Laser Ablation Time-of-Flight (SPLAT II) mass spectrometer built at EMSL to measure the fundamental chemical and physical properties of individual particles at the nano- and micro-scales was one of the first applications of an FPGA at EMSL by the IDL.

- **Digital signal processing** will be more extensively utilized to improve the performance of existing instruments. Doubling the signal-to-noise ratio of an instrument is equivalent to acquiring a second instrument without the associated cost, support, and floor space.

- **Information management (informatics)** remains a challenging problem and an area where the IDL continues to generate impact. Proteomics research results in large data sets requiring information management systems that enable high throughput. The data production from imaging research can easily exceed the data volume produced by proteomics. These emerging areas highlight the importance of information management. EMSL staff have developed several staff-years of experience with the PRISM system. This technology is readily transferred to the imaging domain. As more users rely on data management, an obvious need for a common platform emerges. It is essential to build this capability in EMSL. The development to date has been completed on projects specific to proteomics and imaging. The value of this system is seen in all aspects of mass spectrometry research and in the proteomics capability utilized by many users, as well as to the Genomes to Life protein complex project, and projects funded by DOE Office of Biological and Environmental Research and National Institutes of Health. Continued development of the informatics capability will allow EMSL to support more users and increase the research that can be accomplished with limited resources. In response to this issue, IDL has drafted proposals to improve certain aspects of the data management process and advance informatics analysis.

6.2.10 Computing and Networking Services

Computing and Networking Services (CaNS) provides the infrastructure and computing services that enable EMSL users to effectively operate computer and network resources for their scientific and business requirements. In supporting growing business and research needs of EMSL in the area of information sciences, the CaNS team secures information access to EMSL by providing online remote access to both computing resources and scientific equipment. A large portion of the efforts undertaken by CaNS staff members involves providing customer support to EMSL's onsite and offsite users. For offsite users, the CaNS staff members provide secure information access and dissemination among EMSL researchers and the global scientific user community.



For EMSL users, the CaNS team maintains software repositories with shared access to frequently used data visualization software and other applications.

6.2.10.1 Primary services

The CaNS team provides the following services to EMSL users:

- **Security**: Upgrade infrastructure and applications to better protect EMSL's computing resources while continuing to provide open access for visitors and collaborators.
- **Desktop computing**: Provide computer support services to more than 1,400 Windows and 210 Macintosh computer systems. Work includes application troubleshooting, peripheral device setups, personal digital assistant support, wireless configurations, remote access, and domain account administration, and system upgrades.
- **Scientific computing**: Support computers used to control scientific instruments during experiments or to collect data from experiments. A variety of Windows, Macintosh, and other operating systems are installed on these computers. The CaNS staff also consult with researchers to develop customized clusters or standalone computer systems that meet specific research needs.
- **Infrastructure operations**: Operate, maintain, and develop new or replacement infrastructure to meet changing scientific and security needs.
- **Software application development and deployment**: Provide and maintain software repositories with shared access to frequently used software including freeware and floating license managers for commercial scientific applications. The following applications are in the repository:
  - Computer languages and interpreters.
  - Editors and debuggers.
  - Configuration management tools.
  - Documentation tools and pre-viewers.
  - Communication and collaborative tools.

- Visualization, plotting, and graphing tools.
- Numerical tools and libraries.
- Data acquisition tools.
- Data management, structure, and format conversion. More than 150 applications available via this repository have been built and compiled to operate over the various operating systems that CaNS supports.

- Auditorium and conference room support. Support hundreds of symposia, conferences, and meetings each year.

A large portion of the work undertaken by CaNS staff involves providing customer support.

6.2.10.2 Key capabilities

- Secure Shell remote access gateway (PASCAL) allowing users to securely connect to EMSL and its internal resources using SecurID.

- Virtual VNMR gateway (Vince) that combines Secure Shell access and a feature-rich graphical interface to VNMR and other instrumentation.

- High-performance Internet facing Secure Collaboration Zone (SCZ) that allows direct Internet connection of 10-gigabit Ethernet computers.

- SCZ-attached web server (NWfsWeb) that provides an application framework to deliver content to the Internet with direct access to all data on the EMSL Archive.

- SCZ attached storage system (Ncollab) that provides Internet-facing and multi-protocol (scp, ftp, and bbcp) access to the EMSL Archive.

- Internet-facing source code repository (Subversion) and web-based management of software projects using a Trac-powered wiki.

- AFS shared file system infrastructure that provides cross-platform access to a single collaborative file system.

6.2.10.3 Capability development

- Upgrade the technology of the VNMR gateway to decrease complexity and increase usability. Multiple interfaces on the new server will allow remote access to a greater variety of systems and networks.

- Create framework to launch virtual Windows systems as queue-able supercomputer jobs to perform proteomics processing using idle supercomputer cycles.

- Place platform-independent, high-performance shared (Samba, Lustre, NFS) file system into production (EMSLfs).

7.0 User Outreach and Support

Engaging our user community is one of the major cornerstones to EMSL's success as a national scientific user facility. To attract the best and brightest users, we are putting into place several outreach mechanisms that will inspire colleague-to-colleague contact, including sponsoring workshops and attending national meetings in our staff's area of expertise. We are putting into place programs that will engage leaders in the scientific community in playing a key role in the success and direction of EMSL while also encouraging them to become users.

To provide opportunities to the next generation of scientists, we are hosting educational programs for graduate and undergraduate students that focus on the rapidly growing area of interfacial phenomena. Finally, we are putting into place tools that will foster increased visibility of EMSL by our users, such as a revamped and extensive website that provides easy access to information about EMSL science and capabilities. We are also planning to develop new and modern tools, such as podcasts and online video, which will raise awareness of EMSL by earlier-career scientists.

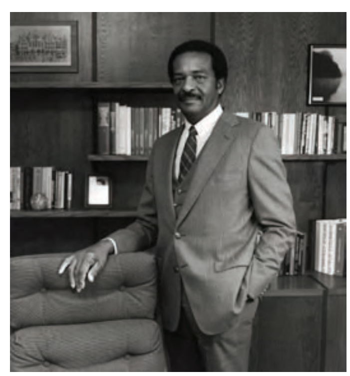
The following provides more detail of the outreach mechanisms EMSL has or will develop in the near future. In addition, the user proposal process is discussed.

7.1 EMSL outreach

Engagement of the external and internal user community in the long-term planning for EMSL is vital to our success. To that end, EMSL has established the following programs aimed at attracting and engaging our user community.

7.1.1 Wiley Research Fellowship

Many researchers have contributed to the area of environmental molecular sciences and the success of EMSL. The Wiley Research Fellowship formally invites researchers who are making significant contributions to EMSL outside their individual research areas and provides them with a new venue for input on EMSL's direction. Also, the fellowship allows them to request special time allocations on high-demand instrumentation, normally reserved for EMSL staff. In addition, travel funding may be made available to fellows outside the Pacific Northwest National Laboratory (PNNL) to assist in their use of and/or service to EMSL.



William R. Wiley

Expectations: Wiley Fellows are expected to actively contribute to the success of EMSL as a user facility including support of EMSL and the user program beyond their own research projects. Examples of this enhanced contribution include the following:

- Participating on EMSL advisory committees.
- Participating on partner proposals for development of new capabilities.

- Acting as a scientific consultant for users.
- Advocating for EMSL and its capabilities in the scientific community.

Fellows are also expected to work with the EMSL scientific leadership team as plans are formulated and provide input, whenever possible, at meetings with the team.

Requirements: All Wiley Fellowships will be evaluated on an annual basis for continued contributions and value to EMSL. Initial appointments require a resume and a one-page description of the researcher's contributions (past and planned) to the EMSL user program. An annual summary of activities and plans for the following year will be required for retention.

7.1.2 Wiley Visiting Scientist Program

The Wiley Visiting Scientist Program recognizes, rewards, and encourages distinguished scientists to come to EMSL and make significant contributions to the user program by providing input to and recommendations on the path forward for EMSL. Two types of visits are considered:

- Short term – visits up to 3 months, with a minimum stay of 1 month.
- Long term – visits up to 1 year, with a minimum stay of 6 weeks.

Wiley Visiting Scientists can request special time allocations on high-demand instrumentation, normally reserved for EMSL staff. In addition, travel funding and per diem expenses are available.

Expectations: Visiting scientists are expected to actively contribute to the success of EMSL as a user facility including support of EMSL and the user program beyond their own research projects. Examples of this enhanced contribution include participating on partner proposals for developing new capabilities, mentoring EMSL staff, and assisting in long-term facility planning. Also, visiting scientists are expected to work with EMSL leadership and provide input, whenever possible, at leadership meetings.

Qualifications: The program is open to scientists working in environmental molecular sciences. In addition to conducting their own research, applicants must be willing to participate in activities to enhance the EMSL user program.

Requirements:

For **short-term fellowships**, the applicant submits their curriculum vitae and describes their proposed onsite research objectives, their proposed additional contribution to the EMSL user program, and the desired funding. Each application is evaluated based on the quality of the research, relevance to EMSL's strategic needs, and the availability of funds. Applications are considered quarterly.

For **long-term fellowships**, the applicant submits a research plan describing their objectives for the visit, special resources needed, and the value of the visit to EMSL. In addition, the applicant includes three letters of reference, their curriculum vitae, and a letter of support from a Laboratory Fellow residing in EMSL.

Each applicant is evaluated using criteria including the quality of the research, the relevance of that research to EMSL, and the availability of funds. Applications are considered quarterly. An applicant may propose a visit up to 1 year in advance.

7.1.3 Workshops

Workshops provide opportunities to bring together experts from across disciplines to discuss future scientific challenges and the new capabilities, including technology advancements, required to overcome those challenges. In the last 3 years, EMSL has sponsored or co-sponsored five workshops related to developing new capabilities.

The Systems Microbiology and Extremophile Research Facility Workshop was held March 26, 2008, and was attended by 30 scientists, including prominent microbiologists and systems biologists from around the nation. The workshop was held to identify the capabilities needed to build a systems-level understanding of microbes and microbial communities, especially those that can withstand extreme environments. Unique capabilities in cell growth and analysis were identified as well as important roles that EMSL can play in driving progress in the emerging field of systems microbiology.

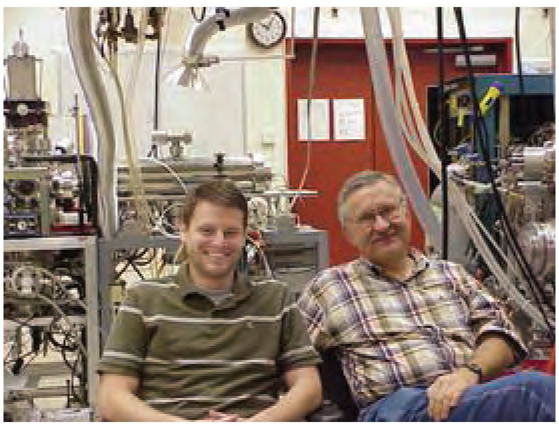
Science Challenges and Design Concepts for the Next-Generation High-Performance Fourier-transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer Workshop was held January 16-17, 2008, at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida (workshop report in Appendix AC). The workshop was jointly sponsored by NHMFL and EMSL, and was attended by 32 experts representing the United States, Germany, Korea, Russia, and Sweden. Presentations and discussion focused on science needs for enhanced FT-ICR mass spectrometry and identification of technological impediments in reaching next-generation performance.

***NWChem* Meeting on Science-Driven Petascale Computing and Capability Development** was held January 25-26, 2007, and included 65 scientists from 22 universities and 5 national laboratories. Discussions centered around status and future direction of *NWChem*—EMSL's computational chemistry software, how to contribute to the growth of *NWChem* related to its scientific capability and computational performance by 2022, and parallel implementation and natural linear scaling of coupled-cluster theory of large molecule applications.

Development of New User Research Capabilities in Environmental Molecular Science Meeting was held August 1-2, 2006, and included 104 expert scientists, many representing EMSL users, from 40 institutions, including 24 universities and 5 national laboratories. Discussions centered around future science and technology challenges and the capabilities that these scientists would need in the future to further their research.

EMSL Radiological Nuclear Magnetic Resonance Spectroscopy Workshop was held May 1-2, 2006 (workshop report in Appendix X), and included scientists from six countries who discussed the possibilities and value of enhancing radiological capabilities at EMSL, with an emphasis on nuclear magnetic resonance and electron paramagnetic resonance capabilities.

Future workshops include a second recapitalization workshop to re-evaluate plans and refine opportunities for investment.



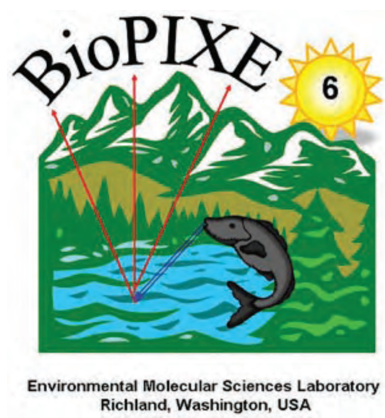
Researchers work with mentors at EMSL as part of the PNNL Summer Research Institute on Interfacial and Condensed Phase Sciences.

7.1.4 Educational Research Programs

To foster the next generation of scientists, EMSL sponsors research programs designed to provide collaborative, hands-on opportunities for undergraduate and graduate students. Two examples of our educational research programs are the nanotechnology course series we co-offer and our participation in Pacific Northwest National Laboratory's (PNNL's) summer institute focused on interfacial and condensed phase research.

Approximately 20 students each year in the PNNL Summer Research Institute on Interfacial and Condensed Phase Sciences perform research in EMSL. The goal of this institute is to educate graduate students and young scientists in theory, simulation, and experimental measurement.

The University of Washington, EMSL, and Washington State University offer a series of two-week courses to enhance education and research in nanotechnology and to speed undergraduate and graduate entry into this exciting field.



7.1.5 Scientific and Technical Meetings

By hosting meetings at EMSL and providing outreach at others, EMSL fosters information sharing, collaboration, and innovation within the scientific community. A few examples from 2006 to 2008 follow.

In June 2008, EMSL hosted the **6th International Symposium on BioPIXE**, an international meeting dedicated to advances in biological, medical, and environmental applications of proton induced x-ray emission (PIXE). Close to 50 participants, mainly from international universities, attended.

As part of the Pacific Northwest Microscopy Society Meeting, participants toured EMSL and our microscopy capabilities.

In April 2008, EMSL hosted the 2008 **National User Facility Organization Meeting**. This meeting was the fifth occasion for all user administrators and user organization chairs to meet and discuss issues of common interest to the community which utilizes these user facilities. Approximately 40 participants from national laboratories and universities participated.

In September 2007, EMSL hosted the annual **Pacific Northwest Microscopy Society Meeting**. More than 40 participants attended to advance the knowledge of the theory and applications of electron microscopy and associated techniques by their usage both in physical and biological sciences.

In June 2007, the **EMSL User Symposium** was held at the 62nd Annual Meeting of the Northwest Region of the American Chemical Society (ACS). The symposium entitled EMSL User Research was organized and chaired by EMSL staff. Fourteen presentations were given by EMSL users. The presentations were attended by potential users throughout a 10-state region.

At the American Chemical Society National Meeting in 2006, members of the EMSL outreach team answered questions and discussed opportunities for working at EMSL.

In 2006, EMSL hosted a booth at the **American Association for the Advancement of Science (AAAS)** meeting in St. Louis, Missouri, and the **ACS National Meeting** in San Francisco, California. At the AAAS meeting, EMSL Director Allison A. Campbell hosted and led a symposium on EMSL's Grand Challenges. At both meetings, booth staff made connections with participants who are potentially future users of EMSL.

The EMSL outreach team plans to work with the EMSL Chief Science Officer and the science theme leads to identify one major professional society meeting per science theme per year where targeted, streamlined outreach can be conducted towards relevant technical programs. The team will purchase lists of attendees so that they can target the desired, potential users before the meeting commences.

Planned meeting activities include the following:

- **EMSL-Led AVS Symposia: *In-Situ* Microscopy and Spectroscopy: Interfacial and Nanoscale Science –** This symposium is a forum for exploring cutting-edge microscopy- and spectroscopy-based techniques and research opportunities in interfacial and nanoscale science. Understanding chemical transformations of nanostructures, surfaces, and materials interfaces is essential to address scientific issues in catalysis and environmental science. Detailed methods for kinetic measurements, for example, need to be developed to allow rapid assessment of how particle size, composition, and shape influence growth, activity, and selectivity in chemical transformations. Especially in nanostructures, understanding the growth mechanisms and reaction pathways is extremely challenging. The surface and interface chemistry of these materials are often poorly understood. Advanced tools to obtain site-specific information in a realistic reaction environment are needed to enable a new level of understanding. The symposium will be held October 2008 in Boston at the National AVS Meeting.

- **Pacific Northwest Chapter of AVS Symposium –** This year's annual symposium will be held in EMSL. The symposium will include two days of invited and contributed talks, a poster session, and vendor exhibit (http://www2.avs.org/chapters/pnw), and it will be held on September 18 and 19.

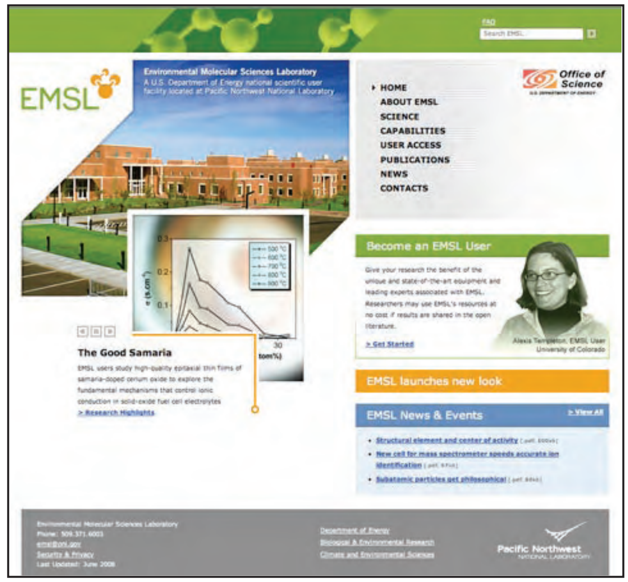
  About 75 people including faculties from the universities, research scientists mostly from PNNL, and students from the Pacific Northwest, Western Canada, and Alaska, are expected to attend the sessions in this conference. Pacific Northwest AVS Chapter encourages student participation by providing subsidies in registration, lodging, and transportation for students, and at least 30 students are expected to attend the conference. About 20 to 25 vendors will be participating in the one-day vendor exhibit. About 25 to 30 people from vendors are expected to be present during the conference in addition to the number of people who attend the sessions.

- **20th International Conference on the Application of Accelerators in Research and Industry (CAARI – 2008) –** CAARI brings together scientists from all over the world who use particle accelerators in their research and industrial applications. CAARI can be considered a collection of symposia on accelerator technology, atomic physics, education, focused ion beams, national and homeland security, ion beam analysis, ion beam modification, medical applications, nano-scale fabrication, nuclear-based analysis and studies, nuclear physics, proton induced x-ray emission, and radiation effects.

In addition, the outreach team will pitch speaking engagements and/or reception-type sessions led by EMSL staff at smaller professional society meetings to discuss EMSL capabilities and science relevant to the meeting. The team will develop a virtual tour or movie of EMSL that, placed on a CD, can be given to attendees with an invitation to submit a proposal. These tours can be tailored to cover the capabilities that are relevant to the meeting attendees.

7.1.6 EMSL Tours

The outreach team at EMSL routinely conducts tours for nationally elected and appointed government officials; local and regional elected officials; senior management from national laboratories; and members of the national and international scientific community. In addition, the team often leads tours for workshop and meeting participants.



The website includes information on science conducted at EMSL, recent news, and contacts.

7.1.7 EMSL Website

To communicate with the scientific community and the public, EMSL provides a website at http://www.emsl.pnl.gov/. The website provides detailed information the science performed by EMSL users and a list of publications produced by that science. In addition, the capabilities of the facility are discussed in detail. News highlights and a history section round out the site.

7.1.8 Targeted Outreach Activities

During the course of a year, the EMSL Director and staff have highlighted opportunities for using EMSL to potential users. These activities included giving invited talks, which showcased EMSL as a national scientific user facility, at universities and meetings. Highlighted examples over the past several years include the following:

- EMSL Director Allison A. Campbell gave invited talks on EMSL opportunities and capabilities at the University of California at Irvine, The Ohio State University, Western Washington University, and MIGRATION ’07 International Meeting.
- Andy Felmy gave an overview of EMSL opportunities and capabilities in biogeochemistry and environmental science at the Environmental Remediation Sciences Program annual meeting in 2007 and 2008.
- Steven Wiley gave an overview poster on EMSL systems microbiology capabilities at the GTL annual meeting in 2008.

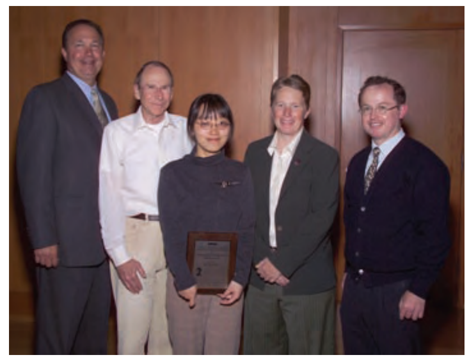
Currently, a plan is being developed to extend EMSL’s work in targeted outreach to distinguished users of EMSL. The plan provides increased focus on colleague-to-colleague outreach and education, bringing our staff and users into field-type situations such as professional society meetings or workshops. Proposed activities in this plan include the following:

- Use the knowledge base of the EMSL Director, Chief Science Officer, science theme lead scientists, Capability Stewards, and Science and User Advisory Committees to identify potential distinguished users in their areas of expertise that could be personally extended invitations to visit, tour, and make a presentation.

- Use PNNL competitive analysis capabilities to obtain information on top universities where research is conducted that is compatible with EMSL's science themes, and then put into place mechanisms to target the heads of those departments with information about EMSL.

- Develop podcasts or YouTube videos on EMSL topics that can be linked from the EMSL website and used to attract "new-generation" users. An "Interview with a Scientist" series could be implemented where an EMSL user is interviewed about their science and how EMSL enables their work, then it can be linked from EMSL's website as well as the user's home institution website—resulting in greater return on investment.

- Take the MT Thomas Award for Outstanding Postdoctoral Achievement a step further by developing a plan to pitch an EMSL Outstanding User of the Year Award.



Jin Zhao (EMSL scientific user, University of Pittsburgh) was the first-ever recipient external to PNNL to receive the M.T. Thomas Award for Outstanding Postdoctoral Achievement in the 11-year history of the award. In the photo: Mike Kluse (PNNL Lab Director), M.T. Thomas, Jin Zhao, Allison A. Campbell (EMSL Director), and Hrvoje Petek (University of Pittsburgh).

7.2 Becoming an EMSL user

7.2.1 The Proposal Life Cycle

Access to EMSL capabilities requires an approved peer-reviewed user proposal. The EMSL User Support Office (USO) is responsible for all aspects of managing the user proposal process from issuing calls for proposals, to facilitating the reviews, scheduling training, and arranging access to EMSL. EMSL Capability Stewards work closely with the USO to ensure that the hand off from proposal acceptance and training to scheduling a visit and conducting the work is smooth and transparent. The entire proposal life cycle is shown in Figure 7-1.

7.2.1.1 Submitting a proposal

User proposals are submitted online via the EMSL User Portal (http://eus.emsl.pnl.gov/Portal). The user fills out the required information, attaches a 3-page description of the proposed work, curriculum vita and any desired supplemental information. Upon submittal, the user receives an email that contains a user proposal number that can be used to track the proposal progress (see also Section 7.2.5).

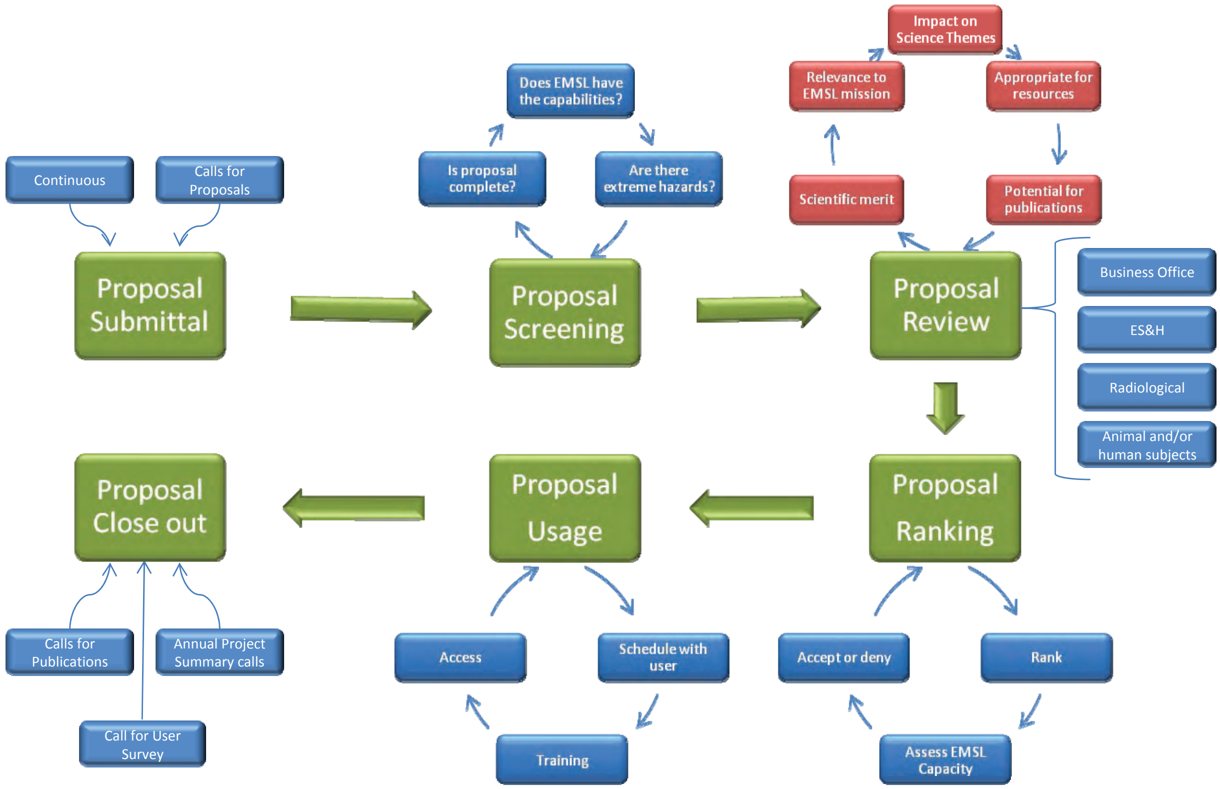


Figure 7-1. Diagram of the EMSL User Proposal Life Cycle. The green boxes are the high-level processes for proposals. Blue boxes depict sub-processes managed by User Support Office (USO) or Capability Stewards. The orange/red boxes represent external peer-review criteria. External review is managed by USO.

7.2.1.2 Proposal screening

Prior to external peer review, proposals are screened to ensure that all the required information is present, that EMSL has the requested capabilities, and that any hazards outside the operating envelope of EMSL are identified. If a proposal fails the screening, the USO contacts the author with an explanation as to why the proposal failed.

7.2.1.3 External peer review

All user proposals undergo an external peer review with the exception of proprietary proposals (see Section 7.2.4), rapid access proposals (see Section 7.2.3), and users who own the requested instrumentation (see Section 9.2.2). A mail review process is used where proposals are sent to three reviewers. Proposals are reviewed against five criteria:

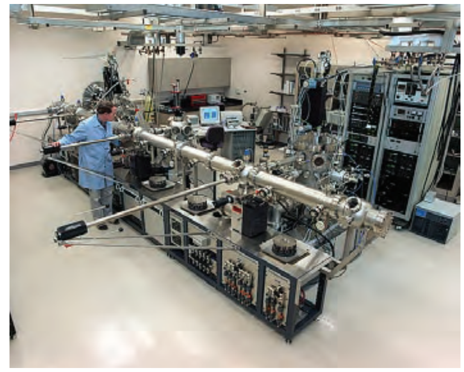
- **Scientific merit and quality of proposed research**. Considerations include the following:
    - How important is the proposed activity to advancing knowledge and understanding?
    - To what extent do the proposed activities suggest and explore creative and original concepts?
    - How well conceived and organized is the proposed activity?
    - Is the proposed research funded and externally peer reviewed?

- **Relevance of proposed research to EMSL's mission**. Considerations include the following:
  - What is the relationship to EMSL's mission?
  - To what extent are both experimental and computational resources synergistically utilized to address the proposed research?
- **Impact of the proposed research on one or more EMSL science themes**. Considerations include the following:
  - Will the proposed research advance scientific and/or technical issues in EMSL's science themes?
  - To what extent does the proposed research suggest and explore creative and original concepts relating to the science themes?
- **Appropriateness and reasonableness of the requested resources**. Considerations include the following:
  - Are EMSL capabilities essential to the proposed research?
  - Are the proposed methods optimal for achieving the scientific objectives of the proposal?
  - Are the requested resources reasonable?
  - Does the complexity and scope justify the requested duration, including any modifications to EMSL capabilities?
  - Is the proposed work plan achievable?
  - Is the requested allocation for each requested capability clearly justified?
- **Potential for highly cited publication(s)**. Considerations include the following:
  - If successful, will the proposed research be publishable in a high-impact journal?
  - Would the results fill gaps required for publication?
  - Does the proposal team have the breadth of skill and knowledge to successfully perform the research?

Each reviewer provides an overall score and a score for each of the criteria along with written comments supporting each rating, noting both strengths and weaknesses. The scores are as follows:

- **Excellent**. Outstanding proposal; deserves highest priority.
- **Very Good**. High-quality proposal; should be supported if possible.
- **Good**. A quality proposal; worthy of support if possible.
- **Fair**. Proposal lacking and issues need to be addressed.
- **Poor**. Proposal has serious deficiencies.

7.2.1.4 Internal approvals



All proposals are assessed for hazards and approved for EMSL's operational envelope.

Concurrent with external review, internal approvals are also obtained (as needed for each proposal) from the following:

- **Business**. All proposals need approved user agreements; proprietary work is assessed for appropriate cost reimbursement, etc.

- **Environment, safety, and health**. All proposals are assessed for hazards and approved as appropriate for EMSL's operational envelope.

- **Animal and/or human subjects**. Proposals with these items are reviewed and approved by the Animal Care and Use Committee and/or the Human Subjects Board.

- **Radiological**. Proposals involving radiological samples are reviewed and approved by a radiological engineer as appropriate for EMSL's operating envelope.

7.2.1.5 Ranking approvals and denials

Once all approvals are obtained, proposals are ranked from highest to lowest, and allocations are awarded based upon availability of resources. Typically, all proposals receiving an overall score of "Excellent" are approved. Pending the availability of resources, a limited number of proposals that score "Very Good" will be granted access. All proposal authors receive a letter of acceptance or denial.

Appeals may be made to the USO. All appeals are reviewed by the Appeals Committee, led by the EMSL Chief Science Officer. The USO coordinates with the committee and notifies the user of the appeal outcome.

7.2.1.6 Usage

A user with an approved proposal may then work with EMSL to schedule visits or remote usage. Prior to any direct access to EMSL capabilities, users work with the USO to complete required training and access requirements.

7.2.1.7 Close out

After all work has been performed and the project duration has elapsed, the user proposal is closed. Users are asked for project summaries and publications that have resulted from the work. For the first 3 years following project close out, users are periodically asked electronically for any additional publications that resulted from the work.

7.2.2 Calls for Proposals

Calls for proposals are part of EMSL's strategy to focus the user program, attract users, and highlight EMSL's capabilities. Proposals are either submitted to a specific call or may be submitted at any time throughout the year. In the last 3 years, EMSL has issued the following calls for proposals:

- **2006 Call for Science Theme Proposals**. EMSL's first call for proposals focused on the science themes.

- **2007 Call for Science Themes Proposals**.

- **2007 Call for Capability-based Proposals**. This call focused only on experiments that would demonstrate new experiments or approaches on select EMSL capabilities, specifically the following:

  - Single and microbeam x-ray diffraction.
  - Dual-beam focused ion beam scanning electron microscope.
  - Transmission electron microscope with cryo-stage and tomography.
  - Bio-solids experiments on the 900-MHz nuclear magnetic resonance spectrometer.

- **2008 Call for User Proposals**. This call had three opportunities:

  - Science theme proposals.
  - Computationally Intensive Research proposals.
  - Partner proposals.

For more details on these proposal calls, see Appendix M.

7.2.3 Proposal Types

Proposals may be from individuals or groups of scientists and may fall into one of several proposal types (also shown in Table 7-1):

Science theme proposals: These proposals are in response to a call for science themes proposals and are focused on advancing the research of EMSL science themes. They are valid for 1 year with eligibility for two 1-year extensions.

Computationally Intensive Research (CIR) proposals: These proposals replace the EMSL Computational Grand Challenge Proposals. They require large amounts of computing time on EMSL's supercomputer but are encouraged to have an experimental component. They are valid for one year with eligibility for two 1-year extensions. Prior to submitting a full proposal, users are asked first for a letter of intent. Based upon internal review of these letters, users are then asked for full proposals which are externally peer reviewed.

Table 7-1. Proposal Types.

	Science Theme	Computationally Intensive Research	Capability Based	Partner	General	Rapid
Duration	1 year	1 year	1 year	1 year	1 year	1 month
Extensions	Up to 2	Up to 2	Up to 1	Varied	0	0
Response to Call	Yes	Yes	Varies	Varies	Continuous	Continuous
Limits	70,000 node hours	2,000,000 node hours	100,000 node hours	No supercomputer	75,000 node hours	Demonstrated Immediate need

Capability-based Proposals: These proposals are in response to a capability-based call for proposals and are focused on demonstrating new approaches or experiments on EMSL's capabilities. They are valid for 1 year with eligibility for a 1-year extension.

General Proposals: These proposals are submitted at any time throughout the year. They are valid for only 1 year. They provide an ideal mechanism for users to get preliminary data or try new ideas in preparation for a science theme proposal.

Partner Proposals: These proposals are submitted by individuals or groups who wish to partner with EMSL staff to develop and build unique capabilities that enhance EMSL's user program. They may be in response to a proposal call or submitted at any time throughout the year. Partner proposals pool resources, expertise, and other assets and build upon EMSL's capabilities in instrument development. In return for co-development, EMSL partner users have priority access to the new capability for a specified period. Two-page letters of intent are used to initiate a discussion with EMSL's Chief Technology Officer on potential impact, total cost, development time, resource sharing, need for the capability, project teams, and partner access requirements. Partner users with successful letters of intent will be asked to submit a 10-page (maximum) proposal.

EMSL recently received a partner proposal to help **add ultra-fast magic angle spinning solid-state probes to the 900-MHz NMR** to help study solid-state materials important in catalysis and hydrogen storage.

Rapid Access Proposals: In limited cases, users may need access to EMSL capabilities where a quick turnaround of data is required (e.g., thesis work, paper publication, proposal preparation). Rapid access proposals, if approved, grant up to one month of EMSL use. The proposal must clearly justify why rapid access is warranted. Proposals are not externally peer reviewed but are subject to the approval of the Capability Steward. All internal approvals are required before work can commence.

7.2.4 Nonproprietary and Proprietary Work

Nonproprietary research: Proposals that plan to fully disclose and disseminate to the public the results and information from research and EMSL usage are considered nonproprietary. Authors of nonproprietary proposals may retain rights to intellectual property resulting from the use of EMSL, but the federal government is granted a non-exclusive license to use the intellectual property. In general, use of EMSL capabilities is free of charge unless the proposal has extraordinary costs associated with the work. Institutions must sign and agree to the terms of a Nonproprietary Use Agreement (NPUA) and users must sign Appendix B of the NPUA prior to access to the facility (see Appendix N).

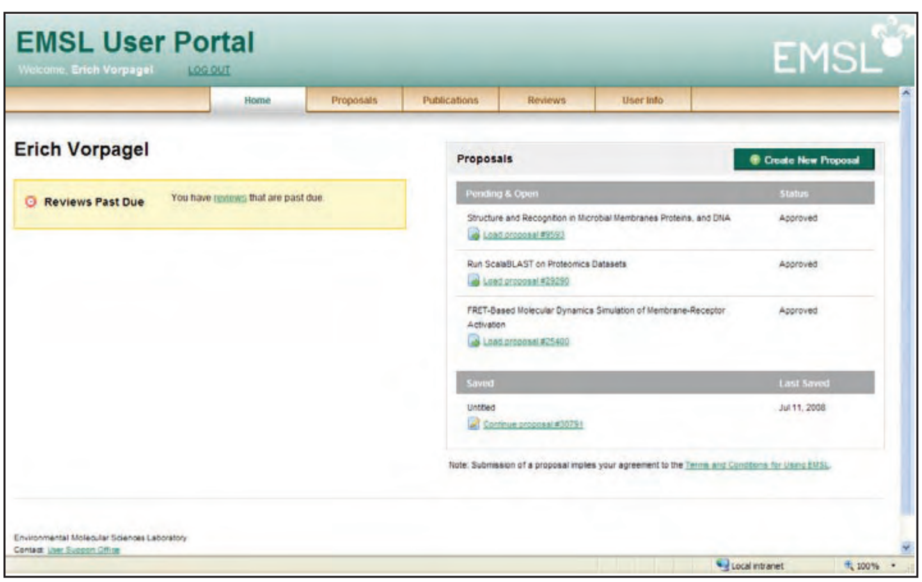
Proprietary research: Proposals that do not plan to disclose or disseminate the results and information to the public are processed as proprietary. DOE requires full-cost recovery for the research. Costs that must be recovered include, but are not limited to, labor, equipment usage, materials and supplies, and travel of EMSL staff.

7.2.5 Management Systems

At EMSL, a single system with multiple interfaces is used to manage user proposals and track use of EMSL resources. The EMSL User Portal interface is accessed by users to submit and track proposals and related information. The EMSL Usage System (EUS) interface is used by EMSL administrative staff to manage all aspects of the proposal process. The EMSL Resource System (ERS) is used by staff to schedule and record resource usage. These tools have enabled EMSL to manage proposals through the life cycle and track equipment use, while minimizing the administrative burden of these tasks.

7.2.5.1 EMSL User Portal

The EMSL User Portal is the interface for users to submit, list, and view their proposals; upload summaries and publications; view and revise their personal information; view scores and reviews of their



"The website layout (User Portal) since last year is conducive to user maintenance. This will save money and reduce data-entry errors." Comment from user on Spring 2008 User Survey proposals; and for reviewers to review and score user proposals. When logged into the User Portal, the front page provides reminders about calls and items that are outstanding (e.g., reviews). The front page also lists proposals that are open or pending review.

7.2.5.2 EMSL Usage System

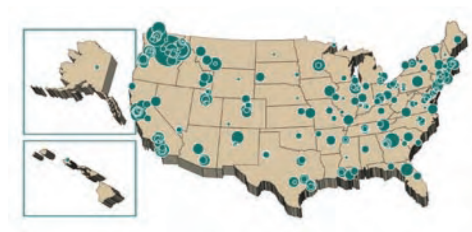
The EUS, also referred to as EUSAdmin, is a workflow-tracking software interface used by EMSL administrative staff to manage all aspects of the proposal process and users. The EUS is also used to manage resources, calls, roles, software agreements, and notifications.

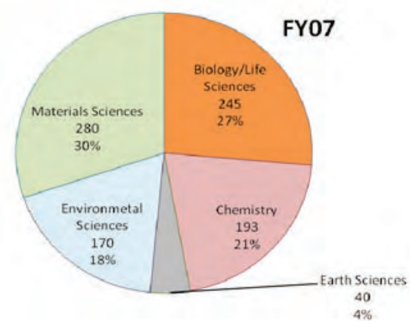
7.2.5.3 EMSL Resource System

The ERS provides an at-a-glance view of multiple resources and enables modification of access schedules and past usage. Primarily, the ERS is used to track past usage of instruments. In addition, the ERS is used to provide resource usage data to DOE. The data in ERS are used by EMSL management to make budget decisions regarding enhancements, acquisitions, consolidation of capabilities, and strategic direction for capability growth.

8.0 User and Proposal Statistics and Trends

Since the doors of EMSL first opened in 1997, EMSL staff have excelled at attracting users from a broad range of locations and disciplines. To date, scientists from all 50 states and many foreign countries have used the facility in support of their scientific efforts. The majority of the users represent disciplines in chemistry, biology, materials, and environmental sciences.





8.1 User definition

To accomplish reliable and consistent reporting to the U.S. Department of Energy (DOE) on the research community using EMSL, the following is the definition agreed upon by DOE's Office of Biological and Environmental Research (BER) and EMSL:

User Definition: Any individual who makes use of the facility as part of an active user proposal in the EMSL Usage System (EUS) is considered an EMSL user.

For each fiscal year, each user will be categorized as a/an:

- onsite user – individuals who are physically present at EMSL, at least once during the reporting period, to conduct their research.
- remote user, operating instrumentation – individuals who remotely access EMSL by logging onto EMSL's network to operate a piece of research instrumentation.
- remote user, not actively operating instrumentation – individuals who remotely access EMSL but do not actively operate instrumentation (such as those who send/receive samples to/from EMSL).

User Counts: Users are counted once per each proposal per fiscal year.

Reporting: Quarterly reports are generated to provide year-to-date counts.

8.2 User counts and trends

Each quarter, EMSL reports user statistics to BER and Pacific Northwest Site Office (PNSO) using the proposal and user statistics report (see Appendix E). Per the definition, users are counted as onsite or remote and are categorized by affiliation. Figure 8-1 shows the onsite and remote user counts for FY 2006, FY 2007, and the third quarter of FY 2008.

Figure 8-2 shows the same user count information by institution type.

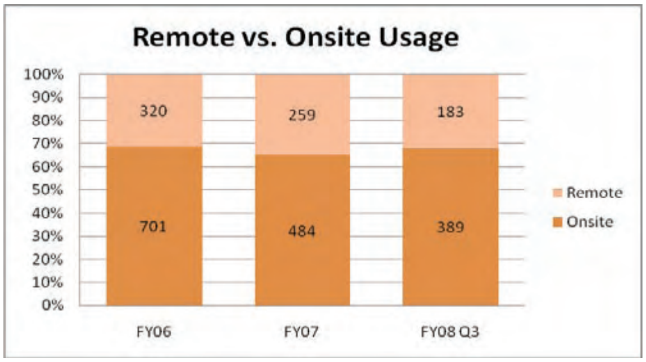


Figure 8-1. Remote versus Onsite Use at EMSL.

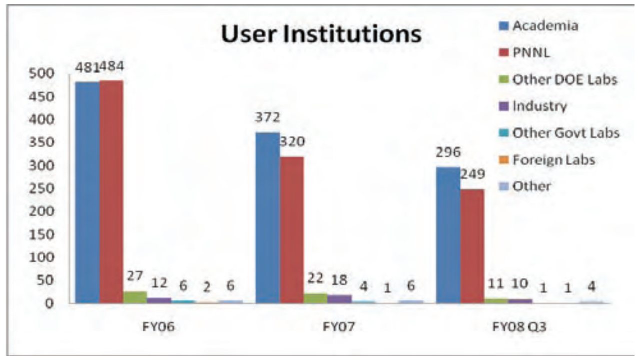


Figure 8-2. Home Institutions of Users.

We also track the number of distinguished users (users that are endowed chairs, National Academy members, Nobel laureates, or noted as highly cited authors by Essential Science Indicators). We had 40, 43, and 34 distinguished users in FY 2006, FY 2007, and FY 2008 (through the third quarter), respectively.

8.3 Proposal counts and trends

Proposals are categorized as science theme, capability (including capability based and computationally intensive), or general (including rapid access). As shown in Figure 8-3, the number of science theme proposals has increased over the last 3 years as a percentage of total proposals. The number of capability proposals has declined due to elimination of nuclear magnetic resonance and supercomputing focused calls, and as users switch from single capability requests to science themes and computationally intensive research proposals. A list of all proposals approved in the last 3 years is in Appendix V.

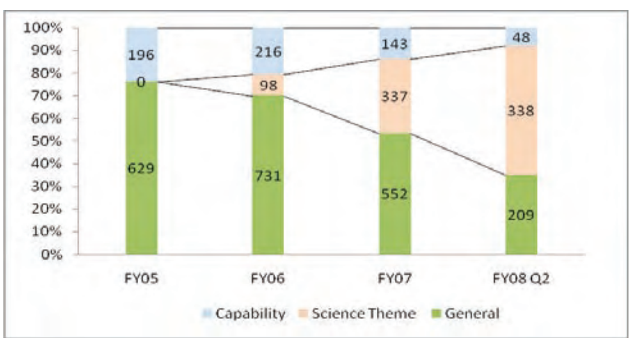


Figure 8-3. Proposal Counts for EMSL.

8.4 Publications

Publications are one of the main mechanisms by which EMSL communicates its research accomplishments to the scientific community. To be counted, a publication must be tied to a user proposal and acknowledge the use of EMSL. While over the past several years publication numbers have declined, the percentage that are published in high-impact journals (including top 10 journals) has increased slightly (Figure 8-4).

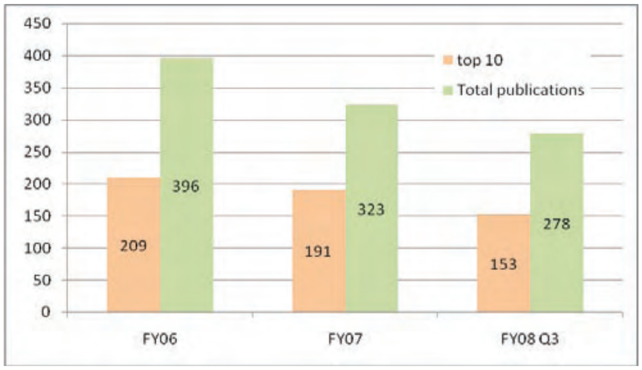


Figure 8-4. Publication Trends Related to EMSL.

Additionally, the number of journal covers resulting from EMSL research has almost doubled over the past 2 years from 7 to 13 through the third quarter of FY 2008. A list of all publications in the last 3 years is in Appendix AA.

8.5 User survey

EMSL conducts a survey to assess the overall satisfaction of a user's experience. Surveys are sent electronically every 6 months to people who used EMSL during the past 6-month period. The user is asked to fill out the online survey and provide any comments on their experience for that 6-month period. Survey results are anonymous unless the user chooses to disclose his or her identity. After each survey, the results are analyzed, and a summary of statistics, generalized questions, and responses are posted on EMSL's website. Results for the last 5 surveys are shown in Figure 8-5. Survey summaries are in Appendix G.

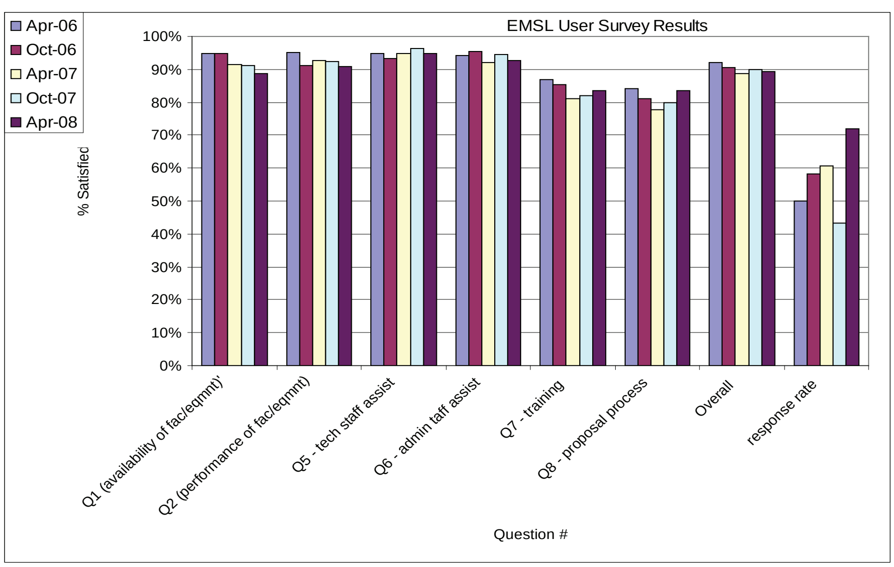
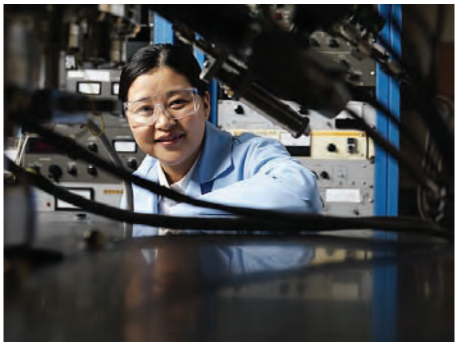


Figure 8-5. EMSL User Survey Results.



EMSL has made gains in user satisfaction around the proposal process, technical support, and training.

We report to DOE user satisfaction as a percentage of respondents who are satisfied or extremely satisfied overall. BER established a metric of 90 percent user satisfaction. As seen in Figure 8-5, we have made gains in user satisfaction around the proposal process, technical support, and training. Slight decreases are seen in access to instruments, instrument performance, and overall performance. The EMSL Core Team evaluates survey data and takes action to address user concerns such as streamlining training.

Finally, survey results are only as good as they are representative of the use community. We worked hard over the past 3 years to improve our survey response rates and are best-in-class with greater than 70 percent rate of return.

9.0 Facilities and Operations

As a national scientific user facility, EMSL houses instrumentation that provides reliable answers to researchers' toughest questions. Developing capabilities, maintaining high-demand instruments, and retiring those instruments that have been superseded by others are critical to maintaining the viability of this 225,000-ft^2 facility. To ensure that EMSL instruments continue to meet user needs, the U.S. Department of Energy's (DOE's) Office of Biological and Environmental Research (BER) is refreshing instrumentation over the next 7 to 8 years. To house these and other instruments, Pacific Northwest National Laboratory (PNNL) is planning to add to the building, including a wing for ultrasensitive equipment.

Research laboratories are enhanced by other spaces in EMSL. The Instrument Development Laboratory and Machine Shop provide the expertise needed to meet the more specific needs of some users. In addition, EMSL contains large collaborative space with whiteboards and discussion spaces as well as 283 offices and 2 large conference rooms, an auditorium, and 6 smaller meeting rooms.

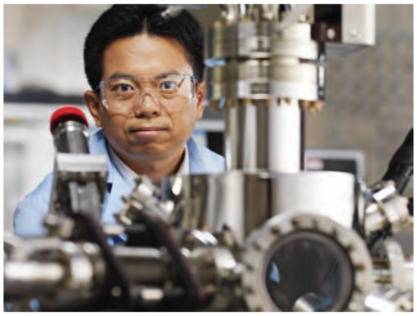
All research done in EMSL is governed by safety, environmental stewardship, and security guidelines. The guidelines are described in the Standards-based Management System. All research is overseen by Cognizant Space Managers.

9.1 Laboratories

Over the past several years, EMSL management has worked to cluster laboratory space around similar capabilities. This creates common safety envelopes in laboratory spaces, minimizing the transport of samples through hallways, and allows EMSL management to more fully showcase the depth and breadth of its capabilities. Figure 9-1 illustrates the current layout of these capabilities within EMSL. Maps by specific capability groups are in Appendix Y.

Figure 9-1. Capability Footprint for EMSL in FY 2008.

9.2 Instruments



The instrumentation available to users is housed primarily within the EMSL building, although users have access to capabilities, such as the radiological nuclear magnetic resonance (NMR) capability, housed in PNNL buildings. All research performed on EMSL instruments must demonstrate a clear benefit to the user program. EMSL contains more than 100 significant experimental and computational resources. Each significant instrument is associated with one or more of EMSL's eight capabilities. A subset of the significant instruments is designated as **major instruments**, which are unique and/or in high demand by EMSL users. These major instruments have the highest funding priority. The list of major instruments is provided annually to BER.

Users may request access to any of these capabilities via the online proposal process. Instruments are cross-referenced to multiple capabilities to facilitate searching for a particular instrument. A listing of all instruments, their location within EMSL, and whether they are considered major instruments can be found in Appendix O.

9.2.1 Instrument Utilization Policy and Tracking

To effectively steward instrument resources, EMSL management must know how often each of the major resources is requested, what research is being done, and when instruments need to be maintained or are unavailable and need of repair. To track instrument use, EMSL developed the EMSL Resources System (ERS) (described in Section 7.2.5). Time on each instrument is recorded in ERS in one of the following designations. In general, the designations are as follows:

- **Available**. Any time not allocated under any other usage type.
- **On-Site Usage**. Use by any person who is part of an active user proposal and who is physically present in EMSL.
- **Remote Usage, Operating Equipment**. Use by any person who is part of an active user proposal and who is remotely accessing EMSL by logging on to the EMSL network to operate an instrument.
- **Remote Usage, Other**. Use by any person who is part of an active user proposal who is accessing EMSL but does not actively operate instrumentation.
- **Broken, Out of Service**. Equipment is not available because it is damaged and cannot be used until it is fixed.

- **Maintenance**. Equipment is not available because periodic maintenance is being performed to keep the equipment in a ready-to-use mode and at peak performance.

- **Capability Development**. Time allocated to develop a new capability and bring it on line. Capability development activities may require extended booking of the instrument.

- **Upgrade**. Equipment is not available because an upgrade is being installed.

- **Unavailable, Staffing**. Equipment is not available because staff are not available to operate the equipment. Additionally, the “Unavailable, Staffing” designator can be used if EMSL user program funds are not adequate to support all of the user demands.

- **Unavailable, Other**. Equipment is not available for reasons other than staff unavailability.

The ERS data are reported quarterly to BER and are used by EMSL management to make decisions regarding staffing, enhancements, acquisitions, consolidation of capabilities, and strategic direction for capability growth. Utilization reports for the past 3 years are in Appendix D.

9.2.2 EMSL Owned, Shared, and Non-EMSL Owned Instruments

The majority of instruments in EMSL were procured using EMSL operations funding and are thus “owned” by the EMSL user program. To fully leverage the operations budget, EMSL co-funds instruments and allows instruments wholly owned by other programs within the walls of EMSL, if there is a clearly defined benefit to the EMSL user program. To ensure that users have access to all instrumentation, time is set aside and allocated (in general terms) as follows:

- **100 Percent User Program-Funded Research Capabilities**

  - At least 95 percent of the available time is allotted for users.
  - Up to 5 percent of the available time is for EMSL staff to perform their independent research. Proposals will be submitted through the EMSL Usage System. Access is subject to review and approval by the Associate Director for Scientific Resources.

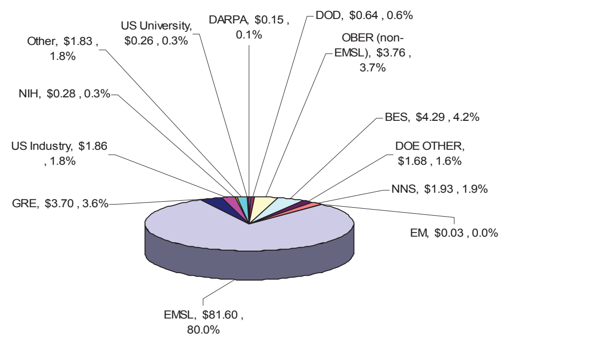
- **100 Percent Other Program-Funded Research Capabilities**

  - At least 20 percent of the available time is available for EMSL users through the user proposal process unless a separate agreement is developed with the EMSL Director. Up to 5 percent of this time can be made available to EMSL staff for their research.

  - The balance of the time is dedicated to the program that procured the systems. The utilization agreement is documented by instrument or system of instruments in the ERS and revisited whenever a major upgrade of the system occurs, and no less than every 3 years.

- **Co-Funded Research Capabilities**
  - User time follows funding split. For example, if the user program paid half the cost of the system, then half of the time is made available to users, although in no case is the available time to users less than 20 percent. Up to 5 percent of this time portion may be allocated to EMSL staff to perform their independent research.
  - The remaining time is allocated to the program that co-funded the research capabilities.

Instruments in EMSL by funding source

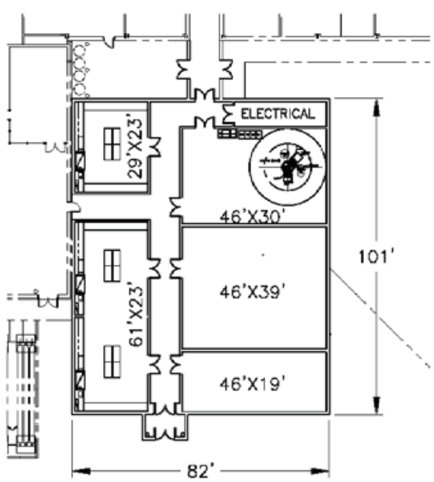


Cost of Active EMSL Resources by funding agency
$102 M total; chart $ in Million
(Data pulled from ERS as of 11/30/2007)

Please note the following caveats:
- Only data in ERS (EMSL Resource System) was used (which was originally pulled in from property and purchasing databases).
- ERS data includes resources in EMSL, 331 and 325 (e.g., Raman, NMRs).
- Data included for 130 Active Resources, which consists (in general) of components that have purchase prices >$25K.
- Components were assigned to one or more 13 possible funding agencies (although 26 funding agency categories exist in ERS).
- #s are conservative (i.e., low).

9.3 Future EMSL expansions

As EMSL moves to build transformational tools that push the limits of sensitivity and resolution, probe dynamic processes, and examine materials in complex native environments, new challenges in infrastructure requirements will emerge. Tight controls on vibration, electromagnetic, and thermal parameters will be required. Networking and cyber needs will arise to enable people to collaborate between distant locations. Laboratory environments that allow for the study of radiological materials in native and simulated environments are needed. To address these needs, EMSL has a long-term vision for future facility enhancements.



Proposed Layout of the Radiological Annex.

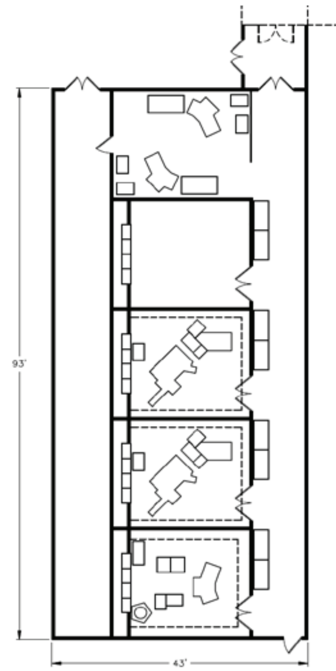
9.3.1 Radiological Annex

Access to specialized equipment for the study of radiological materials is in decline nationwide, and a user facility with these capabilities would provide an important resource to scientists. In addition, providing training for the next generation of radiochemists and associated nuclear scientists is important to the long-term mission of DOE. Expanded radiochemical capabilities in EMSL would provide these opportunities and contribute to high-quality science in areas important to DOE's mission. Laboratories include space for NMR, interfacial science capabilities, and radiotracer laboratory.

The annex is planned to be physically separate from the EMSL facility, thus isolating radiological activities. The annex is designed to rely on the main EMSL facility for such things as compressed air, nitrogen, and electrical power. An alternative analysis for the location of the radiological annex is being developed. This building is being proposed as a $4.9-million facility with an expected completion date of FY 2010.

9.3.2 EMSL Quiet Wing

This wing will support future capabilities within EMSL that require tight controls on electromagnetic interference, vibration, and thermal tolerances. The new Chemical TEM (see Section 6.1.3) planned to arrive in FY 2010 will require space of this nature as will future planned investments such as NanoSIMS and other ultrasensitive instruments.



Proposed layout of the Quiet Wing.

9.3.3 South Electrical Plant

This plant will support the current and future supercomputer capabilities. The need for power and cooling is driven by future computer needs. This $4.9-million general plant projects (GPP) building is expected to be built by the end of FY 2011. This project is in conjunction with the planned PNNL campus electrical infrastructure enhancement with the City of Richland.

9.3.4 Computer Room Addition

This addition will support our fourth supercomputer. The space will lend itself to next-generation technologies of condensed computer arrangements with proper cooling and short-run cable connections, with the existing space used for other computer housing. The expansion is planned for FY 2012 and is expected to be a $4.9-million GPP project.

9.3.5 EMSL North Addition

Long term, EMSL is looking to expand its footprint to the north to meet emerging demands. The proposed EMSL North Addition would include two laboratory modules with an accompanying office pod.

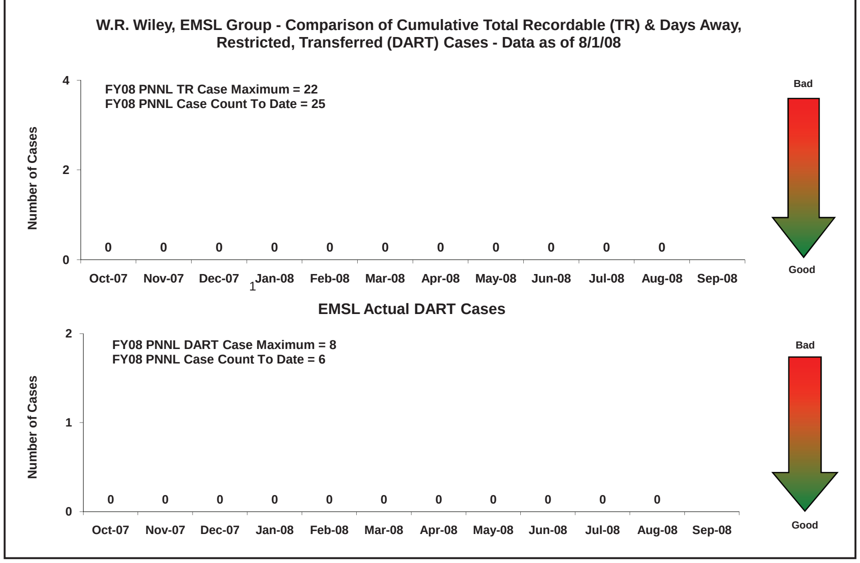
9.4 Environment, safety, health, and security

"Operate with excellence" is among EMSL's highest priorities and involves safety, environmental stewardship, and security. At EMSL, safety is our highest priority. All staff are responsible for safety—their own, their co-workers', and the community's. Staff and user responsibilities include

- Fostering an environment in which staff and users know and understand the safety requirements applicable to their work and are trained to follow and implement those requirements at all times. This principle applies just as soundly to "routine" office work as it does to tasks involving more complex safety requirements.

- Making sure that staff, users, and managers understand the procedures established by PNNL to comply with environmental, safety, health, radiological control, and security requirements.

- Identifying and promptly reporting any potential hazards that could lead to an accident or situations that could result in accident or injury, noncompliance, or stopping work, regardless of the reporting staff member's role in the project or program.



EMSL FY 2008 Safety Metrics

Additionally, the PNNL and EMSL Directors expect line managers to regularly walk through laboratory space, talk with staff and users about safety concerns, and take action for all raised issues.

9.4.1 Safety and Health

The responsibility for managing work safely in a workspace is assigned to a Cognizant Space Manager (CSM). The CSM is responsible and accountable for evaluating workspace hazards, determining work practices needed to control those hazards, and assuring that users have sufficient hazard awareness training and understanding before they work unescorted in the space. A CSM is authorized to make decisions regarding their space, including approving or disapproving activities, approving or revoking a user's access to the space, and correcting environmental, safety, health, and quality (ESH&Q) deficiencies in the space. A CSM is chosen from staff working at the most effective management level to make day-to-day decisions about workspace use.

CSMs, staff, and users heavily rely on the expertise of EMSL's Safety and Health Representative, the single point of contact for the services of PNNL's ESH&Q organization. Because early involvement is essential for integrating safety and health into projects, the ESH&Q organization provides project support from proposal through closeout. Other support this organization provides includes

- Hazards analysis/assessments, with recommendations for engineering and administrative controls and personal protective equipment.
- Procedure review.
- Non-ionizing radiation exposure monitoring.
- Special training needs.
- Laser use permits.

- Chemical process permits.
- Office/lab inspections.
- Workstation ergonomic evaluations.
- Accident, injury, and illness investigations.

Staff and users are encouraged to request ergonomic evaluations.

Staff and users are encouraged to request ergonomic evaluations and to promptly notify their line manager or the Safety and Health Representative if signs of work-related musculoskeletal disorders appear. EMSL's Safety and Health Representative is available to perform ergonomic assessments and answer any safety- and health-related questions.

Voluntary Protection Program: This program defines a single system and structured approach to help people work more safely. The program includes a recognition process for outstanding performers, adopted by DOE from the Occupational Safety and Health Administration, aimed at worksites with successful comprehensive safety and health programs. Staff are encouraged to participate in the Voluntary Protection Program (VPP) and work with management to strive for a safe and healthy workplace.

PNNL has achieved the highest honor bestowed by DOE for this program—STAR status—for outstanding worker safety and health. A steering committee guides PNNL's VPP, and EMSL is represented on the committee. See the VPP website (http://vpp.pnl.gov) for more information.

9.4.2 Environmental Compliance

EMSL conducts its business with respect and care for the environment. Strategies are implemented that build business opportunities and achieve the greatest benefit for EMSL's clients without compromising environmental quality. EMSL supports programs that are implemented under the Environmental Management System through the Standards-based Management System subject areas related to environmental compliance.

EMSL's Environmental Compliance Representative provides the following services to help EMSL achieve these goals:

- Partners with EMSL staff to facilitate the development, execution, completion, and review of activities with environmental issues or concerns.
- Carries out National Environmental Policy Act responsibilities (including review of Prep and Risk forms and EMSL user proposals). Provides review of chemical process permits and biological work permits if identified as a technical reviewer by authors who use the Integrated Operations System permit technical review process.

- Provides technical support to EMSL's management and staff for compliance with environmental laws, requirements, and policy within PNNL.
- Is involved in anticipating environmental issues and requirements and provides specialized training to staff as needed.
- Develops creative approaches to meet PNNL requirements for unique research situations not covered by conduct of operations or policy manuals.
- Fosters and enhances pollution prevention activities.
- Coordinates requests for technical services (e.g., air permits) and sends project and document reviews to Environmental Management technical support services, as necessary.
- Serves as the organization point of contact for environmental compliance issues and projects.
- Coordinates with other Environmental Compliance Representatives and PNNL Field Service Representatives.

EMSL conducts its business with respect and care for the environment.

EMSL's Field Service Representative is the single point of contact for any hazardous materials/chemicals and/or hazardous waste issues, including facilitating purchase, inventories, transfers, recycle, or disposal. The representative sets up all satellite accumulation areas within EMSL and ensures that chemical wastes are properly disposed. A satellite accumulation area is a place for gathering hazardous or radioactive mixed waste in containers during routine operations. The area is at or near the point of generation. The representative also conducts mandatory inspections of these areas.

9.4.3 Security

The very nature of EMSL's core business as a user facility is to maintain an open environment to enable scientific exchange of ideas. However, proper protection of classified and sensitive information and materials and assets is critical to EMSL's success. So, EMSL staff

- Question activities that appear nonroutine.
- Check the badges of people who enter EMSL at the same time they do.
- Understand export control of information and materials.

Security is the responsibility of all staff. If in doubt about the security needs and requirements for EMSL, staff contact their manager or the appropriate organization in the Safeguards and Security Department.

10.0 Integrated Business Planning, Performance Planning, and Assessment

Planning the business (financial) and operational performance of EMSL, and assessing that performance to make informed decisions are critical to the success of the user facility. Through our annual planning process, we solidify our longer term strategic vision and objectives, in addition to the near-term tactical objectives, measures, and targets to guide our work.

10.1 Integrated business planning

EMSL's business planning process is integrated with the U.S. Department of Energy's (DOE's) planning process. Field Work Proposals are submitted for programmatic operating, capital equipment, and General Plant Project funding. In addition, EMSL's business planning process is integrated with Pacific Northwest National Laboratory's (PNNL's) planning process. EMSL provides input to PNNL in setting laboratory-level rates, requesting laboratory-level resources, and approving EMSL-level budgets and rates.

10.1.1 Business Planning Cycle and Process

The annual programmatic planning and budgeting process (see Figure 10-1) begins in June and July with EMSL's Core Team receiving input from the PNNL management, DOE Office of Biological and Environmental Research (BER) management, Science Advisory Committee, and User Advisory Committee. Financial planning guidance and scheduling at both the PNNL and EMSL level are also provided to the Core Team by EMSL's Finance Office.

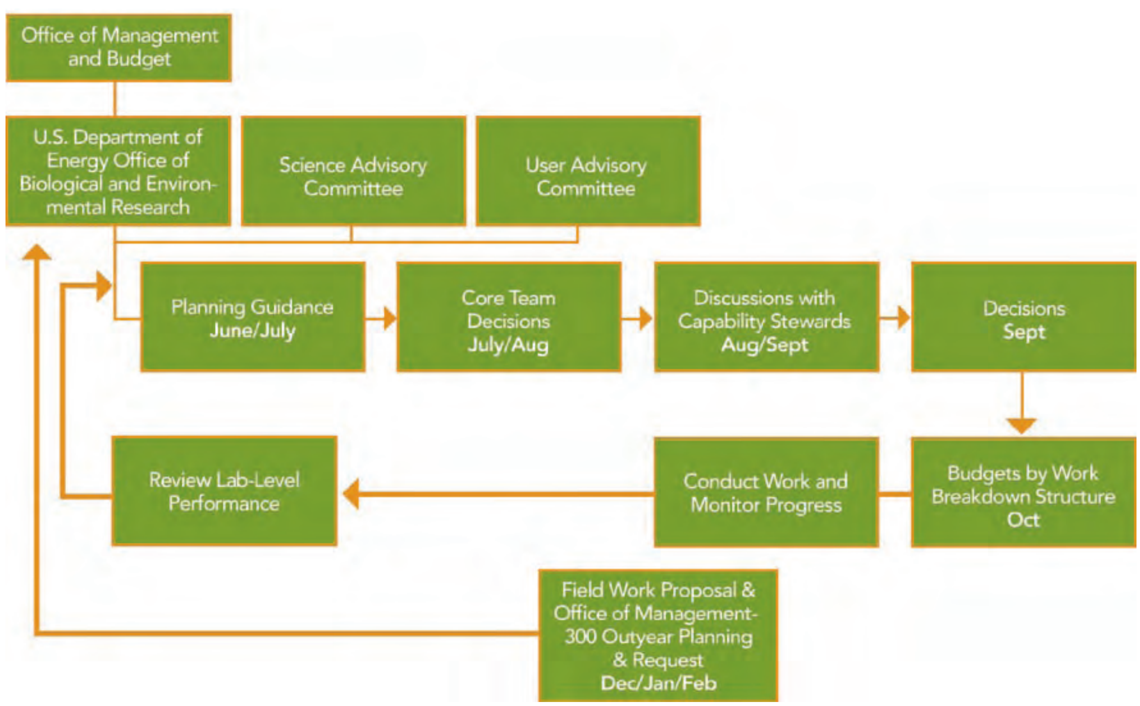


Figure 10-1. EMSL's Annual Programmatic Planning and Budgeting Process. Monthly and quarterly reporting and reviews are an integral part of the process.

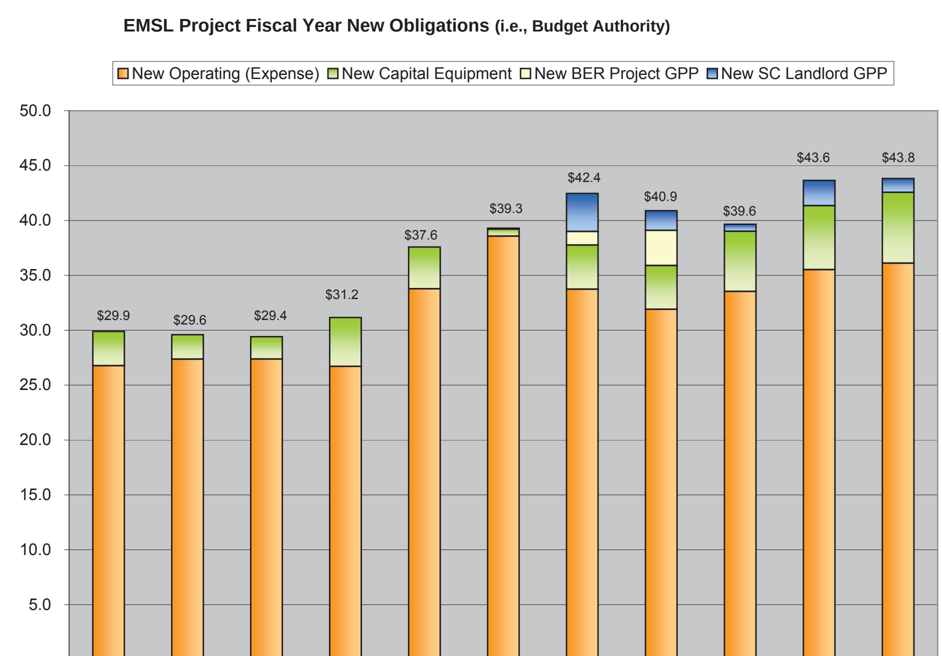
In July and August, the Core Team reviews and meets to discuss all of the information. From these Core Team discussions, EMSL's Associate Directors work with the Capability Stewards to develop tactical plans and budgets for the coming year. In September, the EMSL Director and Associate Directors review and, as appropriate, approve the plans and budgets. With the business plans and budgets approved, the work is assigned as appropriate.

PNNL resources are requested in late July, along with an out-year forecast of programmatic funding, cost, and staff. Decisions and feedback are provided from PNNL to EMSL in late September.

The financial progress of the work is monitored and then reported quarterly in the financial profile report (see Appendix I) and building-based management report (see Appendix J) to BER, Pacific Northwest Site Office (PNSO), and PNNL. Additionally, the EMSL Director reviews a monthly financial report with the EMSL Finance Manager, Peter Smith. The EMSL Associate Directors review more detailed reports with the Finance Manager and program specialists.

10.1.2 Funding Profile

Figure 10-2 shows the DOE fiscal year new obligations (i.e., budget authority) for EMSL from startup in 1998 through the third quarter of FY 2008, in millions of dollars. This financial data has been validated by comparing it with DOE Standard Accounting and Reporting System.



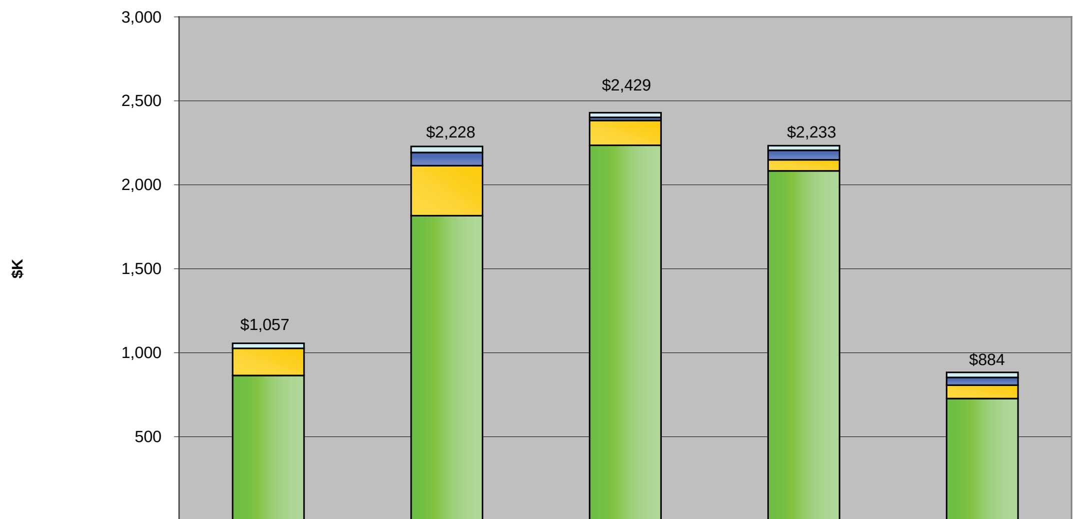
	FY98	FY99	FY00	FY01	FY02	FY03	FY04	FY05	FY06	FY07	FY08
New SC Landlord GPP						0.1	3.5	1.8	0.6	2.3	1.3
New BER Project GPP							1.2	3.2			
New Capital Equipment	3.1	2.2	2.0	4.5	3.8	0.6	4.0	4.0	5.5	5.8	6.4
New Operating (Expense)	26.8	27.4	27.4	26.7	33.8	38.6	33.7	31.9	33.5	35.5	36.1

Figure 10-2. DOE Funding Profile for EMSL ($M) from FY 1998 to Third Quarter of FY 2008.

Operating expense funding is for operation and maintenance of the EMSL user facility (e.g., staff labor, travel, supplies, training users, and maintenance of the equipment); **capital equipment funding** is for upgrades, replacements, and purchases of new capital equipment (e.g., $4.5 million Field Emission Chemical Transmission Electron Microscope that was funded in FY 2008); **General Plant Project (GPP)** funding is for facility improvements and expansion (e.g., the BER-funded raised computer floor expansion, and the Office of Science Landlord funded Office Pod A addition). A list of GPP expenditures can be found in Appendix P. Operating expense costs and workforce full-time equivalents for FY 2004 through FY 2008 estimates are in Appendix Z.

10.1.3 PNNL Investments in EMSL

For EMSL, PNNL management allocates resources such as Laboratory Directed Research and Development (LDRD), Program Development and Management, DOE overhead, and unallowable/non-reimbursable funding. EMSL management participates in the PNNL process. The process is very similar to EMSL's programmatic planning process (Figure 10-1), but it starts earlier, with EMSL's request due to PNNL the latter part of July. The PNNL overhead funded investments in EMSL for the past 5 years are shown in Figure 10-3, with the largest LDRD funding occurring in conjunction with EMSL Grand Challenges.



	2004	2005	2006	2007	2008
UNALLOWABLE	30	35	28	28	30
DOE OH		79	18	56	46
PDM	162	298	148	65	81
LDRD	865	1,817	2,236	2,084	727

LDRD PDM DOE OH UNALLOWABLE

Figure 10-3. PNNL Funding Profile for EMSL ($K) from FY 2004 to Third Quarter of FY 2008. Note: an LDRD project can only be authorized for up to 3 years.

10.1.4 Financial Policy and Guidelines

The user facility financial policy for EMSL that is in PNNL's Finance Manual is in Appendix Q. The policy includes a detailed description of how EMSL charges full-cost recovery for proprietary usage, the original policy of which was approved in FY 2000 by the local DOE Contracting Officer over PNNL.

EMSL staff are provided with charging guidance (see Appendix Q). This guidance provides information for determining when to charge non-proprietary work to the EMSL Operations project and when to charge to other projects that are using EMSL resources. Educational reminders about the guidance are sent to all PNNL staff in the EMSL facility every 6 months.

10.1.5 Capital Investments

EMSL makes capital investments in equipment and laboratories to meet our strategic objectives, to provide essential capabilities to science themes, and to make available to the user community capabilities to solve complex science challenges. Capital investment decisions for EMSL are driven by two primary factors: the science themes and user community input on capability needs to support the science themes. The processes by which EMSL ensures the science themes and user community input drive capital investment decisions are documented in a series of reports, including the EMSL strategic plan, the capital acquisition plan (Appendix W), *Recapitalizing EMSL: Meeting Future Science and Technology Challenges* (Appendix L), and *Scientific Challenges: Linking Across Scales* (see Appendix R).

The process by which BER, PNSO, and PNNL manage EMSL capital investments is described in *DOE Office of Biological and Environmental Research Process for Managing the Acquisition of Capital Investments for the Environmental Molecular Sciences Laboratory (EMSL)*. The document stratifies the investments by total project cost and then applies the appropriate level of federal review, project management rigor using principles from DOE Order 413.3A, and Earned-Value "Lite." The investments are stratified as follows:

1. Total project cost greater than or equal to $5 million up to $20 million.
2. Total project cost less than $5 million but greater than or equal to $2 million.
3. Total project cost of less than $2 million but greater than or equal to $750 thousand.
4. Total project cost of less than $750 thousand.

It is anticipated that no capital investment will exceed the $20-million threshold. If an investment does exceed $20 million, the full force of DOE Order 413.3A will apply.

EMSL has made many critical investments since initiating operations in 1998. In the last 3 years, EMSL has made several significant investments including initiating capital investments outlined in the Recapitalizing EMSL report, mentioned previously. A table detailing capital investments made over fiscal years 2006 through 2008 can be found in Appendix S.

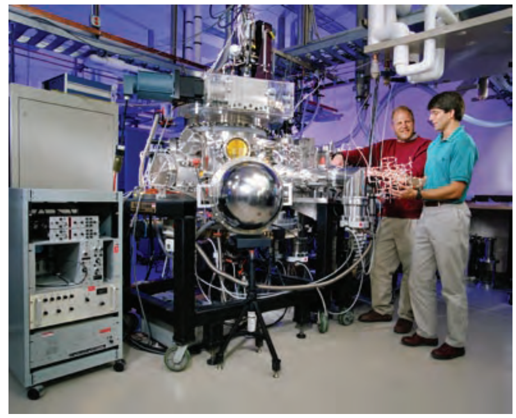
10.2 Performance planning

To turn EMSL's strategy into tactical work that can be assigned, budgeted, performed, tracked, and assessed, EMSL management uses a multi-year and annual performance planning process. The performance planning process allows EMSL management to measure the effectiveness of defined plans, strategies, and operations, as well as overall organizational health. More specifically, the process allows management to evaluate and track performance against defined goals, objectives, and metrics.

Assessments and evaluations are performed using self, independent, internal, and external assessments, audits, and reviews (including peer review of research results). Outcomes of these processes are used to make decisions regarding strategy development and management and to identify and enable improvement.

10.2.1 Annual Performance Planning

While performance planning is done on a multi-year process, annual plans are also developed. These annual plans solidify the objectives, measures, and targets that will guide specific work. A work breakdown structure (WBS) is built so that the tasks identified for the fiscal year can be clearly defined and assigned. WBS data dictionaries are prepared to define work scope and schedule for each WBS element.



EMSL regularly performs assessments.

The plan is monitored monthly by the EMSL Integrated Planning and Assessment Specialist, who works with task leadership to determine status and the percentage of work complete. The EMSL Director is updated monthly, and PNSO is updated quarterly.

10.2.2 Dashboard

To track and analyze the progress of EMSL's aggressive quarterly and annual goals, codified in the tasks in the annual performance plan, the Integrated Planning and Assessment Specialist manages a "dashboard." A dashboard is a list of each task and its progress, summarized as the percent complete versus the percentage of time passed in the fiscal year (e.g., task is 98% complete at the end of January). The dashboard is used to monitor metrics and help management in decision-making and in developing actions to improve performance. Targets not met each quarter are analyzed to determine what approaches could be used to meet future targets. Dashboards for the last 3 years are in Appendix H.

10.2.3 Assessments

Governance employs means such as internal audits and assessments, independent oversight, peer reviews, and benchmarking to provide reasonable assurance that goals are being achieved within approved operational boundaries. Self-assessments are used to obtain information on performance, to validate that management systems are performing effectively and efficiently, and to verify that accurate and reliable data are being delivered to decision-makers. Assurance is also used to verify that our users are being provided high-quality products and services.

At the beginning of fiscal year, an assessment plan is developed. The composition of assessments is determined based on the strategy and business risks. Assessments are done throughout the years, and the plan is updated and the status provided quarterly. The FY 2008 assessment plan can be found in Appendix T.

Assessments include the following:

- Space-based assessments by Cognizant Space Managers or subject matter experts.
- External assessments such as a review by DOE or the Science Advisory Committee.
- Process analysis assessments such as reviewing survey data, publication data, EMSL Usage System (EUS), and/or EMSL Resource System (ERS) data.

Specific examples include the following:

- ***Publication Acknowledgements***: Forty publications were reviewed to see if EMSL was properly acknowledged. Based on the assessment criteria, 32 publications passed and 8 failed. The recommendation due to these poor findings was to perform a 100% assessment of all publications in the future. A copy of the full assessment is in Appendix T.
- ***EUS Proposal Validation***: Sample data entered into the EUS underwent a data integrity check. In general, the assessor reviewed proposals to ensure that the proposal contained enough information for a thorough review, to determine if the proposal form questions were answered appropriately, and determine if the proposal author was contacted if the proposal was denied. A copy of the full assessment is in Appendix T. Recommendations that were implemented based on this assessment included the following:
  - EUSAdmin was modified to send automatic reminders to administrative staff regarding unresolved proposals.
  - A lessons learned was held regarding the 2007 science theme call for proposals.
  - User Support was centralized.
- ***EMSL Reviewers***: On August 7, 2007, a survey consisting of 4 questions was emailed to any non-PNNL person that reviewed a proposal for EMSL to gauge their satisfaction with the process and system. A copy of the full assessment is in Appendix T. In response to the information received, the following changes were implemented:
  - The length of the “description of proposed research” was increased from 2 to 3 pages of text.
  - After the reviewer successfully submits a review, the system automatically sends the reviewer a confirmation note.

- The incremental step in ratings was changed from 1 to 0.25; thus, reviewers can now score a proposal from 5.0 (Excellent), 4.75, 4.5, 4.25, 4.0 (Very Good), 3.75, 3.5, 3.25, 3.0 (Good), 2.75, 2.5, 2.25, 2.0 (Fair), 1.75, 1.5, 1.25, 1.0 (Poor).
- The email requesting a review has been updated to identify the call type, provide a link to the call, and provided guidance with respect to the 2008 call and/or open call.

10.2.4 Benchmarking

On occasion, EMSL benchmarks its policy and procedures against other user facilities. Benchmarking allows EMSL management to evaluate and consider other options and alternatives that might be worth implementing as we strive to be best in class. Examples of areas benchmarked (reports in Appendix U) include the following:

EMSL benchmarks its policy and procedures against other user facilities.

- Shuttle service.
- Example proposals.
- Calls for proposals.
- Publicly shared information.
- User Advisory Committee meetings.
- Review process and success rate.
- User group listservs.
- Funding of User Advisory Committee activities.
- Appeal processes.
- Proprietary user accounting.