



EMSL Quarterly Highlights Report
2nd Quarter, Fiscal Year 2009
(January 1, 2009, through
March 31, 2009)

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EMSL Quarterly Highlights Report: 2nd Quarter, Fiscal Year 2009

MA Showalter
LE Kathmann
KL Manke

May 2009

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Pacific Northwest National Laboratory
Richland, Washington 99352

EMSL—the Environmental Molecular Sciences Laboratory—is a U.S. Department of Energy (DOE) national scientific user facility located at Pacific Northwest National Laboratory (PNNL) in Richland, Washington. EMSL is operated by PNNL for the DOE Office of Biological and Environmental Research. At one location, EMSL offers a comprehensive array of leading-edge resources and expertise.

Access to the instrumentation and expertise is obtained on a peer-reviewed proposal basis. Users are participants on accepted proposals. Staff members work with users to expedite access. The EMSL Quarterly Highlights Report documents research and activities of EMSL staff and users.

Research Highlights

Biological Interactions and Dynamics

Transport Functions Dominate the SAR11 Metaproteome at Low Nutrient Extremes in the Sargasso Sea

SM Sowell,^(a) LF Wilhelm,^(a) AD Norbeck,^(b) MS Lipton,^(b) CD Nicora,^(b) DF Barofsky,^(a) CA Carlson,^(c) RD Smith,^(b) and SJ Giovannoni^(a)

(a) Oregon State University, Corvallis, Oregon

(b) Pacific Northwest National Laboratory, Richland, Washington

(c) University of California, Santa Barbara, California

EMSL proteomics resources were critical to pioneering research in which scientists, for the first time, measured protein expression in microbial communities from the Sargasso Sea. The insight afforded by this research into oceanic microbial communities is important because such bacteria heavily influence biogeochemical cycles, affecting the concentrations of elements such as carbon – and therefore the greenhouse gas, carbon dioxide – in the Earth's air, water, and soil.

The team of EMSL users from Oregon State University, Pacific Northwest National Laboratory, and the University of California conducted these experiments using a new proteomics technique, *metaproteomics*, which allows identification of proteins in mixed cultures even without a complete genome to help. Metaproteomics analyses revealed that the lion's share of peptides detected in Sargasso Sea microbial communities were unique to *Prochlorococcus*, *Synechococcus*, or SAR 11 (*Pelagobacter ubique*) (Figure 1), which is one of the most abundant organisms on earth. Further, these bacteria have adapted to their harsh environment, in which they are subjected to damage by light and oxidative stress, by expressing an abundance of transport proteins for nutrient uptake. This mechanism allows them to

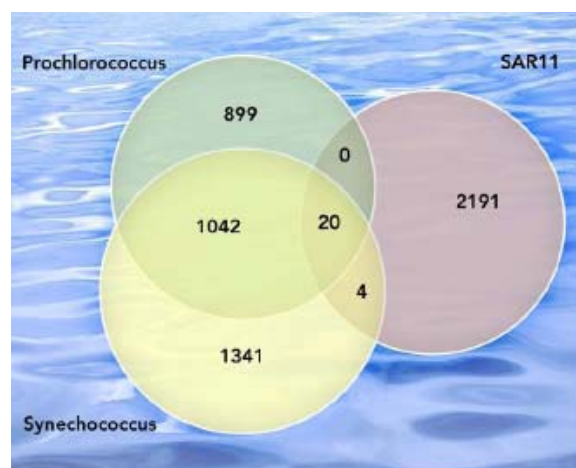


Figure 1. A large proportion of the peptides detected in samples from the Sargasso Sea were unique to *Prochlorococcus*, *Synechococcus*, or SAR 11.

sequester the very limited essential nutrients needed for their survival from the waters that surround them.

The team's work applies new proteomics methods to complex microbial community research and, furthermore, crosses the boundaries of many disciplines, connecting proteomics, microbiology, and climate research. In addition, these studies support EMSL's goal to predict biological functions from molecular and chemical data. In addition, understanding how microbial communities use transport proteins to adapt to seasonal changes and fluctuations in the levels of atmospheric carbon yields insight into global carbon cycling and could help in the design of strategies to address global warming.

The research, supported by a Marine Microbiology Initiative Investigator Award from the Gordon and Betty Moore Foundation and, in part, by the DOE Office of Biological and Environmental Research, was published in *International Society for Microbial Ecology (ISME) Journal*.

Citation

Sowell SM, LF Wilhelm, AD Norbeck, MS Lipton, CD Nicora, DF Barofsky, CA Carlson, RD Smith, and SJ Giovannoni. 2009. "Transport Functions Dominate the SAR11 Metaproteome at Low Nutrient Extremes in the Sargasso Sea." *International Society for Microbial Ecology (ISME) Journal* 3:93-105. DOI:10.1038/ismej.2008.83

MR Imaging of Apparent ³He Gas Transport in Narrow Pipes and Rodent Airways

KR Minard,^(a) RE Jacob,^(a) G Laicher,^(b) DR Einstein,^(a) AP Kuprat,^(a) and RA Corley^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) University of Utah, Salt Lake City, Utah

Biomedical applications of a magnetic resonance imaging method—³He-flow-MRI—newly developed by users at EMSL range from improving inhaled drug delivery to monitoring therapeutic response in patients with breathing disorders like asthma or Chronic Obstructive Pulmonary Disease. The ability to measure alterations in regional lung ventilation also provides a unique opportunity for assessing the subtle effects of inhaled pollutants, and for improving assessment of their potential health risks.

Airflow patterns in the lung not only determine how well you breathe but also how inhaled materials like airborne pollutants or aerosolized drugs are distributed inside the human body. At EMSL, users from Pacific Northwest National Laboratory and the University of Utah have pioneered a new magnetic resonance imaging method for visualizing inhaled airflow patterns. The method uses hyperpolarized ³He gas as an inert tracer for visualizing inhaled air speed and direction at each location within the complex, three-dimensional airways of pulmonary anatomy.

Published results highlighted on the cover of the *Journal of Magnetic Resonance* (Figure 1) reveal a common aerodynamic phenomenon known as air streaming. This was observed as a thin layer of high-speed gas localized along the outside radius of curvature in the



Figure 1. This research was featured on the cover of *Journal of Magnetic Resonance*.

trachea. The results also show, for the first time, how air speed is reduced as flowing gas branches along different paths to fill each of the rat's five lung lobes. This was seen as a transition from high gas speed to a slower flow rate.

The new system is being used in conjunction with its advanced computing resources to develop and test state-of-the-art computer models of inhaled airflow. These models are important not only for predicting where inhaled materials are deposited in the lung, but also for understanding how their fate ultimately affects human health. This work is part of EMSL's ongoing efforts to predict biological functions from molecular and chemical data. EMSL users are also exploiting the system to help understand the risks associated with common pesticides of interest to the Environmental Protection Agency. They have also begun to exploit ³He-flow-MRI for visualizing electrochemistry in operating fuel cells as part of efforts to improve operating efficiency and reliability.

The research is supported by the National Institutes of Health's National Heart, Lung and Blood Institute.

Citation

Minard KR, RE Jacob, G Laicher, DR Einstein, AP Kuprat, and RA Corley. 2008. "MR Imaging of Apparent ³He Gas Transport in Narrow Pipes and Rodent Airways." *Journal of Magnetic Resonance* 194(2):182-191.

A Solution NMR Investigation into the Early Events of Amelogenin Nanosphere Self-Assembly Initiated with Sodium Chloride or Calcium Chloride

GW Buchko,^(a) BJ Tarasevich,^(a) JG Bekhazi,^(a) ML Snead,^(b) and WJ Shaw^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) University of Southern California, Los Angeles, California

New studies performed using EMSL NMR capabilities reveal how the hardest material in the human body, tooth enamel, starts to form at the molecular level. Such studies give insights into the nature of orthodontic diseases such as amelogenesis imperfecta, which results in defective enamel formation and has been tied to N-terminus defects in amelogenin.

EMSL users from Pacific Northwest National Laboratory and University of Southern California used EMSL nuclear magnetic resonance resources to study the mechanisms behind self assembly of the protein, amelogenin, into nanospheres – an initial step in building enamel. Amelogenin provides a matrix upon which another protein, hydroxyapatite, builds a strong three-dimensional structure to form enamel. Using solution-state NMR spectroscopy and dynamic light scattering, the research team followed the initial steps of amelogenin matrix formation in solutions containing different levels of salt, a variable that triggers protein self-association. Two salts were tested (sodium chloride and calcium chloride), and both yielded similar step-wise results for amelogenin interaction (Figure 1). At low pH with no salt in solution, amelogenin exists as individual protein molecules, (monomers). Upon adding salt to the solution, pairs of amelogenin monomers start to interact at their N-termini to form dimers. As the salt concentration is increased further, the interaction between pairs of monomers grows stronger as the association extends to include interactions between the C-termini. Dimer formation is the first step in amelogenin self-assembly; the full self-assembly process yields amelogenin nanospheres.

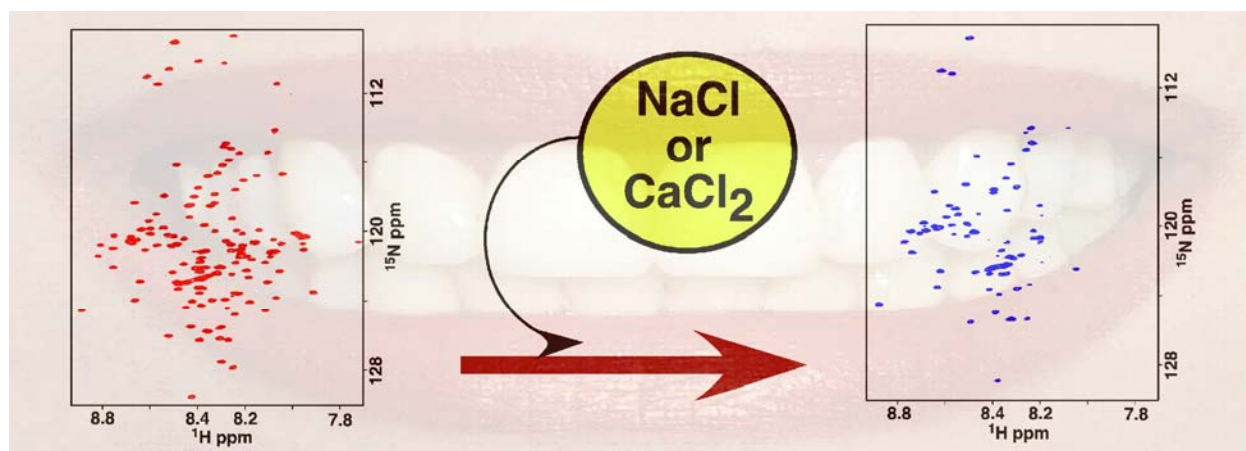


Figure 1. Self-assembly of amelogenin was monitored by following changes to the NMR spectra (¹H-¹⁵N HSQC) of amelogenin without salt (left, monomers) and after the addition of salt (right, dimers and larger).

The team's research provides a better understanding of the formation of nanospheres thought to have an essential functional role in enamel formation. Their work also offers insight into the nature of orthodontic diseases, such as amelogenesis imperfecta, which results in defective enamel formation. Further, this work supports EMSL's goal to predict biological functions from molecular and chemical data.

The research, supported by the National Institutes of Health's National Institute of Dental and Craniofacial Research, was published in *Biochemistry*.

Citation

Buchko GW, BJ Tarasevich, JG Bekhazi, ML Snead, and WJ Shaw. 2008. "A Solution NMR Investigation into the Early Events of Amelogenin Nanosphere Self-Assembly Initiated with Sodium Chloride or Calcium Chloride." *Biochemistry* 47(50):13215-13222. doi: 10.1021/bi8018288.

Enhanced Detection of Low-Abundant Human Plasma Proteins using a Tandem IgY12-SuperMix Immunoaffinity Separation Strategy

W Qian,^(a) DT Kaleta,^(a) BO Petritis,^(a) H Jiang,^(a) T Liu,^(a) X Zhang,^(a) HM Mottaz,^(b) SM Varnum,^(a) DG Camp II,^(a) L Huang,^(c) X Fang,^(d) W Zhang,^(d) and RD Smith^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) EMSL, Richland, Washington

(c) GenWay Biotech, Inc., San Diego, California

(d) Acrotics Corp, San Diego, California

EMSL users have designed a more sensitive protein separations technology, the tandem IgY12-SuperMix, that allows scientists to detect cytokines and other molecules of interest at the low nanogram-per-milliliter to sub-nanogram-per-milliliter range in the presence of other proteins that are more than 8 orders of magnitude higher in abundance. The system will help accelerate the discovery of novel biomarkers for improved diagnosis and prognosis of human diseases such as cancer, which will, in turn, impact the biomedical practice and human health.

Using liquid chromatography, mass spectrometry, and other instruments at EMSL, scientists from Pacific Northwest National Laboratory, EMSL, and GenWay Biotech, Inc. designed a new protein separations system—the tandem IgY12-SuperMix—that enhances the detection of hard-to-find proteins in human plasma (Figure 1). Using this new approach with the proteomics technologies developed at PNNL, the scientists removed the ~60 most abundant proteins from plasma samples. With these proteins removed, the scientists detected numerous low-abundance proteins. This technology makes the discovery of low-abundance disease biomarkers more feasible. The team is developing methodologies to detect breast cancer and other disease state biomarkers.

Funded by the National Institutes of Health's National Center for Research Resources, the National Institute of General Medical Sciences,

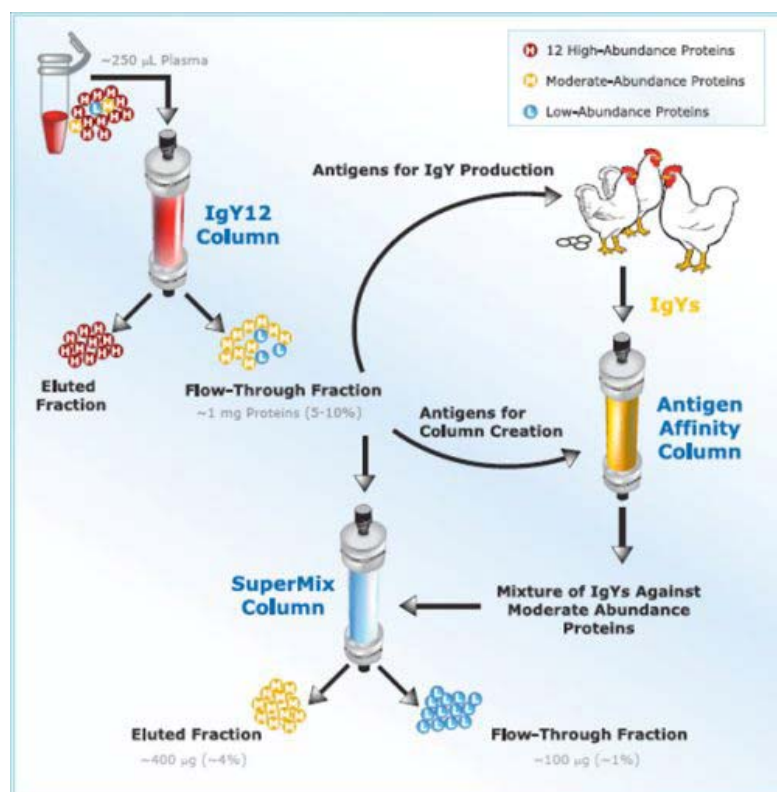


Figure 1. The tandem IgY12-SuperMix immunoaffinity separation strategy was developed by GenWay Biotech, EMSL, and PNNL. Typical recoveries are indicated assuming ~250 µL of plasma is loaded.

the Entertainment Industry Foundation (EIF) and the EIF Women's Cancer Research Fund, this work is part of EMSL's ongoing efforts to predict biological functions from molecular and chemical data. The research was published in *Molecular & Cellular Proteomics*. MCP.

Citation

Qian W, DT Kaleta, BO Petritis, H Jiang, T Liu, X Zhang, HM Mottaz, SM Varnum, DG Camp II, L Huang, X Fang, W Zhang, and RD Smith. 2008. "Enhanced Detection of Low-Abundant Human Plasma Proteins using a Tandem IgY12-SuperMix Immunoaffinity Separation Strategy." *Molecular & Cellular Proteomics*. MCP 7(10):1963-1973.

Geochemistry/Biogeochemistry and Subsurface Science

Enhanced Remedial Amendment Delivery through Fluid Viscosity Modifications: Experiments and Numerical Simulations

L Zhong,^(a) M Oostrom,^(a) TW Wietsma,^(b) and MA Covert^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) EMSL, Richland, Washington

Remediation efforts are often incomplete and laborious because of subsurface contaminants located in hard-to-reach places, such as areas of low permeability in aquifer systems. Using resources at EMSL, a Pacific Northwest National Laboratory and EMSL research team found a way to enhance cleanup effectiveness and efficiency by incorporating the inexpensive and readily available polymer, Xanthan gum, into the remediation process.

Advances in remediation research may lead to improved remediation techniques, positively affecting the environment and human health.

Using flow cell experiments, the Pacific Northwest National Laboratory and EMSL research team simulated the remediation of contaminated areas. The team found that adding Xanthan gum to remediating solutions increased their viscosity, thus helping deliver the remediating agent to areas in which the contaminant may otherwise have been left behind and increasing the portion of the contaminated volume touched by the remediating agent (Figure 1). Further, a version of the Subsurface Transport over Multiple Phases simulator – a general-purpose tool developed by PNNL scientists for simulating subsurface flow and transport – that was modified to account for using the polymer in

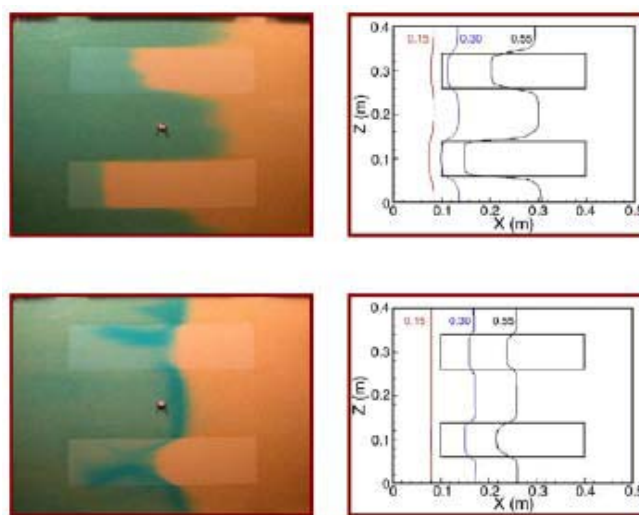


Figure 1. Xanthan gum (lower left) helps remediating agents reach areas of low permeability as compared to a control (upper left) in flow cell experiments (permeated volume shown in blue). STOMP predicts the experimental results well (right).

the system accurately predicted the results of the experiments. The modified version of STOMP may be used to predict subsurface remediation performance in similar systems at larger scales, and the Xanthan gum additive may prove useful in real-world scenarios such as cleanup of uranium-contaminated areas.

Such advances in remediation research demonstrate the feasibility of an inexpensive alternative remediation technique and of using computational tools to predict the effectiveness of such techniques under real-world conditions. In addition, this research supports EMSL's goal to link theory with experiment.

The team's work has led to a Department of Defense Environmental Security Technology Certification Program project, *Enhanced Amendment Delivery to Low Permeability Zones of Chlorinated Solvent Source Area Bioremediation*. For this project, PNNL researchers are collaborating with colleagues from GSI Environmental.

The research, supported by PNNL's Laboratory Directed Research and Development program, was published in *Journal of Contaminant Hydrology*.

Citation

Zhong L, M Oostrom, TW Wietsma, and MA Covert. 2008. "Enhanced remedial amendment delivery through fluid viscosity modifications: Experiments and numerical simulations" *Journal of Contaminant Hydrology* 101:29–41.

Kinetics of Reduction of Fe(III) Complexes by Outer Membrane Cytochromes MtrC and OmcA of *Shewanella oneidensis* MR-1

Z Wang,^(a) L Shi,^(a) C Liu,^(a) X Wang,^(a) MJ Marshall,^(a) JM Zachara,^(a) KM Rosso,^(a) M Dupuis,^(a) JK Fredrickson,^(a) and SM Heald^(b)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) Argonne National Laboratory, Argonne, Illinois

*New details about how bacteria and metals interact highlight the importance of considering metal-ligand complexes as part of bioremediation strategies. Bacteria such as *Shewanella oneidensis* MR-1 hold promise as a bioremediation tool because they exchange electrons with metals, affecting their solubility and thus their level of danger to the environment and human health. This work may lead to enhanced bioremediation strategies to remedy contaminated environments, such as the DOE's Hanford Site in Richland, Washington.*

As part of EMSL's Biochemistry Grand Challenge, scientists have made significant progress toward understanding electron exchange between bacteria and metals. A research team led by EMSL users from the Pacific Northwest National Laboratory carried this Grand Challenge further by using spectroscopy and computational tools at EMSL to determine the kinetics of electron exchange when the metal, iron, is coupled to ligands of geological and environmental significance.

In particular, the research team determined how Fe(III) complexes with the ligands citrate, nitrilotriacetic acid (NTA), and ethylenediaminetetraacetic acid (EDTA) were reduced by two *Shewanella* surface proteins known to be involved in electron transfer: MtrC and OmcA (Figure 1). The team's results were surprising: even though electron transfer from the surface proteins to the Fe(III) EDTA complex is thermodynamically unfavorable compared to reactions involving Fe(III)-citrate and

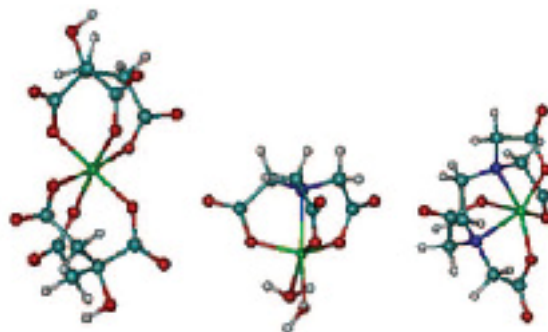


Figure 1. Computed structures of $\text{Fe}-(\text{citrate})_2^{3-}$ (left), FeOH-NTA^- (middle), and Fe-EDTA^- (right).

Fe(III)-NTA, it happened most quickly. For the EDTA reactions, the reaction rate was influenced by the relatively large reorganization energies of the reactants – so much so as to override the strong thermodynamics. This and the geometry of the molecules in the reactions favored the electron transfer kinetics involving EDTA. The team's work demonstrates the importance of metal complexation to bioremediation. For contaminated sediments where radioactive metals are co-disposed with organic chelating agents, any effective bioremediation strategy should take into consideration the ligand complexation effect.

Experimental and computational studies such as these refine the understanding of the fundamental biological process of bacterial electron transfer and contribute to EMSL's goal to rapidly link theory and experiment. Further, such studies contribute heavily to EMSL's Biochemistry Grand Challenge, which supported this research.

This research was published in *Applied and Environmental Microbiology*.

Citation

Wang Z, L Shi, C Liu, X Wang, MJ Marshall, JM Zachara, KM Rosso, M Dupuis, JK Fredrickson, and SM Heald. 2008. "Kinetics of Reduction of Fe(III) Complexes by Outer Membrane Cytochromes MtrC and OmcA of *Shewanella oneidensis* MR-1." *Applied and Environmental Microbiology* 74(21):6746–6755.

Science of Interfacial Phenomena

Imaging Consecutive Steps of O₂ Reaction with Hydroxylated TiO₂(1 1 0): Identification of HO₂ and Terminal OH Intermediates

Y Du,^(a) NA Deskins,^(b) Z Zhang,^(b) Z Dohnalek,^(b) M Dupuis,^(b) and I Lyubinetsky^(a)

(a) EMSL, Richland, Washington

(b) Pacific Northwest National Laboratory, Richland, Washington

Expected but elusive—that's how scientists described two intermediates (Figure 1) that may play an important role in the reaction that turns water into hydrogen. Now, thanks to the work of six researchers at EMSL and Pacific Northwest National Laboratory, these intermediates are no longer a mystery. In a recent article featured on the cover of the Journal of Physical Chemistry C, the researchers provided images of two intermediates that occur during the reaction that changes water into hydrogen.

An intermediate is a transitory product created as a chemical reaction moves from its starting materials to the final product. Some reactions have a few intermediates, others hundreds.

For a long time, people expected some intermediate should be formed during the reaction of oxygen and hydrogen on titanium dioxide. It was expected, but nobody had seen it. Until now. Also, the team found that they could follow all of the steps that occur during oxygen and hydrogen transformation into water.

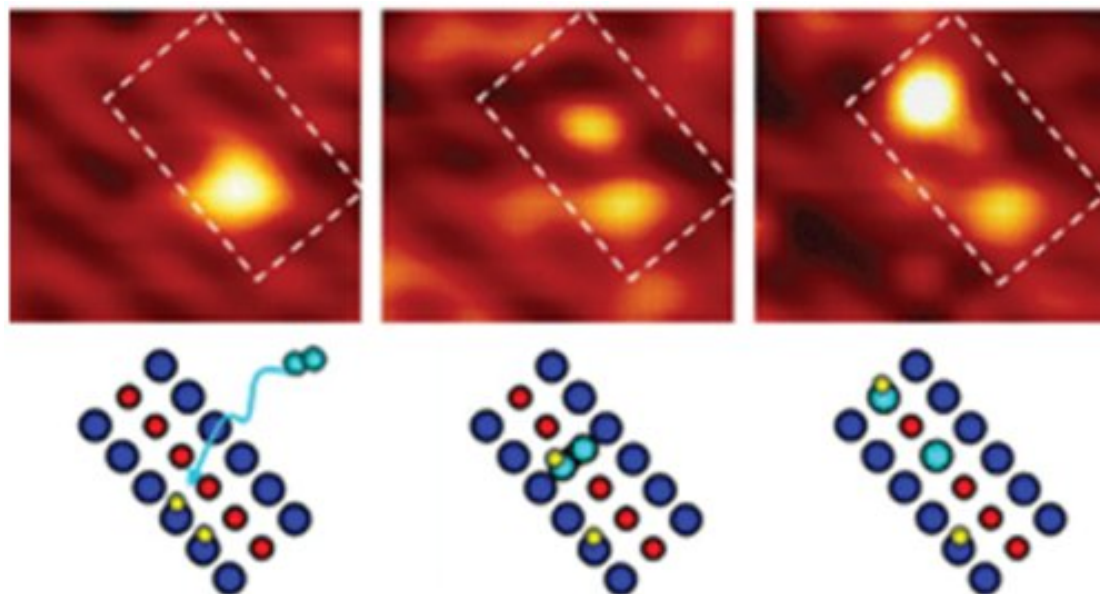


Figure 1. Two intermediates were discovered in the conversion of water to hydrogen (top: scanning tunneling microscope images). Forming these intermediates begins with oxygen (aqua). It snuggles in between the raised oxygen rows (blue), pulling a nearby hydrogen (yellow) on top of it. Later, this intermediate can split apart, creating oxygen and hydrogen (aqua and yellow) bound together and bound to a titanium atom (red).

Discovering the intermediates and uncovering the intricate five-step process may shed light on the catalyzed reactions necessary to mass produce hydrogen. This simple molecule could power fuel cells that provide cleaner, quiet sources of energy.

Fuel cells are in use today, powering large buildings and tiny sensors and computers. Large stationary fuel cells provide backup power to hospitals, nursing homes, and other buildings. They also power remote outposts that do not have access to electricity. In vehicles, smaller cells are replacing or supplementing fossil fuel in cars, trucks, planes, trains, and boats.

The intricacy of the reactions and an exceptionally small number of molecules involved has prevented finding the intermediates until now. To combat these challenges, the team combined experimental techniques with theoretical techniques and computations. They prepared a partially hydroxylated, reduced titanium dioxide catalyst at room temperature so that the surface contained both hydroxyl groups and oxygen vacancies. Next, they exposed the catalyst to oxygen and recorded the reactions. These reactions were imaged using the state-of-the-art scanning tunneling microscope at EMSL. This instrument, available to users from around the world, can show what single molecules and atoms are doing on catalytic surfaces.

Once the team's experimental experts acquired the images, the theorists went to work. Using EMSL computational resources as well as those at the National Energy Research Scientific Computing Center, they performed density-functional-theory calculations to help interpret the images. Based on the theory and experimentation, the team reported the first observed adsorbed hydroperoxyl. Hydroperoxyl is two oxygen atoms bound together and also containing a single hydrogen atom. The hydroperoxyl is attached to the surface, with a single bond forming between one of the oxygen atoms and a titanium atom.

The hydroperoxyl can then break apart. One of the oxygen atoms stays bound to the titanium atom. The remaining oxygen and hydrogen, still bound together, bounce down to bind to another titanium atom. This oxygen-hydrogen combination is the second elusive intermediate: a terminal hydroxyl group on the catalyst surface.

The team will continue to explore catalysts and the reactions involved in producing hydrogen from water and sunlight. Their next paper, to be published soon in a prominent journal, looks at another variation, when the starting catalyst surface has oxygen adatoms.

The research is supported by DOE's Office of Basic Energy Sciences.

Citation

Du Y, NA Deskins, Z Zhang, Z Dohnalek, M Dupuis, and I Lyubinetsky. 2009. "Imaging Consecutive Steps of O₂ Reaction with Hydroxylated TiO₂(110): Identification of HO₂ and Terminal OH Intermediates." *Journal of Physical Chemistry C* 113(2):666-671.

Two Pathways for Water Interaction with Oxygen Adatoms on TiO₂(110)

Y Du,^(a) NA Deskins,^(b) Z Zhang,^(b) Z Dohnalek,^(b) M Dupuis,^(b) and I Lyubinetsky^(a)

(a) EMSL, Richland, Washington

(b) Pacific Northwest National Laboratory, Richland, Washington

Single oxygen atoms dancing on a metal oxide slab, glowing brighter here and dimmer there, have helped chemists better understand how water splits into oxygen and hydrogen. In the process, the scientists have visualized a chemical reaction that had previously only been talked about. The new work improves our understanding of the chemistry needed to generate hydrogen fuel from water or to clean contaminated water.

A research team from EMSL and Pacific Northwest National Laboratory made the discovery while trying to determine the basics of how titanium dioxide -- a compound sometimes found in sunscreen -- breaks down water. The chemical reactions between water and oxygen are central to such varied processes as hydrogen production, breaking down pollutants, and in solar energy.

While exploring titanium dioxide as a way to split water into its hydrogen and oxygen pieces, researchers can use scanning tunneling microscopy to watch the chemical reaction. The surface of a slab of titanium dioxide is like a corn field: rows of oxygen atoms rise from a patch of titanium atoms. The alternating oxygen and titanium rows look like stripes.

Scientists can also see some atoms and molecules that come to rest on the surface as bright spots. One such visible atom is a single oxygen atom that comes to rest on a titanium atom, called an "adatom". Chemists can only see water molecules if they drop the temperature dramatically -- at ambient temperature, water moves too fast for the method to pick them up.

In this work, the research team studied water's reactions with titanium dioxide at ambient temperature at EMSL. Starting with a surface plated with a few oxygen adatoms, they added water -- and the adatoms started to dance, moving back and forth along the titanium row.

Remarkably, the adatoms didn't just slide up and down the stripes. They also bounced out of them and landed in others. Calculating how much energy it would take for the adatoms to move by themselves, much less hop over an oxygen row, the chemists suspected the adatoms were getting help -- most likely from the invisible water molecules.

To make sense of the dancing adatoms, the team calculated how much energy it would take to move adatoms with the help of water molecules. If a water molecule sits down next to an adatom, one of the water's hydrogen atoms can jump to the adatom, forming two oxygen-hydrogen pairs.

These pairs are known as hydroxyls and tend to steal atoms from other molecules, including each other. One of the thieving hydroxyls can then nab the other's hydrogen atom, turning back into a water molecule. The water molecule floats off, leaving behind an adatom. Half the time, that adatom is one spot over -- which makes the original appear to have moved.

The chemists determined that water can help the adatom jump a row as well: If a water molecule and an adatom are situated on either side of a raised oxygen row, a row oxygen can serve as the middleman, handing

over a hydrogen from the water molecule to the adatom. Again, two hydroxyls form, one ultimately stealing both hydrogens (with the help of the middleman) and zipping away as water. If the incoming water molecule has been stripped, the adatom appears to have hopped over.

The calculated energy required for these different scenarios fit well with the team's experimental data. When a row oxygen serves as a middleman, the process is known as "pseudo-dissociation", a reaction suggested by chemists but until now, never verified experimentally.

In the future, the team plans on determining if water can make the adatoms move other species and more than one space at a time. In addition, they will investigate how light affects the reaction.

The research, supported by the Department of Energy's Office of Science, was published in *Physical Review Letters*.

Citation

Du Y, NA Deskins, Z Zhang, Z Dohnálek, M Dupuis, and I Lyubinetsky. 2009. "Two Pathways for Water Interaction with Oxygen Adatoms on TiO₂(110)." *Physical Review Letters* DOI 10.1103/PhysRevLett.102.096102

Macrophage Responses to Silica Nanoparticles are Highly Conserved Across Particle Sizes

KM Waters,^(a) LM Masiello,^(a) RC Zangar,^(a) BJ Tarasevich,^(a) NJ Karin,^(a) RD Quesenberry,^(a) S Bandyopadhyay,^(a) JG Teeguarden,^(a) JG Pounds,^(a) and BD Thrall^(a)
(a) Pacific Northwest National Laboratory, Richland, Washington

The increasing use of nanomaterials in products from semiconductors to sunscreen is revolutionizing products in many industries. This popularity results from significant changes in the chemical reactivity and physical properties of many materials significantly change at the nanoscale—that is, having at least one dimension of 100 nanometers or less. However, the same properties that make nanomaterials attractive for commercial and medical use may also enhance their biological reactivity, raising concerns about their potential toxicity. For example, materials classically considered biologically inert, such as amorphous silica, titanium dioxide and gold have been reported to cause exacerbated biological responses when used at the nanoscale.

Scientists are now closer to determining what a "safe dose" of nanomaterials is to humans, thanks to a comprehensive study published by EMSL users from the Pacific Northwest National Laboratory. Using an *in vitro* model of macrophage cells, they demonstrated that the ability of amorphous silica particles—akin to sand—to stimulate inflammation and toxicity in cells scales closely with the total particle surface area.

To the research team's knowledge, this is the first study to use genome-scale measurements to evaluate whether the cellular effects induced by nanomaterials are dependent on particle size. The results suggest that the surface chemistry properties of amorphous silica that are responsible for its bioactivity do not significantly change as particle size decreases to the nanoscale.

The molecular mechanisms by which nanoparticles stimulate cellular responses are still poorly understood. Yet it is clear that particle surface chemistry is an important driving factor. By identifying the early transcriptional events and pathways activated by amorphous silica in macrophages—white blood cells that surround and kill invaders to the tissues—the research team's results significantly extend previous studies. Because of their role in immune surveillance, macrophages are important sentinels for biological response to pathogens.

To identify hazards and assess human risk from nanoparticle exposure, researchers must extrapolate dose-response data from animal studies to human systems. Therefore, accurate interpretation of size-dependent biological responses to nanoparticles depends on the dose metric used for comparison—in this case, particle size. This is because for a given mass of particles, the total surface area increases with decreasing particle diameter, making it an essential determinant of the fraction of reactive groups on particle surfaces.

Using EMSL's particle characterization capability and transmission electron microscopy, this study demonstrated that the particle surface properties that dictate biocompatibility of amorphous silica are essentially the same at the nanoscale as a function of surface area. The generalized strategy described in this study can be extended to other nanomaterials both to identify mechanism of action and to prioritize more expensive toxicity studies in animals.

The team used a genome-wide approach to investigate whether the cellular pathways activated by amorphous silica are size dependent. Amorphous silica was chosen because of its increasingly important role in nanotechnology. It is used in production of high-efficiency photovoltaics and tires, and in consumer products such as drug delivery vehicles, toothpaste, sunscreen, cosmetics and nutraceuticals.

They performed whole genome microarray analysis of the early gene expression changes induced by 10- and 500-nm particles. These showed that the magnitude of change for the majority of genes affected correlated more tightly with particle surface area than either particle mass or number. The researchers also identified particle size-specific gene expression changes (Figure 1).

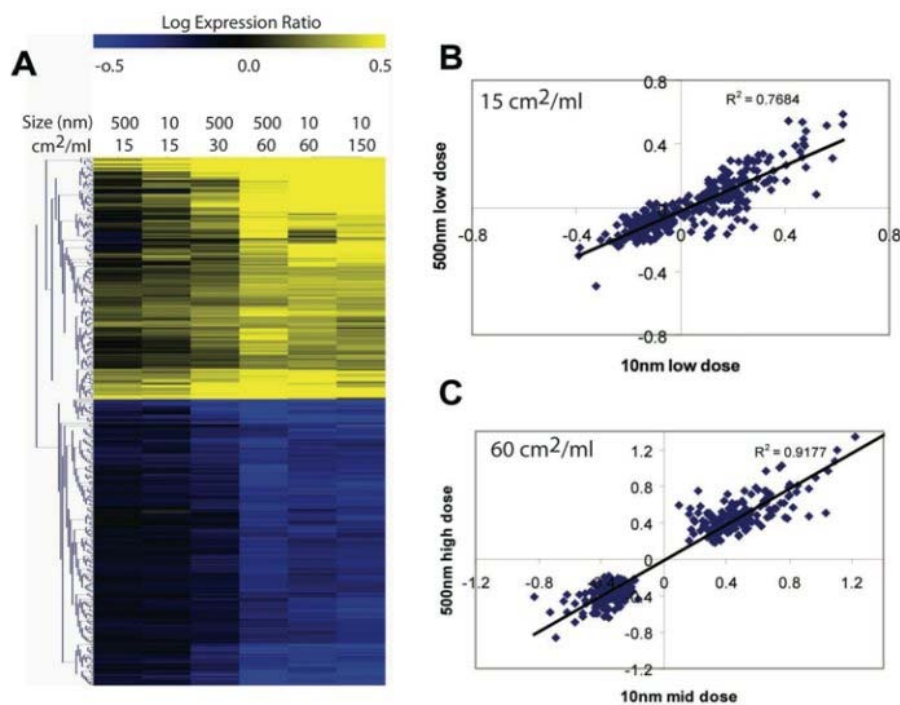


Figure 1. The relationship between mRNA abundance changes and particle surface area dose for 404 genes regulated in response to 10- and 500-nanometer amorphous silica particles. Genes shown in the majority pattern A naturally clustered according to the particle surface area dose. In contrast, the genes for patterns B and C continued to separate by particle size and mass dose (data not shown). Correlation analysis for the majority pattern A genes indicated a strong overall correlation between the gene expression ratio and particle surface area dose across all treatment groups.

Using advanced bioinformatics approaches, the team was able to demonstrate that the biological pathways represented by the size-specific gene expression changes were nearly identical, irrespective of particle size. Direct comparison of the cell processes represented in the 10- and 500-nm particle gene sets using gene set enrichment analysis revealed that among 1009 total processes represented in the data, none were statistically enriched for one particle size group over the other.

The key mechanisms involved in silica nanoparticle-mediated gene regulation and cytotoxicity have yet to be established. For example, scientists don't know whether macrophage cell responses are initiated by particle contact with the cell membrane or if receptor binding or particle internalization is required. Such studies should help in developing strategies for enhancing the beneficial properties of nanomaterials while reducing potential adverse health effects mediated through macrophage interactions.

The research, sponsored by the National Institutes of Health and internal funding at PNNL, was published in *Toxicological Sciences*.

Citation

Waters KM, LM Masiello, RC Zangar, BJ Tarasevich, NJ Karin, RD Quesenberry, S Bandyopadhyay, JG Teeguarden, JG Pounds, and BD Thrall. 2009. "Macrophage Responses to Silica Nanoparticles are Highly Conserved Across Particle Sizes." *Toxicological Sciences* 107(2):553-569.

Electronic Effects on the Surface Potential at the Vapor–Liquid Interface of Water

SM Kathmann,^(a) IFW Kuo,^(b) and CJ Munday^(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

(b) Lawrence Livermore National Laboratory, Livermore, California

One of the toughest challenges in molecular simulation is to construct computational models that contain enough of the right physics to produce results scientists can trust. EMSL users from the Pacific Northwest National Laboratory and Lawrence Livermore National Laboratory have solved part of that problem. They have produced the first model to faithfully depict the electric field present at the point, or interface, where the liquid and vapor forms of water meet. The model also comes closer than other simulations to matching calculations derived from experiment.

In molecular simulation, a model is only as good as the physics that goes into it. More physics leads to better models. The effects of electrons and how to include them in models can make a big difference in the accuracy of a model. A research team from Pacific Northwest National Laboratory and Lawrence Livermore National Laboratory found that researchers have to consider the electrons individually if they want an accurate representation of an electric field.

A new model developed by the team provides an improved tool for acquiring that information (Figure 1). The model calculates the molecules' full electronic charge distribution—all of the water electrons and how they interact with other electrons. The type of information this model can provide is significant in many areas of chemical physics research, including energy, biology, materials science and global warming.

Scientists know that the dominant interaction among molecules is electrical and that very interesting chemistry occurs at interfaces, where one form of matter meets another. From electricity on a child's balloon

that makes your hair stand up, to electron transport in transistors, electric fields are what make things move. Yet calibrating an electric field is immensely complex, even for a molecule as simple as water. Surface potential is the term given to the measurement of an electric field at an interface. Scientists use surface potential calculations to describe and predict chemical reactions at a vapor-liquid interface. Many scientists have attempted to determine the surface potential of the vapor-liquid interface of water. But, they do not agree on the importance of the field or if the charge distribution is positive or negative.

The primary obstacle has been lack of computing power. The high-performance computing resources enabled the research team to apply quantum physics to the problem. These resources are located at EMSL and Lawrence Livermore National Laboratory.

The new model revealed that the strength of the electric field is much smaller than previously estimated and that the charge is always negative.

The team started by calculating the behavior of the electronic cloud that envelops every water molecule at the vapor-liquid interface. In water that is either all liquid or all gas, it is the

intermingling of these electronic clouds that holds the molecules together. However, electrons behave differently where the liquid and vapor meet. This interface is a sort of no-man's-land, where electrons move from one state to the other and back again, aiding or restricting chemical processes and other molecular interactions.

The team then compared the new model with previous models and experiments. Earlier models viewed the electrons in water as set along certain pathways or gathered at the nuclei of the atoms. Dealing with the electrons as a cloud confirmed predictions that the density of the electrons significantly influences the electronic properties of the vapor-liquid interface of water.

Future studies will seek to further quantify explicit inclusion of the electronic charge cloud. For example, researchers will address the surface potential and electric field at the interface between a salt crystal and liquid water, as well as electronic effects on the reaction path of various ions through the vapor-liquid interface of water.

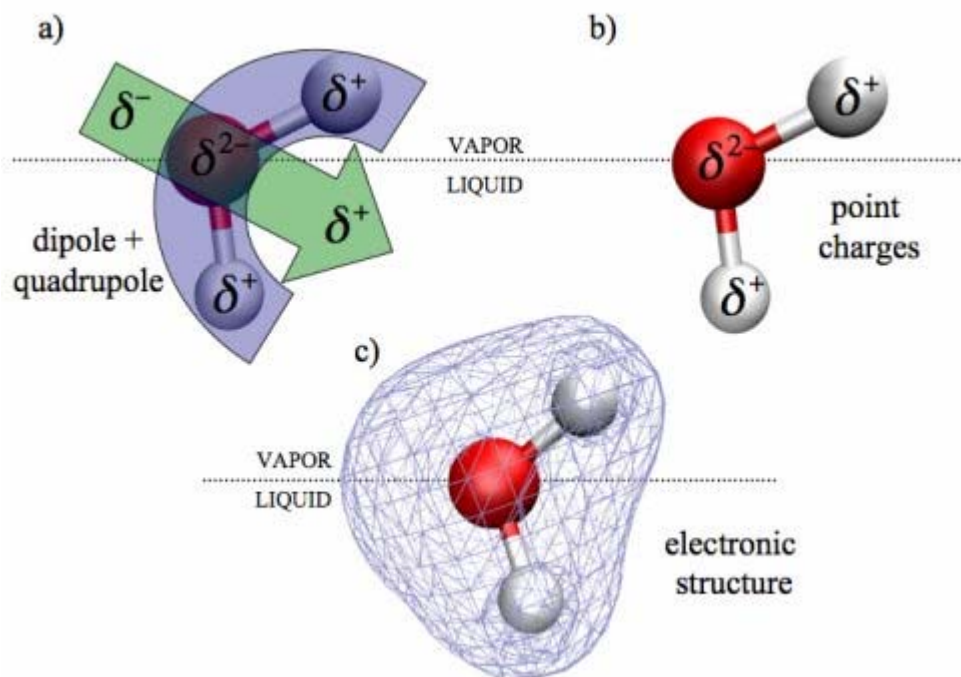


Figure 1. Unlike previous models (top), a new computational model (bottom) includes the full “cloud” of electrons in a water molecule.

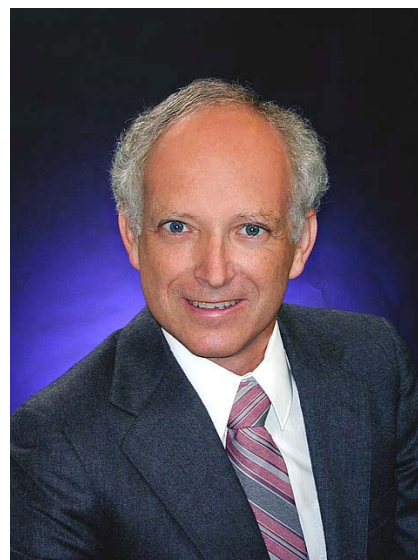
This research was supported by the DOE Office of Basic Energy Sciences and was published in the *Journal of the American Chemical Society*.

Citation

Kathmann SM, IFW Kuo, and CJ Mundy. 2008 "Electronic Effects on the Surface Potential at the Vapor-Liquid Interface of Water." *Journal of the American Chemical Society*, 130:16556-16561.

Awards and Recognition

Baer named AAAS Fellow. Don Baer, EMSL Lead Scientist for Interfacial Chemistry, was named Fellow of the American Association for the Advancement of Science. At EMSL, Baer specializes in the use of spectroscopy and other advanced techniques to reveal the behavior of atoms and molecules at or near the surfaces of materials. AAAS honored him "for research and capability development that significantly advance molecular-level understanding of environmentally important interfacial processes relevant to nanoparticle reactivity, mineral dissolution and stress corrosion cracking." He is a Laboratory Fellow at Pacific Northwest National Laboratory and a Fellow of AVS. He also is an adjunct professor of physics at Washington State University, Tri-Cities, and an adjunct professor of chemistry at the University of Washington. Baer is a graduate of Carnegie Mellon University and received his doctorate from Cornell University. He has authored or co-authored more than 200 peer-reviewed scientific journal publications and edited three books and four special journal issues. He was also recently named Reviews Editor for *Surface and Interface Analysis*, a refereed journal devoted to publishing papers and applying techniques for characterizing surfaces, interfaces, and thin films. Baer joins 485 other high-caliber researchers who were elected as Fellows in November, including EMSL users Cindy Bruckner-Lea, Michel Dupuis, Chuck Peden, and Yong Wang. He was honored with his fellow recipients at the AAAS Annual Meeting to be held in February in Chicago.



Don Baer

Wiley invited to join National Research Council review panel.

Steven Wiley, EMSL Lead Scientist for Biology, was selected to serve as a reviewer on the 2009 National Research Council Research Associateship Programs. The programs fund postdoctoral fellows, senior scientists and engineers, and faculty to work on research problems of their choice in federal laboratories. The Council receives around 800 applications every year for these programs. The NRC selects about 300 of these applications for funding based on a competitive process that includes a review by one of five NRC panels. One of the five panels is the Life Sciences panel, where Wiley will serve. On this panel, he will evaluate the impact and the approach of the research proposed in the applications four times a year. Also, he will discuss his recommendations with his colleagues on the panel, working to promote only the best possible research. Wiley will serve on the panel for three years.

Wiley was chosen because of his scientific expertise in molecular and systems biology, such as the research into large-scale protein-protein interactions and cell signaling networks. In addition, he is an experienced leader, currently working as the steward for EMSL's Biological Interactions and Dynamics science theme and as Director of Pacific Northwest National Laboratory's Biomolecular Systems Initiative. Further, he has experience with advisory committees, including the National Institutes of Health and Burroughs Wellcome Fund.



Steve Wiley

Raff receives prestigious NSF award. Jonathan Raff, an EMSL user from the University of California Irvine, was awarded a prestigious American Competitiveness in Chemistry Postdoctoral Fellowship from the National Science Foundation. The award is designed to support post-doctoral associates in chemistry and seeks to build ties between academia and industry/the national laboratory system while also involving beginning scientists in efforts to broaden participation in chemistry. Raff is one of four researchers nationwide who received the award, which is in its inaugural year. A research associate at the university's Environmental Molecular Sciences Institute, AirUCI—or Atmospheric Integrated Research for Understanding Chemistry at Interfaces, he received the award in the amount of \$200,000 from the NSF's Division of Chemistry for his proposal to study the heterogeneous reactions of nitrogen oxides under atmospherically relevant conditions. Nitrous acid—which results from the heterogeneous reaction of nitrogen dioxide and water—is the most important daytime source of reactive hydroxyl free radicals, an important oxidant that removes pollutants and drives important radical reaction pathways in the atmosphere. However, there is

currently very little understanding about how nitrous acid forms on surfaces, so Raff's goal is to use EMSL's surface science instruments, such as infrared spectroscopy, X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and Auger electron spectroscopy to help identify its precursors on surfaces and gain insight and understanding of how the chemistry leading to nitrogen dioxide adsorption and photochemical nitrous acid formation affects the composition of aerosol and thin-layer film surfaces.



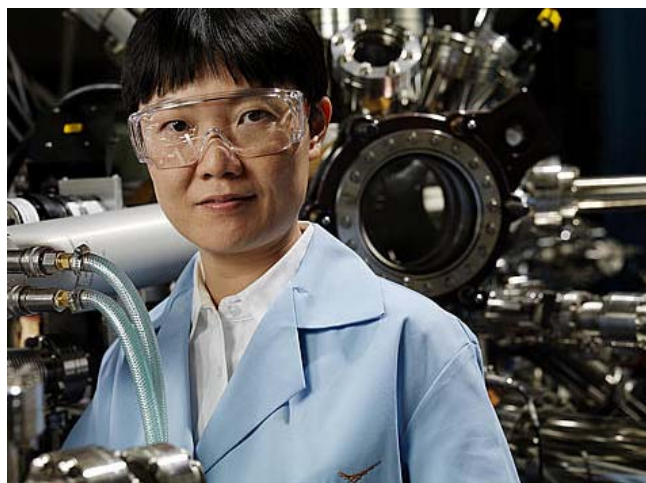
Jonathan Raff

Qian named Rising Young Star by *Genome Technology*. EMSL user Wei-Jun Qian, a Pacific Northwest National Laboratory scientist who conducts leading-edge proteomics work at EMSL, was named one of the 30 rising young stars of science by *Genome Technology* magazine in its third annual “Tomorrow’s PIs” special edition. The magazine offers readers a chance to see large-scale biological research through the eyes of some of the best and the brightest young scientists who are poised to make significant contributions in advancing the scientific frontiers. Qian was selected for this honor because of his work in developing and applying innovative techniques that have enabled large-scale, quantitative investigations of proteins in challenging clinical samples. Currently, he is developing and applying novel mass spectrometry-based approaches to measure changes in proteins from mammalian cells, tissues, and biofluids. His work is helping other scientists better understand cell signaling and discover mechanistic or diagnostic protein biomarkers for human diseases. The magazine’s interview with Qian, titled “Step by Step, a Better Mass Spec,” appears in the December 2008/January 2009 issue.



Wei-Jun Qian

Zhang invited to editorial board. EMSL researcher Yanwen Zhang was invited to serve a 3-year term on the advisory editorial board of *Nuclear Instruments & Methods in Physics Research, Section B*. This journal, published by Elsevier, covers all aspects of the interaction of energetic beams, such as ion, electron, and photon beams, with solids. Related topics, such as applying ion beam analysis to biological, archaeological and geological samples, are covered. Notable conferences publish their proceedings in this peer-reviewed journal. At EMSL, Zhang leads materials analysis and modification research projects in the ion accelerator laboratory. Her work covers topics such as single ion impact, nanoscale defect engineering, ion/electron-solid interaction, radiation detector physics, ion-beam modification and synthesis of materials, electrochemical oxidation of nuclear reactor fuel cladding, and application of ion-beam analysis techniques. With her collaborators around the world, she has written or co-written more than 120 journal articles. She is a co-editor for a book *Ion Beams in Nanoscience and Technology* (Springer Verlag, Berlin).



Yanwen Zhang

Major Facility Upgrades

Chinook is accepted. EMSL’s new supercomputer, Chinook, achieved final acceptance on March 20, 2009. Chinook is a \$20M system with peak performance of 164 teraflops, nearly 15 times faster than EMSL’s previous 11.2 teraflop system named MPP2. Chinook can perform more 160 trillion calculations per second, ranking it in the top 20 fastest computers in the world. Speed isn’t its focus though: Chinook’s designers made sure the supercomputer can handle the kinds of complex scientific problems the researchers who use it tackle. Researchers studying complicated worldly questions -- from climate scientists who are trying to

reproduce the tiniest particles in the atmosphere to chemists watching how atoms tug at each other in a molecule -- need a different kind of supercomputer than physicists studying the big bang.

News Coverage

EMSL stimulus funding in Tri-City Herald. PNNL has received \$124 million of funding under the American Reinvestment and Recovery Act through the Office of Science for capital upgrades and instrumentation for EMSL and the Atmospheric Radiation Measurement Climate Research Facility. EMSL is expected to receive \$60 million of the funding, which will accelerate the user facility's recapitalization plan in areas such as nuclear magnetic spectroscopy, computing, microscopy, and mass spectrometry over the next 18 months. See the article at http://www.tri-cityherald.com/kennewick_pasco_richland/story/519807.html.

Visitors and Users

During the second quarter of Fiscal Year 2009, a total of 386 users benefited from EMSL capabilities and expertise. This total included 231 onsite users and 155 remote users.

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