the Molecular Bond

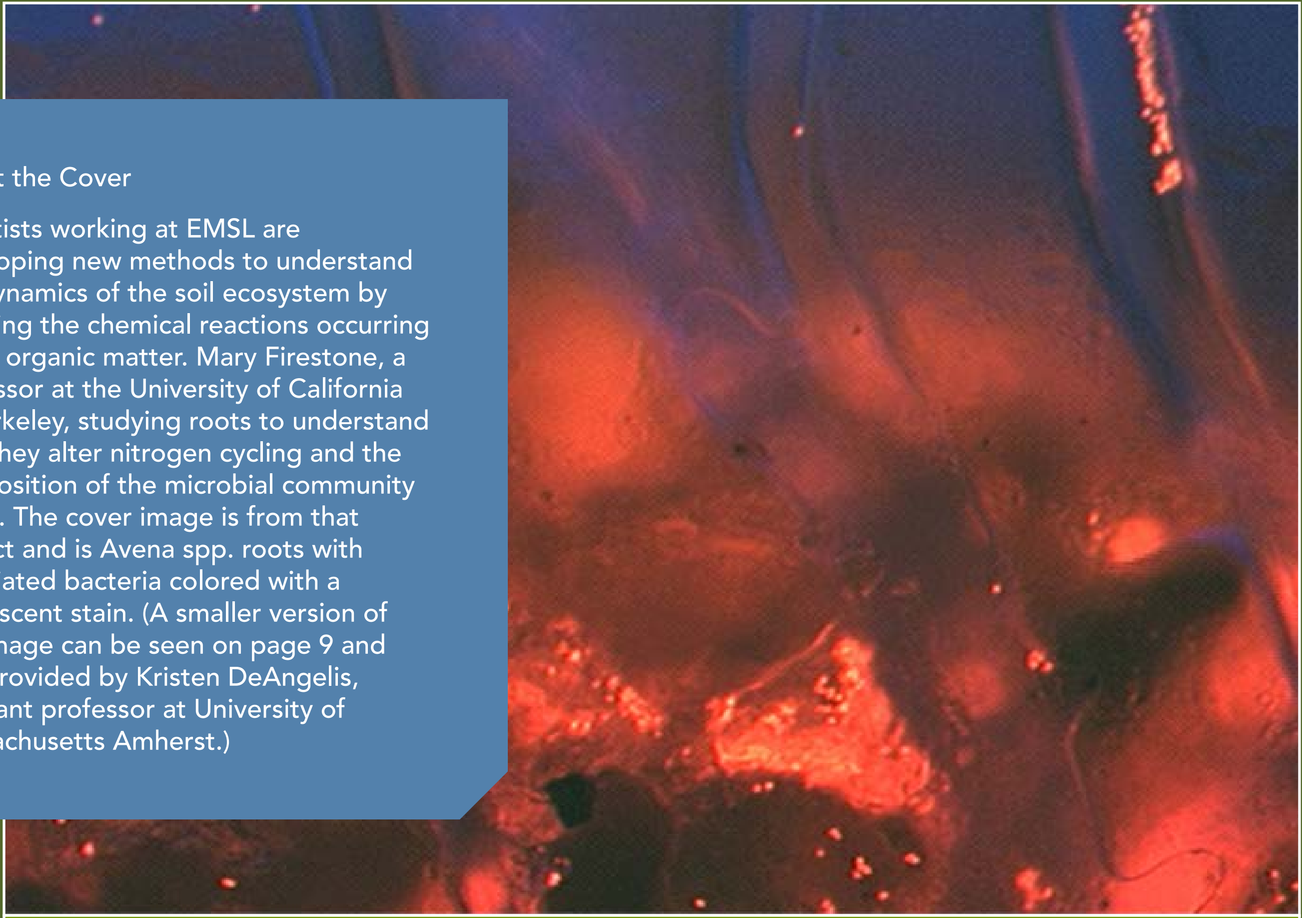
EMSL

SCIENTIFIC INNOVATION THROUGH INTEGRATION

April 2015

Ground Control

Also inside this issue:



About the Cover

Scientists working at EMSL are developing new methods to understand the dynamics of the soil ecosystem by studying the chemical reactions occurring in soil organic matter. Mary Firestone, a professor at the University of California at Berkeley, studying roots to understand how they alter nitrogen cycling and the composition of the microbial community in soil. The cover image is from that project and is Avena spp. roots with associated bacteria colored with a fluorescent stain. (A smaller version of this image can be seen on page 9 and was provided by Kristen DeAngelis, assistant professor at University of Massachusetts Amherst.)

About *The Molecular Bond*

The Molecular Bond is EMSL's bimonthly newsletter for users, potential users and other interested individuals. EMSL Communications oversees the production of *The Molecular Bond*.

EMSL, the Environmental Molecular Sciences Laboratory, is a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research in the Office of Science. Located at Pacific Northwest National Laboratory in Richland, Wash., EMSL offers an open, collaborative environment for scientific discovery to researchers around the world. Its integrated computational and experimental resources enable researchers to realize important scientific insights and create new technologies. More information about EMSL is available at:
www.emsl.pnnl.gov

To request additional copies or to subscribe, contact: EMSL Communications at email: emslcom@pnnl.gov

EMSL

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

U.S. DEPARTMENT OF ENERGY

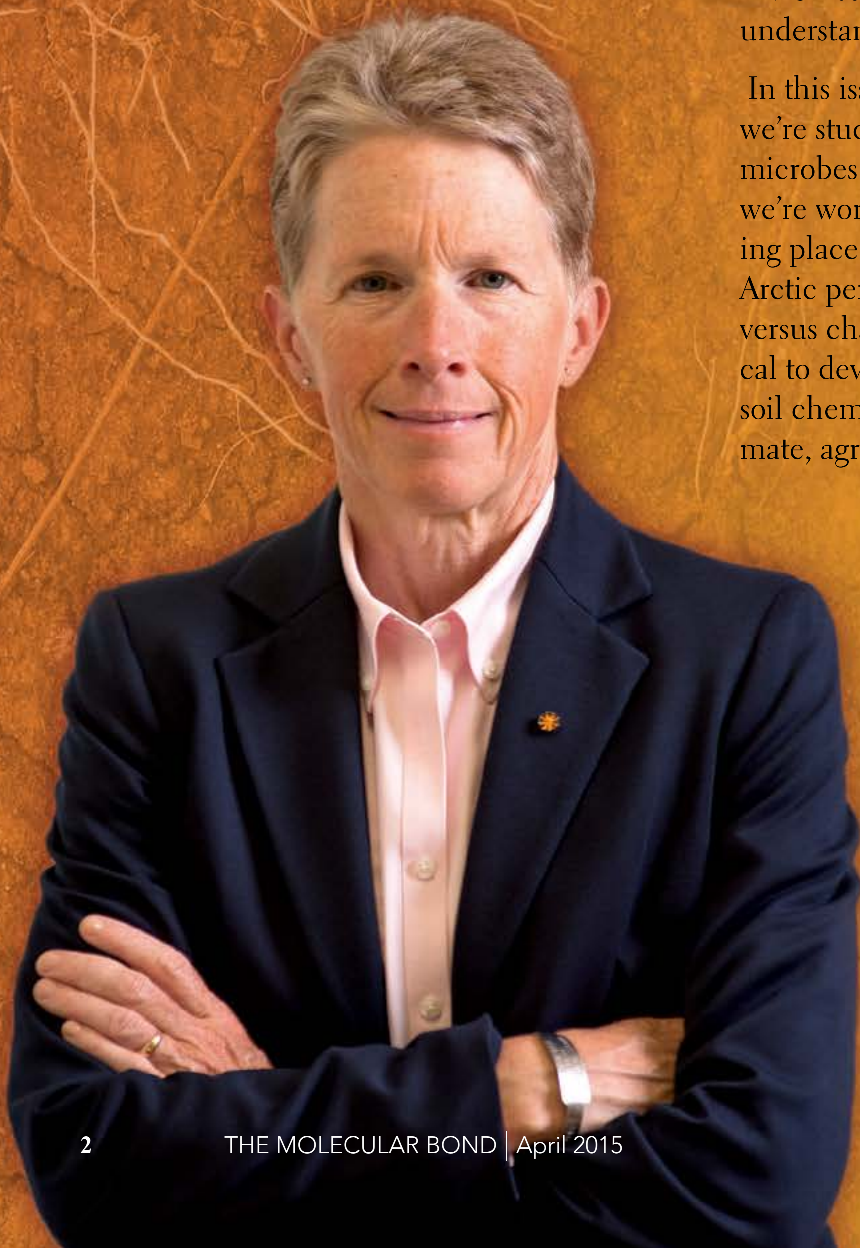
Used for energy and environmental applications, an EMSL scientist works at the environmental transmission electron microscope, or ETEM, housed in EMSL's Quiet Wing. EMSL's ETEM provides *in situ* capabilities that enable atomic-resolution imaging and spectroscopic studies of materials under dynamic operating conditions. It captures atomic-level processes as they occur, enabling vital research across a range of scientific fields. Read more about the Quiet Wing and other capabilities at EMSL in the feature "Special Science Call Projects Announced" on page 11. (EMSL file photo)

INSIDE THIS ISSUE

EMSL

FROM THE DIRECTOR

Allison Campbell



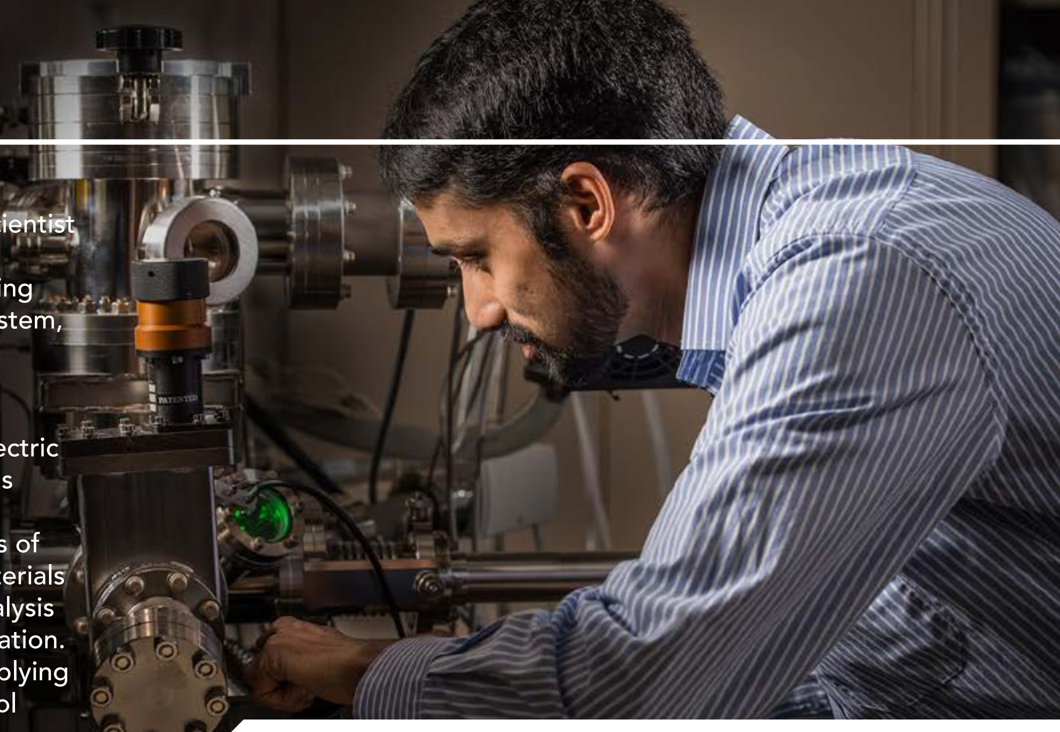
It's appropriate that in the year designated "International Year of Soils" by the United Nations General Assembly, we should highlight the exemplary work being done by EMSL scientists and our collaborators to advance the understanding of soils.

In this issue of *The Molecular Bond*, you'll learn how we're studying the mysterious happenings of carbon and microbes in the soil beneath our feet. With our users, we're working to understand the chemical reactions taking place in soil organic matter, the role of carbon in Arctic permafrost, and the interaction of carbon in soil versus char, or burned biomass. These insights are critical to developing more accurate models to predict how soil chemistry might change based on changes in climate, agricultural practices or other factors.

Earlier this year, we kicked off a new seminar series that will feature some of the country's top soil scientists, including our inaugural speaker Dr. Rattan Lal who visited EMSL in February. I'm looking forward to continue dialogue on the important role soil plays in addressing many of the vital environmental challenges we face.

I encourage you to reach out to our scientific staff to discuss how we can collaborate to advance your research into soils.

—Allison



Arun Devaraj is a senior research scientist in the Interface Spectroscopy and Diffraction group in EMSL. He is using EMSL's atom probe tomography system, or APT, which uniquely provides comprehensive and accurate 3-D chemical imaging of low electrical conductivity materials, such as dielectric and semiconductor materials. APT is assisting EMSL's efforts to further scientific advancements in the fields of energy storage and conversion materials by providing powerful interface analysis and 3-D microstructural characterization. More recently Devaraj has been applying APT to advance atmospheric aerosol research. (EMSL file photo)

NEWS & KUDOS

Analytical Innovations Bring Millions in Royalties

Yehia Ibrahim, a scientist at PNNL, is part of a team developing the new Ion Mobility Spectrometry-Mass Spectrometry Proteomics system at EMSL.

A suite of analytical innovations that provide early detection of environmental, national security and health concerns have realized $10 million in licensing income for Pacific Northwest National Laboratory, or PNNL, and its operator Battelle. The technologies were developed at PNNL and EMSL.

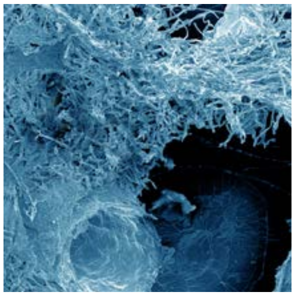
It's the first time income tied to a specific technology developed at PNNL has reached this level. The income was earned from multiple licenses over nearly a 20-year period and the annual amount has steadily increased over the past five years.

Since the 1990s, dozens of PNNL and EMSL researchers have been enhancing the performance of mass spectrometers – at first for use in PNNL's and EMSL's own environmental, national security and health-related research programs, and then as part of efforts to improve the science impact of mass spectrometers in the marketplace.

Read more in the PNNL news release at http://www.pnnl.gov/news/release.aspx?id=4192.

T&SE Postdoc Position Now Open

EMSL is now accepting applications through May 19 for its Terrestrial and Subsurface Ecosystems Postdoctoral Appointment.

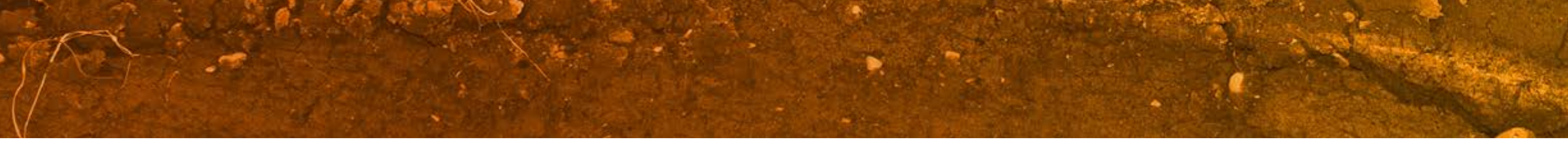


This is a colorized scanning electron microscopy image of a pine tree root surrounded by a soil fungus. The rhizosphere represents a critical zone where plant roots, microbes and minerals interface, and where biogeochemical weathering provides nutrients to plants.

The recipient will conduct integrated experimental and modeling research in below ground terrestrial carbon cycle processes that impact the dynamic exchange of carbon in the atmosphere-water-land system using diverse experimental and computational platforms available at the EMSL. The recipient will also participate in research projects in EMSL's Terrestrial and Subsurface Ecosystems Science Theme and aligned science at Pacific Northwest National Laboratory, as well as assist users in EMSL's User program. The appointment is funded directly by the Department of Energy's Office of Biological and Environmental Research Terrestrial Ecosystem Science program.

The appointment is open to recently graduated PhD scientists (received a PhD within the past five years from an accredited college or university). The recipient will serve a one-year term, with the possibility of the appointment being renewed for a total of three years.

See PNNL's jobs website at http://jobs.pnnl.gov/ for the job posting or to apply for this position.



Hess Serving on Editorial Advisory Board

Nancy Hess

Nancy Hess recently joined the editorial advisory board for the third edition of the *Encyclopedia of Soil Science*. Rattan Lal, Distinguished University Professor of Soil Science at The Ohio State University and editor-in-chief of the encyclopedia, extended the invitation to Hess.

Hess is the lead for EMSL's Terrestrial and Subsurface Ecosystems Science Theme.

The editorial advisory board comprises "prominent world-class scholars and experts in the field" of soil science. Tenure on the board is for three years, but may be extended.

In addition to Hess' involvement, three EMSL and Pacific Northwest National Laboratory scientists have been invited to author or co-author three chapters for the reference book.

The *Encyclopedia of Soil Science* is a comprehensive collection of academic articles covering all branches of soil science. The third edition is schedule to be published in early 2016.

Jakowski Named a Wiley Visiting Scientist

Jacek Jakowski

Jacek Jakowski has been selected as a 2015 EMSL Wiley Visiting Scientist. He is a computational scientist at the Oak Ridge National Laboratory Joint Institute for Computational Sciences and the University of Tennessee, Knoxville, National Institute of Computational Sciences.

At EMSL, Jakowski will work with EMSL scientists Edo Apra and Niri Govind to develop a pilot implementation of density functional tight binding, or DFTB, in NWChem, an open-source computational chemistry software suite developed at EMSL. Jakowski will also help develop a long-term plan for a complete implementation of DFTB within NWChem to provide a unique computational capability suitable for large-scale atomistic simulations relevant to all EMSL Science Theme areas.

A leader in DFTB development in the U.S., Jakowski recently developed a massively parallel computational capability based on the DFTB approach to tackle large scale dynamics of energy materials under diverse environmental conditions. He holds doctorate and master's degrees in theoretical chemistry from the University of Warsaw.

EMSL Scientists Part of UD-led Phosphorous Cycling Study

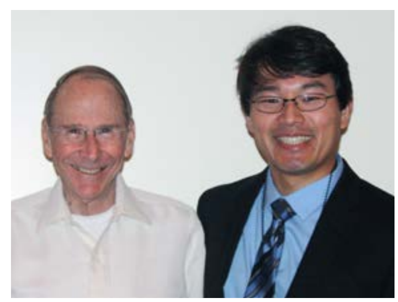
Scientists from the University of Delaware, Old Dominion University and EMSL have identified for the first time the predominant pathway for the phosphorous cycling that occurs during the summer in the Chesapeake Bay. Their findings were published in the journal *Environmental Science and Technology*.

University of Delaware scientists Deb Jaisi (left) and Sunendra Joshi are studying phosphorous cycling in the Chesapeake Bay.

A recent article in the University of Delaware's *UDaily* newsletter highlights the research findings and the scientific collaboration. The article recognizes EMSL scientists Ravi Kukkadapu and Mark Bowden and their collaboration with the researchers from the other institutions.

EMSL Accepting the M. T. Thomas Award Nominations

Nominations for EMSL's M. T. Thomas Award for Outstanding Postdoctoral Achievement are due April 30.



2013 M. T. Thomas Award recipient Ernesto Nakayasu (right) stands with award namesake M. Tom Thomas.

The selection committee bestows the award on one postdoctoral fellow each year who has used EMSL capabilities to make significant contributions on projects relevant to the EMSL mission. All postdoctoral fellows who have participated in research on an EMSL project during calendar year 2014 are eligible for the award.

As part of the award, the committee invites the honoree to present a seminar on his or her research to the EMSL community. The awardee also receives a $1,000 cash award.

The award is named in honor of M. Tom Thomas, who joined the EMSL project team in 1987 and served as the EMSL project manager and later operations manager before retiring in 1995.

Visit the M. T. Thomas Award page at http://www.emsl.pnnl.gov/emslweb/mt-thomas-award-outstanding-postdoctoral-achievement for more information or contact Tamas Varga at Tamas.Varga@pnnl.gov.

Review Paper: Brown Carbon Changes Environment, Climate

Brown carbon is an important contributor to air pollution and climate change. A recently published comprehensive review article focusing on atmospheric chemistry of this aerosol paves the way for more accurate climate models as well as strategies to curb negative effects.

Researchers from EMSL, Pacific Northwest National Laboratory and University of California, Irvine, recently published a comprehensive review article on the chemistry of atmospheric brown carbon – a type of organic carbon aerosol characterized by an absorption spectrum that smoothly increases from visible to ultraviolet wavelengths.

In the review article, authors presented a summary of field observations, laboratory experiments and modeling studies describing the potential role of brown carbon in air pollution and climate forcing – the difference of sunlight absorbed by earth and energy radiated back to space.

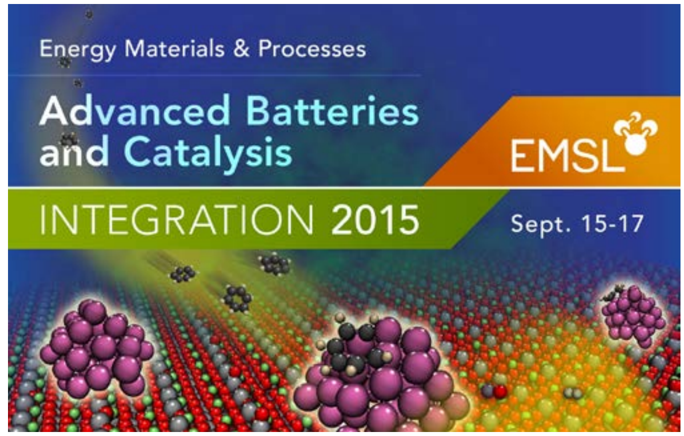
Brown carbon may be a key contributor to air pollution and climate change. By reviewing recent evidence on physical and chemical properties and prioritizing topics for future research, the article paves the way for more accurate climate model predictions as well as strategies to curb negative effects of brown carbon on climate and environment.

Researchers recommended topics for future research, such as examining potential effects of brown carbon on climate and environment. Current climate modeling often neglects brown carbon because researchers assume black carbon and mineral dust are the two significant types of light-absorbing aerosols on the global scale. The accuracy of atmospheric and climate models is also limited because relatively little is known about chemical properties of brown carbon. Thus, more basic research on brown carbon chemistry is needed to understand the most important properties and parameters to include in these models.

Many previous and ongoing research projects were conducted at locations around the world and used U.S. Department of Energy national scientific user facilities such as EMSL, the Atmospheric Radiation Measurement Climate Research Facility and the Advanced Light Source at Lawrence Berkeley National Laboratory.

Reference: Laskin A, J Laskin and S Nizkorodov. 2015. "Chemistry of Atmospheric Brown Carbon." *Chemical Reviews*. DOI: 10.1021/cr5006167

Annual User Meeting Dates Set



EMSL's annual meeting will be Sept. 15-17 and is titled "EMSL Integration 2015: Energy Materials and Processes for Advanced Batteries and Catalysis." This year's meeting focuses on advanced batteries and catalysis research at the molecular level.

Researchers from around the world and from academia, industry and government research labs are encouraged to attend. The meeting is open to EMSL users and non-users.

Don Baer, lead for EMSL's Energy Materials and Process Science Theme and a PNNL Fellow, chairs the organizing meeting.

Confirmed plenary speakers include:

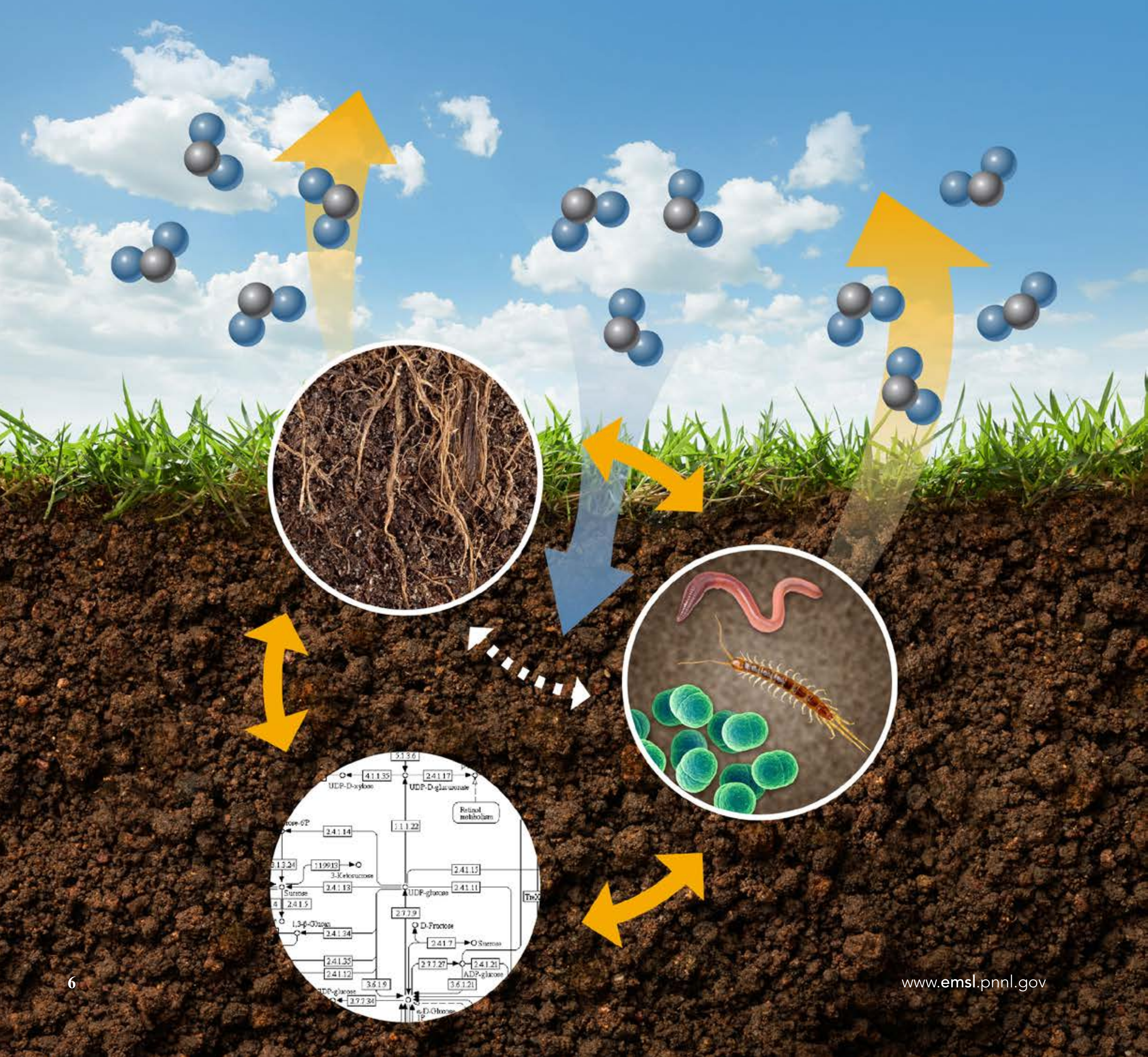
- Baris Key, Research Chemist, Argonne National Laboratory
- Linda Nazar, Professor of Inorganic Chemistry, Nanotechnology and Materials Chemistry, University of Waterloo, Canada
- Susannah Scott, Professor of Chemical Engineering, Chemistry and Biochemistry, University of California, Santa Barbara
- Johannes Lercher, Battelle Fellow at Pacific Northwest National Laboratory and Professor of Chemistry at Technische Universität München, Germany

Cost is $55 for students and $135 for nonstudents. Registration will open later this spring. Registration costs will cover refreshments and lunch both days.

Additional information is available on the Integration 2015 website including accommodations, badging and contacts at http://www.emsl.pnl.gov/emslweb/emsl-integration-2015.

Ground Control

EMSL scientists develop new methods to dig deeper into soil organic matter



Under our feet lies a key resource for environmental health and human wellbeing. Every day, we walk across the substrate that provides global food security, the habitat for one quarter of the world's biodiversity, and a carbon sink with huge storage potential. For this critical role, the United Nations declared this to be the "International Year of Soils."

But none of these benefits would be possible without carbon-transforming microbes, fungi and decaying debris. This organic matter enriches the soil and can either drive the storage of carbon into the ground or release carbon into the atmosphere. Increasingly, human activities and climate conditions are disrupting this underground ecosystem, depleting this non-renewable resource. Yet scientists at EMSL are developing new methods to understand these dynamics, leading to insights and tools that could lessen our environmental impact and create more sustainable approaches to land management.

Traditionally, soil has been studied by bulk analyses to determine percentages of essential elements, such as carbon, or quantify various components of soil – the clay, silt, detritus and so on. Some techniques, such as thermal degradation, also get at molecular-level composition of functional groups.

"But there hasn't been enough information to write a chemical formula," says Nancy Hess, lead for the Terrestrial Ecosystem & Subsurface Science Theme at EMSL. "In every other branch of chemistry, the ability to write the relationship between reactants and products is something we take for granted. That's been entirely missing in the characterization of soil organic matter."

Without that level of detail, it's impossible to make accurate models that can show how soil chemistry might change with climate, alternative agricultural practices, or other ecosystem perturbations.

To address that big gap, EMSL researchers have been developing high-resolution spectrometric techniques that can measure the mass–in parts per million accuracy–of thousands of organic molecules that exist in as little as a thimbleful of soil. When combined with information from other techniques such as nuclear magnetic resonance, infrared or fluorescence spectroscopy, even more information about these molecules can be teased out.

"These new methods are revolutionary," says Hess. "They allow us to characterize soil in terms of molecular composition and in a spatially resolved way. That's important because soils are incredibly heterogeneous."

The Nitty Gritty

One of the scientists spearheading many of these new spectrometry efforts is Malak Tfaily, a postdoc at EMSL. She's working with numerous researchers at other institutions (EMSL users) to understand how soil organic matter (SOM) behaves under altered environmental conditions.

"Right now, there are not many studies that talk about the actual composition of SOM," says Tfaily. Without that knowledge, it's difficult to know how climate change could affect these crucial soil elements.

Tfaily also worked with statistical approaches to help scientists correlate organic matter data with genomics. In this way, soil microbial transformations of elements like carbon can be linked to genetic information about the microbial community. Then, scientists can decipher not only the chemical reactions taking place, but also discern which microbes might be responsible for those reactions and the metabolic pathways involved.

For Hess, this innovative approach is helping her investigate the surprising results of a 17-year "reciprocal experiment" on soil transplants from Rattlesnake Mountain, a treeless sub-alpine ridge just a few miles from EMSL. There, to mimic environmental changes in climate warming, core samples from the bottom of the mountain were placed at the cooler and wetter 3,500-foot summit. In turn, the upper soil samples were replanted near the warmer and drier base. Then researchers looked for microbial genomic changes that might reflect adaptations in structure and function, and any resulting changes in soil chemistry caused by this change in climate.

Although the work is still in its early stages, researchers have already examined about 200 different soil samples and identified 300,000 different organic molecules. Generating a list of that size has never been done before, says Hess. They can assign chemical formulas to about 70 percent of those molecules. But it's still just a list.

In this study, the microbes that relocated up to the summit didn't adapt to the cooler temperature zone as expected. Hess wants to relate that long list of molecules to genomic data from the microbial community and information about enzymes the microbes are making.

"We're really looking for evidence of activity," Hess says. "That's very different from the traditional approach of soil characterization where someone might take a sieve and separate the soil into fractions based on particle size." (Continued on page 8)

The United Nations General Assembly declared 2015 the International Year of Soils. Soil is critical for food production and climate regulation. It's a complex underground ecosystem of organisms that process decaying debris to enrich the land as well as store and release carbon into the atmosphere. However, human activity and changing climate are impacting this environmental system. Scientists working at EMSL are trying to understand the complexities of soil to develop better sustainable land management to protect the soil.

The Deep Freezer

Another study benefitting from EMSL's mass spectrometry expertise is a study on permafrost supported by the DOE Joint Genome Institute (JGI)-EMSL Collaborative Science Initiative. Tfaily is one of 18 mass spectrometry experts at EMSL working on user projects.

Understanding carbon cycling in this frozen territory is critical, says Virginia Rich, a molecular microbial ecologist, from the University of Arizona who is leading this study. Permafrost is a big "freezer" that currently stores about twice as much carbon as the atmosphere. As the freezer thaws from climate change, that carbon will become available to microbes.

"So, it's a big open question: How much of that frozen carbon will be released? We also want to know if that carbon will be respired as CO_2 or as methane, which is 32 times more potent as a greenhouse gas over a 100-year time frame. This dynamic controls whether thaw will create a positive feedback to climate change," she says.

Rich works with a team of researchers at a permafrost site in the Arctic. With advanced monitoring equipment, her colleagues collected detailed field observations of methane isotopes and fluxes from the study site–more than have ever been published before. Combining those observations with soil samples, Rich and her colleagues can then ask: What's in "the guts" of the peat that leads to those emissions? Further, with the proteomic data Rich anticipates getting at EMSL this summer, the researchers hope to determine what the microbes are actively expressing. With all those levels of data, scientists can follow the organic matter transformations occurring across the thawing gradient and trace how that may lead to CO_2 or methane emissions.

In addition, new organic matter and new carbon will be generated when the permafrost thaws, due to plant growth. Then, it will be important to understand how much of the "old" carbon will be transformed by microbes, and where the "new" carbon ends up. Through partnering with Tfaily, Rich says they can "really get into the nitty-gritty," assigning chemical formulas to organic molecules across the gradient and finding signatures of the old and new carbon.

Burning Questions

Big thaws aren't the only aspect of climate change causing soil carbon storage concerns. Historically, fire has been a dominant determinant of carbon cycles in terrestrial ecosystems, says Johannes Lehmann, a biogeochemist at Cornell University. Even though we've been suppressing fire globally, research in the last decade shows that soils around the world contain a surprisingly large amount of "char," the blackened byproduct of burned biomass. In Australia, for example, the soil char carbon can range up to 99 percent of soil organic carbon, while five to 50 percent of char is found in U.S. Midwestern land.

"It's an underappreciated but very important part of SOM," Lehmann says. This pyrogenic organic matter contains carbon that can be sequestered in soil and can also boost soil health. Lehmann wants to know what drives the decomposition of char – the slower it breaks down, the longer carbon stays in the soil – and what that might mean for the retention of nutrients and other organic carbon in soil.

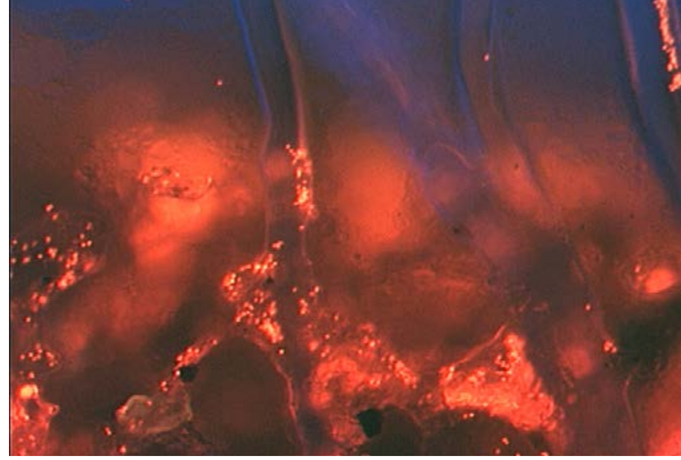
At EMSL, Lehmann has worked with its scientists and used instruments such as NMR and Fourier Transform Infrared Spectroscopy to analyze the distribution of char carbon at a fine scale. This is especially critical, he notes, because soil carbon is largely particulate and has critical surface

Pictured are Nancy Hess, EMSL: Malak Tfaily, EMSL; Virginia Rich, University of Arizona; Johannes Lehmann, Cornell University; Mary Firestone, University of California at Berkeley; and Amity Andersen, EMSL.

interactions. His research reveals that profound surface effects occur when char is oxidized: In this form, char retains more nutrients per unit of carbon, and per unit of surface area, than other organic matter.

In addition, many studies show that char can increase soil microbial populations and change community composition in ways that aren't explained by simple effects such as changes in acidity, nutrients or added energy. Probing this mechanism, Lehmann found that surface interactions between soil carbon and char carbon may be responsible for reducing mineralization of existing carbon. Understanding more about these surface interactions could then help predict whether soils will gain or lose carbon through the addition of char.

To refine a soil carbon model that incorporates these mechanisms of "priming," Lehmann plans to return to EMSL for expertise with the nanoSIMS (nanoscale Secondary Ion Mass Spectrometry) and Laser Ablation-Accelerator Mass Spectrometry.



For Mary Firestone's project, *Avena spp*. roots with associated bacteria are stained with a fluorescent stain. (Image provide by Kristen DeAngelis, assistant professor at University of Massachusetts Amherst.)

Root of the Matter

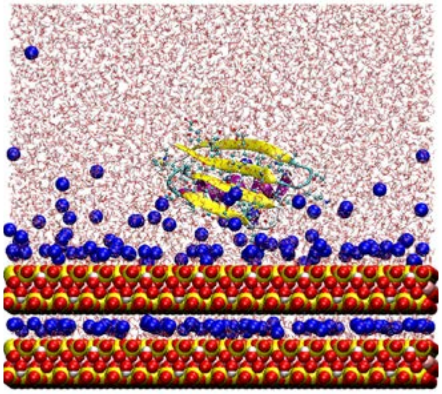
Perhaps microbes themselves have been another underappreciated component of soil organic matter.

"We've progressed from older ways of looking at roots and how their carbon is transformed to soil organic matter," says Mary Firestone, a professor of environmental science at the University of California in Berkeley. "It's only really been understood, in the last 10-15 years, that root carbon is stabilized through the eye of a needle, and the eye of the needle is the microbes."

With a joint DOE JGI-EMSL study, Firestone follows carbon from the roots of *Avena fatua*, a common Mediterranean grass, into microbes and then into stabilized material. She's also looking at how the carbon supply by roots disperses into the surrounding decomposing community, where it then enables or facilitates that community's capacity to degrade older soil organic matter. (Continued on page 10)

Mary Firestone researches root carbon in *Avena fatua*, a common Mediterranean grass.

Rattlesnake Mountain is a treeless ridge in Eastern Washington overlooking the Hanford Site. It's the field location where Nancy Hess is investigating the results of a 17-year "reciprocal experiment" on soil transplants mimicking environmental changes in climate warming. (Image taken by Scott Butner)



This image shows a hydrated Gb1 protein interacting with the Na+-montmorillonite clay mineral basal surface. The work was done as part of an internal EMSL research project using EMSL's Cascade supercomputer. The research team included Amity Andersen, Patrick Reardon and Nancy Washton, all from EMSL; Nikolla Qafoku, from Pacific Northwest National Laboratory; and Stephany Chacon and Markus Kleber, both from Oregon State University. (Image provided by Amity Andersen, EMSL scientist.)

Her work will improve understanding of how roots may alter the rates of decomposition.

"We have a poor handle on this," says Firestone. "We know roots can have large impacts–that can be as important as climate change–but we have a really hard time predicting these effects because we don't understand the mechanisms well enough."

By parsing the molecular mechanisms through which roots impact the rates of decomposition, and understanding how roots impact the enzymes and proteins produced by the surrounding microbial community, Firestone hopes to better predict how soil carbon stabilization processes will respond to environmental change. While Firestone is characterizing the metagenome through JGI, the soil bacterial proteomics are being sorted out at EMSL.

Digging Deeper

One advantage for scientists who bring their soil samples to EMSL is the capability to run up to 500 samples.

"That's more than other labs. In geochemistry, the first question anyone asks is about replication," says Tfaily. "Even within the same site, there can be a lot of heterogeneity, so you need all those samples."

Fortunately, Tfaily has also developed streamlined techniques for soil extraction that allow faster processing with solvents that don't interfere with sample chemistry. The technique is also sequential, meaning smaller samples are needed for testing.

In a few months EMSL scientists will be able to work with an even higher resolution mass spectrometer.

"We'll get better identifications and perhaps another 20 percent of what we can't get now," says Hess.

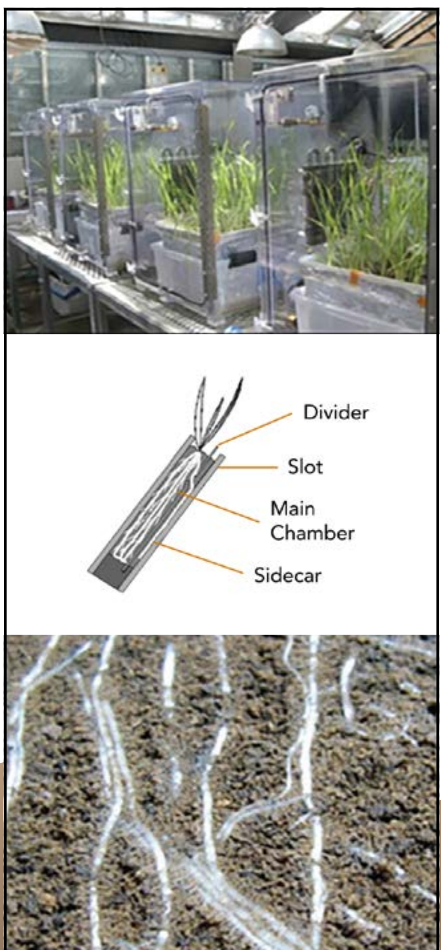
In addition to these advances, EMSL research scientist Amity Andersen is refining computer models that simulate interactions of protein and other biologically–sourced organic molecules with mineral surfaces–a factor that can affect the stabilization of soil carbon. With these models, Andersen says she'll be ready to "tackle other user projects that need large-scale simulations to understand these systems."

With these state-of-the-art tools, Hess says, "We're really on forefront of enabling so many advances, not only to create more predictive models, but also to better design more sustainable land use practices to preserve soil. ■

Funding for the research mentioned in this article comes from:

- *DOE's Office of Biological and Environmental Research (Tfaily and Rich)*
- *EMSL's Intramural Program (Amity Andersen)*
- *USDA's National Institute of Food and Agriculture's Carbon Cycle Science (Lehmann)*
- *National Science Foundation (Lehmann)*
- *DOE's Office of Biological and Environmental Research (Firestone)*
- *PNNL Laboratory-Directed Research and Development Signature Discovery Initiative (Hess)*

Elizabeth Devitt is a science journalist and freelance writer.



For Mary Firestone's research, *Avena spp*. is grown in chambers designed to control carbon dioxide concentration and allow 13C labelling of plant carbon and root carbon supply to associated microbes. (Image provided by Mary Firestone, professor at University of California, Berkeley.)

Special Science Call Projects Announced

23 High-Impact Research Proposals Accepted

EMSL's Special Science Call for Proposals challenged prospective users to submit high-impact research projects, and they delivered. The findings from some of the accepted projects will help in the development of more accurate climate models, next-generation biofuels and biochemicals, and improved nuclear waste management and contaminated site remediation.

"It was great to see the proposals submitted for the Special Science Call incorporated some very creative science utilizing our radiological capabilities – that was very exciting," says Nancy Hess, Science Theme lead and RadEMSL contact for the Special Science Call. (Continued on page 12)

EMSL Scientist Nancy Washton inspects a nuclear magnetic resonance, or NMR, spectrometer used for environmental and radionuclide science. Located in RadEMSL, the 750MHz wide-bore NMR is a multimodal high-field system that offers solids, liquids and imaging capabilities. This NMR allows EMSL users to investigate radiologically active samples at high field rather than proxy model compounds, leading to an enhanced understanding of radionuclide behavior in the environment. (EMSL file photo)

EMSL's Special Science Call for Proposals ran from mid-April through September and generated 23 accepted studies. The call challenged prospective users to submit high-impact research projects that took advantage of EMSL's technical resources including RadEMSL, the Quiet Wing microscopy and NanoSIMS capabilities, and HRMAC. The research associated with the call is progressing, and the projects will soon start delivering important scientific findings.

Lili Paša-Tolić, EMSL mass spectrometry line manager and call contact for the HRMAC, or high resolution and mass accuracy mass spectrometry capability, also praises the quality of submissions. "The projects requesting to use the HRMAC were exceptional, and the majority of them were submitted by leading scientists in their fields," she says.

Potential users submitted a total of 42 proposals during the Special Science Call. The external peer reviewers accepted 23 of those projects.

The Call

The Special Science Call ran from mid-April through Sept. 15, 2014. The peer reviewers tried to evaluate and approve projects upon receipt of the proposals to help expedite users' access to EMSL's expertise and capabilities.

"Our goal was to get our unique scientific capabilities out to the users as soon as possible to enable them to do great science as soon as possible," says Hess.

Call guidelines encouraged users to submit proposals advancing the scientific missions of the Department of Energy's Office of Biological and Environmental Research through support of EMSL's Science Themes. The projects were expected to focus on atmospheric aerosols, feedstocks for bioproducts and biofuels, global carbon cycling, biogeochemistry and energy materials.

The proposals were also expected to take advantage of recently established or developing technical resources at EMSL. Those unique scientific resources include RadEMSL, formerly called the Radiochemistry Annex; the Quiet Wing microscopy and NanoSIMS capabilities; and HRMAC. (Note: the HRMAC is also referred to as the 21 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

"In the case of the instruments in the Quiet Wing and the NanoSIMS, it's important for us to build communities in the terrestrial ecosystems, biofuels and atmospheric sciences, which typically haven't utilized these high resolution instruments," says Scott Lea, EMSL microscopy capability lead and call contact for the Quiet Wing and NanoSIMS capabilities. "Projects such as biomass deconstruction, carbon turnover and aerosol characterization could all take advantage of the novel, molecular scale studies these instruments provide."

The Projects

The 23 accepted proposals by unique EMSL scientific resource include:

HRMAC

- A combined top-down and bottom-up glycoproteome analysis of O-glycoform diversity of the secretome of the lignocellulose degrading fungus Neurospora crassa, PI-Christopher Somerville, University of California at Berkeley
- Building the lignin metabolic map for the production of advanced biofuels, PI-Blake Simmons, Sandia National Laboratory
- Dissolved organic matter transformations in wet tropical soils: The effects of redox fluctuation, PI-Jennifer Pett-Ridge, Lawrence Livermore National Laboratory
- Glycosylation isoforms of heterologous fungal cellobiohydrolases (CBH1) determined by "top-down" high resolution/high accuracy mass spectrometry, PI-Jonathan Walton, Michigan State University
- High-resolution, parallel measurements of wetland organic carbon and microbial community metabolism under changing redox conditions, PI-Kelly Wrighton, The Ohio State University
- The effect of biogenic-anthropogenic interactions on the physical and chemical properties of atmospheric organic aerosols, PI-Sergey Nizkorodov, University of California at Irvine

Quiet Wing Microscopy and NanoSIMS Capabilities

- A single cell approach to understanding a bacterial-protist food web, PI-Steven Singer, Lawrence Berkeley National Laboratory
- High-resolution imaging of *Rhodobacter sphaeroides* strains with increased lipid accumulation, PI-Timothy Donohue, University of Wisconsin at Madison
- Improved climate records and new biodesign strategies through a mechanistic understanding of sub-micron heterogeneity in environmental materials, PI- Alexander Gagnon, University of Washington

- Isotope-resolved mapping of Fe(II)/Fe(III)-oxide redox exchange interfaces, PI-Kevin Rosso, Pacific Northwest National Laboratory
- Liquid and environmental TEM as transformative capabilities in carbon cycle research, PI-James De Yoreo, Pacific Northwest National Laboratory
- Multimodal imaging and chemical analysis of sea spray aerosols, PI-Nathan Gianneschi, University of California at San Diego
- Spatial partitioning and differential expression by wood-degrading fungi, PI- Jonathan Schilling, University of Minnesota
- Visualizing plant biomass degradation by Aspergillus niger, PI- Ronald de Vries, CBS-KNAW Fungal Biodiversity Centre

RadEMSL

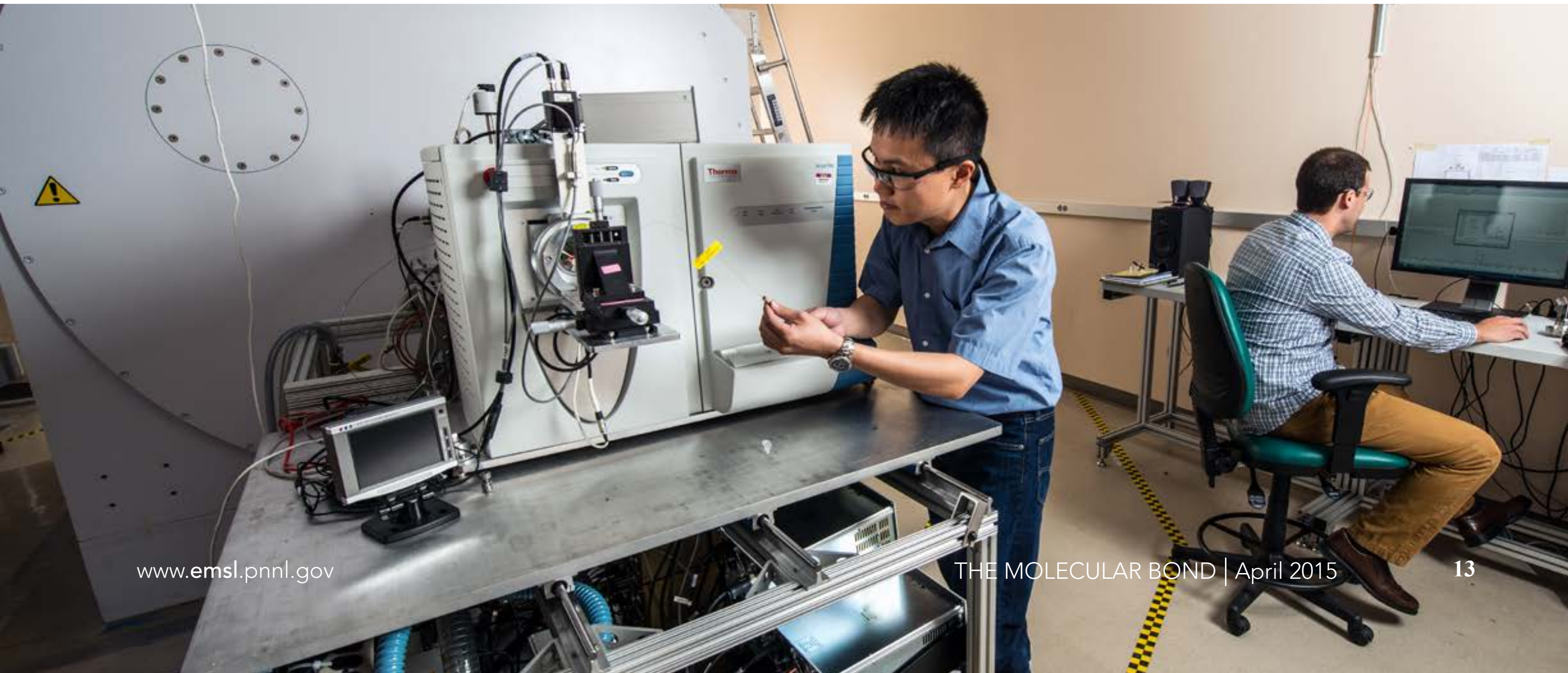
- Chemistry at the hematite-technetium interface. Implication for technetium mobility, PI- Nathalie Wall, Washington State University
- Elucidating the behavior of technetium in spinel ferrites and polyoxometalates, model systems for oxide waste forms and naturally occurring magnetite, PI-Wayne Lukens, Lawrence Berkeley National Laboratory
- Exploring the molecular driving forces for f-element complexation and organization in mixed solvents at interfaces, PI-Sue Clark, Washington State University
- NMR spectroscopy of plutonium systems, PI- Herman Cho, Pacific Northwest National Laboratory
- Nucleation and precipitation processes that affect U(VI) sequestration following phosphate addition to contaminated sediments, PI-Jeffrey Catalano, Washington University in St. Louis
- Oxidative corrosion of uraninite (UO_2) surfaces, PI-Joanne Stubbs, University of Chicago
- Plutonium in the environment: Probing mineral surface reactions relevant to Pu transport using NMR and EPR spectroscopy, PI-Harris Mason, Lawrence Livermore National Laboratory
- Rhizosphere iron and carbon influence on uranium redox cycling in a wetland environment, PI-Daniel Kaplan, Savannah River National Laboratory
- Understanding ferrichrome structural interaction with uranium compounds, PI-David Wunschel, Pacific Northwest National Laboratory

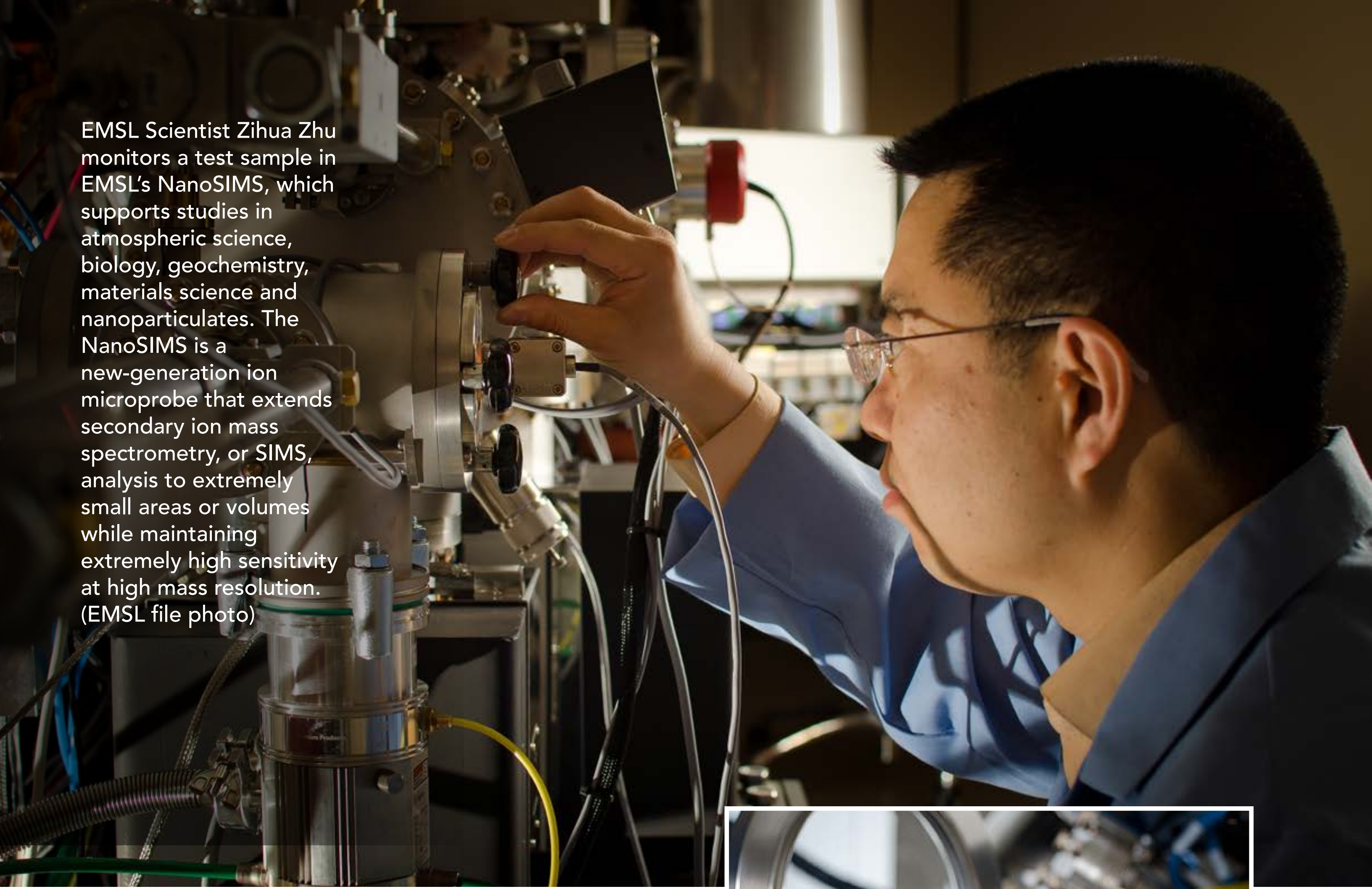
The Science

The research associated with the Special Science Call is underway, and the call contacts are optimistic the projects will deliver important scientific findings.

"Many of RadEMSL proposals have a common element – the users are trying to understand molecular chemistry at a level they couldn't access previously due the lack of appropriate instrumentation," says Hess. "This expanded understanding of molecular chemistry will improve predictive models of contaminant fate and transport. The most important outcome from this call is better predictive models of radionuclide transport." (Continued on page 14)

EMSL's new high resolution and mass accuracy mass spectrometry capability, or HRMAC, is a 21 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. The HRMAC's higher resolution and mass accuracy measurements ensures identification of molecular constituents in complex samples and materials. EMSL post-doctoral research assistants Tzu-Yung "Terry" Lin (center) and Jared Shaw are shown with the instrument. (EMSL file photo)





EMSL Scientist Zihua Zhu monitors a test sample in EMSL's NanoSIMS, which supports studies in atmospheric science, biology, geochemistry, materials science and nanoparticulates. The NanoSIMS is a new-generation ion microprobe that extends secondary ion mass spectrometry, or SIMS, analysis to extremely small areas or volumes while maintaining extremely high sensitivity at high mass resolution. (EMSL file photo)

Paša-Tolić is looking forward to the high-impact science made possible by the Special Call scientists using the HRMAC. She considers all of the HRMAC studies impactful in the areas of bioenergy, atmospheric prediction and climate change.

For Lea, the discoveries from the Quiet Wing- and NanoSIMS-related projects will add to the knowledge base of biological systems. "Some of the best science to come out of this call will be the greater understanding of the mechanisms for biofuel production and biomass deconstruction. There are plenty of sources for biomass, but being able to efficiently break it down into the source or precursor components for a certain chemical is the Holy Grail. Understanding these deconstruction mechanisms and being able to make them more efficient will open new pathways for energy and biochemical production." ■

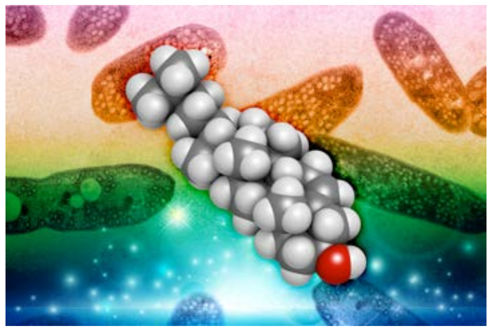
More information about proposal opportunities is available on the EMSL website under the Working With Us tab or by contacting User Support Office at emsl@pnnl.gov or 509-371-6003.

Advancing the scientific understanding of various phenomena, including interfacial behavior, biological transformations, and geochemical processes is the helium ion microscope in EMSL's Quiet Wing. EMSL's helium ion microscope is useful for high-resolution imaging of native microstructures and chemical analysis using a sub-nanometer probe. Shown is the sample holder. (EMSL file photo)

SCIENCE HIGHLIGHTS

Lipid Biofuels

Enhancing microbial lipid production



Lipids derived from oil-rich microorganisms such as bacteria, yeast and microalgae offer a promising source of renewable fuels and chemicals. However, genetic and biochemical mechanisms regulating lipid accumulation in microorganisms are poorly understood. This study examined how the photosynthetic bacterium *Rhodobacter sphaeroides* increases its membrane lipid content under low-oxygen and anaerobic conditions, which are ideal for synthesis of valuable fuels and chemicals.

By revealing a novel molecular pathway involved in microbial lipid accumulation, this study could lead to the development of strategies for engineering microbes to increase the production of lipid biofuels and chemicals. The ability to increase the yields of such compounds could improve society's ability to produce fuels and chemicals from renewable non-fossil-derived sources, ultimately paving the way for industrial biorefineries that produce these compounds in an environmentally and economically sustainable manner.

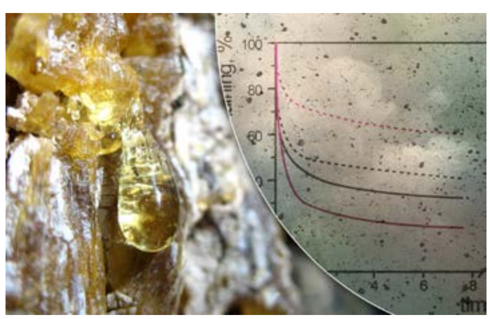
Program Funding: Great Lakes Bioenergy Research Center and Department of Agriculture National Institute of Food and Agriculture.

Publication: Lemmer K, A Dohnalkova, D Noguera and T Donohue. 2015. "Oxygen-dependent regulation of bacterial lipid production." *Journal of Bacteriology*:JB.02510-02514. DOI:10.1128/jb.02510-14.

Participating Organizations: Great Lakes Bioenergy Research Center, University of Wisconsin-Madison and EMSL.

Atmospheric Particulates

Study reveals how organic aerosols evaporate



Secondary organic aerosol, or SOA, particles represent a major component of atmospheric particulates and are known to affect climate, air quality and health. Despite prevalence and importance of SOA particles, the lack of experimental data has precluded a detailed understanding of the formation, properties and atmospheric evolution of these particles, resulting in model predictions significantly at odds with field observations. A recent study addressed this gap in knowledge by measuring the effect of relative humidity on SOA particles' evaporation kinetics.

By shedding light on factors that affect formation and evaporation of SOA particles, this study provides data and understanding needed to properly represent formation, loadings and atmospheric evolution of these particles in air quality and climate models.

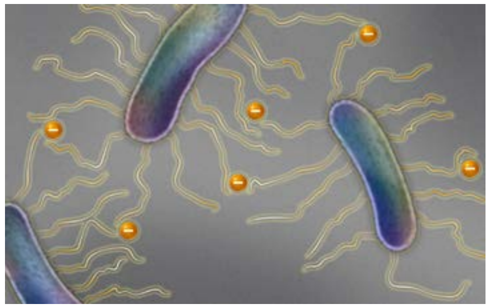
Publication: Wilson J, D Imre, J Beranek, M Shrivastava and A Zelenyuk-Imre. 2014. "Evaporation Kinetics of Laboratory-Generated Secondary Organic Aerosols at Elevated Relative Humidity." *Environmental Science & Technology*. http://dx.doi.org/10.1021/es505331d.

Program and Funding: Department of Energy's Office of Science's Office of Basic Energy Sciences and Office of Biological and Environmental Research.

Participating Organizations: PNNL, Imre Consulting and EMSL.

Metal Mechanisms

Bacteria breathe metals in different ways



Geobacter bacterial species use metal reduction pathways to respire metals such as uranium, rendering it insoluble. This is of interest for bioremediation of contaminated groundwater. However, mechanisms of metal reduction by *Geobacter* species found in subsurface environments have not been clear. This study addresses this question through proteomic analysis of *Geobacter bemidjiensis*, which is a major species that uses acetate to reduce uranium in aquifers and thus is particularly important for potential bioremediation applications.

The results suggest there is not just one mechanism of metal reduction in microbes and *Geobacter bemidjiensis* exists with distinct physiological states in different ecological niches. Shedding light on metal reduction pathways in key microbial species paves the way for future widespread bioremediation efforts.

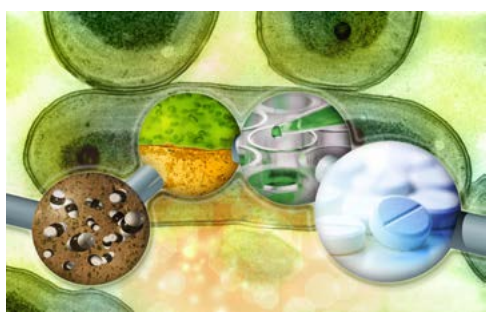
Program and Funding: Department of Energy's Office of Biological and Environmental Research for Pan-Omics Technologies Development, Implementation and Applications, and a Subsurface Biogeochemical Research grant.

Publication: Merkley E, K Wrighton, C Castelle, B Anderson, M Wilkins, V Shah, T Arbour, J Brown, S Singer, R Smith and M Lipton. 2014. "Changes in protein expression across laboratory and field experiments in Geobacter bemidjiensis." *Journal of Proteome Research*. DOI:10.1021/pr500983v.

Participating Organizations: PNNL, The Ohio State University, University of California at Berkeley, Lawrence Berkeley National Laboratory, University of Washington at Seattle and EMSL.

Ideal Microbe for Industrial Purposes

Strain has highest growth rate to date of any cyanobacteria



Cyanobacteria are of considerable interest as production organisms in biotechnology. They can grow by harvesting energy from sunlight, an abundant energy source, and they consume carbon dioxide, a greenhouse gas. However, commonly used cyanobacterial strains grow slow. Furthermore their genetic and metabolic networks are not as well understood when compared with other bacteria and yeast models used for industrial applications. This study identified a novel cyanobacterial strain that grows rapidly and is amenable to genetic manipulation that makes it ideal for a wide range of synthetic biology and metabolic engineering applications.

A cyanobacterial strain that can grow rapidly and is amenable to easy, targeted genetic manipulation will expedite the process of characterizing the cellular biology and genetic and metabolic networks of cyanobacteria. The strain will also enable development of new synthetic biology tools for these microbes.

The newly identified strain could pave the way for widespread use of cyanobacteria for carbon sequestration, biofuel production, biosynthesis of valuable chemicals, and search for novel pharmaceuticals.

Program and Funding: Department of Energy's Office of Biological and Environmental Research, the National Science Foundation and the EMSL Synthetic Biology Research Campaign.

Publication: Yu, J, M Liberton, P Cliften, R Head, J Jacobs, R Smith, D Koppenaal, J Brand and HB Pakrasi. 2015. "Synechococcus elongatus UTEX 2973, a fast growing cyanobacterial chassis for biosynthesis using light and CO_2." *Scientific Reports* 5:8132. DOI:10.1038/srep08132.

Participating Organizations: Washington University in St. Louis, PNNL, EMSL and University of Texas at Austin.

About this Art

The fungus *Trichoderma reesei*, shown here growing on finely-ground pieces of discarded corn waste, could foster rapid conversion of biomass to fuels. The fungus is known for its profuse production of biomass-degrading enzymes, which enhance the conversion process. Researchers have studied the genomes of *Trichoderma reesei* and other fungi, seeking to better understand enzyme production, and how enzymes might achieve biofuel breakthroughs. The research was conducted at EMSL located at Pacific Northwest National Laboratory. Funding was provided by Department of Energy's Office of Biological and Environmental Research. The image was captured with EMSL's helium ion microscope.

Team members

Scott Baker, Bruce Arey and Kyle Pomraning, all of EMSL; and Sue Karagiosis of Pacific Northwest National Laboratory. (Image colorized.)