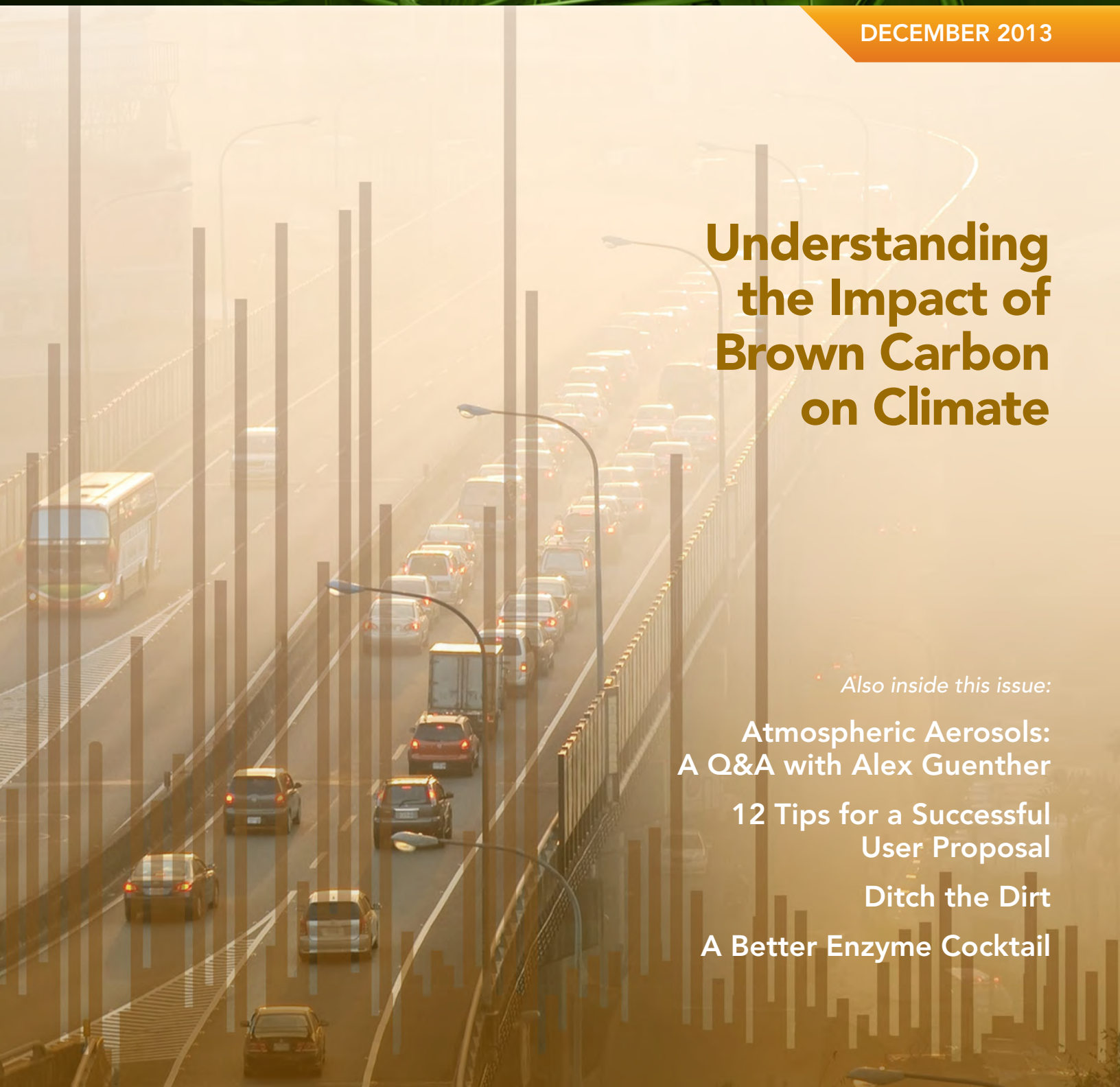
EMSL

THE MOLECULAR BOND

SCIENTIFIC INNOVATION THROUGH INTEGRATION

DECEMBER 2013



Understanding the Impact of Brown Carbon on Climate

Also inside this issue:

Atmospheric Aerosols: A Q&A with Alex Guenther

12 Tips for a Successful User Proposal

Ditch the Dirt

A Better Enzyme Cocktail

About the Cover

Better known as smog, the familiar haze of brown carbon aerosols hovers over major metropolitan areas. But it's more than a visual problem; it's an important environmental issue. The impact of brown carbon aerosols on atmospheric warming is not well understood. A joint project with EMSL is studying brown carbon aerosols with a goal of adding new data into climate models to better predict climate change.

The cover shows a mass spectrometry spectrum of a brown carbon sample created at EMSL overlaid on the image of a brown carbon event.

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

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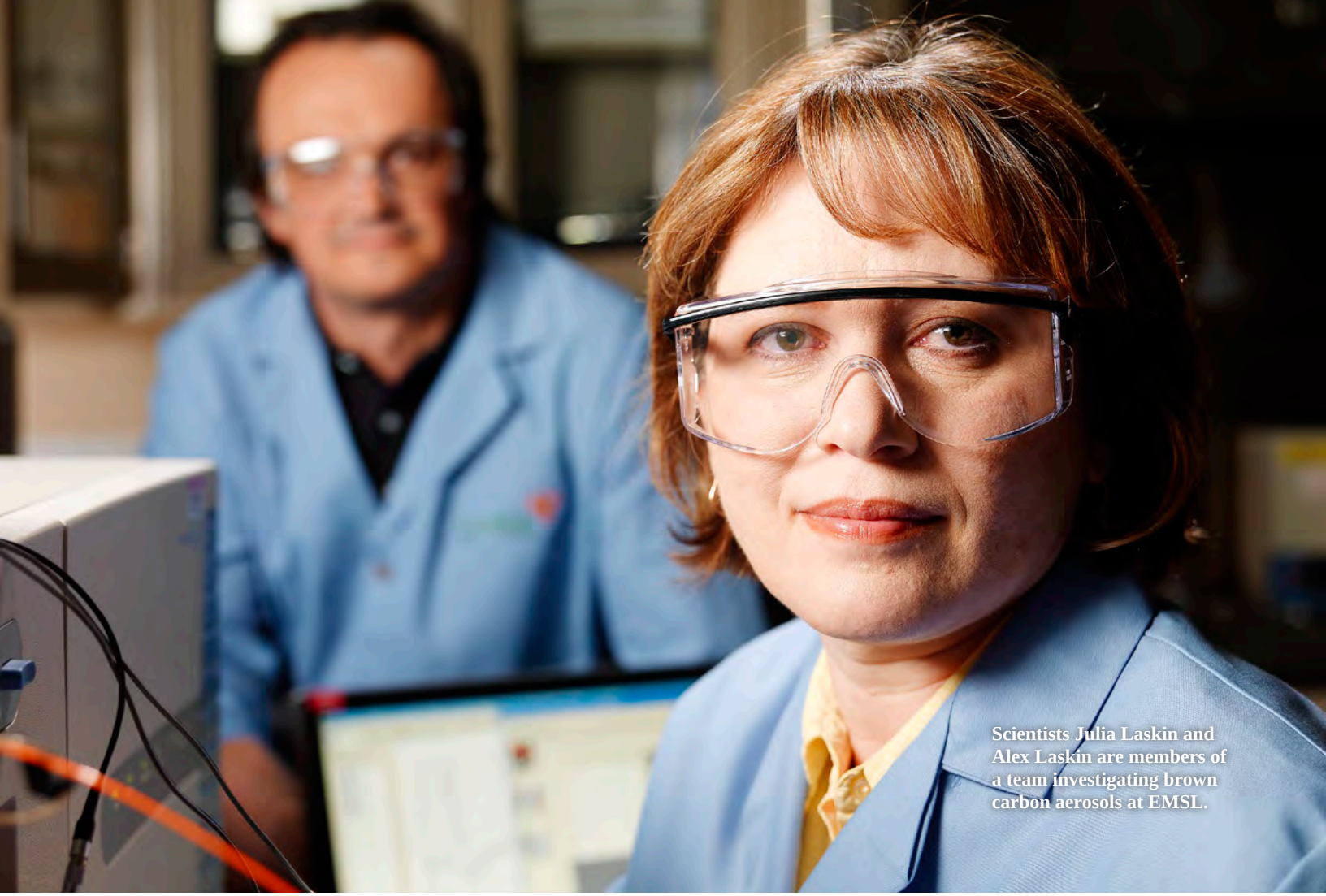

Scientists Julia Laskin and Alex Laskin are members of a team investigating brown carbon aerosols at EMSL.

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FROM THE DIRECTOR

Allison Campbell

I'm pleased to share with you the latest news and scientific perspectives from EMSL and our users. This issue marks the first time we're offering our news in a hard copy and web-zine format, in addition to our traditional email version.

It's a time of honing and enhancing what we do and how we do it at EMSL. We've recently refocused our Science Themes by expanding with a new theme focused on Atmospheric Aerosol Systems. And we've refined our others to represent Biosystem Dynamics and Design; Energy Materials and Processes; and Terrestrial and Subsurface Ecosystems. Our annual call for proposals, which opens later this month, will reflect these refined Science Themes.

In this issue, you'll learn more about the Atmospheric Aerosol Systems Science Theme, led by Alex Guenther, an international expert in land ecosystem and atmospheric research who recently joined EMSL.

With the addition of Alex's leadership, we're building on the people, facilities and instrumentation expertise we've developed over the years to address significant problems associated with aerosols and their role in climate changes.

Most recently, our researchers and users studied brown carbon, one of the least understood aerosols. Brown carbon aerosols aren't easily binned into descriptions of either scattering or absorbing light. Their chemistry is unknown and complex. Yet we anticipate they are important to our ability as a scientific community to build the most accurate climate models possible. With that in mind, we've teamed up with colleagues from the University of California, Irvine, and Pacific Northwest National Laboratory to tackle this challenge.

I hope you enjoy reading about our research and put forward your own proposals during the annual call for how we can collaborate to advance the understanding of atmospheric aerosols.

—Allison

EMSL Scientist Karol Kowalski co-authored a paper named one of the 80 best by *The Journal of Chemical Physics*.

NEWS & KUDOS

Paper by EMSL Scientists Named One of 80 Best

Marat Valiev

The Journal of Chemical Physics selected an article by EMSL scientists Marat Valiev and Karol Kowalski as one of the best 80 papers in the journal's 80 years. It was included in the Journal's *80th Anniversary Collection*.

"Congratulations, Karol and Marat, for having an article selected as one of the best 80 papers in 80 years of *The Journal of Chemical Physics*," says Don Baer, EMSL lead scientist. "Some of the other authors named for this honor are the most well known in their fields. It's a wonderful honor and great company to be associated with."

Titled "Hybrid coupled cluster and molecular dynamics approach: Application to the excitation spectrum of cytosine in the native DNA environment," the journal published the article in 2006.

Started in 1933, *The Journal of Chemical Physics* is the leading and most cited journal in chemical physics.

Annual Call for Proposals Opens Dec. 20

EMSL's will accept user research proposals through its annual call starting Dec. 20. EMSL encourages researchers to submit proposals focused on its four science themes. New EMSL capabilities offer prospective users the possibility of innovative and unique experiments.

Scientists can submit proposals using the User Portal. Details about this year's focused topics, as well as contact information and links to the 2014 review criteria and proposal package guidance, are available at EMSL 2014 Call for User Proposals web page on the EMSL website.

Questions regarding EMSL's user program or specifics about this call may be directed to the User Support Office, 509-371-6003.

12 Tips for a Successful User Proposal

Access to use EMSL capabilities is becoming more competitive, and it's even more important to make sure your submission stands out from the other proposals. Here's how:

1. Contact an EMSL capability lead or science theme lead prior to starting your proposal to talk about your research ideas and what instruments you are planning to use. The leads can help you develop a much stronger submission.
2. Requirements change – carefully read the proposal guidance for the call, and fully understand what should be included in your submission.
3. Follow the guidance on the recommended number of words per section. A successful proposal can be, and has been, written within the prescribed limits.
4. Ensure your proposal is concise and well written. For those who may be submitting a proposal someone else authored, carefully review it and put your personal stamp on it.
5. Have clear definable hypotheses and specific science objectives.
6. Provide a measured assessment of the benefits of your research. Overstatements of benefits harm a proposal.
7. Clearly explain how your research addresses specific mission areas and advances the science pertinent to DOE's Office of Biological and Environmental Research. Just stating there is a linkage is not as compelling as describing the linkage in detail.
8. Have an explicit research approach – clearly state what steps you are going to follow, why you want to use a particular instrument and what you are going to do with the data.

One of the fastest computer systems in the world, Cascade's processing units perform at 2.35 petaflop per second.

9. State the role of each key contributor on the project. If aspects of the study are outside your areas of expertise, indicate who and how others will support those science areas.
10. Explain why you need to do your research at EMSL and link those reasons to specific instruments. Make a strong case why you should be selected to use national user facility capabilities. Just stating an interest in using a specific instrument isn't as compelling.
11. State if your proposal is part of a phased project. Make sure the reviewers know there will be more phases in this project.
12. Don't cut and paste your proposal from previous documents. Take the time to write an integrated proposal for each call. Proposals that are cut and pasted are often disjointed and are noticed by the peer reviewers.

The peer reviewers will be looking at many proposals. Make sure yours stands out with clear and concise writing, strong ideas, and impactful science. Good luck.

Cascade #13 of Top 500 Computers in World

EMSL's new supercomputer, named Cascade, earned a top 20 ranking on the international Top 500 List released in early November. Ranked at No. 13, Cascade performs at 2.35 petaflop per second.

While one of the fastest systems in the world, Cascade was intentionally designed to run computationally intensive climate and biological simulations aligned with the mission of DOE's Office of Biological and Environmental Research.

It is the newest DOE Office of Science supercomputer in the top 20 and the sole supercomputer located at an institution in the Pacific Northwest in the top 20.

Earlier this year, EMSL acquired Cascade from Atipa Technologies for $17 million with a theoretical peak of 3.4 petaflop. The system was delivered in July, accepted in October and anticipated to be operational for users in December.

More than 250 scientists from around the world performed calculations on Cascade's predecessor system, Chinook, each year.

EMSL/DOE JGI Partnership Advances Biofuel and Carbon Cycling Research

EMSL and the Department of Energy Joint Genome Institute teamed up in a joint call to integrate their research capabilities. The inaugural round of eight accepted proposals showcase the synergy between these two DOE user facilities.

Five of the eight new EMSL/DOE JGI proposals will focus on carbon cycling and three relate to improvements in biofuels production. Each of these projects will tap the capabilities at both facilities to further the research in ways that would not otherwise be possible, and all are targeted for completion within an 18-month time window.

Two of the carbon cycling projects focus on soil microbial communities. The leads are Mary Kathryn Firestone from the University of California, Berkeley, and Kirsten Hofmockel from Iowa State University.

Two other carbon cycling projects study cyanobacteria. The principal investigators are Matthias Hess at Washington State University-Tri Cities and Philip Weyman from the J. Craig Venter Institute.

A carbon cycling project from Colleen Hansel at the Woods Hole Oceanographic Institute studies wood-degrading fungi.

The last three projects are all related to biofuels production and are also all fungal projects. The leads on these projects include: Steve Harris, University of Nebraska-Lincoln; Michelle O'Malley, University of California, Santa Barbara; and Harold Kistler, U.S. Department of Agriculture-Agricultural Research Service.

EMSL Annual Meeting Scheduled for May 6–7

Mark your calendar for EMSL Integration 2014 on May 6 and 7 in Richland, Wash.

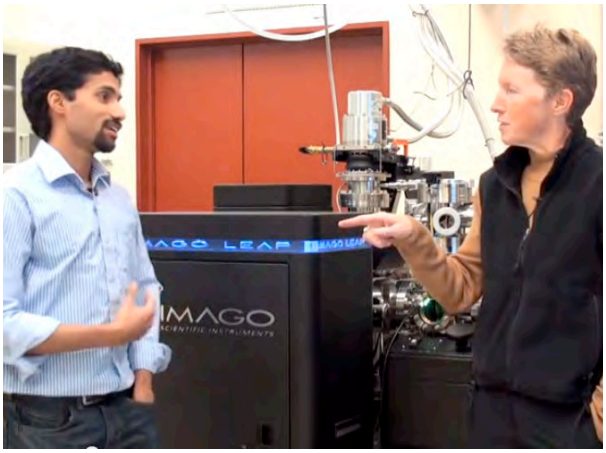
The focus of the 2014 annual user meeting is atmospheric organics. Scot Martin, Gordon McKay Professor of Environmental Chemistry at Harvard University, is the keynote speaker. The meeting also features half-day workshops and a poster session with awards for top student posters.

The meeting is open to all members of the scientific community, including past and current users and interested researchers.

Watch EMSL on YouTube

The EMSL YouTube channel is EMSLatPNNL. In a monthly interview series, *iDirector*, EMSL Director Allison Campbell talks with Staff Scientist Arun Devaraj about his background and research interests. He is doing chemical imaging using EMSL's atom probe spectrometer for the 3-D characterization of materials at sub-nanometer resolution.

Also on YouTube, watch an amazing 3-D video entitled *X-ray Computed Tomography of a Porous Silicon Carbide Structure*. Researchers are creating and studying porous crystalline silicon carbide for its many scientific and industrial uses. Part of the research effort included imaging with EMSL's X-ray computed tomography to create 3-D images of the porous sample.



UNDERSTANDING THE IMPACT OF BROWN CARBON ON CLIMATE

A joint research project seeks to integrate brown carbon insights into climate models

If you've ever flown into a major metropolitan area and noticed haze hovering over the city, then you've seen brown carbon aerosols. While most people are familiar with the visual impact of brown carbon, scientists are learning more about the formation of brown-colored aerosols and how they influence climate.

"Brown carbon aerosols are an important environmental issue, and their impact on the atmospheric warming is not well understood," says Alex Laskin, an EMSL senior research scientist. "We've just started to understand what brown carbon aerosol are, how they can be formed and in what amounts. Given the complexity, it will take years of research to provide knowledge on this broad spectrum of compounds, their chemistry and their impact on the environment."

"We're studying brown carbon because it's climatically relevant and not well characterized in climate models."

In partnership with University of California, Irvine, researchers at EMSL have been studying different aspects of the chemical composition, formation and atmospheric evolution of brown carbon aerosols for several years. The DOE's Office of Biological and Environmental Research Atmospheric Systems Research Program funded the EMSL/UC-Irvine research. UC-Irvine was also supported by the National Science Foundation.

"During the past three years we've made significant discoveries that have triggered the next level of understanding about brown carbon aerosols," says Sergey Nizkorodov, professor of chemistry at UC-Irvine and EMSL collaborator. "Through multiple projects we've explored an area that was barely touched by the research community."

The scientists at PNNL's Atmospheric Measurements Laboratory, part of the Atmospheric Sciences and Global Change Division, have also been studying brown carbon aerosols for several years.

Research groups at UC-Irvine and AML synthesize brown carbon aerosols in environmental chambers. These facilities mimic what is happening in the atmosphere, but under controlled conditions, to produce a variety of aerosols, including those with brown carbon.

A recently started joint project between EMSL and ASGC combines the knowledge and expertise of these groups into a creative team with a goal of adding brown carbon aerosol data into climate models. The study is intended to develop capabilities that will support BER's mission to advance the understanding of Earth's biogeochemical systems in order to improve climate prediction.

"We're studying brown carbon because it's climatically relevant and not well characterized in climate models,"

(continued on page 8)

Scientist John Shilling stands in the Aerosol Test Chamber located in the Atmospheric Measurements Laboratory at Pacific Northwest National Laboratory. The chamber is used to study the aerosol lifecycle, and the data derived from experiments using the chamber will be used for model validation and directly incorporated into climate models.

What are Brown Carbon Aerosols?

Brown carbon aerosols are non-graphitic organic materials that are brown or yellowish in color. They come from different sources, including the burning of biomass, industrial emissions, combustion of fossil fuels and automobile exhaust. Brown carbon aerosols can also be formed in the atmosphere from reactions of biogenic organic gases, given off naturally by trees and other organisms, that condense to form aerosol particles.

Researchers classify organic materials in the atmosphere by their ability to absorb or scatter sunlight. The scattering of sunlight has a cooling affect overall on the climate, while the absorption of sunlight heats the air. Carbon rich materials in the atmosphere range between predominantly scattering and strongly absorbing. The chemical and optical properties of the two extremes of the absorbing materials are known and relatively well studied. The compounds between the two extremes are brown carbon aerosols. Brown carbon aerosols are made of thousands of different complex compounds, and because of this complexity they present a significant challenge to the investigators.

says John Shilling, an AML scientist and co-principal investigator on the joint project. “We know brown carbon can have an impact on climate. It can change the Earth’s energy balance and that will affect how climate responds to changes in air emissions.”

The joint research project will study species of brown carbon formed in the atmosphere from reactions of gases that condense to form aerosol particles. Specifically, researchers hope to identify chemical reactions that cause particles to turn brown, either when they are formed or as they age in the atmosphere.

“Brown carbon aerosols are an important environmental issue, and their impact on the atmospheric warming is not well understood.”

The joint project identified the types of research where EMSL’s expertise, particularly in molecular-scale characterization, could be used to solve problems important for global climate. The project also takes advantage of PNNL expertise in molecular modeling, atmospheric aerosol chemistry and climate modeling. In addition to Shilling and Alex Laskin, the other co-principal investigators on the joint project are PNNL scientists Shawn Kathmann, Rahul Zaveri, Phil Rasch and Julia Laskin.

“Brown carbon is one area where we really need an integrated approach across disciplines to solve some of these large-scale problems in climate change,” says Shilling. “It’s the type of problem national labs and user facilities should be solving. It would be difficult for a single principal investigator working alone to tackle such a big problem.”

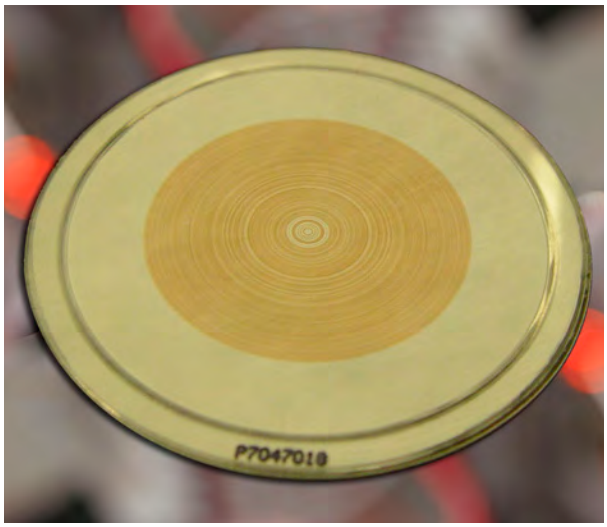
The Properties of Brown Carbon

According to Alex Laskin, “To accommodate this complex world of brown carbon, more laboratory and field studies are needed to describe this material’s chemistry and optical properties and to understand the fundamental relationship between composition and optical properties.”

The EMSL/UC-Irvine team has aged aerosols in the lab so they turn brown, and they quantified the optical properties of the browning effect and have a better understanding of the chemistry behind the color transformation.

A major challenge the EMSL/UC-Irvine team faced was identifying chromophores, specific molecules responsible for color, in aerosols during transformation from white to brown. The team needed a sensitive technique that allows detection of individual aerosol species that may exhibit strong light absorption properties.

“Conventional analysis didn’t help us very much, because changes in the chemical composition are really, really minor,” says Alex Laskin. “It turns out changes are hardly detectable



A brown carbon sample prepared at EMSL.

by many traditional approaches. It's the presence of very minor compounds that make this material brown. It's really a task of finding a needle in the haystack."

The sensitive technique that finally allowed the EMSL/UC-Irvine team to detect small changes in chemical composition was EMSL's newly developed method of nanospray desorption electrospray ionization, or nanoDESI, in conjunction with high-resolution mass spectrometry.

"Brown carbon research was one of the first applications of the nanoDESI setup to a scientific problem, and it gave us really unique and unparalleled results," says Alex Laskin. "It was the technique that gave us clear answers to what is happening within brown carbon aerosols."

Nizkorodov agrees, adding "nanoDESI has proven to be a powerful analytical technique for the study of brown carbon aerosols. It has helped us move to that next level of understanding."

Based on numerous laboratory and field studies, the EMSL/UC-Irvine team has determined brown carbon aerosols are complex systems containing thousands of various organic molecules. The formation of brown carbon materials strongly depends on the aerosol composition – one type of aerosol may show browning but a nearly identical aerosol may not. The team also discovered that incorporation of nitrogen into the organic material contributes to the formation of certain brown carbon aerosol species.

Experiments and Modeling

A PNNL Laboratory Directed Research and Development project, the ultimate goal of the EMSL and ASGC effort is to include detailed brown carbon aerosol characterization data in a form atmospheric modelers can use in predicting climate change.

"Our focus is on fundamental chemistry – the molecular-level understanding of brown carbon aerosols," says Alex Laskin. "The scope of the project is to make sense out of molecular-level chemistry and transfer that knowledge to climate models."

The joint project is part of a much loftier goal – to ultimately understand exactly how brown carbon (at all times, in all places and from all sources) affects climate, according to Shilling. The joint project continues the search for the chromophores and chemical processes and mechanisms involved in the browning of carbon aerosols. Critical to this project is EMSL's expertise in molecular-level characterization of aerosol mixtures.

"There are thousands and thousands of compounds in these aerosol particles, and we're looking for the ones that are specifically making the material brown," says Shilling. "Research efforts of Julia and Alex Laskin finally made it possible, but it's extremely difficult and extremely rare – only a few people in the world can do it."

To date, the scientists have identified a series of reaction conditions that produce brown carbon and have made some preliminary measurements of the optical properties of brown carbon. The next step is to produce samples for advanced molecular-level analysis. They will partner with Alex Laskin in using EMSL instrumentation, including nanoDESI, in conjunction with high-resolution mass spectrometry and chromatography, to analyze aerosol samples with strong brown carbon capacity. As a result, they'll identify specific molecules out of the many thousands in the sample that are absorbing the light and causing the material to be brown.

The team also discovered that incorporation of nitrogen into the organic material contributes to the formation of certain brown carbon aerosol species.

The other team members have been developing the necessary computer codes and analyses, including molecular- and process-scale modeling, so that the data from EMSL's analysis can be added into a global climate model. The model should then be able to predict the climate forcing – the excess solar power retained at the Earth's surface – associated with brown carbon aerosols. Climate forcing is a metric commonly used by climate scientists that is directly related to Earth's temperature changes.

"We've measured the optical properties and we know brown aerosols will form under a broad range of conditions," says Shilling. "What we need to learn now is what effects certain brown aerosols have on the radiation balance, and how much they will change the Earth's temperature. Our ultimate goal is to determine the impact brown carbon aerosols have on climate." ■

Atmospheric Aerosols: A Q&A with Alex Guenther

The importance of aerosol research

Alex Guenther is a renowned atmospheric and ecosystem scientist, as well as a Laboratory Fellow at Pacific Northwest National Laboratory and lead scientist for atmospheric aerosols science at EMSL. He recently took time while traveling in Brazil to answer some questions about the importance of atmospheric aerosol studies. Here's what he had to say:

Q. Why is the scientific understanding of aerosols important?

A. The scattering and absorbing of light by atmospheric aerosols, and also by clouds that are modified by aerosols, impacts the Earth's radiation balance resulting in cooling (from scattering) or warming (from absorbing) at the Earth surface. Aerosols can also degrade visibility and are harmful to human health.

Q. How will a greater understanding of aerosols improve climate models?

A. Predictive climate models need to include numerical representations of the relevant processes that influence climate. This means we need to understand aerosols well enough to account for their role in climate with numerical model code that calculates their impact on the Earth's radiative balance.

Q. What are the societal implications of aerosol research?

A. Aerosol research improves the numerical models decision makers use to develop strategies for sustainable development and to balance energy needs with the need for a stable environment.

Q. What is EMSL's role in aerosol research?

A. EMSL research provides a fundamental understanding of the molecular scale processes that determine aerosol production, evolution and fate. This knowledge forms the basis for the numerical algorithms and parameterizations in climate models.

Q. What is the next major milestone in aerosol research?

A. I view the next major milestone as identifying the specific molecules within organic aerosol responsible for absorption of light and characterizing the processes responsible for their formation and properties.

Q. What are the science priorities of aerosol research in the next five to 10 years?

A. It's critical that the scientific community develop a molecular-scale understanding of the processes that enhance the formation of biogenic organic emissions – those produced by living organisms – and determine the radiative properties of organic aerosols to improve the accuracy of climate model simulations.

Q How does aerosol research support the mission of the DOE's Office of Biological and Environmental Research?

A. It addresses BER Atmospheric System Research programmatic goals by building a physical understanding and an accurate representation of the important aerosol-cloud-precipitation processes that drive precipitation and the atmospheric radiation balance. The research is key to advancing BER priorities by successfully incorporating this understanding of aerosols into regional and global climate models.

Q. How do EMSL users fit into the aerosol research being done at EMSL?

A. Users have historically utilized some EMSL capabilities to enhance their atmospheric research. Recently, they've been considering how they can apply other EMSL tools and expertise not previously used by the atmospheric community – this opens the possibility of new and innovative discoveries. In addition, input from users helps determine future capabilities for EMSL to drive high-impact science.

In this computer reconstruction done at EMSL, multiple Geobacter pilin structures are overlaid on Gonorrhea's fiber.

SCIENCE HIGHLIGHTS

Structure of Bacterial Nanowire Protein

Electrically conducting bacteria important for energy, environment and technology

Many bacterial species have fingerlike projections along their bodies, called pili, to adhere to surfaces, create films or recognize objects in the environment. Some bacteria even use them like electrical wires.

EMSL scientists Patrick Reardon and Karl Mueller are studying the protein pilin that makes up one such nanowire, and they have determined the protein's structure. Their findings have implications for producing energy, recycling Earth's carbon and miniaturizing computers.

To better understand how pilins contribute to conduction, Reardon and Mueller used EMSL's nuclear magnetic resonance capabilities to picture the shape of the pilin from *Geobacter sulfurreducens*, an electrically conducting bacteria. To better visualize the structure of the nanowire, the scientists overlaid the shape of the pilin from Geobacter over an existing computer model of an assembled fiber from an unrelated species, the bacteria that cause gonorrhea.

Reardon and Mueller's study provided useful information about the protein structure of a nanowire, but more research is needed to determine how electrons travel along Geobacter's pilin.

Funding: This work was supported by the William Wiley Post-Doctoral Fellowship from EMSL, a national scientific user facility supported by the DOE's Office of Biological and Environmental Research.

Publication: Reardon PN and KT Mueller. 2013. "Structure of the Type IVa Major Pilin from the Electrically Conductive Bacterial Nanowires of *Geobacter sulfurreducens" Journal of Biological Chemistry*. DOI: 10.1074/jbc.M113.498527.

Participating Institution: EMSL.

Patrick Reardon

Ditch the Dirt

Soil pretreatment boosts protein recovery

Scientists have significantly boosted the recovery and identification of proteins expressed by soil-dwelling microbes over what was previously possible, thanks to a new method of soil pretreatment being used at EMSL. The new strategy for processing samples reveals additional insight into the function of microbial communities in their native environments.

Studying the proteins expressed by soil-dwelling microbial communities helps to define their fundamental biogeochemical roles in carbon cycling, nitrogen cycling, phosphorus cycling and climate regulation. It also helps to determine how microbial communities might assist with environmental cleanup – for example, bacterial protein expression could be used to remediate sites contaminated with toxic metals or radionuclides.

Funding: This research was supported by the DOE's Office of Biological and Environmental Research Genomic Science Program. Portions of the work were performed at EMSL.

Publication: Nicora CD, BJ Anderson, SJ Callister, AD Norbeck, SO Purvine, JK Jansson, OU Mason, MM David, D Jurelevicius, RD Smith and MS Lipton. 2013. "Amino acid treatment enhances protein recovery from sediment and soils for metaproteomic studies." *Proteomics* DOI 10.1002/pmic.201300003.

Participating Institutions: PNNL; Lawrence Berkeley National Laboratory; Florida State University; Instituto de Microbiologia Paulo de Góes, Universidade Federal do Rio de Janeiro.

A Better Enzyme Cocktail

Tapping fungus to unlock energy

Trichoderma reesei

Scientists are trying to create more effective blends of enzymes to transform plant materials into fuels. Producing biofuels from plentiful non-food plant materials is possible, but the research process is expensive and time consuming. A team of scientists from PNNL and EMSL may have found a way to reduce laboratory research time from months to days, and their findings provide more options for biofuel development.

"The ultimate goal is to begin with a plant material like corn stalks, for instance, and to subject it to a cocktail of enzymes that would convert those plants to fuel," said chemist Aaron Wright, who led the team. "It takes a series of steps to do that, and the cost has to come down if these fuels are to compete seriously with traditional hydrocarbon-based fuels."

Researchers are studying the fungus *Trichoderma* reesei, because of its ability to produce enzymes that break down complex sugars. Scientists are trying to create a highly efficient chemical cocktail using the fungus' many enzymes.

The study focused on the fungus' glycoside hydrolases enzymes. The team developed a chemical probe that monitors the activity of the individual enzymes and whole mixture. Using activity-based protein profiling, the chemical probe binds to glycoside hydrolases and provides information indicating the activity of the individual enzymes. Instead of running a series of experiments, each focusing on a separate enzyme, the team runs one experiment and tracks precisely how each of dozens of enzymes are reacting to changing environmental conditions like temperature and pH.

Many of the measurements for the study, such as the measures of protein activity using mass spectrometry, were done at EMSL.

Funding: This work was supported by PNNL. It used instrumentation and capabilities developed under the National Institute of General Medical Sciences and the DOE's Office of Biological and Environmental Research.

Publication: Anderson LN, DE Culley, BA Hofstad, LM Chauvigné-Hines, EM Zink, SO Purvine, RD Smith, SJ Callister, JM Magnuson and AT Wright. 2013. "Activity-based protein profiling of secreted cellulolytic enzyme activity dynamics in Trichoderma reesei QM6a, NG14, and RUT-C30." *Molecular BioSystems*, DOI: 10.1039/c3mb70333a.

Participating Institutions: PNNL; EMSL.

Scientists Capture 'Redox Moments' in Living Cells

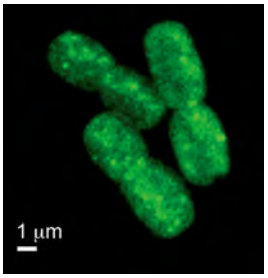
Better understanding of hardy bacteria enhances tool for biofuel creation

Scientists using EMSL's mass spectrometry and microscopy capabilities observed for the first time protein reduction–oxidation modification, known as redox reactions, inside living cells of the microbe *Synechococcus*. These findings will help scientists create biofuels by using this microbe's ability to convert sunlight into useful energy. The results were published in *ACS Chemical Biology.*

"Redox activity tells us where the action is going on within a cell," said chemist Aaron Wright, the leader of the Pacific Northwest National Laboratory team. "We've been able to get a look at the redox system while it's still operating in a living cell, without destroying the cell first. This allows us to tell who the players are when the cells are engaged in the activity of our choice, like making components for biofuels."

Redox modification allows microorganisms to sense environmental changes and initiate cellular responses. The researchers identified 176 proteins involved in the redox signaling system. Before this study, just 75 of those proteins were known to be part of a redox signaling network.

Wright developed chemical probes that identified redox events. The team used EMSL capabilities, such as fluorescent imaging and mass spectrometry, to analyze the events. The analysis indicated when and where within the cell redox activity occurred.



Synechococcus cells

Funding: This research was supported by the Genomic Science Program of the DOE's Office of Biological and Environmental Research and is a contribution of the PNNL's Biofuels and Foundational Scientific Focus Areas.

Publication: Sadler NC, MR Melnicki, MH Serres, ED Merkley, WB Chrisler, EA Hill, MF Romine, S Kim, EM Zink, S Datta, RD. Smith, AS Beliaev, A Konopka, and AT Wright. 2013. "Live Cell Chemical Profiling of Temporal Redox Dynamics in a Photoautotrophic Cyanobacteriu." *ACS Chemical Biology*. DOI: 10.1021/cb400769v.

Participating Institutions: PNNL and Marine Biological Laboratory.

About this Art

Researchers are developing nanoscale 3-D characterization tools to analyze biological materials. This is a scanning electron microscopy, or SEM, image of the protein ubiquitin mixed with a MALDI matrix from the samples fabricated for atom probe tomography.

Team members: Arun Devaraj, Suntharampillai Thevuthasan, Daniel Perea, Leach Franklin and Ron Heeren

Image was captured using instrumentation at EMSL and the research funded by PNNL Chemical Imaging Initiative.