EMSL NEWS
ATMOSPHERIC AEROSOL CHEMISTRY
An Emerging Science Theme
Vol 5, Issue 2

Taking the Laboratory into the Great Outdoors

Collaborative endeavor brings EMSL instrument to the skies over Alaska

As a birthplace for clouds, the Arctic provides an excellent location to study climate change, and that is exactly the research 80+ U.S. and Canadian climate scientists did in a massive field campaign in northern Alaska. The campaign, known as the Indirect and Semi-Direct Aerosol Campaign, was designed to understand aerosols and Arctic clouds, which help determine how much precipitation and heat reach the Earth's surface.

"Our objective was to obtain a data set that will allow scientists to compare and contrast Arctic aerosol and cloud properties from the spring and fall," said Pacific Northwest National Laboratory's Beat Schmid, aerial vehicles program technical director for the campaign.

At the request of the Indirect and Semi-Direct Aerosol Campaign, EMSL's capabilities in particle measurement were requested aboard the aerial vehicles in the campaign and on the ground. The campaign believed that EMSL's SPLAT II would provide valuable data during the airborne campaign, which involved packing more than 40 instruments into a Canadian National Research Council Convair 580.

SPLAT II. EMSL's SPLAT II, or the second generation of the Single Particle Laser Ablation Time-of-Flight Mass Spectrometer, provides such measurements. The instrument allows researchers to establish inter-relationships among different particle properties such as size, composition, density, morphology, hygroscopicity, and cloud activity. The measurements from this instrument are one to two orders of magnitude more sensitive than any other mass spectrometer in the field.

Getting airborne. For this campaign, SPLAT II had to be reconfigured to fit within its allocated space in the aircraft. The four laser beams and internal particle beam responsible for measuring the aerosols had to be isolated from onboard vibrations. Further, the entire instrument had to meet safety regulations to protect the crew during turbulence and other upsets.

Onboard a research aircraft, SPLAT II gave researchers a first look at the composition of ice nuclei.

Together, the researchers and EMSL machinists, crafts people, and the drafting department reconfigured the frame and the components into a smaller, more robust system that met all of the demands of travelling on the research aircraft. Next, the instrument was installed on PNNL's Gulfstream-1 research aircraft for test flights.

"This allowed the team to test instrument performance onboard the aircraft, something that has never been done with this equipment," said Alla Zelenyuk, an EMSL user from Pacific Northwest National Laboratory and one of the original developers of SPLAT II.

The instrument was operated at altitudes between 5,000 and 15,000 feet. The results demonstrated that SPLAT II should perform as expected during the field campaign.

During the flights over northern Alaska and the Pacific Ocean, SPLAT II measured the size and chemical composition of more than a million particles, including aerosols that serve as cloud condensation nuclei and ice nuclei.

Part of the larger picture. The airborne measurements from EMSL's SPLAT II are just some of the data collected. EMSL's

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EMSL DIRECTOR'S MESSAGE

An emerging science theme to support greater understanding of atmospheric particles

Allison A. Campbell
EMSL Director

The chemistry of atmospheric aerosols—which play an important role in global climate change—represents an emerging science theme here at EMSL. The effect of aerosols has been one of the greatest sources of uncertainty for scientists who attempt to interpret climate change that has occurred in the past century or who try to predict future climate change.

EMSL's interest in atmospheric aerosol chemistry is designed to help our users advance the knowledge of aerosol physics and chemistry from the molecular level to regional and global scales and how they impact climate change. Our staff and users are providing the research community with the expertise and state-of-the-art instrumentation needed to characterize the size, composition, density, morphology, chemical reactivity, and cloud interactions of aerosol particles.

In this issue, you will read about how our staff and users supported a recent field campaign in Alaska designed to understand aerosols and Arctic clouds. We'll also introduce you SPLAT II—EMSL's in-house-designed and –developed portable mass spectrometer that was deployed as part of this campaign on a Canadian National Research Council Convair 580 aircraft to measure the size and chemical composition of more than a million particles. And we'll provide you with details on some exciting projects undertaken by users from Pacific Northwest National Laboratory, University of California at Irvine, and Lawrence Berkeley National Laboratory.

Finally, I'd like to invite you to check out EMSL's newly designed website (www.emsl.pnl.gov) and see how you, too, can become a user.

Allison A. Campbell, Ph.D.
EMSL Director

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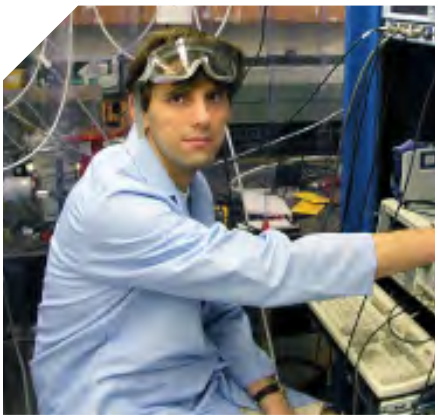
Travelling Down Unexplored Pathways

Scientists discover unrecognized reaction mechanism that forms atmospheric aerosols

A large portion of the particle mass in the atmosphere is secondary organic aerosols, created when volatile organic compounds such as limonene enter the atmosphere and react with ozone and other oxidants. Secondary organic aerosols can impact local air quality and global climate. Yet, little is known about the reaction mechanisms that generate these particles. For example, in the oxidation of limonene by ozone, the known pathways account for a dozen or so chemical compounds, which is inconsistent with the complexity of the experimentally observed products. More pathways exist and need to be discovered to get a more accurate picture of particle formation.

An unrecognized reaction of the oxidation of limonene—a chemical created by vegetation and found in both outdoor and indoor air—that yields secondary organic aerosols with a significantly more complex composition than that predicted by previously reported mechanisms was discovered by users of EMSL. Aerosols formed by this mechanism can impact local air quality and global climate.



Sergey Nizkorodov from University of California, Irvine conducts research to uncover mechanisms responsible for aerosols in the atmosphere.

The research team from the University of California at Irvine, EMSL, and Pacific Northwest National Laboratory used EMSL's high-resolution Linear Ion Trap Quadrupole Orbitrap Mass Spectrometer with a modified electrospray ionization source to characterize secondary organic aerosol samples produced by ozonation of limonene.

The instrumentation provided highly accurate mass measurements of the resulting chemical compounds, making it possible to unambiguously determine the molecular composition of hundreds of individual compounds in the samples.

"Previous studies dealt with way smaller number of products," said Sergey Nizkorodov, an investigator on the study from UCI.

The complex composition of the secondary organic aerosol constituents led the team to propose the extended network of isomerization and decomposition pathways of key radical intermediates that have been disregarded by previous studies. With these new reactions added, the team accounted for up to 75 percent of the chemical compounds detected in the samples.

The hundreds of reaction products detected in the samples show the level of challenges involved in studying the chemistry of laboratory-generated aerosols. In the real world, the chemical and physical conditions as well as the number of organic compounds are far greater.

This study was supported by the U.S. Department of Energy's Office of Basic Energy Sciences and the National Science Foundation through the Environmental Molecular Science Institute Program and the Atmospheric Chemistry Program. Additional funding was provided by the National Science Foundation Graduate Research Fellowship.

Walser, ML, Y Desyaterik, J Laskin, A Laskin, and SA Nizkorodov. 2008. "High-Resolution Mass Spectrometric Analysis of Secondary Organic Aerosol Produced by Ozonation of Limonene." *Physical Chemistry Chemical Physics* 10(7):1009 – 1022. DOI: 10.1039/b712620d.

OTHER INSTRUMENTS THAT SUPPORT ATMOSPHERE AEROSOL CHEMISTRY RESEARCH

With EMSL's **Time-of-Flight Secondary Ion Mass Spectrometer**, researchers can direct a pulsed beam of carbon-60 fullerenes or buckyballs at a material. When this polyatomic ion beam hits the sample, it will produce more secondary ions with a higher mass, giving researchers richer data to help characterize the sample's chemistry. The C[60] ion beam will present new opportunities for analyzing compounds on the surface and, in some instances, in the bulk of samples.

The **Desorption Electrospray Ionization Mass Spectrometer** records mass spectra on samples in their native environments. The instrument directs electrically charged droplets at the sample. The interaction between the droplets and the sample releases ions that are then drawn into a mass analyzer. This instrument presents opportunities for rapid and highly sensitive chemical analysis of samples in ambient atmosphere.

SPLAT II: Studying Particles in the Lab and in the Field

An instrument available to users at EMSL is helping answer fundamental questions about the properties and behavior of small particles, which play a role in climate, public health, and national security. Designed and developed by EMSL user Alla Zelenyuk from Pacific Northwest National Laboratory, the Single Particle Laser Ablation Time-of-Flight Mass Spectrometer (SPLAT II) simultaneously measures, with high sensitivity and precision, the size, composition, density, shape, hygroscopicity, and fractal dimension of individual particles.

Using this instrument allows researchers to study fundamental processes in the atmospheric lifecycle of aerosols. For example, in Columbus, Indiana, the Cummins Company brought in SPLAT II when traditional methods failed to provide detailed diesel emission information. The scientists began by performing real-time analysis of diesel emissions, examining the particles with and without treatment. The resulting data allowed the computer scientists to design and run more simulations of filters and particle behavior. The instrument's capabilities combined with its portability make it valuable for understanding the behavior of particles in both the laboratory and the field.

Instrument Detail

SPLAT II uses an extremely efficient aerodynamic lens inlet to produce a narrow particle beam with low divergence. Two stages of differential pumping separate particles and gas. Two stages of optical detection use light scattering to detect each particle twice and to measure its velocity, from which the particle aerodynamic diameter is obtained. Pulsed, synchronized infrared evaporation followed by ultraviolet ionization of semi-volatile fractions and ablation of non-volatile fractions creates ions. From these ions, time-of-flight mass spectra are generated for compositional analysis.

The spectra are analyzed and visualized using SpectraMiner, software built to explore single-particle mass spectra. SpectraMiner provides controls that connect particle data from SPLAT II with other relevant parameters, advancing knowledge beyond simple statistical analysis.

SPLAT II QUICK SPECS

Multidimensional Characterization: Simultaneously measures particle size, density, dynamic shape factor, morphology, fractal dimension, hygroscopicity, and composition

Particle Type: Yields quantitative information about all particle types

Size Range: Detects particles from 50 nm to 3 μm

Analysis Rate: Measures up to 100 particles/second

Sensitivity: Detects 125 nm particles at a concentration as low as 1 particle/cm^3 at a rate of 1 particle/second

Sizing Precision: Better than 1 nm

Ion Formation: IR-UV operation mode yields reproducible and quantitative particle mass spectra

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Zelenyuk, A, D Imre, JH Han, and S Oatis. 2008. "Simultaneous Measurements of Individual Ambient Particle Size, Composition, Effective Density, and Hygroscopicity." *Analytical Chemistry* 80(5):1401-1407.

One Particle at a Time

Molecular-level characterization of sulfur in particles sheds light on cloud chemistry

Collecting field data off the California coast, scientists have developed a rich data set on the chemistry of phytoplankton-created sulfur species found in clouds.

Decisions with broad social and economic implications, driven by climate change, are made based on computer models. These models need reliable field data on particles involved in cloud formation to compare to the models' output.

So, a team led by EMSL scientist Alexander Laskin and Lawrence Berkeley National Laboratory researcher Mary Gilles is providing data on the composition of individual particles that are not obtainable with bulk measurements. The team has developed a data set on the chemical speciation of sulfur in marine cloud droplets and particles. The study presents the first quantitative assessment of different forms of sulfur present in sea salt particles.

The major source of sulfur in marine particles is dimethyl sulfide (DMS) generated by ocean-dwelling phytoplankton. In the atmosphere, DMS undergoes a complex sequence of oxidation reactions, yielding non-sea salt (nss) sulfate and methane sulfonate in aerosol particles. The partitioning between the nss-sulfate and methane sulfonate products affects the number and size of cloud condensation nuclei, which, in turn, impacts the chemistry-cloud-climate feedback in the marine atmosphere. Large fluxes of DMS significantly impact the radiative budget over oceans on regional and global scales.

The atmospheric chemistry of DMS and its possible impact on aerosol and cloud droplets has been the subject of many computer modeling studies. The high level of detail used in models is sufficient, in principle, to calculate the different forms of sulfur in marine particles pertinent to different atmospheric conditions and ocean areas. However, validating these calculations requires field and laboratory data with a similar level of specificity, a substantial challenge.

The team began their research by collecting the dry residues of cloud droplets off the California coast. The samples were then sent to EMSL and the Advanced Light Source at Lawrence Berkeley National Laboratory. At EMSL, researchers analyzed the particles using time-of-flight secondary ionization mass spectrometry and computer-controlled scanning electron microscopy with energy-dispersed analysis of x-rays. At ALS, analyses were performed using a scanning transmission x-ray microscope with near-edge x-ray absorption fine structure spectroscopy.

Combined data sets obtained in these analyses have facilitated unambiguous speciation of sulfur-containing compounds and quantitative assessment of the methane sulfonate to the nss-sulfate ratios. The reported results offer a rich set of qualitative and quantitative information important to atmospheric processes in the marine boundary layer involving sea salt and marine sulfate particles.

The team found the methane sulfonate to the nss-sulfate ratios were distinctively high for the droplets and particles representative for the geographic area and the atmospheric conditions of the field experiment, which was in good agreement with modeling predictions.

DOE's Offices of Biological and Environmental Research and Basic Energy Sciences and the Summer Research Institute on Interfacial and Condensed Phase Chemical Physics provided funding.

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Taking the Laboratory into the Great Outdoors *(continued from page 1)*

SPLAT II, shown here during a research flight aboard the Convair 580, allows real-time single particle analysis.

time-resolved aerosol collector and cloud condensation nuclei counter was also part of the campaign.

In addition, flights were conducted by the National Oceanic and Atmospheric Administration and the National Aeronautics and Space Administration. Ground-based instruments and radars measured cloud, aerosol, and other atmospheric properties. Satellite data were also incorporated.

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For additional details about the capabilities and research being performed at EMSL, please visit our website at http://www.emsl.pnl.gov.