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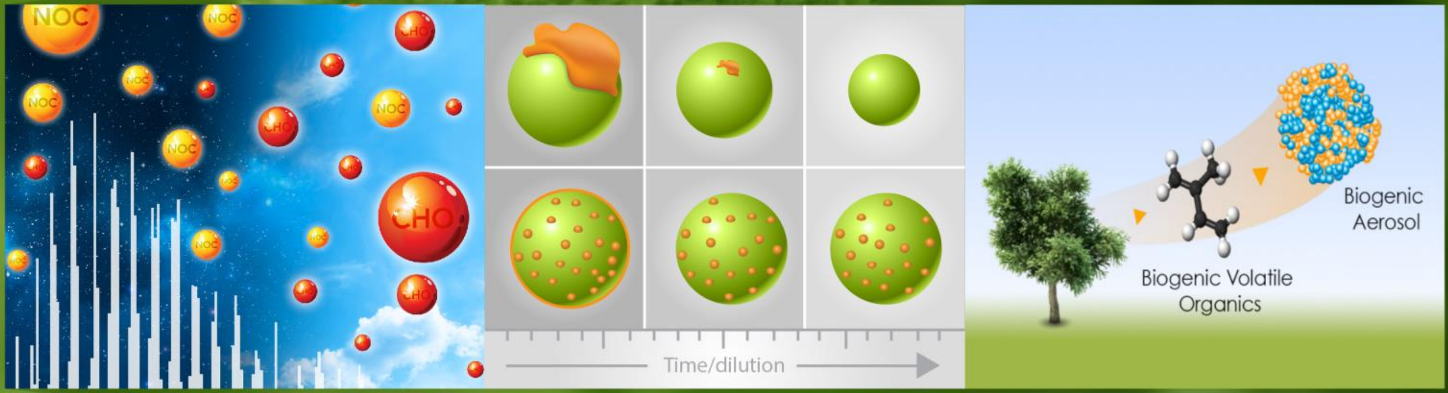
EMSL

Atmospheric Aerosol Science Theme

Advisory Panel Report

Workshop Date
May 8, 2014



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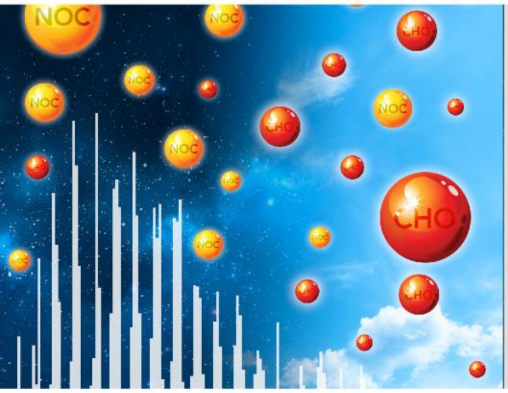
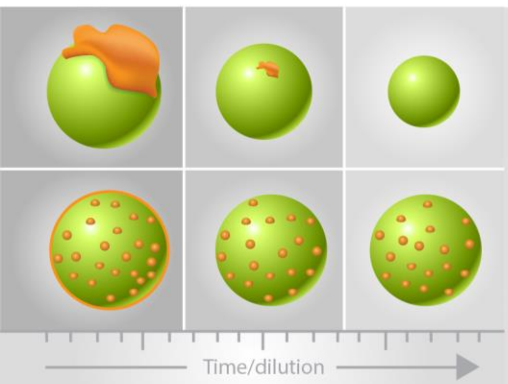
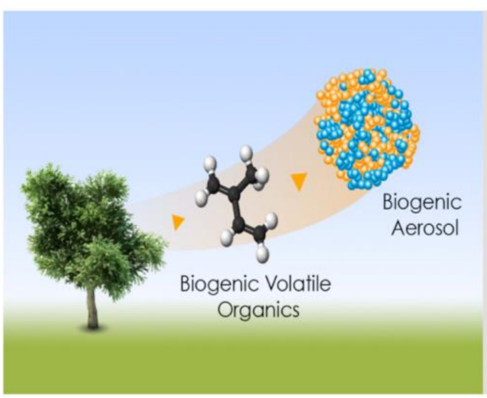


Unexplored organic molecules
Organic molecules are known to play an important role in particle formation, growth, and optical properties but it is not known which ones are the most important molecules. New analytical techniques are needed to target organic compounds that are currently not being detected in atmospheric aerosol and chemistry studies.



Particle evolution and mixing
Atmospheric particles are not homogeneous mixtures and they can evolve throughout their atmospheric lifetime. The processes controlling the aging and lifetime of atmospheric particles are not fully understood and advanced approaches are needed for examining atmospheric particles with better spatial and temporal resolution.



Interactions
Plants, microbes, organic gases, aerosol, clouds, and other earth system components interact and may have feedback couplings. Characterizing these processes is complicated by the large number of interactions that occur simultaneously in the earth system. Laboratory studies using environmental control chambers can complement field observations by investigating the response of a change in a single variable in a carefully controlled earth system simulator.

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PNNL-24039

Atmospheric Aerosol Science Theme Advisory Panel Workshop

Prepared for the U.S. Department of Energy's Office of Biological and Environmental Research under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Acronyms and Abbreviations

AAS	Atmospheric Aerosol Systems
ASR	Atmospheric Systems Research
BER	Biological and Environmental Research
BOA	biogenic organic aerosol
DOE	U.S. Department of Energy
EMSL	Environmental Molecular Sciences Laboratory
FTICR	Fourier transform ion cyclotron resonance
PILS	Particle-Into-Liquid-Sampler
PNNL	Pacific Northwest National Laboratory
SIP	Science of Interfacial Phenomena
SOA	secondary organic aerosols
STAP	Science Theme Advisory Panel

Contents

1.0 Introduction

Atmospheric aerosols have been identified as important contributors to the earth system processes that control the climate of the earth, yet they are among the least understood. Although increasingly sophisticated instruments and computer models have helped scientists discover more about these complex particles and their atmospheric impacts, big gaps remain between theoretical models and the findings of laboratory or field studies and this an active area of scientific research. The Environmental Molecular Sciences Laboratory (EMSL) Atmospheric Aerosol Systems (AAS) Science Theme is aligned with U.S. Department of Energy's (DOE) Office of Biological and Environmental Research (BER) Atmospheric Systems Research (ASR) program. The mission of ASR is to quantify interactions among aerosols, clouds, and radiation to reduce the uncertainty in climate simulations. The aerosol component of the ASR program includes a focus on the formation and properties of secondary organic aerosols. This is challenging because achieving ASR goals requires research across scales ranging from molecular processes to the global climate system. The EMSL AAS Science Theme provides an important contribution to BER's efforts through molecular-scale research that informs global-scale models.

The AAS Science Theme supports outstanding research proposals on all aerosol types and sources related to the climate system. In recognition of limited resources for this work, AAS is emphasizing controllable biogenic organic aerosol (BOA) as a research area that is aligned with the BER ASR priorities and is a topic where EMSL has the potential to be a world leader. The BOA area includes organic matter that is produced in the atmosphere from volatile organics emitted from terrestrial ecosystems. Only small amounts of BOA are formed in a pristine environment, but large quantities form in polluted air. Controllable BOA indicates this aerosol, while produced from natural volatile organics, can be controlled by reducing levels of pollutants that determine that rate at which volatile organics are transformed into aerosol.

EMSL focuses on BOA for three reasons. First, it is a relatively unexplored research topic that makes a large contribution to the total uncertainty in climate models. Until recently it was not included in models and yet we now know it comprises about half of the total aerosol. Second, organics are relatively difficult to characterize and no single analytical tool is sufficient; however, the comprehensive suite in EMSL can enable progress. Third, EMSL scientists have expertise to lead the community in defining the key scientific questions.

EMSL capabilities and activities will enable BER-funded scientists to address new and innovative scientific questions associated with the roles of controllable BOA on climate resulting in high-impact scientific publications and a knowledge base for quantitative climate models. Identification of the most important controllable BOA constituents and processes that have a critical impact on the atmospheric environment and climate will allow researchers to focus on key BER programmatic priorities in climate science. Advanced understanding and quantification of these processes will be used to improve parameterizations in the land surface and atmospheric components of DOE climate models and increase accuracy of model predictions leading to effective mitigation strategies that will improve the environment and reduce climate change.

EMSL has a strong record of aerosol research that until recently was conducted as a component of the Science of Interfacial Phenomena (SIP) Science Theme. Starting in 2012, EMSL initiated a process of realigning and refocusing Science Themes with updated priorities of BER, DOE, and with societal needs. Atmospheric aerosol research was emphasized in this realignment and became one of four EMSL Science Themes. To engage the scientific community in identifying specific research areas where EMSL capabilities and expertise can be focused, EMSL's scientific management team often engages the scientific community via Science Theme Advisory Panels (STAP), associated with EMSL's Science Themes. A STAP typically forms around a workshop with national and international experts to identify specific research in areas where EMSL capabilities and expertise can be focused for maximum benefit of the research community and to identify new capabilities that will enable breakthrough research. A STAP for the SIP Science Theme was held in

January 2013 to obtain community input on potential EMSL research priorities on the life cycle of aerosols and to make molecular-level models accurate for application in large-scale climate models. The participants discussed how EMSL could have a major impact on atmospheric aerosol research including new particle formation, growth and properties of particles, and reactions in and on particles.

The process of focusing EMSL aerosol expertise and extending research capabilities continued with the first AAS STAP held at Pacific Northwest National Laboratory (PNNL), Richland, Wash. on May 8, 2014. Twenty-seven scientists participated in the workshop, with 11 from institutions external to EMSL or PNNL. The participants are shown in Appendix 3. This STAP workshop report summarizes the workshop recommendations that will be considered in planning EMSL's strategic investments in new facilities and development of scientific expertise. These recommendations will also influence future EMSL calls for research proposals.

2.0 Workshop Overview

2.1 EMSL User Meeting

The 2014 annual EMSL user meeting was designed to facilitate scientific discussions of how EMSL capabilities are enabling new scientific discoveries in atmospheric sciences with an emphasis on atmospheric organics; communicate EMSL's future directions and new capabilities to users and potential users; and expose students to advanced instrumentation and innovative science. The meeting was open to existing and potential users from academia, government, and industry in the U.S. and overseas. Technical sessions focused on microscopy, computation, and mass spectrometry. In addition, the user meeting identified key challenges and outstanding scientific questions associated with atmospheric aerosols. This was accomplished through the insightful presentations from leaders in the atmospheric sciences community. This included the keynote speaker, Scot Martin (Harvard University), as well as distinguished speakers Barbara Finlayson-Pitts (University of California, Irvine), Allen Goldstein (University of California, Berkeley), Jose Jimenez (University of Colorado), Joel Thornton (University of Washington), Jim Smith (National Center for Atmospheric Research), and Doug Worsnop (Aerodyne Research).

The user meeting was held on May 6 and 7, 2014, immediately before the AAS STAP. The user meeting served to present a comprehensive view of outstanding challenges and questions in atmospheric aerosol science, especially related to atmospheric organics, and provided the AAS STAP attendees with a starting point for discussions of the EMSL research priorities for atmospheric aerosol science.

2.2 Breakout Session 1: Atmospheric Systems Research Scientific Focus Areas

In the first of two breakout sessions, the scientists took more science topical approaches to the focus questions. Four small groups discussed aerosol aging and mixing states, ice nucleation, secondary organic aerosols (SOA), and new particle formation.

Three groups indicated interest in developing innovative 3-D imaging techniques to enhance understanding in each of their science areas. It was clear that aerosols are complex – changing with time, location, chemical coatings, and many other environmental variables. Yet studies now yield only "snapshots" of these processes. Thus they recognized images that track particle aging on a continuum would be more useful. Similarly for ice nucleation, researchers want to know which particles nucleate first, at what site on the particle, and under what conditions. Currently ice nucleation researchers perform *ex-situ*, "post mortem," experiments, figuring out what happens after the fact. To improve their representation in climate models, experiments ideally need to be performed *in situ*, with multi-dimensional imaging. It was noted that PNNL has an ongoing chemical imaging initiative, and recently announced a new biological imaging initiative. Developing additional imaging applications would complement these efforts.

Additionally, the SOA group emphasized that models do not currently connect all phases of the carbon cycle. The key is to understand the important processes and then see how they relate to climate-relevant properties of aerosols. The transformation and fate of carbon would be better understood with experiments that measured the majority of the gas and particle-phase organic species using ultra-high resolution mass spectrometry, connecting gas-phase precursors to particle-phase products. Participants also pointed out that having the ability to relate chemical composition and optical properties of particles, with a focus on brown carbon, would make a strong link with ongoing work in that area. This is an area where EMSL could make a contribution, but would require developing more expertise.

For researchers investigating new particle formation, the need to close the gap between observed and modeled particle growth rates led to suggestions for more accurate analytic techniques to determine the chemical composition of particles. "If we get the chemical composition right, we can build better models," said one participant. Suggestions included field-deployable instrumentation with high resolution and wide mass ranges; flexible, streamlined data analysis to manage and interpret large data sets; and a collector for size-resolved offline analysis, such as nanoPILS (Particle-Into-Liquid-Sampler). The mass spectrometers currently used for most atmospheric aerosol studies do not have the mass resolution, accuracy, and range required to adequately characterize the composition and structure of all of the compounds that are thought to play important roles in the production and growth of secondary particles. EMSL atmospheric aerosol applications of innovative mass spectrometry, including ultra-high mass resolution Fourier transform ion cyclotron resonance (FTICR) capabilities, could advance atmospheric aerosol research.

2.3 Breakout Session 2: Research Approaches

The second breakout session divided participants into three groups to discuss and prioritize potential new research capabilities that would enable the EMSL community for greater impact on unanswered scientific questions driving the field. These groups considered the feasibility of building a community aerosol and earth system chamber, new field-deployable instruments, and methods to improve approaches to collect samples in the field and bring them to the laboratory for analysis.

A community chamber could diminish disparities between laboratory and field research. Although several chambers have been built in Europe and Japan, they do not cover the entire scope of aerosol and earth system research and do not solve key experimental concerns, such as avoiding wall effects and contamination. There is no adequate facility in the U.S. for investigating biosphere-atmosphere interactions, including biogenic emissions and aerosol production and growth, in a chamber system that does not have significant wall effects. If EMSL constructed such a chamber it would need to complement and integrate existing field and laboratory approaches. EMSL would need to provide "standard" measurements as well as innovative instrumentation and on-line monitoring capabilities. In addition, the facility would also enable researchers to bring their own unique instruments to the chamber.

The list for field-deployable instruments was long, but included 1) development of a field-deployable high-resolution (e.g., Orbitrap) mass spectrometer and 2) development of an advanced platform equipped with different front-end ionization capabilities as a springboard for such a field-deployable system and also as a tool available for off-line analysis. EMSL is developing an ultra-high mass resolution FTICR capability to provide unequivocal resolution and mass accuracy measurements on biogenic and other organic aerosol components. Used in conjunction with field measurements, this capability can help advance our process-level understanding of SOA, for example, measurements of particle-phase organic nitrates to uncover the origins of SOAs and brown carbon. The idea of a low-cost, hand-held mass spectrometer was also put forward. A field microscope to image suspended sub-micron particles, as a way to avoid filters or other collection techniques that might alter molecules under study, was also mentioned.

Improved approaches for off-line analysis requiring transport of field samples to the laboratory were also considered. One limiting factor is the sample size needed to take advantage of some EMSL instrumentation. Therefore, developing analytic techniques that work with smaller sizes is important. Pushing size limits for single-particle composition analysis down to one nanometer would allow researchers to get information about earlier stages of particle formation and enable studies of how new particles form.

3.0 Recommendations: Research priorities and EMSL Capabilities

In a final review session, the workshop participants agreed on three science focus areas and discussed capabilities that EMSL could develop over the next five years that would build on existing EMSL strengths and leverage its measurement capabilities and computational resources to develop innovative methods for investigating atmospheric aerosols.

1. Unexplored organic atmosphere: What compounds are responsible for particle formation, growth, and optical properties? This could be addressed with the development of a sensitive and portable ultra-high resolution mass spectrometer with a flexible front end(s) to target various compounds that are currently not being detected in atmospheric aerosol and chemistry studies.

2. Particle evolution and mixing state: What are the processes controlling the aging and lifetime of atmospheric particles? Addressing this question would require advanced approaches for examining atmospheric particles by both in situ and by off-line spectro-microscopy methods, with better spatial and temporal resolution. Those methods could include multi-modal techniques to provide high throughput 3-D tomography and dynamic imaging of atmospheric particle formation and evolution.

3. Plant-microbe-aerosol-climate interactions: How do plants, organic gases, aerosol, clouds, and climate interact in the earth system? This could be addressed with the development of a multi-component chamber that minimizes wall effects and artifacts and enables investigations of interactions between key earth system components (e.g., plants, soil, aerosol, and clouds).

4.0 Path Forward

EMSL science and technology leadership will give initial consideration to the STAP recommendations to determine which ones, if any, of the three focus areas listed in Section 3 should move forward. For each area that is considered to be a good candidate for developing a future EMSL capability, a community workshop will be held to determine if it is a priority for the atmospheric aerosol community, and define the science drivers, the capability and expertise required, as well as the approach. The development of these capabilities and areas of expertise should enable EMSL to offer a unique user facility that can better advance understanding of aerosol sources, formation, growth, properties, and impact on regional and global climate.

Appendix A

Appendix A Workshop Agenda

www.emsl.pnl.gov

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Atmospheric Aerosol Science Advisory Theme Panel

Thursday, May 8, 2014

Contact Information:
Viviana Burgueno (509) 371-6002 (office), (541) 861-9239 (cell)

AGENDA

8:00 a.m. – 8:30 a.m.
Badging
- US. Citizens – EMSL Lobby
- Non - US Citizens – ETB 1113
- Morning Refreshments – EMSL Board Room

8:30 a.m. – 9:00 a.m. – EMSL Board Room
Plenary Session –
- Welcome & charge – D. Koppenaal
- Introductions & Agenda – A. Guenther
- Summary of previous AAS – D. Baer

9:00 a.m. – 10:20 a.m. – Breakout Rooms
Breakout groups to prioritize EMSL contributions to the DOE/BER/CESD atmospheric aerosol research program by identifying the science challenge where EMSL staff and user community can have the greatest impact in each of the following science areas. This should include a prioritized list of associated capabilities including recommendations for EMSL investments in new instruments and/or staff.

1. **New Particle Formation, Room 1185**
   - McMurry - discussion leader
   - H. VanDam – rapporteur

2. **Secondary Organic Aerosol, Board Room**
   - J. Shilling – discussion leader
   - M. Shrivastava – rapporteur

3. **Aerosol Aging and Mixing State, Room 1385**
   - N. Riemer - discussion leader
   - Zelenyuk – rapporteur

4. **Ice Nucleation, Room 1075**
   - G. Kulkarni - discussion leader
   - B. Kabius - rapporteur

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Agenda: Atmospheric Aerosol Science Advisory Theme Panel
Thursday, May 8, 2014
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10:20 a.m. – 10:40 a.m.
BREAK

10:40 a.m. – 12:00 p.m. – Breakout Rooms
Breakout groups to prioritize EMSL contributions to the DOE/BER/CESD atmospheric aerosol research program by identifying the science challenge where EMSL staff and user community can have the greatest impact using the following research approaches. This should include a prioritized list of associated capabilities including recommendations for EMSL investments in new instruments and/or staff.

1. **Community Aerosol Chamber/Instruments, Room 1185**
   - Smith – discussion leader
   - S. Ghan - rapporteur

2. **Field Deployable Instruments, Board Room**
   - Martin - discussion leader
   - R. Zaveri - rapporteur

3. **Samples Transported to EMSL for Analysis, Room 1385**
   - Nizkorodov - discussion leader
   - Laskin - rapporteur

12:00 p.m. – 4:00 p.m. – EMSL Board Room
Plenary Session

12:00 p.m. – 1:00 p.m.
Working Lunch
Discussion and prepare breakout reports

1:00 p.m. – 2:00 p.m.
Summarize/discuss breakout #1 session
5 minute summary + 10 minute discussion for each group

2:00 p.m. – 2:45 p.m.
Summarize/discuss breakout #2 session
5 minute summary + 10 minute discussion for each group

2:45 p.m. 3:30 p.m.
Discussion and identification of highest priorities for EMSL contributions to DOE/BER/CESD atmospheric aerosol research program.

3:30 p.m. – 4:00 p.m.

Summarize panel conclusions. This will consist of a ranked list of the top ~3 science challenges and the required capabilities including any new EMSL investments in instruments and/or staff.

4:00 p.m. Adjourn

Appendix B

Appendix B Workshop Participants

Organizer

Alex Guenther

External Participants

Allen Goldstein, University of California, Berkeley

Doug Worsnop, Aerodyne

Jim Smith, University Corporation for Atmospheric Research

Joel Thornton, University of Washington

Peter Buseck, Arizona State University

Scot Martin, Harvard University

Sergey Nizkorodov, University of California, Irvine

Sasha Madronich, University Corporation for Atmospheric Research

Peter McMurry, University of Minnesota

Nicole Reimder, University of Illinois

Jian Wang, Brookhaven National Laboratory

Qi Zhang, University of California, Davis

EMSL and PNNL Participants

Lizabeth Alexander	David Koppenaal	Ljiljana Pasa-Tolic
David Asner	Gourihar Kulkarni	John Shilling
Donald Baer	Alexander Laskin	Manishkumar Shrivastava
Jerome Fast	Julia Laskin	Hubertus Van Dam
Steven Ghan	Jim Mather	Rahul Zaveri
Alex Guenther	Karl Mueller	Alla Zelenyuk-Imre