Atmospheric Aerosol Chemistry, Climate Change, and Air Quality
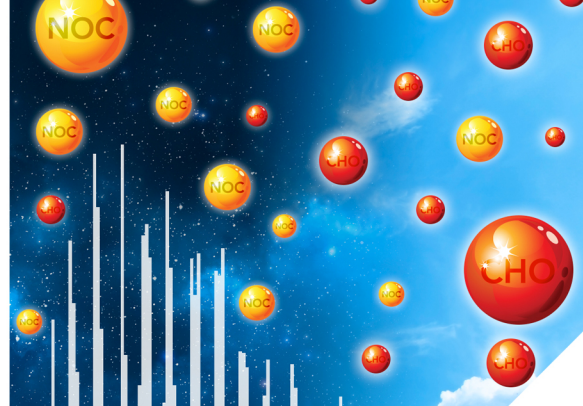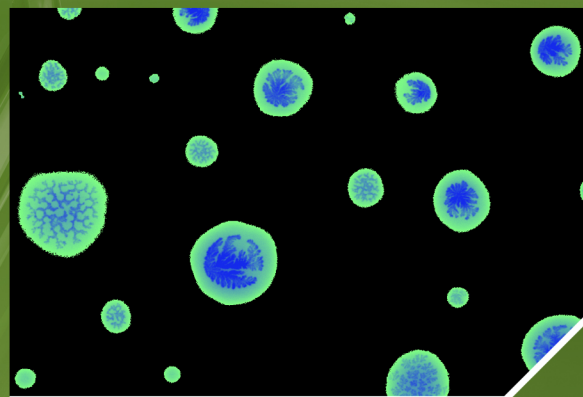
Science Theme Advisory Panel Workshop

January 30, 2013

Report: July 2013

EMSL

Atmospheric Aerosol Chemistry, Climate Change, and Air Quality

An EMSL Science Theme Advisory Panel Workshop

Workshop Date: January 30, 2013

Cover image details: (top) Scientists used EMSL's nano-DESI and mass spectrometry capabilities to analyze the molecular composition of atmospheric organic aerosols, or OA, containing nitrogen-containing organic compounds (NOC) and only carbon, hydrogen, and oxygen (CHO). They uncovered a new method for investigating OA that may lead to more precise climate models. (middle) The common understanding of the birth of soot, created by combustion sources such as aircraft, cars, and power plants, is really oversimplified. Scientists showed that aliphatic carbon, thought to be excluded from soot formation, often is present and may play an important role in creating this common pollutant. (bottom) The internal structure of mixed sea salt/secondary organic aerosol (SOA) particles. The reactions between sea salt and SOAs, two major particle types in the atmosphere, are unique for airborne particles and can have profound consequences on these particles' physicochemical properties.

Executive Summary

Environmental quality and climate change are major challenges facing our nation and the world—with current and potential impacts in the near and distant future. Fundamental understanding of atmospheric processes and coupling between the atmosphere, oceans, and biosphere are needed to understand and predict the interactions between climate and environmental processes and energy production practices. This is critical for providing policy makers with accurate information needed to develop cost-effective strategies to monitor, control, mitigate, and adapt to a changing climate. Reducing uncertainties in key components necessary to understand the Earth's complex climate and environmental systems is an important scientific objective, as discussed in National Research Council and National Science Foundation reports and embraced by the Climate and Environmental Sciences Division (CESD) within the Department of Energy's Office of Biological and Environmental Research (DOE-BER).

The Environmental Molecular Sciences Laboratory (EMSL), a DOE scientific user facility located in Richland, Washington, encourages and enables molecular-level research that leads to discovery and innovation which enhances the quality of life, now and for generations to come. Because of the growing recognition of atmospheric aerosol chemistry impacts on climate change, regional pollution, and weather patterns, EMSL conducted a Science Theme Advisory Panel (STAP) workshop focused on atmospheric aerosol chemistry. Thirty-eight scientists from 11 institutions participated in the workshop held on January 30, 2013. Workshop participants were asked to evaluate areas where understanding the chemical details and time evolution of aerosol formation and development, as well as their chemical and physical properties, could have the largest impact on the development of reliable process-level understanding of regional and global atmospheric climate models.

The workshop discussions identified two categories of scientific gaps: 1) those associated with understanding and predicting the formation, growth, chemical evolution, and other climate-relevant properties of aerosols and 2) those associated with translating molecular-level understanding into parameterization schemes that are applicable over a large range of length and time scales in climate models. Common themes that the workshop participants agreed would advance quantitative understanding and lead to improved predictions included:

- Advancing the accuracy of regional and global models will require close interaction of observational (field studies), experimental (lab studies), theoretical, and computational efforts at the molecular level (to understand and predict formation and growth of particles) and in modeling atmospheric processes at scales from regional to global. Initially, atmospheric modeling should focus on regional scales because regional models can handle more detailed aerosol parameters than traditional global models. In addition, there are data from many regional-scale field studies that can be used to test the accuracy of the parameterizations used in models before extrapolating to the global scale. Linking these disciplines will be critical to success.

- The current understanding of aerosol properties is limited by overly simple concepts of aerosol composition and structure and by relying on methods that determine average properties. Information about the heterogeneity of aerosols, their three-dimensional (3D) composition, and the phase and structure of individual particles, including the presence of minor components that may dominate climate-relevant properties, will be needed to advance aerosol science.

- There is a range of infrastructure and technology needs associated with obtaining the required data on heterogeneity, composition, phase, and structure of particles in 3D, as well as in characterizing individual particles in real time in ambient air. EMSL is ideally suited to address these needs. Potential new capabilities that enhance time, spatial, and/or molecular resolution, such as ultrafast microscopy, high-sensitivity nuclear magnetic resonance (NMR), and experiments enabled by a compact light source, will help to address these issues.

- Significant progress could be made if EMSL coordinated and focused a team effort on one or two specific projects, such as (but not intended to be exclusive): ice nucleation, brown carbon formation and chemistry, or new particle formation and growth.

Acronyms and Abbreviations

3D	three-dimensional
AAAR	American Association for Aerosol Research
ACS	American Chemical Society
ARM	Atmospheric Radiation Measurements Facility
ASR	Atmospheric System Research
BER	Office of Biological and Environmental Research
CCN	cloud condensation nuclei
CESM	Climate and Earth System Modeling
DFT	density functional theory
DNP	dynamic nuclear polarization
DOE	U.S. Department of Energy
EMSL	Environmental Molecular Sciences Laboratory
EXAFS	extended X-ray absorption fine structure
FT-MS	Fourier transform mass spectrometry
IPCC	Intergovernmental Panel on Climate Change
MD	molecular dynamics
MSC	Molecular Science Computing
NMR	nuclear magnetic resonance
PNNL	Pacific Northwest National Laboratory
SciDAC	Scientific Discovery through Advanced Computing
STAP	Science Theme Advisory Panel
TEM	transmission electron microscopy
UTEM	ultrafast transmission electron microscopy

Content

1.0　Introduction

1.1　Background

The Environmental Molecular Sciences Laboratory (EMSL), a Department of Energy (DOE) scientific user facility located at Pacific Northwest National Laboratory (PNNL) in Richland, Washington, encourages and enables molecular-level research that leads to discovery and innovation which enhances the quality of life, now and for generations to come. Addressing environmental quality and climate change are major challenges for the DOE, the nation, and the world community—with current and potential impacts in the near and distant future. Fundamental understanding of atmospheric processes and coupling between the atmosphere, oceans, and biosphere are necessary to understand and predict the interactions between climate and environmental processes and energy production practices. These areas are critical for providing policy makers with accurate information needed to develop cost-effective strategies for monitoring, control, mitigation, and adaptation to climate changes. Reducing uncertainties in key components needed to understand the Earth's complex climate and environmental systems is an important scientific objective, as discussed in National Research Council and National Science Foundation reports and embraced by the Climate and Environmental Sciences Division (CESD) within DOE's Office of Biological and Environmental Research (BER).

In 2012, CESD issued a strategic plan for all of the research programs and user facilities (including EMSL) within the division.[1] One of the five goals articulated in the CESD Strategic Plan is to develop, test, and simulate process-level understanding of atmospheric systems and terrestrial ecosystems, extending from the bedrock to the top of the vegetative canopy. Within CESD the Atmospheric Systems Research (ASR) program seeks to:

".....quantify the interactions among aerosols, clouds, precipitation, radiation, dynamics, and thermodynamics to improve fundamental process-level understanding, with the ultimate goal to reduce the uncertainty in global and regional climate simulations and projections."

The field of aerosol chemistry is sufficiently "young" that molecular-level understanding of the processes leading to the formation of new particles from gaseous precursors and to their growth, which are important for understanding and predicting local and regional changes in air quality, weather patterns, and long-term climate change, currently is quite primitive. Without such understanding, the ability of climate models to reproduce past changes and predict those in the future will be fraught with significant uncertainty. The current state of understanding (or lack thereof) of aerosol chemistry is, in large part, due to the lack of approaches for characterizing and following particles over a wide, atmospherically relevant range of diameters, times, and conditions. In addition, theoretical approaches to predict new particle formation from first principles in complex, multi-component systems are required. With the explosion of new technologies and opportunities to develop the next generation of both experimental and theoretical approaches, the time is ripe for advancing molecular-level understanding of particle formation and growth in atmospheric systems.

Many of EMSL's existing capabilities can be applied to study aerosol particle formation and evolution, including various types of mass spectrometry, microscopy, optical, and surface chemistry tools. Planned new capabilities will further expand the ability of EMSL users to investigate aerosols. A number of EMSL users and scientists have been investigating particles using EMSL capabilities for several years. The combination of unique experimental and computational resources, in addition to growing expertise at EMSL/PNNL, positions EMSL to play an important role in advancing this environmentally important area of research.

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[1] DOE-BER. 2012. "Biological and Environmental Research Climate and Environmental Sciences Division Strategic Plan." Last accessed on June 01, 2013 at http://science.energy.gov/ber/news-and-resources/.

To identify 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, or STAPs, associated with one of EMSL's existing three 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.

Due to the growing recognition of the impact of atmospheric aerosol chemistry on climate change, regional pollution, and weather patterns, a 2013 EMSL STAP (within the Science of Interfacial Phenomena (SIP) Science Theme) focused on atmospheric aerosol chemistry. Specifically, the STAP were asked to evaluate the areas where understanding the chemical details and time evolution of aerosol formation and development and their chemical and physical properties may have the largest impact on the development of reliable process-level understanding of atmospheric climate models.

The purpose of this STAP workshop was to gather the insights and data needed to inform EMSL's strategic investments in new experimental facilities and develop scientific expertise as it relates to atmospheric aerosol chemistry and its impact on air quality and climate prediction. The STAP participants evaluated the science gaps to assess potential areas where EMSL's capabilities are well suited to make significant impact and ascertain what actions, insights, and capabilities are needed to address these disparities. In a larger context, EMSL leadership also must be cognizant that the integration of EMSL and PNNL's Fundamental & Computational Sciences Directorate (FCSD), especially its Atmospheric Sciences and Global Change (ASGC) division, capabilities represent a unique resource to build a world-class atmospheric research platform.

2.0   Workshop Scope

The STAP addressed four high-level questions:

1. Where are the opportunities and greatest needs for a fundamental and detailed molecular-level understanding of aerosol chemistry that can impact air quality, regional weather patterns, and climate prediction?

2. What is the research and capability space that EMSL should/could uniquely occupy and to what extent is there a sufficiently robust scientific community interested and working in the area that could provide a basis for an EMSL user community?

3. How could EMSL's current and planned capabilities impact that need and how should they be deployed for the greatest impact?

4. What new capabilities would significantly advance scientific understanding or fill the science gaps?

This STAP workshop report summarizes STAP workshop recommendations that will be considered in planning EMSL's strategic investments in new facilities and development of scientific expertise. It also will influence the nature of the 2014 and future EMSL calls for research proposals.

This workshop was organized to encourage experts with a variety of areas of expertise to engage in discussion that identified 1) the significant scientific gaps, 2) the types of information needed and related capabilities required to gather that information, and 3) approaches that could optimize EMSL's impact in improving understanding of aerosols, hence the accuracy of the predictive capabilities of regional and global models. The workshop was divided into blocks focusing on each of these areas. Discussions after informal plenary presentations and breakout discussion group topics provided the forum addressing science gaps and capability needs.

2.1   Identifying Science Gaps

2.1.1   Plenary Talks

The workshop began with four informal presentations, allowing experts to provide their perspectives on the status of aerosol chemistry and challenges associated with understanding and modeling the impacts of aerosols on climate change and air quality. Workshop Co-Chair, Professor Barbara Finlayson-Pitts, provided her perspective on the current understanding of aerosol chemistry and some challenges faced in moving forward. Dr. Dorothy Koch and Dr. Ashley Williamson presented DOE-BER perspectives on climate modeling and atmospheric system research, respectively. Professor Joyce Penner discussed science gaps and challenges associated in linking molecular understanding and data to climate models, and Professor Scot Martin discussed molecular science questions in relation to the planned GoAmazon field campaign.

2.1.2   Breakout Session 1: Group Discussions

These four main presentations introduced many topics and issues that were then discussed in detail during a breakout session designed to identify critical research areas, important areas for EMSL activity, and challenges that must be addressed. The workshop participants were divided into three groups focusing on topics (as follows):

1. New Particle Formation

    – Jim Smith (discussion lead), Doug Tobias (recorder), Barbara Wyslouzil, Joyce Penner, Sotiris Xantheas, Liz Alexander, Craig Murray, Bill Shelton, Scott Lea, and Ian Kraucunas.

2. Growth and Properties of Particles

    – Allan Bertram (discussion lead), Donald Dabdub (recorder), Heather Allen, Kim Prather, Phil Rasch, Alla Zelenyuk, Alex Laskin, and Hongfei Wang.

3. Reactions In and On particles

    – Paul Ziemann (discussion lead), Julia Laskin (recorder), Sergey Nizkorodov, Filipp Furche, John Hemminger, Theva Thevuthasan, John Shilling, Nancy Hess, and Vicki Grassian.[2]

These groups were specifically asked to address two questions:

1. **What are the big/important unknowns or major challenges in each area (or what missing information is needed to link to other critical processes)?**

2. **What needs to be done to address the identified challenges and unknowns?**

2.2 Capability Focus

2.2.1 EMSL Capabilities

As a start to exploring capability needs, Don Baer shared a presentation that showcased EMSL's capabilities—current and planned—relevant to aerosols. The potential major new equipment items related to ultrafast microscopy, next-generation nuclear magnetic resonance (NMR), and a compact light source all have the potential to enable new high-resolution or time-resolved aerosol science. The discussion noted capabilities currently applied to aerosols, as well as some that might be applied. Panel members noted that other capabilities currently applied to biological areas also would be important to understanding and characterizing aerosols. EMSL's capability development themes of *in situ*, real-time measurements; unprecedented resolution; and providing a close link between theory and experiment fit with the needs for advancing aerosol science.

2.2.2 Breakout Session 2: Discussion Groups

To focus discussion on capability needs and a direction for possible development, the STAP workshop participants were broken into three groups:

1. Laboratory-focused Capabilities

    – Barbara Wyslouzil (discussion lead), Sergey Nizkorodov (recorder), Paul Ziemann, Heather Allen, Craig Murray, John Shilling, Scott Lea, Hongfei Wang, Sherry Cady, and Vicki Grassian.[3]

2. Field-deployable Capabilities

    – Kim Prather (discussion lead), Alex Laskin (recorder), Liz Alexander, Jim Smith, Allan Bertram, Alla Zelenyuk, Ian Kraucunas, Ray Teller, and Theva Thevuthasan.

3. Modeling/Theory Tools along with Linking Models to Fundamental Data

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[2] Grassian provided input after the meeting.
[3] Grassian provided input after the meeting.

–   Phil Rasch (discussion lead), Filipp Furche (recorder), Joyce Penner, Donald Dabdub, Doug Tobias, Sotiris Xantheas, Bill Shelton, Dave Cowley, and Nancy Hess.

These groups were asked to consider what new laboratory, field, and computational tools are necessary to address the science gaps (previously noted). They also addressed: what are the next-generation of tools that are needed and how do we get the information needed to develop and test models?

2.2.3   Maximizing Impact

The final discussion section of the workshop focused on what can be done to enable EMSL-facilitated research to have the greatest impact. A range of general questions apply including:

- What needs should be addressed first?

- What tools, either new ones or innovative applications of existing tools, must be developed to fill the most critical gaps?

- How could current tools best be deployed?

- What useful partnerships could be created?

3.0   Gap identification and Recommendations

The workshop benefited from highly engaged and enthusiastic participants. Many important topics reappeared in slightly different forms throughout the discussion. Input and discussions related to science, capabilities, and areas for action occurred throughout each discussion. The general themes and areas identified as of "high importance" or "impact" are collected under the general categories identified in the workshop agenda: *Science Gaps*, *Capability Needs*, and *Maximum Impact*. The breakout groups each identified important issues and topics. Although many of these fit into the preceding categories, they also are individually summarized herein.

3.1   Scientific Gaps

The scientific gaps identified during workshop discussions generally fit into one of two categories: 1) those associated with understanding and predicting the formation, growth, and properties of aerosols or 2) those associated with translating molecular-level understanding into parameterized schemes applicable over a large range of length and time scales. Although clearly different, these two areas must be highly coupled to enhance the reliability of predictive models.

3.1.1   Elucidation of Aerosols at the Molecular Level

Developing physically based information relevant to regional and global models requires understanding a system in sufficient detail so the processes can be accurately parameterized for use in atmospheric models. The STAP workshop participants identified several major gaps in understanding aerosol formation, as well as their evolution in time and their important properties that currently limit progress toward this goal.

The current models often consider aerosols to be "identical" spheres either uniformly mixed or with simple coatings. Current evidence suggests this is wrong in many ways:

- Aerosols are three-dimensional (3D) objects that are neither simple core-shell particles nor uniformly mixed. There is an urgent need for 3D characterization to understand their properties, including, for example, interactions with light and a variety of gases.

- Changes in composition and phase with size need to be known and understood for different environments and conditions.

- The differences among particles—composition, phases, and other properties—must be understood. It is likely that a minority of particles, or of species in particles (particle heterogeneity), can have major effects. Average size, structure, and composition can mask important processes.

- Trace components can be present and have important effects on the physical properties of particles, which easily can go unrecognized.

Water in particles also can significantly alter their properties, especially reactivity and environmental update. Currently, both the amounts of water present and impacts are largely unknown.

Different assumptions for gas-particle interactions that determine the growth and composition of particles are used in various models. There is a critical need to understand at a molecular-level the factors that drive these gas-particle interactions and control uptake of species from the gas phase. For example, depending on particle phase, the uptake could either be a kinetically controlled, condensation-type mechanism or a quasi-equilibrium (steady state) process.

The time and spatial scales associated with particle formation, growth, and aging must be understood.

Because the presence of aerosols can have a significant impact on air pollution and climate, it is important to understand their formation and the conditions under which their formation is accelerated or inhibited. The nature of aerosol nucleation and the impacts of different conditions on nucleation must be understood, including:

- Can we distinguish between a cluster and a particle to learn additional details about what drives or controls aerosol formation?

- Can the role of trace atmospheric species in aerosol formation be elucidated and quantified?

- Can theory provide insight into cluster or particle survival probabilities?

3.1.2   Using Molecular Information to Improve Predictive Models

Workshop participants recognized the major challenge of linking molecular-level understanding of aerosols to regional and global models. Some relevant questions raised at the workshop included:

- How much detail is required in the models?

- Are the models predicting the most relevant parameters?

For example, testing global models often involves comparing predicted-to-measured mass concentrations. Meanwhile, the particle number concentration may be most relevant for impacting the formation, properties, and lifetimes of clouds. The workshop participants felt that improving the reliability and accuracy of regional and global models required that parameterization used in the models be physically based. An appropriately detailed understanding of the underlying processes (having a detailed model) enables an accurate, but simplified, parameterization that can improve the larger-scale models. In other words, regional and global models do not need to accurately incorporate all of the processes taking place at the molecular level, but the molecular-level processes need to be sufficiently well understood so that simplified parameters used in the models are based on and evolve from the processes that actually occur.

Considerable discussion was devoted to understanding how best to link molecular-level information to parameterizations useful for larger-scale models. Several themes emerged a number of times throughout the workshop, including:

- There is a need to couple or coordinate laboratory studies, field measurements, and computational approaches. Laboratory studies allow more control and, in conjunction with theoretical approaches, enhance mechanistic understanding. Field studies reveal the degree to which relevant processes actually take place under natural conditions, and predictive atmospheric modeling integrates the understanding from laboratory/theory and field studies.

- Another common theme was recognition of a need for intermediate (or mesoscale) models to help "codify" the molecular-level understanding. These models can help provide physically and chemically grounded parameters that bridge between molecular-scale understanding and regional- or global-scale models. They also allow more extensive testing of the parameterizations under a variety of conditions due to the availability of a large amount of data from field studies conducted on a regional scale.

- There is a need to understand the sensitivity of larger-scale models to different types of molecular-level aerosol properties. It is clear, for example, that aerosols often change as a function of time and space. However, the rate and timing of these changes and their impact on "steady state" processes might make these changes either of high importance to be included in models or indicate their inclusion is unnecessary.

- One high-level important conclusion of the workshop is that advancing the accuracy of regional and global models will require closer interaction—including working on linked projects—of researchers working at the laboratory/theory and field scales and modelers working at larger scales. Integration of these approaches is critical for identifying the most important gaps that affect the accuracy of model predictions, as well as the sensitivity of the predictions to uncertainties in the mechanisms and kinetics of key processes.

3.2 Capability Needs

Capability needs were identified in all six breakout groups. Suggestions from each group are included in Section 3.4. Many of the needs highlighted on multiple occasions are noted herein. The science needs already described directly identify some areas where current measurement technology is inadequate. Although specific tools are identified in some cases, analysis needs often were noted without identification of specific approaches. In fact, at present, appropriate analytical tools to address a number of the important gaps do not exist, and finding mechanisms for attending to these breaches is a key role that EMSL is uniquely positioned to fill.

Many aspects of aerosol, structure, composition, and chemistry are not well understood. Improved particle analysis could significantly enhance understanding. Specifically, techniques that effectively "peel away the onion skin" of individual aerosol particles to understand the detailed 3D structure and chemistry of these materials are needed. Scientists also need to observe the dynamic nature of aerosols. Capabilities that allow real time for tracking of these changes *in situ* will become critical in the future. As already noted, it is critical that this fundamental knowledge be translated into aerosol parameterizations that can be incorporated into existing or improved climate models. Currently, most aerosol models are based on a set of "average" particles and do not recognize the range or variation in properties within a population—despite the fact such variations can be central to climate impacts. The ability to characterize single particles and their variations in time and space is clearly an important goal. While laboratory studies often enable a greater degree of characterization than field studies, many of the needs are similar and applicable to both, such as:

- Enhance the current capabilities of analyzing individual particles, rather than distributions:
  - Improve sensitivity to enable identification of trace gases that may control the formation, growth, and properties of particles
  - Determine 3D structures of aerosol particles on a molecular (not just elemental) basis
  - Quantify the amounts of water in aerosols and the distribution within particles
  - Speed throughput in analysis methods to allow for greater understanding of the distribution of various properties of the particles
  - Increase the methodologies that can characterize individual aerosol particles (e.g., push the technology limits of detection, including the NMR application, to obtain molecular information from single particles)
  - Apply biological approaches, such as those used in cell sorting techniques, that might allow characterization of aerosol particles with similar properties.
- Determine optical properties (scattering and absorption coefficients) at multiple wavelengths for particles at different states of growth, different environmental conditions, and as a function of time.
- Expand experimental methods for collecting and analyzing data in ambient (*in situ*) environments to minimize sampling and analysis-induced changes.

- Focus on improving the ability to determine the composition for all-sized particles with the most need for smaller particles down to 1 nm.

- Increase capabilities for determining the time variation of properties.

- Make multi-modal measurements linking various characteristics to properties:

  – Conceptual EMSL capabilities involving ultrafast microscopy, high-resolution mass spectrometry, highly sensitive NMR, and a compact light source can increase the spatial, energy, or time resolution that can advance aerosol science.

- Incorporate particle nucleation:

  – Develop and extend current theoretical methods to identify processes involved in cluster formation and transformation from cluster to particle

  – Develop approaches that allow the roles of trace gases in nucleation to be determined.

- Improve modeling and data analysis:

  – Improve ability to analyze/mine large data sets

  – Enhance existing modeling tool boxes that may include the intermediate, or mesoscale, models that facilitate the links between molecular data and larger-scale models

  – Establish a platform for linking data from laboratory and field measurements and modeling

  – Develop new approaches to pass information from molecular and mesoscale to larger-scale models.

3.3 Maximizing Impact

Clearly, there are exciting challenges and opportunities to significantly advance the field of aerosols and climate models, particularly to use molecular-level insights of aerosol processes to improve the predictive capabilities of models. EMSL is in a distinct position to contribute both to itself, as well as to the broader PNNL community. In addition, as a user facility, it is able to marshal resources from the much broader atmospheric chemistry community, including university, government, and industrial laboratories. Some areas where EMSL's impact could be optimally employed in this context include:

New or Enhanced Capabilities (some tools needed to fill the gaps)

- Single-particle NMR

- Atom probe (for cryogenically immobilized aerosol particles)

- Secondary time of flight analysis in the helium-ion microscope (probing the surface and below)

- Expand field-deployable methods

- Apply dynamic transmission electron microscopy (DTEM) and eventually the ultrafast TEM, or UTEM

- Microscopy and other tools for ice nucleation studies

- 3D molecular analysis

- Composition down to 1 nm

- Advanced light sources to probe particles

- Improved resolution high-throughput mass spectrometry (possibly using upgraded Orbitraps).

- Data sharing, data mining, enhanced data analytics, and availability/integration of information at multiple levels.

Team Formation and Projects

Throughout the workshop, the need for coordinated research projects that link appropriate components of fundamental chemistry, laboratory-based aerosol studies, field studies, and multi-levels of models was a pervasive message. The coordination of EMSL and PNNL's FCSD provides an important set of capabilities and expertise that, in combination with involvement of the wider research community, could successfully address many important issues. As a user facility that can create focused campaigns, the STAP workshop participants felt that great impact could be achieved with EMSL-initiated or coordinated studies that integrated laboratory/theory and field studies with multiscale modeling and focused on an important unsolved problem. Some suggested areas included: 1) "brown carbon," an area where EMSL already has significant activity; 2) ice nucleation with emphasis on the role of biological particles and black carbon; 3) particle nucleation, an important area for which new tools would be needed; 4) particle growth, an area where EMSL already has significant activity and a topic of immense recent scientific interest; and 5) elucidating particle phases and coatings in 3D and linking these to optical properties.

Make EMSL Capabilities More Widely Known

Existing EMSL capabilities can help advance the understanding of aerosols and determine their impacts on regional or global models. However, the range of capabilities and understanding of how to access them is not well known in the community. Therefore, it was recommended that steps be taken to increase this visibility. It was specifically recommended that EMSL consider having a presence at the American Association for Aerosol Research meetings. The next meeting will be in Portland, Oregon, September 30–October 4, 2013.

3.4   Scientific Gap Breakout Group Report Summaries

Although each breakout addressed the questions posed to them in slightly different ways, they all identified important issues and needs (summarized in the following sections).

3.4.1   New Particle Formation

J. Smith, discussion lead, and D. Tobias, recorder

The new particle formation group noted that models suggest new particle formation impacts climate by modifying the amount and properties of cloud condensation nuclei (CCN). A fundamental question is: what information about new particle formation is required to improve the accuracy of a global model? Understanding the conditions that facilitate particle formation and growth and how fast both occur would provide important foundational information to identify the aspects of new particle formation growth that are important to global climate models.

The panel discussed several specific areas where additional understanding was needed:

- The early stages of particle formation are difficult to study experimentally and incorporate into models.

  – There is little understanding of the connection between the formation of clusters and the transition of clusters to particles.

  – Can survival probabilities of small particles be represented by simple distributions?

- What is the relationship between ambient conditions, including trace gases, and particle formation and growth, both in the field and in laboratory studies? What are the roles of trace species, such as amines and low-volatility organics, in field measurements and laboratory studies? How could this be accounted for in regional or global models?

- How does the surface (and bulk) chemistry of particles vary as they grow and how does that impact the growth rate? Although aerosols as small as 1 nm can be detected, there is little information about the composition of particles in this size range. What is the role of organic condensation versus quasi-equilibrium partitioning on particle growth (and structure)?

- What are the spatial and time scales involved?

- Current models of particle structure that impact nucleation and growth are very simple, consisting of spherical particles, sometimes with a core-shell structure. Information about the 3D structure of particles is likely to be crucial to making progress. What is really on the surface? How are components mixed?

- Models of nucleation and growth rates of atmospheric nanoparticles that can be incorporated into regional and global models need to be based on laboratory/theory and field studies and linked to molecular-level modeling. These models require molecular understanding of nucleation and early growth.

  - These mechanistic process-level models need to be incorporated into regional models and evaluated.

  - It would be useful to identify data sets that might serve as a guides or benchmarks for incorporating understanding new particle formation into global climate models.

Other capabilities to pursue include:

- Infrared and other methods for defining neutral particle composition that would not involve changing neutral aerosols into charged particles for analysis.

- Exploiting new-generation laser technology.

3.4.2   Growth and Properties of Particles

A. Bertram, discussion lead, and D. Dabdub, recorder

The group noted that particles have a variety of important properties that influence important atmospheric processes which impact models of environmental processes. It is important to understand how particles grow, how they influence ice nucleation, how much water is included in particles, and how they interact with light.

General Issues–Progress will be facilitated by:

- Combining field and laboratory studies to gain better understanding, e.g., make some techniques now used only in laboratory studies field deployable

- Connecting laboratory, field, and modeling studies

- Making measurements in ambient conditions. In some cases, this requires expanding capabilities and developing new technologies.

- Making measurements at the single-particle level, not average, accounting for the heterogeneity of particles in measurements and models

- Making quantitative measurements and moving beyond qualitative observations.

Particle Growth–Regarding growth of particles, there are many unknowns:

- What is the mechanism of growth: equilibrium within bulk or condensation mechanism?

- Do certain mechanisms dominate under certain conditions?

- Do current theoretical frameworks of growth match experiments?

- Are there chemical reactions involved in growth? What species are involved?

- What are the uptake coefficients of organics and other species on organic particles?

- How does the size distribution evolve (secondary organic aerosol + others) during particle growth?

The measurements necessary for understanding particle growth also include:

- Uptake coefficients

- Chemical composition of the sub-50 nm particles

- Activation energies of adsorption

- Viscosities as function of relative humidity

- Evolution of the size distribution.

Particles Properties–Discussion focused on particle properties related to ice nucleation, water uptake, and interaction with light:

1. Ice nucleation:
   – Unknowns include:
     ○ The mechanism of ice nucleation
     ○ The relationships between active sites for ice nucleation versus total surface area
     ○ Why do some particles cause ice nucleation?
   – Needed measurements or experiments:
     ○ Detailed studies of the chemical composition and morphology of ice nucleation
     ○ Spectro-microscopy
     ○ Sum frequency generation (SFG) microscopy.

2. Water uptake properties/hygroscopicity:
   – Unknowns include:
     ○ Is the hygroscopicity of the average the same as the hygroscopicity of individual particles?
     ○ How important is heterogeneity?
     ○ Does heterogeneity when modeling hygroscopicity need to be considered?
     ○ How does water partition on or in particles (i.e., on the particle surface or in the bulk of the particle)?

- ○ The CCN ability of certain types of particles
- ○ In cases where CCN is not well predicted in models, is this a limitation of the models or the chemistry?
- – Properties to measure or methods to apply:
  - ○ Single particle measurements (to determine heterogeneity)
  - ○ 3D structure of single particles
  - ○ Size-resolved chemical composition
  - ○ Phase of particles
  - ○ Water content of particles on a per particle basis
  - ○ Surface properties (what is actually on the particle surface)
- – Ambient pressure effects
- – Levitation techniques.

3. Light absorption
   - – Unknowns include:
     - ○ Chemistry that changes light absorption of particles
     - ○ What chemistry is most important for light absorption (e.g., brown carbon)?
   - – Measure:
     - ○ Wavelength-dependent optical properties on particles at different states of growth, different environmental conditions, and as a function of time
     - ○ Determine particles chemistry in greater detail, especially aspects that influence interactions with light.

3.4.3   Reactions In and on Particles

P. Ziemann, discussion lead, and J. Laskin, recorder

This session group focused on questions surrounding the challenges and unknowns involving particle reactions. Aerosol particles interact with their surroundings, including water and light, and may change phase or structure as they grow or with temperature changes.

Particle reactivity depends on a number of factors, many of which are currently either unknown or not well known. Often, chemical reactions mostly occur at the surface of particles. As such, what is on the surface makes a difference. In addition, the overall reactivity of a particle will differ, at least to some degree, if it is liquid or solid and the extent to which the particle is hydrated. This distribution of components within the particle determines their availability to react. These issues provide the background for the questions raised by this group.

Understanding the 3D composition and structure of particles appears to be an important component of understanding their reactivity. It is necessary to understand and be able to characterize structure, compositional, and phase changes in 3D as a function of particle aging/transformation. There are several aspects to this general need:

- Optical properties are sensitive to composition, but minority molecules may play dominant roles in determining optical properties. Determining the dominant chromophores may be like finding a needle in a haystack. Does it matter how stable they are and where they are located within the particle?

- Aerosol water plays in important role in determining aerosol properties and reactivity. The nature of the chemistry that occurs in the highly concentrated solutions in aerosols is not well known. There is a need to understand the differences in chemistry of bulk solutions and small droplets. There also is a need to determine how much water is contained in aerosols and how that may depend on size.

- The surfaces and surface composition of aerosols are critically important to understanding reactivity at particle surfaces. Uncertainty of sticking coefficients limits understanding. How do particle phase and structure impact rates of reactions?

- What are the critical descriptors of particles that will impact regional and global models? What information needs to be incorporated into those models?

There is a critical need to merge or link laboratory and field observations. Laboratory observations may provide information that allows the nature of reactions in field systems to be probed. The understanding obtained (and targeted) should be directed toward information that either provides quantitative information of value to systems models or offers useful constraints for those models.

3.5 Capability Needs Breakout Session Report Summaries

3.5.1 Laboratory-focused Capabilities

B. Wyslouzil, discussion lead, and S. Nizkorodov, recorder

Answering the science questions with enough detail to provide useful mechanistic-based input into regional and global models requires a better understanding of heterogeneity in particles, which could be defined by a list of measurement and information needs. It is realized that some of these needs are beyond current capabilities.

Information needs include:

- Composition of particles (from clusters to nanoparticles)

- Particle structure (from clusters to nanoparticles)

- Distribution of matter and phases within the structure and on the surface

- Optical properties

- How much water and its distribution within a particle

- How does heterogeneity impact reactivity, water uptake, etc.?

There are several issues that cut across these measurements including: 1) the need to compare and contrast laboratory and field measurements and link these to theory; 2) the need to make microscopy and other measurements in ambient conditions without particle damage, 3) the ability to obtain information from individual particles versus determining an average property, and 4) the ability to determine any time variation in properties (kinetics versus equilibrium).

Instrument Needs and Development Objectives

To meet information needs, a range of instrument development targets apply, including:

- Pushing the size limit for single-particle chemical composition measurements down to the ~1 nm regime

- Increasing throughput of single-particle measurements to allow characterization of >105 particles on a reasonable time scale

- Employing multi-modal imaging and chemical and structural characterization (such as tomography of single particles coupled to other methods, such as extended X-ray absorption fine structure, or EXAFS)

- Improving software for analysis of structure of nanoparticles

- Providing tools for localized extraction of organics from 100 nm-plus particles, affording simultaneous mass spectroscopy, imaging, and optical measurements on the same particle

- Developing state-of-the-art tools for broadband absorption measurements (refractive indexes) from aerosols

- Pushing the sensitivity limits of NMR and other probes to single-particle measurements

- Employing real-time measurements of phase distribution in individual particles

- Increasing the resolving power of mass spectrometers dedicated to aerosol research or used for routine, high-throughput characterization of molecular-level composition of aerosols, e.g., upgrading the Orbitrap-based instrument to obtain intermediate resolving power and pursuing high-field Fourier transform mass spectrometry (FT-MS)

- Creatively adapting cell sorting and characterization tools to aerosol measurements (e.g., flow cytometry), as well as sorting by reactivity or other properties rather than by mass or mobility

- Coupling particle suspension methods to UTEM to investigate, for example, phase transitions in particles

- Developing ambient-pressure analysis for studies of atmospheric aerosols.

3.5.2   Field-deployable Capabilities

K. Prather, discussion lead, and A. Laskin, recorder

The field-deployable capabilities group started with a laundry list of ideas, but they focused on a few areas thought to be most important and missing from current field-deployable tools. Quantifying molecular speciation of single-particles and measurements (smaller sizes, cluster-to-particles 1–20 nm) would be key to addressing new particle nucleation and growth. The group discussed how, in the field, researchers can do imaging to get optical data, including morphology and shape properties, but that time-resolved measurements or coupled single-particle hygroscopicity still are needed. There was much discussion surrounding single-particle phase viscosity information, brown or black carbon, and molecular-level and optical properties measurements (chemical imaging or spectroscopy of non-volatile organic carbon, semi-volatiles, etc.).

Although the group identified a long list of desirable field-deployable measurement needs, they noted there were some high-priority target areas that that could help resolve important scientific topics. To that end, there was considerable discussion of a possible focus on ice nucleation and brown (or black) carbon as appropriate target areas.

The comprehensive list of desired field measurements included:

- Addressing indirect and direct effects
  - *In situ* measurements
  - Samples-to-laboratory measurements.
- Addressing gas-particle versus aqueous processes
- Analytical chemistry of bioaerosols
- Gas-particle partitioning and the ability to measure low-volatility gas-phase species
- Optical measurements with wavelength dependence
- Surface versus bulk spectroscopic analysis
- Room-temperature ambient kinetics
  - Evaporation/condensation
  - Reactivity
  - Differentiation.
- Understanding water impacts on reactivity
- Understanding water impacts on secondary organic aerosols formation
- Using in-field high-resolution spectroscopy to measure isotopes ^{12}C and ^{13}C (also can be used with C, S, N, and O)
- Chemistry of aerosols with cloud microphysics
  - What about linking it with precipitation?
- Distinguishing between non-volatile, semi-volatile, and volatile compounds
- Capabilities to link atmospheric-water-soil processes.

3.5.3   Modeling/Theory Tools Along with Linking of Models to Fundamental Data

P. Rasch, discussion lead, and F. Furche, recorder

This study group focused on areas where molecular calculations could make a difference to measurements and larger-scale models. As characteristic of the experimental groups, the objective was to provide or enable information that allows the regional- or global-scale models to have increased accuracy and reliability by including mechanism-based information at the required levels. Modeling is appropriate at multiple levels, and one challenge is the transfer of necessary information in a simplified form between levels. The group called attention to the following areas:

- The importance of connecting molecular and macroscopic scales and a need to identify intermediate steps between molecular and other scales
- The need to design mesoscale models (e.g., interaction of aerosol particles)
- Identifying what information is needed and what accuracy level is necessary for macroscopic models

- – Macroscopic parameters
- – Need box tools
- – What are the essential mechanisms?

- What are the important parameters and basic assumptions associated with sensitivity analysis?

- What are the areas where molecular calculations can make a difference? How do they impact regional or climate models?
  - – Chromophores and their interactions (oxidation, photobleaching, formation) with the environment
  - – Particle morphology/composition
  - – Prediction of uptake coefficients
  - – Confinement effects
  - – "Computer experiments" to guide other experiments
  - – What are the important mechanisms and species involved?
  - – Characterization of transient species
  - – Series of benchmark calculations and experiments.

- How do we relate this to "big picture" goals (e.g., climate models)?

Appendix A: Workshop Agenda

www.emsl.pnl.gov

EMSL

Environmental Molecular Sciences Laboratory
902 Battelle Boulevard • P.O. Box 999 • Richland, WA 99352

Atmospheric Aerosol Chemistry, Climate Change and Air Quality
EMSL Science Theme Advisory Panel (STAP) Workshop
January 30, 2013
Sand & Surf Resort, Laguna Beach, CA

AGENDA draft

January 29, 2013

7:00 pm   **Introductory Dinner** *(attendees need pay for their own meal – location being finalized)*

Four workshop questions:

- Science Gaps - Where are the opportunities and greatest needs for molecular-level understanding of aerosol chemistry that can impact air quality, regional weather patterns and climate prediction?
- What is the research and capability space that EMSL should/could uniquely occupy, and to what extent is there a sufficiently robust scientific community interested and working in the area that could provide a basis for an EMSL user community?
- How do EMSL's current and planned capabilities impact that need and how should they be deployed for the greatest impact?
- What new capabilities would significantly advance scientific understanding or fill the science gaps?

January 30, 2013

8:15 am   **I) Welcome and plans for the day – Top of the Surf room**
- EMSL Future Vision – Allison Campbell
- Review of objectives – Don Baer

8:30 am   **II) Science Status and Gap Identification**
Informal Presentations/Discussions
- 8:30 am - Status of aerosol chemistry and current challenges - Barbara Finlayson Pitts
- 9:00 am - Discussion of BER perspective on needs for advancing climate models - Ashley Williamson and Dorothy Koch
- 9:20 am - Challenges to linking molecular data to climate models – Joyce Penner
- 9:40 am - Molecular Science questions related to field campaigns - Scot Martin
- Questions and discussions with presenters
- **10:00 am - Breakout Session 1** - critical areas, open space, unaddressed challenges (see details below)
- **11:15 am - Reports from breakout sessions and discussion**

Contact Information:
Don Baer 509-781-1326 cell

EMSL is located at PNNL

Pacific Northwest
NATIONAL LABORATORY

12:00 Noon   Lunch

12:30 pm   III) Capability Focus
Informal Presentation and Discussion
- 12:30 pm - EMSL capabilities relevant to aerosols: current, planned and limitations – Don Baer
- Questions and discussion
- **1:15 pm - Breakout Session 2** - what tools are needed in the lab, field and modeling to address gaps, what are the tool gaps, what are the next generation of tools needed? How do we get the information needed to help develop and verify models?
- **2:30 pm - Reports from breakout sessions**

3:15 pm   IV) Maximizing Impact – questions and discussion topics
Addressing needs, current and future tools in the context of our current environment:
- What research space/gap needs to be filled first?
- What tools most need to be developed to fill the gaps?
- What leadership or expertise gaps does EMSL need to fill?
- How best should EMSL tools be deployed?
- Are there coming opportunities that we need to focus on?
- Are there opportunities to raise the visibility of aerosol chemistry on the national research agenda?
- Does an appropriate user/partner community exist?

4:15 pm   Tabulation of Recommendations/Final comments

5:00 pm   Adjourn

BREAKOUT GROUPS FOR STAP DISCUSSIONS

[**]Discussion Leaders
[*]Recorders

Breakout Session #1 - 10 am to 11:15 am January 30
(1) *What are the big/important unknowns or major challenges in each of these areas (or missing information needed to link them to other critical processes)?*
(2) *What needs to be done to address these?*

Group 1 -New Particle Formation:
[**]Jim Smith
[*]Doug Tobias
Barbara Wyzlouzil
Joyce Penner
Sotiris Xantheas
Liz Alexander

Group 2 - Growth and Properties of Particles:

[**]Allan Bertram
*Donald Dabdub
Heather Allen
Kim Prather
Phil Rasch
Alla Zelenyuk
Alex Laskin
John Shilling

Group 3 - Reactions In and on Particles:

[**]Paul Ziemann
*Vicki Grassian
Julia Laskin
Sergey Nizkorodov
Filipp Furche
John Hemminger

Breakout Session 2 - 1:15 to 2:30 pm

(1) *What new tools are needed in lab, field and modeling to address the gaps noted earlier and to link to models*

Group 1 - Laboratory Focused Capabilities:

[**]Barbara Wyslouzil
*Sergey Nizkorodov
Paul Ziemann
Heather Allen
Vicki Grassian
John Hemminger

Group 2 - Capabilities that are field deployable:

[**]Kim Prather
*Alex Laskin
Liz Alexander
Jim Smith
Allan Bertram
(Scot Martin)
Alla Zelenyuk

Group 3 - Modeling/Theory Tools along with linking of models to fundamental data:

[**]Phil Rasch
*Filipp Furche
Joyce Penner
Donald Dabdub
Doug Tobias
Sotiris Xantheas
Bill Shelton

Appendix B: Attendees

Appendix B: Attendees

STAP Members

Barbara Finlayson-Pitts, University of California, Irvine (*Workshop Co-Chair*)
Heather Allen, Ohio State University
Allan Bertram, University of British Columbia
Vicki Grassian,* University of Iowa
Scot Martin,** Harvard University
Joyce Penner, University of Michigan
Kimberly Prather, University of California, San Diego
Phil Rasch, PNNL
Ruth Signorell, ETH Zurich (Swiss Federal Institute of Technology) and University of British Columbia
Jim Smith, the National Center for Atmospheric Research (NCAR)
Barbara Wyslouzil, Ohio State University
Paul Ziemann, University of California, Riverside

Travel problems prohibited attendance, but provided input after the meeting.
**Web participation during part of the workshop.*

Other Workshop Participants and Observers

Donald Dabdub, University of California, Irvine
Filipp Furche, University of California, Irvine
John Hemminger, University of California, Irvine
Sergey Nizkorodov, University of California, Irvine (*EMSL User Executive Committee member*)
Zeev Rosenzweig, National Science Foundation
Doug Tobias, University of California, Irvine

PNNL Staff

Julia Laskin
Ian Kraucunas
John Shelling
Sortiris Xantheas
Alla Zelenyuk-Imre
Charity Plata (scribe/editor)

EMSL Staff

Don Baer (*Workshop Co-Chair*)
Liz Alexander
Allison Campbell
Sherry Cady
Dave Cowley
Alex Laskin
Scott Lea
Bill Shelton
Ray Teller
Nancy Hess
Theva Thevuthasan
Hongfei Wang