ELECTRIC POWER RESEARCH INSTITUTE

2008 August Mini-Intensive Gas and Aerosol Study (AMIGAS)

Motivation

Recent scientific studies suggest that the interactions between biogenic and anthropogenic emissions in the formation and transformation of particulate matter (PM), particularly secondary organic aerosol (SOA), may be important. However, there is not a clear understanding of the mechanisms involved in these interactions and the extent to which they contribute to increased PM levels.

In fact, most mechanisms regulating the concentrations and chemical composition of organic particulate matter are still quite unclear. Other recent studies have shown the importance of particle-phase reactions (chemical reactions occurring within or on the surface of particles) to the "aging" of primary and secondary organic aerosol. These aging processes can add additional aerosol mass, change the chemical nature of the material, or lead to the decomposition of the organic PM. Moreover, further oxidation and condensation of gas-phase products formed from the initial oxidation of volatile organic compounds (VOC) emissions can also contribute to organic PM mass. Understanding these processes under daytime and nighttime conditions requires detailed characterization of the components of particulate matter.

Several components of PM may act as tracers of specific chemical or physical transformations, and thus help elucidate the mechanisms of interest. Carbonaceous compounds have historically been used most frequently, but recent instrumentation advances allow for the use of sulfur- and nitrogen-containing compounds as well.

Sulfur-containing compounds, such as organosulfates and nitroxy-organosulfates, have been detected in ambient air. Laboratory studies suggest that these compounds may serve as unique tracers for biogenic SOA formation processes occurring in the presence of SO_2 and elevated aerosol acidity. However, the applicability of these lab studies to ambient conditions is unclear.

Nitrogen-containing compounds, such as ammonia and nitric acid, contribute to ambient particulate matter and to nitrogen loading to watersheds and ecosystems via atmospheric deposition. However, other nitrogen-containing compounds in the atmosphere have gone undetected for years due to instrument limitations. Recent state-of-the-art measurements for one class of organic nitrogen compounds, amines, indicate they may play a previously unknown but significant role in SOA and new particle formation. Moreover, toxicology studies have shown amine exposure can lead to adverse health effects such as thrombosis (formation of blood clots), thus further necessitating the need to measure those compounds.

Highly time-resolved measurements of many nitrogen-containing chemicals such as ammonia, nitric acid, ammonium and nitrate are essential to determine the contribution of different sources of nitrogen emissions to air quality and atmospheric deposition. With support from the Program on Technology Innovation, EPRI has developed novel analytical methods to obtain continuous data on these nitrogen compounds. The resulting continuous datasets are important because particle formation and chemistry occur on scales of hours or less, and would not otherwise be resolved with daily sampling. In addition, the Program on Technology Innovation has also

supported the development of instrumentation to detect and quantify organic nitrogen compounds such as organic nitrates and amines in the ambient aerosol. The emergence of these methods has made possible investigations into the atmospheric abundance of various nitrogen-containing compounds and could help support future health studies.

Objectives

The 2008 August Mini-Intensive Gas and Aerosol Study was designed in order to answer several questions related to interactions of biogenic and anthropogenic emissions:

1. How do anthropogenic emissions interact with biogenic emissions in the atmosphere? In particular, how do these reactions impact formation of secondary organic aerosol?
2. What are the mechanisms regulating the chemistry of primary and secondary organic particulate matter? How do these processes differ during day and night?
3. Which compounds contribute to the atmospheric nitrogen loading? How do these ambient nitrogen compounds impact atmospheric chemistry and ensuing air quality?

Campaign Details

A field campaign was designed to meet the above objectives and to investigate the influence of acidity and other parameters to SOA formation and particle nucleation. The Southeastern Aerosol Research and Characterization (SEARCH) network served as the operating platform for the campaign due to its location in a region experiencing both biogenic and anthropogenic emissions, and the extensive high-quality long-term datasets available.

Numerous pieces of additional instrumentation from multiple laboratories were installed at the urban Atlanta (Jefferson Street) and rural Yorkville, Georgia, sites and were complemented by the ongoing SEARCH measurements in those locations.

Several scientific themes were investigated during the campaign.

One was to determine how much of the total amount of reactive nitrogen in the atmosphere can be accounted for, using both novel and established measurement techniques. Reactive nitrogen is comprised of all forms of nitrogen other than N_2 and includes organic and inorganic nitrogen, in the gas and particle phase, in both oxidized and reduced form. [1]

A similar accounting of sulfur compounds will be attempted with measurements of total sulfur, sulfate, organosulfates, nitroxyorganosulfates, and other forms of sulfur, using multiple techniques.

The relative contributions of various organic aerosol formation pathways, including the roles of biogenic and anthropogenic emissions, primary and secondary compounds, and combinations thereof, will be evaluated. The differentiation of daytime and nighttime organic aerosol processing and resultant composition will be investigated.

Measurement Details

The campaign allowed for field testing and cross-comparison of two EPRI-developed instruments for measurement of organic and inorganic nitrogen, and will demonstrate their capabilities in a high-visibility forum.

The inorganic nitrogen instrument, the Inorganic Continuous Aerosol Monitoring System (iCAMS) fills a gap of routine monitoring methods for gas phase nitric acid (HNO_3) and ammonia gases (NH_3) and particle phase nitrate (NO_3^-) and ammonium (NH_4^+). Previous techniques could not measure all of these compounds in a single system, but required individual, highly labor-intensive research-grade instruments. In contrast, the iCAMS provides continuous 1-hour data, is easy to use and maintain, can be operated remotely, and is constructed in three components for maximum flexibility to the operator.

The organic nitrogen instrument, the Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) and Chemical Ionization ATOFMS (CI-ATOFMS), were developed by the University of California, San Diego. These are the only existing instruments to provide detailed information on amines. While the previous ATOFMS instrument is extremely sensitive to amines and provides some information about other chemical constituents of PM and insights on new particle formation, it is a qualitative instrument. In contrast, the CI-ATOFMS can accurately and quantitatively confirm chemical identity.

[1] Reactive nitrogen also includes nitrous oxide, N_2O, a potent greenhouse gas. However, in this study, N_2O was not included in the reactive nitrogen calculations.

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The suite of measurements performed on-site during the field campaign, and off-site using filter samples collected during the campaign, also included the following:

- Inorganic soluble ions (e.g. SO_4^-, NO_3^-), organic soluble ions (e.g., formate, acetate) which may undergo heterogeneous chemistry, and total water soluble organic carbon (WSOC) representing from 20 to 70% of aerosol organic PM. WSOC of is particular interest since it can impact cloud formation (and thereby impact climate) and rapidly deposits to surface and ground waters. Georgia Institute of Technology
- Radiocarbon analysis for amounts of modern versus fossil carbon mass. National Ocean Sciences Accelerator Mass Spectrometry Facility at the Woods Hole Oceanographic Institute.
- Physical properties related to particle formation and growth (such as cloud condensation nuclei, hygroscopicity, and surfactant measurements). Georgia Institute of Technology.
- Analysis of tracers of biogenic SOA formation (e.g. organosulfate and nitroxyorganosulfate compounds) under acidic conditions with liquid chromatography mass spectrometers and electrospray ionization time-of-flight mass spectrometers. California Institute of Technology
- Gas chromatograph-mass spectrometer analyses of organic carbon tracer compounds. Georgia Institute of Technology.
- Comprehensive aerosol composition measurements from the mobile air quality laboratory of the Tennessee Valley Authority.
- Routine air quality and meteorological measurements from the SEARCH Network. Atmospheric Research and Analysis, Inc.

Project Status

Researchers were in the field in from August 1 to September 15, 2008. Additional chemical analyses and data analyses will continue into 2009. A number of peer-reviewed literature manuscripts and presentations at scientific conferences are planned. Topics will include evaluation of the new instrumentation field-tested during the campaign, as well as comparison and integration of data from various types of instrumentation and participating laboratories to address the study's goals.

Contact Information

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