

Formation Mechanisms for Secondary Organic Aerosol in Ambient Air

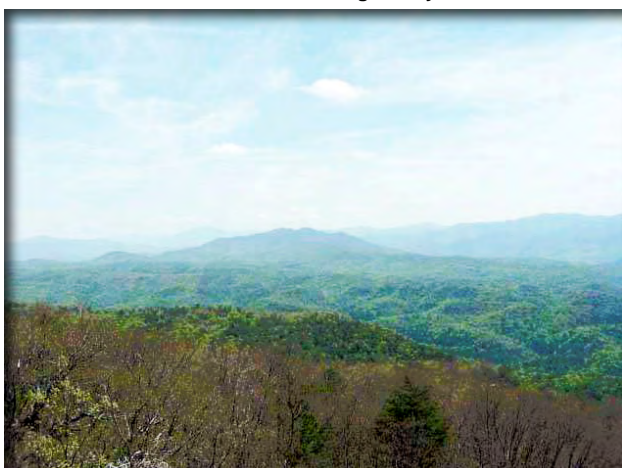
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Abstract. An integrated laboratory and field research program is underway at the National Exposure Research Laboratory to characterize organic carbon in PM_{2.5} formed through chemical reactions. Information from this study will provide critical data needed to improve the treatment of secondary organic aerosol (SOA) formation in the Community Multiscale Air Quality (CMAQ) model. In the laboratory portion, SOA-producing hydrocarbon precursors are irradiated in a smog chamber in the presence of NO_x and SO₂. Identifiable organic compounds are formed indicative of the precursors which are then compared to field study samples to ensure that relevant chemical systems are being studied. In collaboration with the California Institute of Technology and the University of Antwerp, analytical methods and instruments are used to identify the products. Collaborative efforts are also underway with the Atmospheric Modeling Division of the NERL to incorporate findings from the field and laboratory measurements to improve the treatment of SOA within CMAQ. The project results should provide the Office of Air Quality Planning and Standards with critical data on important regulatory issues, among them (1) contributions of each SOA precursor to the PM_{2.5} concentration, (2) relative contributions of anthropogenic and biogenic hydrocarbons to ambient SOA concentrations, and (3) impacts of SO₂ reductions on SOA formation. This information will improve the treatment of SOA in the CMAQ model and help states evaluate control strategies for reducing ambient PM_{2.5}. These results will support effective regulations and information that improves public health and reduces ecological impacts.

Goals and Objectives

- Identify the major SOA precursors important in PM_{2.5}
- Identify tracer compounds for the major SOA precursors
- Determine reaction mechanisms for SOA formation
- Work with the NERL Atmospheric Modeling Division (AMD) to improve treatment of SOA in CMAQ.
- Use the NERL smog chamber to generate atmospherically relevant air mixtures for exposure studies

The haze from Look Rock in the Great Smokey Mountains shows the presence of secondary organic aerosol from photooxidation reactions or ozone reactions with biogenic hydrocarbons.

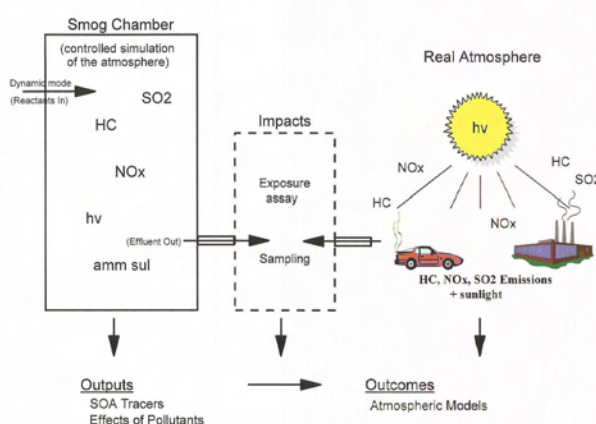


Approach for Research Studies

- Conduct field studies to measure the organic fraction of ambient PM_{2.5}. Identify tracer compounds in the ambient samples, such as those that would be collected from the atmosphere depicted above.
- Conduct laboratory experiments to identify reaction systems responsible for the observed tracer compounds. Use the NERL smog chamber to generate these atmospheres. Establish reaction mechanisms for SOA formation.
- Conduct modeling studies to predict the formation and partitioning of SOA within PM_{2.5}.
- Collaborate with the Atmospheric Modeling Division (AMD) in NERL to incorporate the findings in CMAQ.

The figure below shows graphically the research approach taken to conduct combined field and laboratory studies.

Schematic of Approach for Implementation Studies



Experimental Methods

- Irradiate individual aromatic and biogenic hydrocarbons in the presence of NO_x and SO₂ in the NERL smog chamber and measure their formation SOA masses.
- Analyze chamber SOA samples using LC/MS, derivative-based GC/MS, Ion Trap MS, and MALDI methods to identify SOA tracer compounds.
- Compare chamber composition and concentration data with model predictions whose formation mechanisms include contributions from gas-aerosol partitioning, acid catalyzed reactions, and polymer formation, and others.
- Assess whether tracer concentrations can be used to determine contributions of SOA precursors to ambient PM_{2.5}.

Types of Experiments Conducted

Lab Irradiation Experiments	Field Studies
Toluene/NO _x /SO ₂	RTP, NC 2000 summer
α-Pinene/NO _x /Air + SO ₂	RTP, NC 2003
β-Pinene/NO _x /Air	Baltimore, MD 2001 summer
α-limonene/NO _x /Air	Philadelphia, PA 2001 summer
Isoprene/NO _x /Air + SO ₂	New York City, NY 2001 summer
Toluene/α-Pinene/NO _x + SO ₂	Detroit, MI 2004 summer
α-Pinene/β-Pinene/d-limonene/NO _x	
Isoprene/α-Pinene/NO _x	
Isoprene/α-Pinene/Toluene/NO _x + SO ₂	

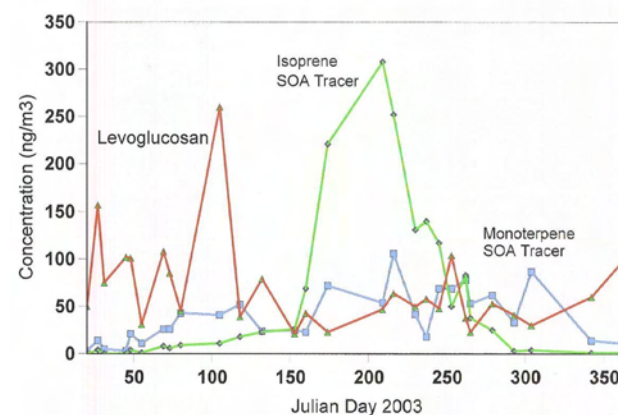
Nature of the Collaborations

- The identification of individual polar organic compounds requires highly specialized instruments and the skill to operate them and interpret the data.
- The identification of tracer compounds requires gas chromatography to measure individual compounds. We currently conduct these measurements for samples taken in the United States. We are collaborating with researchers at the University of Antwerp who are using similar techniques for samples taken in Europe and South America.
- We also have a collaboration with researchers at the California Institute of Technology who are developing techniques using liquid chromatography and mass spectroscopy to measure oligomeric and polymeric components of PM_{2.5}.
- Physical scientists in the Human Exposure and Atmospheric Sciences Division are collaborating with meteorologists in the Atmospheric Modeling Division to incorporate the field and laboratory findings from this study into CMAQ.
- We are working closely with NERL MCEAD in developing MALDI analysis techniques to explore the potential of oligomer formation in the atmosphere.

Results and Conclusions

- Smog chamber irradiations of biogenic hydrocarbons (emitted from trees and other vegetation) and aromatic hydrocarbons (emitted mainly from cars) show that these compound can be converted to SOA by chemical reaction.
- For compounds, such as isoprene and α-pinene, the addition of SO₂ increases the amount of SOA formed above that obtained in its absence.
- Laboratory results suggest that several chemical processes must be included in a model to explain SOA formation. The types of processes that appear to be important include (1) exchange of organic compounds between the gas and particle phases, often referred to as partitioning, (2) acid catalyzed reactions within the particle, (3) polymer formation, and possibly (4) cloud water reactions could be contributing to SOA formation.
- Toluene, α-pinene, and isoprene SOA tracer compounds detected in ambient PM_{2.5} samples collected in the eastern USA indicate these emitted hydrocarbons are contributing to SOA. Analysis of field data suggests that SOA in the summer is significant, but decreases considerably in the colder seasons.
- The figure below shows how the concentrations of the tracer compounds change with season. The isoprene tracer is only seen in the summertime, while the tracer compound for α-pinene is detected in the spring, summer, and fall. Levoglucosan, a primary product from wood combustion, is detected throughout the year but mainly during the winter and spring.

2003 RTP PM_{2.5} Concentrations Data



Outputs, Outcomes and Future Directions

- Continue comparing chamber concentrations and compositions of SOA formed with atmospherically relevant individual and mixtures of hydrocarbons irradiated in the presence of NO_x and SO₂ with model results for proposed SOA formation mechanisms.
- Assess whether SOA yields in complex hydrocarbon mixtures are additive.
- Work with AMD modelers to develop the CMAQ version of the PM chemistry model. Results of the laboratory and field studies are used by AMD in the CMAQ model that will be available to the RPOs for State Implementation Plan modeling studies.
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- Some of the laboratory methods, developed under this program, will be used in EPA-NOAA collaborative research to assess the impact of N₂O₅ reactions on PM_{2.5} nitrate levels.

Disclaimer

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.



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