



What are the Precursors and Formation Processes for Secondary Organic Aerosol ?

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research
and
development

Objectives

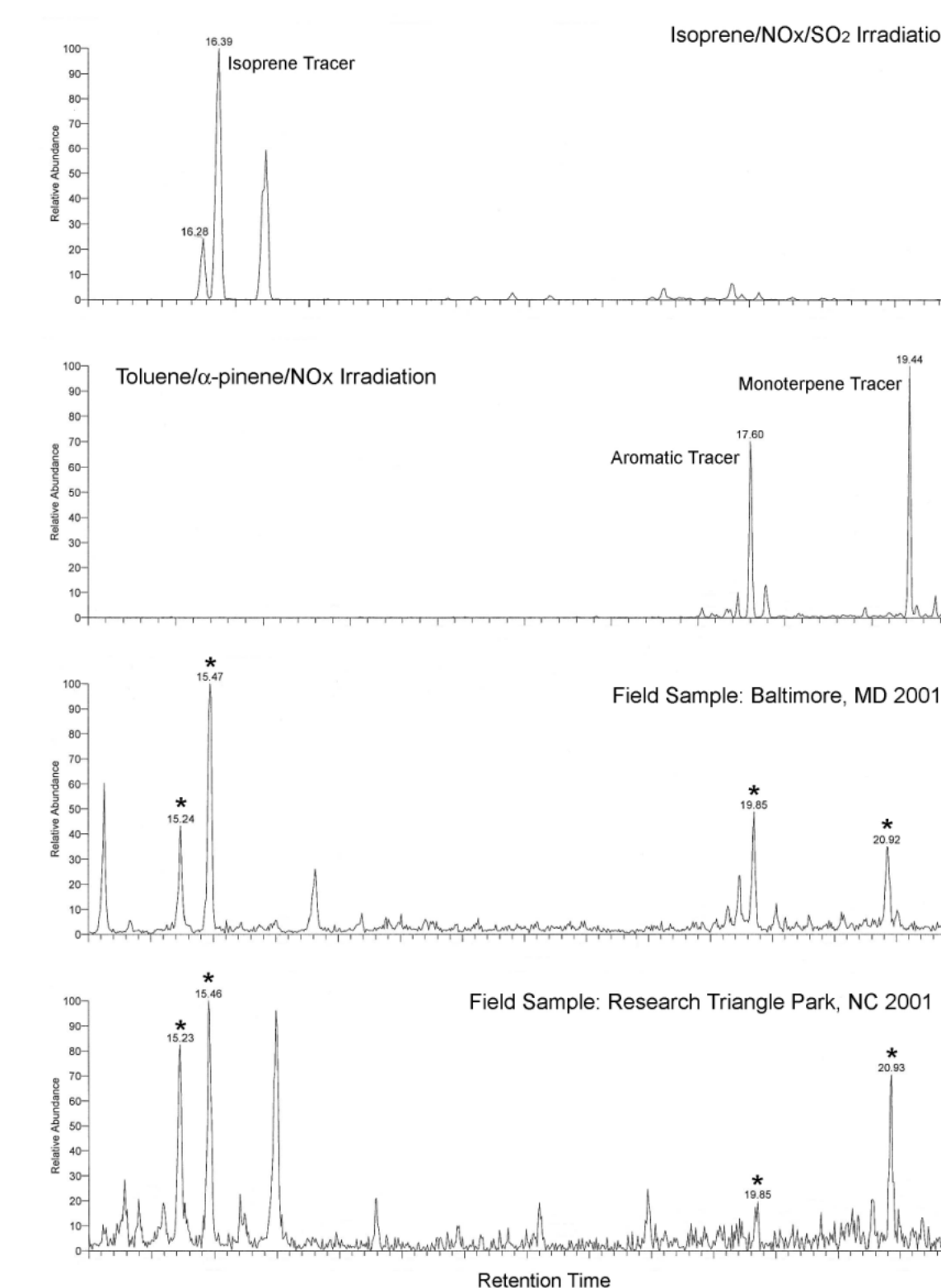
- Identify the major SOA precursors
- Identify tracer compounds for the major SOA precursors
- Determine reaction mechanisms for SOA formation
- Work with the NERL Atmospheric Modeling Division (AMD) to improve treatment of SOA in CMAQ.
- Use the NERL smog chamber to generate atmospherically relevant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

Methods/Approach

- Irradiate individual aromatic hydrocarbons, isoprene, monoterpenes, and sesquiterpenes in the presence of NO_x and SO₂ in the NERL smog chamber and measure SOA yields.
- Analyze chamber SOA samples using LC/MS, derivative-based GC/MS, Ion Trap MS, and MALDI methods to identify SOA tracer compounds.
- Analyze chamber SOA samples using a modified SMPS method to determine their thermal properties.
- Compare chamber composition and concentration data with model predictions whose formation mechanisms include contributions from gas-aerosol partitioning, acid catalyzed reactions, and oligomerization.
- Assess whether tracer concentrations can be used to determine contributions of SOA precursors to ambient PM_{2.5}.
- Based on laboratory and field study results, recommend improvements to AMD for treating SOA formation in CMAQ.

Results/Conclusions

SOA Tracer Compounds from Laboratory and Field Samples



- HC/NO_x/Air results show toluene and α -pinene, β -pinene and *d*-limonene can contribute to SOA formation.
- HC/NO_x/SO₂/Air results for α -pinene demonstrate the addition of SO₂ increases the SOA yield above those obtained in its absence.
- While isoprene/NO_x/air mixtures in the absence of SO₂ produce only very low levels of SOA, in its presence, the yield increases greatly suggesting isoprene could be contributing to summertime SOA.
- Laboratory results suggest traditional reversible gas-aerosol phase partitioning may not be sufficient to explain SOA formation and other mechanisms including (1) acid catalyzed reactions, (2) oligomer formation and possibly (3) cloud water reactions could be contributing to SOA formation.

• Toluene, α -pinene, and isoprene SOA tracers detected in ambient PM_{2.5} samples collected in the eastern USA indicate these hydrocarbons are contributing to SOA. Ongoing analyses of field data suggest the contribution of SOA in the summer is significant, but decreases considerably in the colder seasons.

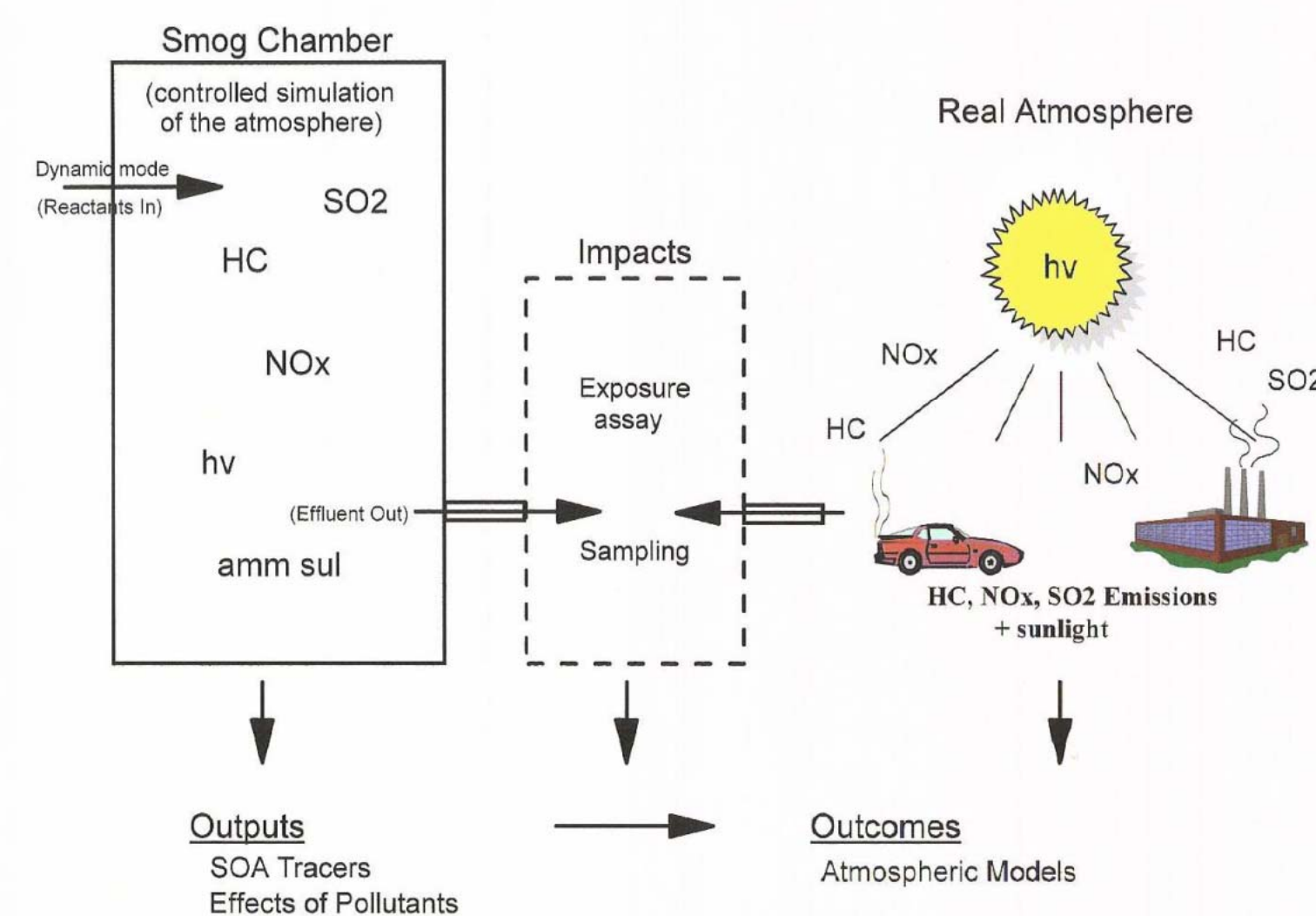
- Our ability to determine the contributions of a particular SOA source to ambient PM_{2.5} samples depends on whether the ratio of the tracer concentration to the SOA for that hydrocarbon, λ , obtained from laboratory irradiation experiments, can be used for ambient samples.

Future Directions

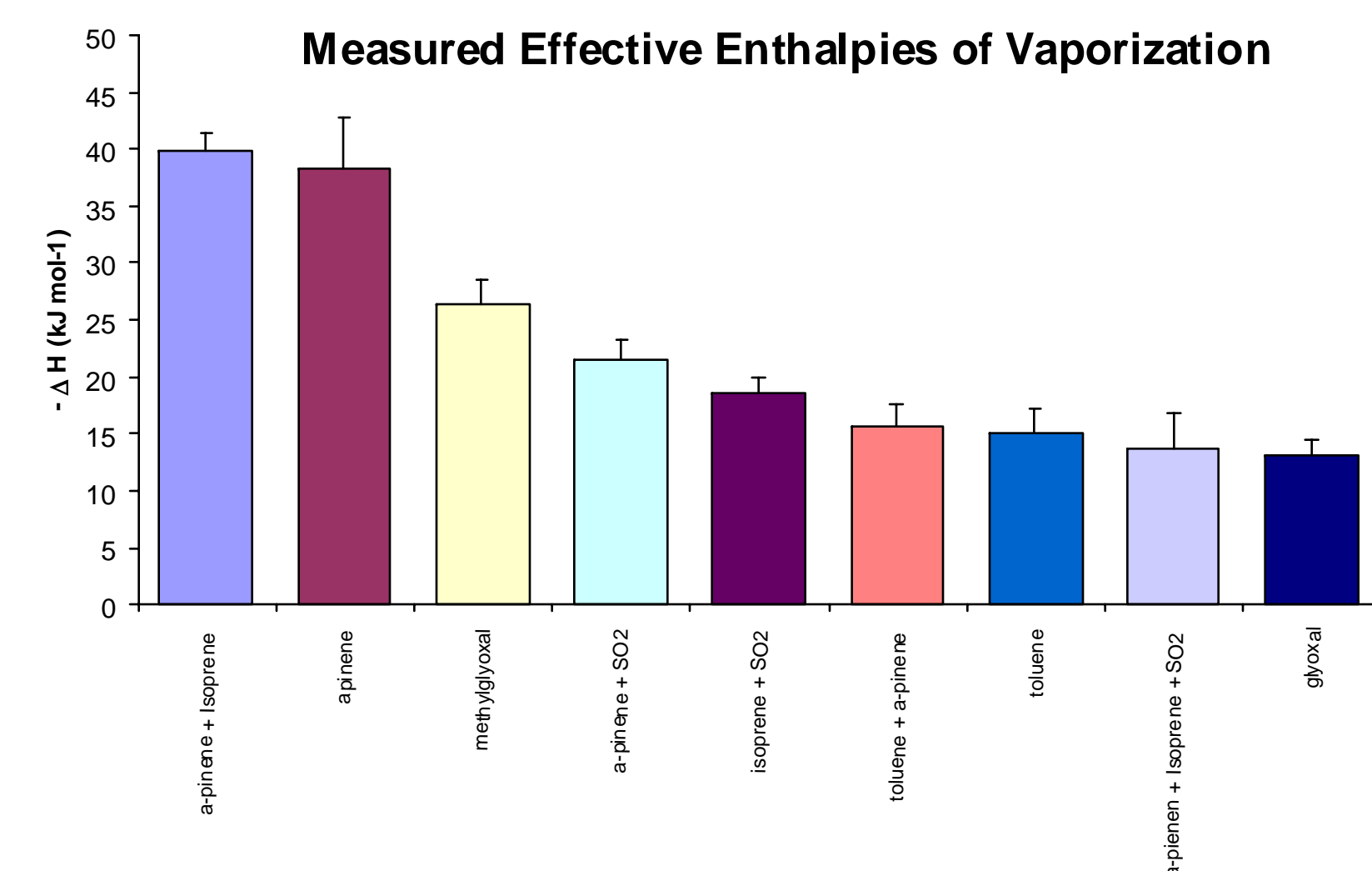
- Continue comparing chamber concentrations and compositions of SOA formed with atmospherically relevant individual and mixtures of hydrocarbons irradiated in the presence of NO_x and SO₂ with model results for proposed SOA formation mechanisms.
- Identify SOA tracer compounds for sesquiterpenes.
- Continue measuring and refining values for λ for SOA precursors and use them to estimate contributions of SOA precursors to ambient PM_{2.5} concentrations.
- Assess whether SOA yields in complex hydrocarbon mixtures are additive.
- Work with AMD modelers to develop the CMAQ version of the PM chemistry model.

Research Approach

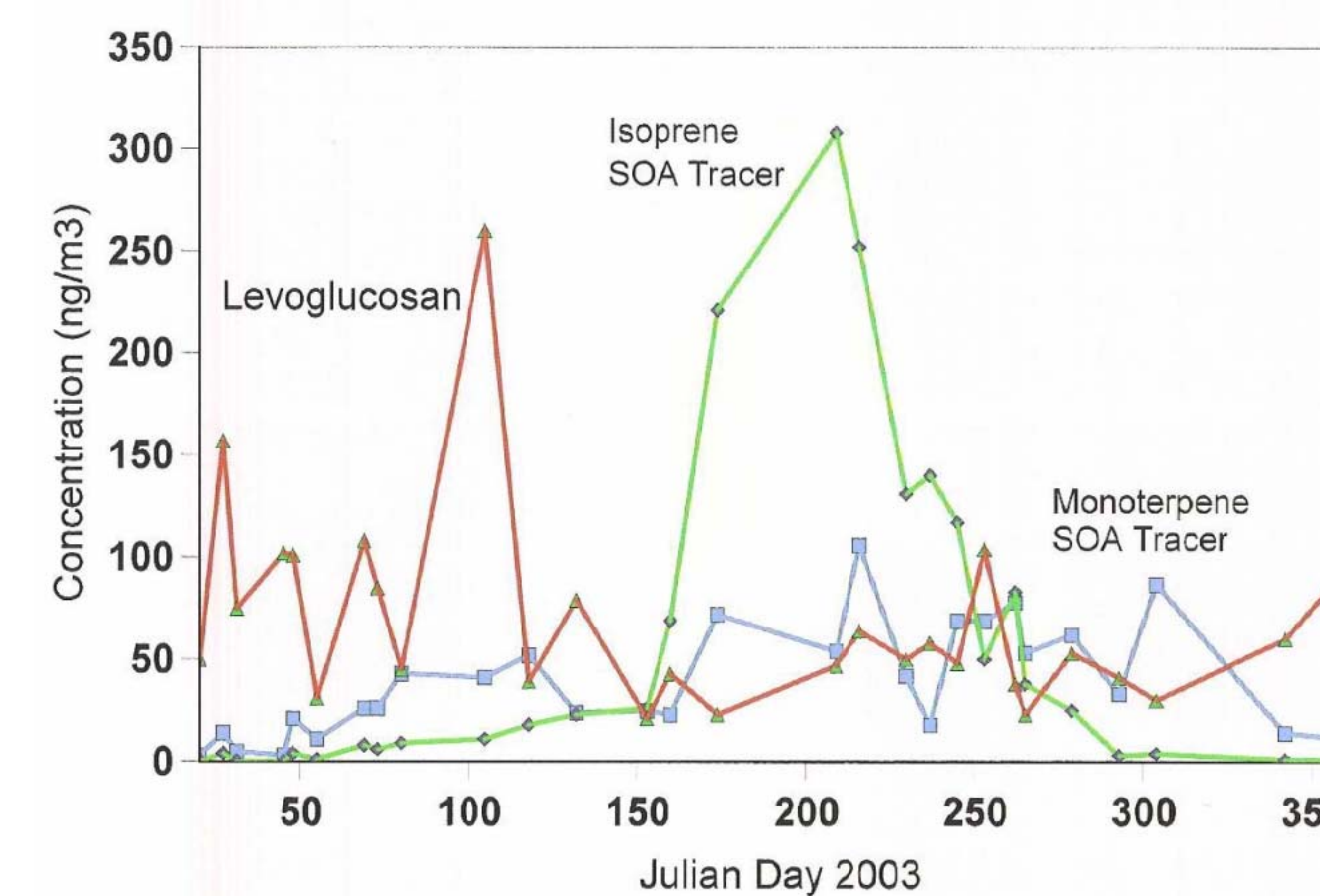
Schematic of Approach for Implementation Studies



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
<i>d</i> -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/ <i>d</i> -limonene/NO _x	
Isoprene/ α -Pinene/NO _x	
Isoprene/ α -Pinene/Toluene/NO _x + SO ₂	



2003 RTP PM2.5 Concentrations Data



Air Quality