Daytime vs. nighttime NOx effects on aerosol formation: Constraints from ambient measurements and chamber studies

Juliane L. Fry, Joshua D. Katz, and Rhiana D. Meade
Chemistry Department, Reed College, Portland, OR, USA

Major results
- SOA yield is greater from O₃ + α-pinene under low-NOx, dark conditions
- In the presence of NOx, SOA yield is greater under dark conditions
- Ambient aerosol functional group characterization is possible using ATR-FTIR
- Organic aerosol functional group composition depends on oxidants and supports NOₓ-initiated nighttime SOA formation

Background: NOx effects on aerosol formation
- Aerosol represents the largest uncertainty in understanding of Earth's climate (IPCC 2007)
- Secondary organic aerosol (SOA) sources are particularly uncertain, with recent estimates ranging from 12 – 70 Tg yr⁻¹ (Kanakidou et al, 2005) to 140 – 910 Tg yr⁻¹ (Goldstein and Galbally, 2007)
- NOx has been shown to both enhance (Ng et al, 2007) and suppress (Presto, et al 2005) SOA formation, depending on the hydrocarbon precursor and relative volatility of products:

  Volatile Organic Compound (VOC)

  \[ \text{Nitrate} \to \text{Oxidant} \to \text{Oxidized SOA} \]

Additional NOx-enhanced SOA formation channel:
- NOx oxidation of hydrocarbons

  \[ \text{NO}_x + \text{Hydrocarbon} \to \text{SOA} \]

  NOₓ-initiated SOA formation has received less attention than other oxidants despite the fact that it accounts for loss of a large fraction of VOCs, especially at night
- \( \text{NO}_x + \text{VOC} \) provides a mechanism that couples an anthropogenic oxidant with biogenic carbon, resulting in a source of modern carbon in OA that only occurs in combustion-influenced aerosols, potentially resolving an apparent paradox in aerosol source attribution (de Gouw, JGR 2005, Volckarner GFL 2005)

Reed College Atmospheric Simulation Chamber
- 430 L rectangular FEP Teflon bag
- Light/Dark, temperature control

Inputs:
- O₃: Prozone air purifier
- Dry air: Sabroe zero air source
- NOx tank
- Hydrodosing: syringe injected into roundbottom, evaporated into chamber

Output measurements:
- [O₃⁻]: Dasibi photometric ozone analyzer
- [NO]: Thermo chemiluminescent NOx analyzer
- Particle concentration and size distribution: Brechtel Scanning Electrical Mobility Sizing system (SEMS)

First chamber experiments: NOx & light effects on SOA formation from O₃ + α-pinene
Under 4 sets of initial conditions, 0.1 mL liquid α-pinene was evaporated into the bag containing ~200 ppb ozone. Ozone loss and particle formation were monitored to assess relative SOA yield.

Ambient measurements of organic aerosol composition by ATR/FTIR
- Filter-collected aerosol is extracted by 24-hour Soxhlet (below) and concentrated by rotary evaporator and N₂ purge
- Extracted, concentrated samples are reconstituted in a small amount of acetone and dropped onto an ATR-FTIR crystal for functional group analysis (right)
- Standard compounds are used to identify peaks (right), then absorbances are scattered against oxidants to assess correlations (bottom)

Quantification of organic functional groups in SOA
- Creation of standard curves using known-functionality compounds will enable quantification of functional group concentrations in ambient aerosol samples. The above were created for ketone and aliphatic CH groups using 2-tridecanone (C₁₃H₂₆O) as a test compound.

Future work
- Standard curve for all SOA components using synthesized multifunctional limonene nitrate:
  - simultaneous standardization of all functional groups
- Compare NOx production of aerosol under light and dark conditions across different biogenic hydrocarbons, including real plant emissions
- Develop method for online measurement of hydrocarbons in chamber experiments
- Collect more day/night aerosol filter samples to verify correlation trends

Contact information
Juliana Fry, jfry@reed.edu

Acknowledgements
Funded in part by a Reed College Science Research Fellowship
Thanks to Linda George (Portland State University) for the loan of the O₃ monitoring equipment