

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

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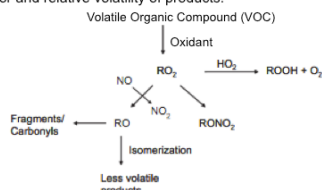
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Major results

- 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 NO₃-initiated nighttime SOA formation

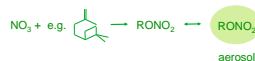
Background: NOx effects on aerosol formation

- Aerosols 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:



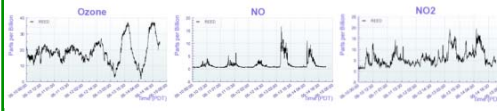
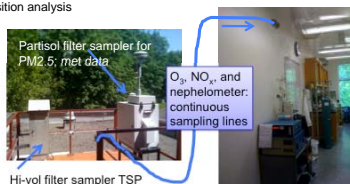
Additional NOx-enhanced SOA formation channel: NO₃ oxidation of hydrocarbons

- NO₃-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
- NO₃ + bVOC 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 airmasses, potentially resolving an apparent paradox in aerosol source attribution (de Gouw, JGR 2005, Volkamer GRL 2005)



Reed College Atmospheric Sampling Site

- Continuous monitoring of O₃, NO, NO₂, and aerosol scattering (bscat)
- 24-hour or 12-hour day/night filter collections of aerosol for offline chemical composition analysis



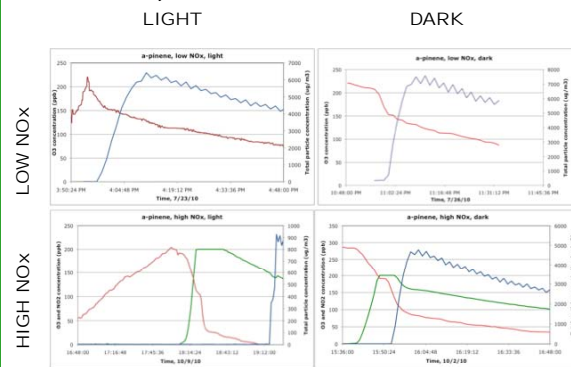
Reed College Atmospheric Simulation Chamber



- 430 L rectangular FEP Teflon bag
- Light/Dark, temperature control
- Inputs:**
 - O₃: Prozone air purifier
 - Dry air: Sabio zero air source
 - NO₂ tank
 - Hydrocarbon: syringe injected into roundbottom, evaporated into chamber
- Output measurements:**
 - [O₃]: Dasibi photometric ozone analyzer
 - [NO], [NO₂]: 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.

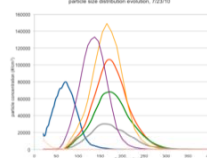


Experiment	Δ O ₃ (ppb)	Δ SOA (μ g/m ³)
Low-NOx, light	100	6000
Low-NOx, dark	80	7500
High-NOx, light	200	900*
High-NOx, dark	100	4800

*The high-NOx, light experiment may have produced more aerosol but SEMS did not initially detect it.

At right: Watching aerosol grow...

Size distribution traces at 16:00 (blue), 16:04 (purple), 16:09 (yellow), 16:33 (red), 17:03 (green), and 18:04 (grey). As SOA material is created and condenses, particles rapidly grow to a mean diameter of 160 nm, then simply dilute.

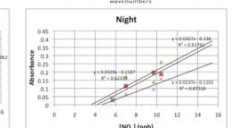
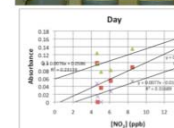
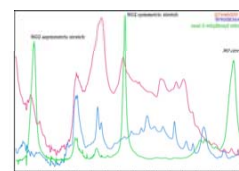
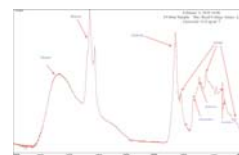


Ambient measurements of organic aerosol composition by ATR/FTIR

- Filter-collected aerosol is extracted by 24-hour Soxhlet (below) and concentrated by rotovap and N₂ purge

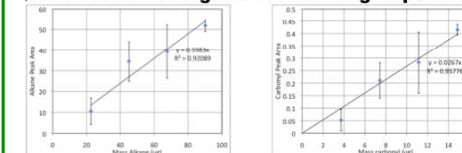
- Extracted, concentrated samples are resuspended in a small amount of acetone and dropped onto an ATR-FTIR crystal for functional group analysis (right)

- Standard compounds are used to identify peaks (right), then absorbances are scattered against oxidants to assess correlations (bottom)



- Correlation of 3 distinct organic nitrate peaks is stronger (R²=0.87 vs. 0.32) and has a steeper slope (0.024 vs. 0.0077) for nighttime samples, corroborating an NO₃-mediated SOA formation pathway

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 CH₂ 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

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