Changes in composition and volatility of biogenic secondary organic aerosol from nitrate radical oxidation during night-to-day transition

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ACM UCDavis
Interactions of NOx and BVOCs – intersection between natural and anthropogenic emissions, air quality and climate change

Edwards et al., Nature Geoscience, 2017
Chamber experiments to explore

1. Chemical composition of NO$_3$-initiated biogenic secondary organic aerosol (BSOA)

2. Changes in the chemical composition of BSOA during dark aging

3. The volatility of BSOA

4. Changes in the chemical composition and volatility of BSOA after turning on the lights
List of experiments and BSOA precursors
Paul Scherrer Institute Simulation Chamber for Atmospheric Chemistry (PSI-SCAC)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Experiment plot symbol</th>
<th>Reacted VOC (ppb)</th>
<th>$\mathrm{O_3/N_2O_5}$ (ppb)</th>
<th>Max. OA load (µg cm$^3$)</th>
<th>SOA yield (%)</th>
<th>Thermodenuder $D_{sel.}$ (nm)</th>
<th>Thermodenuder $C_{sel.}$ (cm$^3$)</th>
<th>Isothermal evaporator $D_{sel.}$ (nm)</th>
<th>Isothermal evaporator $C_{sel.}$ (cm$^3$)</th>
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</table>

Graham et al., EGUsphere, 2022
Instruments and methods

• Chemical ionization mass spectrometer with a filter inlet for gases and aerosols (FIGAERO-CIMS)
• Extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF)
• Volatility tandem differential mobility analyser (VTDMA)
• Isothermal evaporation chambers
Chemical composition of NO$_3$-initiated biogenic secondary organic aerosol (BSOA)

Wu et al., ACP, 2021
Particle-phase reactions during dark aging
Measured volatility of BSOA

Graham et al., EGUsphere, 2022
Volutility distributions derived from the molecular composition

- Parametrizations based on BSOA molecular composition
  - IvWA: Isaacman-VanWertz and Aumont, ACP (2021)
  - PRK: Peräkylä et al., ACP (2020)

Graham et al., EGUsphere, 2022
Comparison of evaporation calculated with a kinetic model to measured evaporation

Grey: Measurements

Graham et al., EGUsphere, 2022
The same after optimizing the nitrate influence in the parametrizations

Graham et al., EGUsphere, 2022
Changes in number and mass during dark-to-light transition

Wu et al., ACP, 2021
Changes in chemistry during dark-to-light transition

- Isoprene tracers $C_{10}H_{17}N_3O_{12,13}$
- $\alpha$-pinene tracers $C_{20}H_{32}N_2O_{8-10}$
- $\beta$-caryophyllene tracers $C_{30}H_{48}N_2O_{8-10}$

Wu et al., ACP, 2021
Changes in volatility during dark-to-light transition

Wu et al., ACP, 2021
Summary

• Composition of NO$_3$-derived SOA from biogenic precursors is dominated by dimers formed through RO$_2$–RO$_2$ reactions under the experiment conditions in this study.

• After formation in the gas phase, dimers will condense to the particle phase, where further reactions will proceed (oxidation, fragmentation, dimer decay to monomers).

• NO$_3$-BSOA of α-pinene is more volatile than the corresponding α-pinene ozonolysis products; nitrate oxidation of β-caryophyllene produces less volatile SOA than α-pinene and isoprene.

• Thorough re-evaluation of the parameters describing the magnitude of the vapor pressure reduction due to nitrogen-containing functional groups is warranted, shifting the volatility distribution from the ELVOC towards the LVOC range.

• 44-60 % of the total signal of isoprene, α-pinene, and β-caryophyllene SOA is sensitive to photolytic ageing. Fragmentation of nitrate groups is not the main loss pathway on the timescale of our experiments, but oligomer fragmentation.