NO₃-initiated oxidation of plant emissions as a source of secondary organic aerosol: Speciated BVOC yield parameterization and policy implications

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Major results

- Chamber experiments show widely varying but strong (0 – 64%) aerosol formation from NO₃ + BVOC
- This variation likely indicates unappreciated regional variation in radiative forcing.
- Future GIS-based work will determine NO₃ BVOC SOA production “hot spots” based on existing tree cover and NOx point source.
- Findings inform regulatory policy regarding sites and operation of NOx point sources.
- Existing tree stock may determine location of new point sources, while both new and existing sources may benefit from planting specific tree species.

Background

NOx radicals provide a mechanism by which NOx can enhance the sink of BVOC (biogenic volatile organic compounds) and source of condensible oxidation products that lead to secondary organic aerosol production. This nighttime chemistry adds to the traditional picture of NOx controlling NOx radical fate, producing organic nitrates and thus affecting the volatility of atmospheric organic gases.

Methods

NCAR community lab chamber experiments

Chamber and free atmosphere chamber experiments: Oct-Nov 2011 (box reactor chamber for NO₃ BVOC)

Chamber experiments (10-12 h) for NO₃ BVOC were done in the laboratory chamber, which was thermostatically controlled with constant temperature of 22 ± 1°C and 22 ± 1°C RH. NO was added to the chamber in constant concentration, while BVOC were added to the chamber (5% NO, 5% NO₂, 5% NO₃, 5% NO₃ + BVOC). BVOC concentrations were added to the chamber in constant concentration, while NO and NO₂ were added to the chamber in constant concentration.

Chamber results show that while the SOA yield from NO₃ + β-pinene, 27%, is in midrange of observed aerosol yields from NO₃ BVOC, the range for other BVOC is wide, from a low of 0% for α-pinene to a high of 63% for limonene and β-pinene. As shown in the table below, global modeling studies typically employ a single yield for NO₃ + all monoterpene, which in the case of Pye et al (shown in the column at right) is based on previously measured yields for β-pinene. This yield number makes the modeled NOx BVOC source comparable to the observed yield for β-pinene.

Preliminary Volatility Basis Set (VBS) fitting of SOA yields

- To quantitatively compare SOA mass yields from the various BVOC, we are in the process of fitting the aerosol mass fraction in each experiment using a volatility basis set of C + 1 (0.1 – 10) µg m⁻³. Below are shown preliminary fit results for two BVOC, derived by using measured NOx decay to determine hydrocarbon reacted in each time step. Limonene appears to yield lower volatility products than β-pinene.

Implications and policy considerations

- Cooling effect of variability in terpenes offers a new point of information in decisions to site and operate sources of NOx.
- Planting tree species that reduce terpene with the optimal reactivity with NOx emissions to mitigate radiative forcing.
- Locations for power plants should consider existing potential for tree cover in combination with strength of NOx emissions and scientific data regarding wind plumes.
- Other known, reliable NOx sources (e.g., diesel engines) should be buffered with appropriate terpene-emitting biomass.
- Implications with regard to urban reforestation efforts – type of trees chosen for planting could have marketability of tree for other uses.

Chamber experiment results

SOA growth rates

- Conducted a series of chamber experiments with 5 (pyrrol and β-pinene) and 15 (pyrrol + 1.5 pmol mm⁻³) of each BVOC + NOx observed oxidation delay, organic nitrate production and evolving aerosol size distribution.
- Observed strong new particle formation events (see left) from all BVOC except α-pinene.
- Aerosol yield varies significantly across BVOC.

Chamber experiment results

SOA growth rates

- At left, time evolution of peak aerosol diameter for all experiments. Note diversity of growth rates. Analyze using the growth equation.

How much could this NO₃ + BVOC source add to U.S. regional climate forcing?

- Pye et al. (2010, left) estimate up to 100% increase in regional surface-level aerosol from oxidation of terpenes when including the NOx oxidation pathway. This analysis uses a 26% mass yield of SOA for all terpenes when oxidized by NO3.
- Based on studies reported here, varying BVOC could result in actual yields from zero (where α-pinene dominates), to double this source estimate (where limonene or β-pinene dominates).

In search of NO₃ BVOC “hot spots”

- Anthropogenic contributions to SOA have been shown in a modeling study (Chung and Seinfeld 2002, above) to result in ~3 W m⁻² regional cooling over the southeastern U.S. and ~0.5 W m⁻² over the northeastern U.S.
- Since NO₃ oxidation may contribute from zero to a doubling of surface SOA, this could add up to ~4 W m⁻² in the southeast and up to ~1 W m⁻² in the northeast. To improve this estimated contribution, speciated BVOC and NOx sources are required.

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