SOA yield from ozonolysis of BVOC at varying NO_2 concentrations

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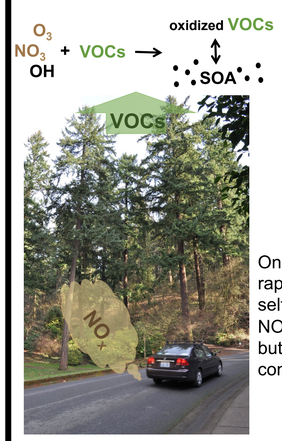
Major results

- NO_x suppresses SOA formation from α-pinene but may enhance SOA formation from other monoterpenes.
- SOA yields vary dramatically from different monoterpenes and different oxidants.
- This significant variation is not currently included in large-scale atmospheric chemistry models; its incorporation could improve predictions of SOA formation.

Background

Secondary organic aerosol (SOA) forms from the reaction of volatile organic compounds (VOCs) with atmospheric oxidants (OH, O_3, NO_3). Some of these oxidized organic products are much less volatile than their precursors and are able to form particles.

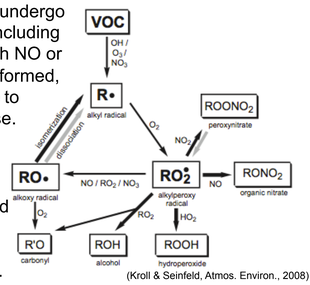


Estimates indicate that close to 90% of global VOC emissions originate from biogenic sources (i.e. trees), but anthropogenic pollution contributes to the majority of the oxidants in the atmosphere. NO_x (NO and NO_2) is formed in the process of combustion and contributes to both O_3 and NO_3 formation:

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$NO_2 + O_3 \rightarrow NO_3^* + O_2$$

*NO_3 is rapidly photolyzed and thus is relevant primarily at night.

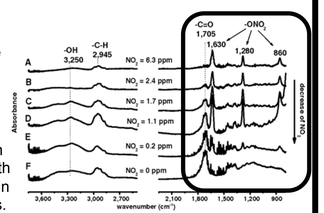
Once VOCs are oxidized, they undergo rapid radical chemistry (right) including self-reactions and reactions with NO or NO_2. A variety of products are formed, but only some of them are able to condense into the particle phase.



(Kroll & Seinfeld, Atmos. Environ., 2008)

Previous studies (Perraud, 2011; Presto, 2005) have observed that NO_2 suppresses SOA formation in the reaction of O_3 with α-pinene, which is taken to be representative of the NO_2 effect on SOA formation from ozonolysis of any monoterpene.

In both cases, the observed results are explained by the formation of organic nitrates ($RONO_2$), which are assumed to be less volatile than some other oxidation products. These organic nitrates can be formed either through RO_2 + NO_x channels or as a direct result of NO_3 oxidation (formed from the O_3 and NO_2 present).



(Right) FTIR spectra of SOA from the Perraud study show an increase in intensity of the three characteristic NO_3 peaks with increasing NO_2 concentration and a simultaneous decrease in intensity of the carbonyl peaks – indicating a shift in products.

(Perraud et al., 2011, PNAS)

Methods

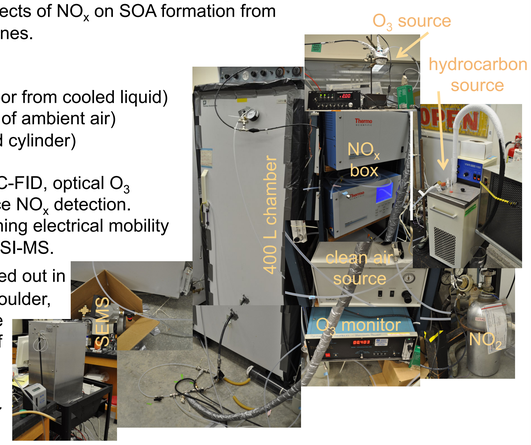
A series of dark chamber experiments were performed in Reed College's environmental chamber (400 L Teflon bag) beginning December 2012 to assess the effects of NO_x on SOA formation from ozonolysis of different monoterpenes.

Reagents include:

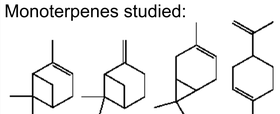
- 300 ppb monoterpene (vapor from cooled liquid)
- 500 ppb O_3 (UV photolysis of ambient air)
- 0-1700 ppb NO_2 (calibrated cylinder)

Reagents are measured using GC-FID, optical O_3 detection, and chemiluminescence NO_x detection. Aerosol is measured with a scanning electrical mobility sizer (SEMS) and offline HPLC-ESI-MS.

Additional experiments were carried out in a 10000 L chamber at NCAR in Boulder, CO using 10-50 ppb monoterpene and comparable concentrations of N_2O_5 as a NO_3 radical source.



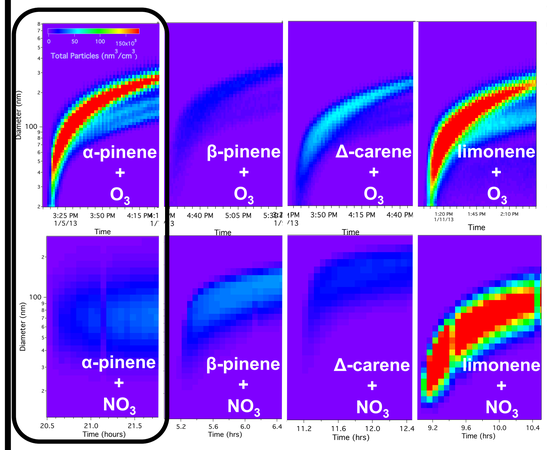
Monoterpenes studied:



These 4 VOCs encompass the dominant monoterpene emissions in the US.

Chamber experiment results

Size Distribution Data:



Aerosol growth curves from chamber experiments for different monoterpenes:

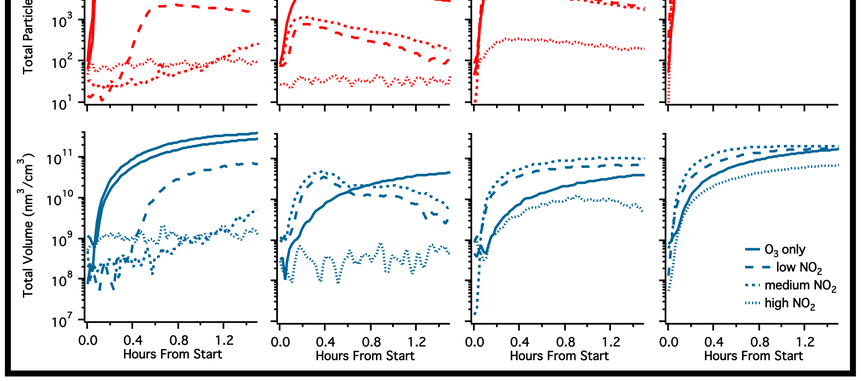
- O_3 experiments used 500 ppb O_3 with 300 ppb VOC
- NO_3 experiments used 50 ppb each of N_2O_5 and VOC and the α-pinene experiment included $(NH_4)_2SO_4$ "seed" aerosol, which did not grow.

Observations:

- **α-pinene makes an especially large amount of aerosol with O_3 and NONE with NO_3.**
- vastly different aerosol yields are observed for different monoterpenes
- endocyclic double bonds (α-pinene and Δ-carene) exhibit higher yields with O_3 oxidant; exocyclic double bonds with NO_3.
- limonene (2 double bonds) makes copious aerosol with either oxidant.

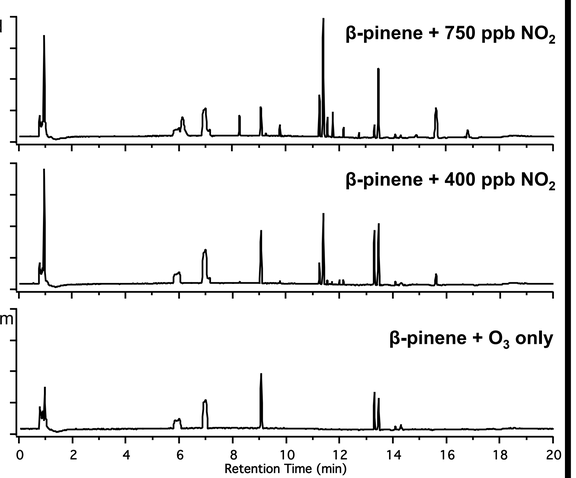
What if the aerosol suppression observed in previous studies is simply an artifact of α-pinene's anomolous behavior when oxidized? ↑ $[NO_2]$ leads to ↑$[NO_3]$ leads to ↓SOA

Number concentrations and derived **particle volume concentrations** are plotted below for all four monoterpenes studied. NO_2 is observed to suppress total number of particles and total mass from **α-pinene** ozonolysis, as observed in other studies. Suppression is observed in total number, but enhancement of total mass is observed for both **β-pinene** and **Δ-carene** with increasing $[NO_2]$. **Limonene** yields are enhanced in both number concentration and mass with the addition of NO_2.



Compositional Data:

- Aerosol samples were collected on filters during each chamber experiment
- Filters were extracted and shipped to CSU for offline analysis by HPLC-ESI-MS
- Qualitative compositional differences are observed in SOA formed from different precursors



(Right) Chromatograms shown from SOA generated from β-pinene ozonolysis at varying $[NO_2]$. As **↑$[NO_2]$** new peaks appear in addition to the ozonolysis peaks.

Ongoing Analysis

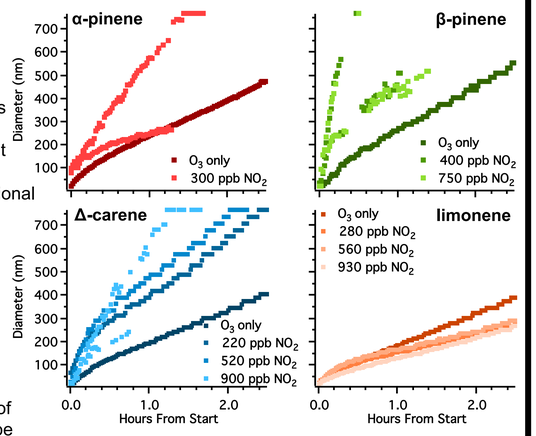
Growth Rates:

- Aerosol growth curves were plotted for each experiment, tracing the diameter at which the peak # concentration occurs
- Growth rates differ drastically for different terpene and oxidant conditions.
- Growth rates should be proportional to the concentration of the gas-phase condensing species (χ_∞) according to the equation:

$$\frac{dD_p}{dt} = \frac{4D_v\chi_\infty F(D_p)}{\rho_p D_p}$$

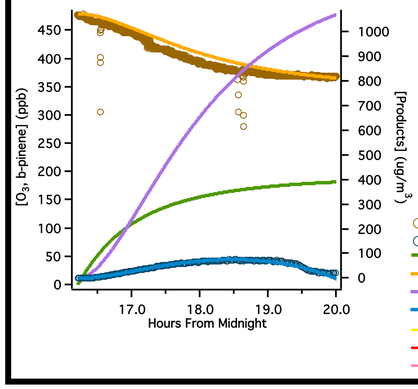
(Brock et al., GRL 2011)

- χ_∞ values provide a kinetically-driven, lower limit constraint on the steady state concentration of condensable vapor, which will be compared to box model simulations.

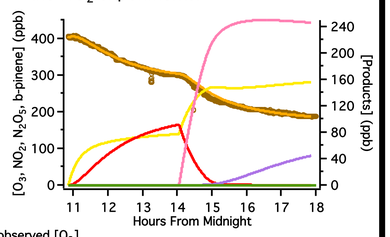


Kinetics Modeling:

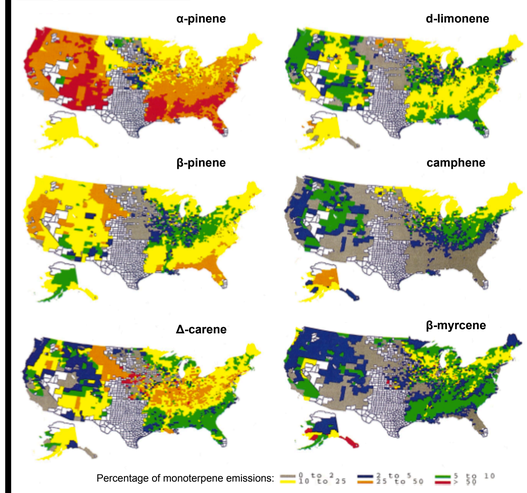
Box model simulation of β-pinene + O_3 experiment. Observed aerosol mass can be fit as a fixed 12% of the total O_3 oxidation products, accounting explicitly for gas and aerosol dilution losses, suggesting a kinetically-driven condensation mechanism.



Box model simulation of gas-phase chemistry in the β-pinene + O_3 + "low" NO_2 experiment. β-pinene introduced at hour 14 Comparing O_3 products and NO_3 products shows the dominance of NO_3 chemistry in the NO_2 experiments.



Implications



(Geron, 2000, Atmos. Environ.)

- NO_x influence on SOA formation from terpenes is much more variable than the accepted suppression theory.
- Map of terpene distribution in the US (left) shows that α-pinene is dominant in many locations, but not everywhere.
- Most large scale regional atmospheric models include a single monoterpene as representative of the class of compounds.
- If NO_x enhances aerosol growth from some monoterpenes but not others, models including only a single monoterpene could be under-predicting SOA formation.
- Could help decrease the gap between modeled and measured SOA.

Acknowledgements

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