New insights into atmospheric particle formation in forests

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BEACHON-RoMBAS field study, July-Aug 2011, Colorado Front Range

Follow-up expts, 2011-2012, NCAR Community Lab Chamber

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SABBATICAL 2011-2012:
NCAR ASP & CIRES/NOAA Visiting Fellow
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Itinerary

• Motivation: aerosol’s role in global climate
  – Secondary organic aerosol (SOA) formation in forests (why focus on biogenic sources?)
  – Human impacts: NOx effects on aerosol formation
• Field evidence of the importance of nitrate-initiated aerosol formation
• Laboratory quantification of aerosol yields from NO$_3$
• Ongoing work at Reed College: chamber & lab studies & ambient measurements to elucidate NOx effects on SOA formation
Particle (="aerosol") hazes in forests

Great Smoky Mountains, Tennessee, USA; wikimedia commons
Aerosols influence regional & global climate

Source: SeaWiFS satellite

Source: Terra/MODIS satellite

http://visibleearth.nasa.gov
Aerosols in the global climate system
Aerosols in the global climate system

What do we need to learn to narrow uncertainties on these aerosol climate forcings?

- Aerosol formation mechanisms & kinetics
- Atmospheric lifetime (loss processes)
- Chemical composition
- Optical properties
- Cloud interactions (hydrosopicity, etc.)
Secondary Organic Aerosol (SOA) formation

Volatile organic compounds (VOCs) \[\rightarrow \cdot \rightarrow \text{oxyVOCs}\]

- \(\text{OH}, \text{O}_3, \text{NO}_3\)

Formation of secondary organic aerosol

- Interesting multiphase chemistry
- Important regional climate forcing
- Organic aerosol contributes 20-50% of total fine aerosol mass at continental mid-latitudes & up to 90% over tropical forests (Kanakidou et al. 2005)
- Models continue to underestimate field-observed organic aerosol (Hallquist et al. 2009)
Why focus on forests?

- *Biogenic SOA may be globally dominant*

Heald et al, 2010: Max continental OA production = 150 Tg C yr$^{-1}$ (+/- 80%)

“Net BSOA could be nearly zero, or it could be as much as 185 Tg C/yr”

Hallquist et al, 2009. Figure follows Goldstein & Galbally, 2007
Why focus on the role of NOx in biogenic SOA formation?

→ We can (in principle) *control* NOx emissions
Why focus on the role of NOx in biogenic SOA formation? ➞ We can (in principle) *control* NOx emissions

- VOCs ➔ OH, O₃, NOx ➔ NOx ➔ oxyVOCs
  
  biogenic VOCs

- anthropogenic NOx

Formation of secondary organic aerosol

Highest [NOₓ] in urban areas:

Whence NOₓ?

Combustion sources:
- vehicles
- power generation

Lightning
Soils

OMI NO₂ column, Aura
What are the possible effects of NO$_x$ on SOA formation?
What are the possible effects of NO$_x$ on SOA formation?

1) [NO] controls fate of RO$_2$ radical
What are the possible effects of NO$_x$ on SOA formation?

1) [NO] controls fate of RO$_2$ radical

2) Adds an additional mechanism of aerosol formation: NO$_3$ + BVOC

NO$_2$ + O$_3$ $\rightarrow$ NO$_3$ + O$_2$

Mostly nighttime b/c NO$_3$ photolyzes rapidly
SOA from NO$_3$ + monoterpenes

- Monoterpane ($C_{10}$ alkenes) emissions are temperature-dependent (not light); therefore also emitted at night
- Reaction with NO$_3$ is much faster than O$_3$ at typical \([\ ]\)’s
- Measured NO$_3$ SOA yields are large (Hallquist et al, ES&T 1999; Griffin et al. JGR 1999, Fry et al ACP 2008, 2011), compared to OH and O$_3$ oxidation, but data is sparse

<table>
<thead>
<tr>
<th>VOC</th>
<th>Rate(NO$_3$+VOC)/Rate(O$_3$+VOC)</th>
<th>North American Emissions, Tg C yr$^{-1}$</th>
<th>RONO$_2$ (molar)</th>
<th>Aerosol (mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-pinene</td>
<td>52</td>
<td>4.5</td>
<td>19%</td>
<td>0.3 - 16%$^H$</td>
</tr>
<tr>
<td>$\beta$-pinene</td>
<td>122</td>
<td>3.2</td>
<td>61%,$^H$ 40%$^F$</td>
<td>10 - 52%,$^H$ 50%$^F$</td>
</tr>
<tr>
<td>$\Delta^3$-Carenne</td>
<td>183</td>
<td>2.0</td>
<td>66%</td>
<td>15 - 62%$^H$</td>
</tr>
<tr>
<td>Limonene</td>
<td>44</td>
<td>0.4 - 1.1</td>
<td>48%,$^H$ 30%$^F$</td>
<td>17%,$^H$ 25-40%$^F$</td>
</tr>
</tbody>
</table>

Calculated @ O$_3$=30 ppb, NO$_3$=20 ppt

Substantial nighttime emissions

Sakulyanontvittaya, ES&T 2008
Spatial patterns of emissions of monoterpenes

Geron et al, Atmos Env 2000
Modeling NO$_3$ + BVOC SOA formation

Chung & Seinfeld, JGR 2002: NO$_3$ + BVOC contributes ~ 1 Tg/yr SOA (9% of total BSOA production)

Pye et al., ACP 2010: NO$_3$ + BVOC contributes 4 Tg/yr SOA (20% of total BSOA production)

With large REGIONAL variability!
Change in organic aerosol loading due to inclusion of NO$_3$ oxidation pathways for BVOC in GEOS-Chem:
> 3 $\mu$g m$^{-3}$ for terpenes over the southeast U.S.

NOTE: these global models use $\beta$-pinene SOA yield parameterization for ALL NO$_3$+terpene reactions!

NO$_3$ BSOA production remains a very underconstrained process!
How do we model SOA formation from individual BVOCs, retaining chemical information?

Calculating SOA yields

Guess/model gas-phase oxidation products and calculate gas/aerosol partitioning with estimated $P_{vap}$'s in the absorptive partitioning formalism:

$$K_p = \frac{F/TSP}{A} = \frac{760 \cdot RT \cdot f_{om}}{MW_{om} \cdot 10^6 \cdot \zeta \cdot P_{vap}}$$

F: aerosol-phase conc.  
A: gas-phase conc.

Partitioning governed by $P_{vap}$

Estimate $P_{vap}$ by “group contribution methods”: start with $C_n$ backbone assumed $P_{vap}$, each functional group lowers $P_{vap}$ by some amount (determined empirically from a large number of compounds)
Back to the big picture: Two mechanisms of NO$_x$ affecting SOA formation

- Do these day & night mechanisms make 2 distinct classes of nitrates, with different consequences for SOA formation?

- Could rapid NO$_3$-initiated chemistry play an important role in new particle growth?
Tools for measuring oxidized N compounds

NO$_3$ PAM chamber

Inlet ovens for TD-LIF meas. of NO$_2$ and gas/aerosol NOy

CRDS meas. of NO$_3$/N$_2$O$_5$
NO$_3$ & N$_2$O$_5$ Cavity Ringdown Spectroscopy (CRDS) Instrument

**NO$_3$:** 662-nm optical extinction
L.O.D. = 0.2 - 3 pptv, 20% Accuracy

**N$_2$O$_5$:** Thermal conversion + 662-nm
L.O.D. = 0.5 - 3 pptv, 10% Accuracy

**Instrument from lab of Steve Brown, NOAA**
Thermal Dissociation – Laser Induced Fluorescence (TD-LIF) measurement of NOy

**TWO MODES OF OPERATION:**

**3-gas mode**
- Ch. 1 @ 30°C Ambient channel: NO₂
- Ch. 2 @ 180°C; \( \Delta_{180-40} = \Sigma PN \)
- Ch. 3 @ 320°C; \( \Delta_{320-180} = \Sigma AN \)
  (denuder bypassed)

**Gas/aerosol mode**
- Ch. 1 @ 30°C Ambient channel: NO₂
- Ch. 2 @ 320°C; \( \Delta_{320-40} = \Sigma PN+\Sigma AN, \text{ gas+aero} \)
- Ch. 3 @ 320°C, denuded; Ch. 3 = \( \Sigma PN+\Sigma AN, \text{ aero only} \)

Instrument loan courtesy Ron Cohen lab, UC Berkeley
Field data: BEACHON-RoMBAS 2011

July – August 2011, campaign studying biogenic aerosol in Colorado pine forest:
http://tinyurl.com/BEACHON2011
Montane ponderosa pine; 8000 ft elevation
BEACHON NO$_2$ measurements: variability

Regular *nighttime* peaks > 2 ppb!
BEACHON NO$_2$ measurements: average diurnal pattern

Campaign average: 7/21/11-8/25/12

Why does NOx peak at midnight?

Fry et al., in prep
Tracer modeling shows origins of nighttime NO$_2$ peaks: transport from Denver, Colo Springs

WRF/Chem model courtesy Alma Hodzic Roux, NCAR
RO$_2$+NO reactions are significant @ BEACHON

Using rates for RO$_2$ = isoprene-O$_2$

\[
[\text{NO}]_{ss} = \frac{j_{\text{NO}_2} [\text{NO}_2]}{k_{\text{NO}+\text{O}_3} [\text{O}_3]}
\]

HO$_2$/RO$_2$ data courtesy Chris Cantrell, NCAR
Higher [monoterpenes] at night; Dominated by a/b-pinene, d-carene.
[Monoterpenes], [MBO] average diurnal pattern

PTR-MS measured monoterpenes (ppb)

Fraction of day

Monoterpenes
MBO

C_{10}H_{16}

PTR-MS measurements (ppb)

Fraction of day

PTR-MS data courtesy Lisa Kaser, Uni Innsbruck
TD-LIF NOy meas: Production of organic nitrates every morning at sunrise (RO$_2$ + NO, R probably MBO-derived)

Fry et al., in prep
Fraction of organic nitrates in AEROSOL phase peaks at night.

Fry et al., in prep.
Oxidation mechanism & the role of NOx: NO$_3$ oxidation of α-pinene

Predicted $P_{vap}$ ≈ $1 \times 10^{-5}$ Torr
-Not much aerosol should form!

Wängberg et al. ES&T 1997
How much (maximum) SOA could this NO$_3$ initiated chemistry produce in the real atmosphere?

**Potential Aerosol Mass (PAM) measurements at BEACHON-RoMBAS:**
Apply a (known) dose of oxidant to ambient air, detect changes in aerosol composition & loading via Aerosol Mass Spectrometer
Potential Aerosol Mass (PAM) from NO$_3$ reactions

- Trap Flow 0-100 SCCM
- Cold Trap -78 °C controllable
- Solid N$_2$O$_5$

N$_2$O$_5$ injection ring

Ambient airflow

N$_2$O$_5$ <-> NO$_3$ + NO$_2$

NO$_3$ + VOC -> products

PAM chamber (15L)

Stainless steel

ToF-AMS

SMPS

Teflon

CRDS (NO$_3$/N$_2$O$_5$)

<- front

back ->
PAM organic aerosol enhancement $f(\text{NO}_3\text{ reacted})$
Are apparent aerosol mass yields from $\text{NO}_3 + \text{monoterpenes}$ reasonable?

Aerosol Mass Yield $\approx 20\%$ for $[\text{MT}] \sim 0.3$ ppb including Org and NO3 mass enhancement.
Compare absolute organic and NO$_3$ enhancement to estimate condensing RONO$_2$ structure

@ nighttime “saturation” point:

\[
\frac{\Delta (\text{organic mass})}{\Delta (\text{NO}_3 \text{ mass})} = \frac{0.2 \mu g}{0.05 \mu g/m^3} = 4
\]

If condensing species is a C$_{10}$ organic nitrate:

+ 5 OH
or +2 COOH

\[
\frac{(\text{org. mass})}{(\text{NO}_3 \text{ mass})} = \frac{153 \frac{g}{mol}}{62 \frac{g}{mol}} = 2.5
\]

\[
\frac{(\text{org. mass})}{(\text{NO}_3 \text{ mass})} = \frac{169}{62} = 2.7
\]

... or there are co-condensing organics along with RONO$_2$
Off to the NCAR community lab to investigate further...
BVOCs studied in NCAR chamber/flow tube

α-pinene  β-pinene  Δ-carene  limonene  β-caryophyllene
Selected chamber results

- limonene
- \( \beta \)-pinene
- \( \beta \)-caryophyllene
- \( \Delta \)-carene

10/3/11
9/28/11
9/22/11
9/19/11
9/15/11

\( \alpha \)-pinene (seeded at 20:30)
$\beta$-pinene: “High” vs “low” [VOC]

$\beta$-pinene chamber expts axes same scaling

50 ppb $\beta$-pinene, $N_2O_5$

10 ppb $\beta$-pinene, $N_2O_5$
Compare $N_{\text{tot}}$ timeseries for all BVOC experiments.
Compare $N_{tot}$ timeseries for all BVOC experiments

The diagram illustrates the total particle concentration (in #/cm$^3$) over time (hours from start) for various BVOC experiments. The largest $N_{tot}$ peaks are observed for $\beta$-caryophyllene and limonene, both with 2 double bonds. The plot is color-coded for different BVOC species and their concentrations, including b-pinene, d-carene, b-caryophyllene, limonene, sabinene, and various combinations with nitric oxide ($NO_3$) and ozone ($O_3$).

- b-pinene high conc
- b-pinene low conc
- d-carene high conc
- d-carene low conc
- b-caryophyllene high conc
- b-caryophyllene low conc
- limonene high conc
- limonene + NO$_3$ low conc
- limonene + O$_3$ + NO$_2$
- sabinene low conc
Compare $V_{\text{tot}}$ timeseries for all BVOC experiments.

![Graph showing the total volume and total mass timeseries for various BVOC experiments.](image)

- seeded a-pinene high conc
- b-pinene high conc
- b-pinene low conc
- d-carene high conc
- d-carene low conc
- b-caryophyllene high conc
- b-caryophyllene low conc
- limonene high conc
- limonene + NO$_3$ low conc
- limonene + O$_3$ + NO$_2$
- sabinene low conc

The graph illustrates the growth of $V_{\text{tot}}$ over time for different BVOC concentrations.

- The largest $V_{\text{tot}}$ growth occurs in all high concentration experiments.
Growth rates for various BVOC + NO$_3$
Compare organic nitrate yields for different BVOC

<table>
<thead>
<tr>
<th></th>
<th>Δ-carene (9/19) 16 ppb</th>
<th>β-pinene (9/28) 41 ppb</th>
<th>limonene (10/3) 40 ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>RONO$_2$ molar yield</td>
<td>25%</td>
<td>20%</td>
<td>40%</td>
</tr>
<tr>
<td>Nitrate fraction of aerosol</td>
<td>~60-70%</td>
<td>~90-100%</td>
<td>&gt;100%!? More functionalized or dinitrates?</td>
</tr>
</tbody>
</table>
Compare SOA mass yields for different BVOC using Volatility Basis Set (VBS) fits to time-dependent yields

\[ Y = \frac{C_{OA}}{\Delta HC} = \xi_1 \alpha_1 + \xi_2 \alpha_2 + \xi_3 \alpha_3 + \xi_4 \alpha_4 \]

\[ \xi_i = \frac{1}{1 + \frac{C_i}{C_{OA}}} \]

**Bins used:**
1: 0.1 ug/m³
2: 1 ug/m³
3: 10 ug/m³
4: 100 ug/m³

C*: saturation concentration of each product bin
### Summary of VBS fitting parameters

<table>
<thead>
<tr>
<th>BVOC</th>
<th>Yield @ 10 μg m⁻³</th>
<th>dDp/dt nm hr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-pinene</td>
<td>27%</td>
<td>20</td>
</tr>
<tr>
<td>Δ-3-carene</td>
<td>21%</td>
<td>21</td>
</tr>
<tr>
<td>limonene</td>
<td>63%</td>
<td>12</td>
</tr>
<tr>
<td>sabinene</td>
<td>17%</td>
<td>21</td>
</tr>
<tr>
<td>β-caryophyllene</td>
<td>64%</td>
<td>14</td>
</tr>
<tr>
<td>α-pinene</td>
<td>0%</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

**Farina et al JGR 2010, NO₃ + monoterpenes**  
12%

**Pye et al ACP 2010, NO₃ + all terpenes**  
26%

**Pathak et al ACP 2007 O₃ + α-pinene**  
32%

- Wide range of SOA mass yields
- Not correlated with growth rate
Neither α-pinene nor β-pinene is a good representative of the monoterpenes for NO$_3$ reactions!

**α-pinene:** ✓ dominant emission globally
   ✗ atypically low SOA yield

**β-pinene:** ✓ Several SOA formation datasets exist (Hallquist, Griffin, Moldanova, Fry)
   ✗ looks like atypically *high* SOA yield for mono-alkene
Why doesn’t NO$_3$ + α-pinene make any aerosol?
Conclusions: FIELD

BEACHON-RoMBAS field study:

- Significant morning production of alkyl and peroxy nitrates is observed in a “remote” forest
  - Not much NOx is needed to make NO$_3$ SOA formation chemistry important!

- Aerosol fraction of nitrates peaks at night, coincident with NO$_2$ peak, suggesting NO$_3$-initiated chemistry produces lower-volatility nitrates than photochemistry

- Apparent “field” NO$_3$ SOA mass yield of ~ 20%, with large variability
Conclusions: LAB

• Chamber studies show wide diversity in aerosol yields and growth rates from NO$_3$ + various BVOC (from 0 to >60%!)

• Dominantly emitted $\alpha$-pinene produces no SOA; model compound $\beta$-pinene has atypically high SOA yield
  
  — Models need to track individual monoterpenes to accurately predict SOA from NO$_3$ reactions.
  
  — Our ‘conventional wisdom’ that NOx suppresses SOA formation may be due to overuse of $\alpha$-pinene as a representative monoterpene
Ongoing work

• Test suppression vs. enhancement of SOA formation from $O_3 +$ various BVOC, at varying $[NO_2]$ at Reed Environmental Chamber

• Analyze chemical composition of particles offline with FTIR (Reed) and HPLC-ESI-MS (collaboration with D. Farmer, Colorado State Univ.)

$\leftarrow$ do the analog of this with $\beta$-pinene, $\Delta$-carene, limonene, etc.

Perraud et al., PNAS 2012
Reed College Environmental Chamber

- 430 L rectangular FEP Teflon bag
- *Light/Dark, temperature control*

**Inputs:**
- \(O_3\): Prozone air purifier
- Dry air: Sabio zero air source
- \(NO_2\) tank
- Hydrocarbon: syringe injected into roundbottom, evaporated into chamber

**Output measurements:**
- \([O_3]\): Dasibi photometric ozone analyzer
- \([NO], [NO_2]\): Thermo chemiluminescent NOx analyzer
- Particle concentration and size distribution: Brechtel Scanning Electrical Mobility Sizing system (SEMS)
Sample growth event: $O_3 + \alpha$-pinene with oxalic acid seed particles

- Monitor gas-phase oxidation products during SOA formation
- Filter-collect SOA for offline analysis
Ongoing work, cont’d

• Quantitatively analyze organic nitrate component of ambient SOA, with focus on day vs. night, seasonal changes (FTIR)

• Assess mechanistic reasons for high SOA yield from NO$_3^-$-initiated reactions by probing gas-phase BVOC products (GC-FID) and oligomerization in model systems (liquid chromatography)
FTIR functional group analysis of extracted aerosol samples

Soxhlet extracted into acetone/dichloromethane/hexane solvent mix, ATR-FTIR
Observed correlation of organic nitrate & level of oxidation with $[\text{NO}_2]$}

More RONO$_2$ in higher-NO$_x$ days’ aerosol: *suggests* nitrate enhancement

Positive correlation between NO$_x$ and “level of aerosol oxidation”
Quantify FTIR-measured organonitrate aerosol; look for day/night differences in correlation

Created FTIR standard curve by synthesizing:

![Chemical Structure](image)

**Graph:**
- **Title:** Summer [RONO2] vs. [NO2]
- **X-axis:** [NO2] ppb
- **Y-axis:** [RONO2], µg/m³ (1.630 cm⁻¹)
- Points for day and night are plotted.
- Day points are blue diamonds.
- Night points are red squares.
In search of evidence for oligomerization

O3 + a-pinene SOA on various seeds:
H$_2$SO$_4$ final (072412 Ac p.d); NH$_3$ seed (081412 NH3 Seed p.d); NH$_3$ final (081712 NH3 p.d)
Thanks!

NCAR ASP & CiRES fellowships

The whole BEACHON-RoMBAS 2011 Team

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Laura Krause (‘13), Danielle Draper (‘13) & Josh Katz (‘12), Reed College

Steve Brown

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John Ortega

Paul Winkler

Pete Edwards & Bill Dube

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