Nitrate radical initiated atmospheric particulate matter formation in forests:
Anthropogenically-triggered biogenic aerosol production

Juliane L. Fry, Associate Professor of Chemistry & Environmental Studies, Reed College, Portland, OR SEAS, Harvard University, 2. Mar 2018
What’s to come in this talk:

• Why do we think that NO$_3$ chemistry is an important contributor to secondary organic aerosol (SOA) formation?

• Two short stories about NO$_3$ + BVOC SOA formation:
  – Estimating SOA yields from NO$_3$ + isoprene based on nighttime aircraft power plant plume transects during SENEX 2013
  – Resolving the mystery of α-pinene’s anomalously low NO$_3$ SOA yield with computational comparison of RO$_2$ fate from NO$_3$ + α-pinene vs. NO$_3$ + Δ-carene
Global organic carbon budgets and biogenic SOA

Emissions 1350 TgC/yr

- Primary Anthropogenic: 5 TgC/yr
- Primary Biomass: 11 TgC/yr
- Ox Low Volatility Anth.: 5 TgC/yr
- Ox Low Volatility Bio.: 14 TgC/yr
- Anth SOA: 10 TgC/yr
- BB SOA: 17 TgC/yr

BSOA: 88 TgC/yr

Ox. to CO + CO₂: 400 TgC/yr

Particle Deposition: 150 TgC/yr

Vapor Deposition: 800 TgC/yr

MEGAN model estimates 760 TgC yr⁻¹ global BVOC emissions, of which >60% is isoprene:

=> Which biogenic VOC precursors?

Hallquist et al., ACP 2009

Sindelarova et al., ACP 2014
Oxidation of isoprene & monoterpenes ($C_{10}$ BVOCs)

$$\text{O}_3 + \text{NO}_3 + \text{OH} \rightarrow \text{oxidized VOCs}$$

BVOCs:

- isoprene
- α-pinene
- β-pinene
- Δ-carene
- limonene

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$$
$$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$$
$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$$
$$\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}$$

*NO$_3$ is rapidly photolyzed and thus active primarily at night

BVOC lifetimes w.r.t. each oxidant

<table>
<thead>
<tr>
<th>BVOC</th>
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@ “typical” conc’s: 12-h daytime avg [OH]: 2x10$^6$ #/cm$^3$; 24 h avg [O$_3$]: 7x10$^{11}$ #/cm$^3$; 12 h nighttime avg [NO$_3$]: 5x10$^8$ #/cm$^3$ = 20 ppt (Atkinson & Arey, 2003)
Oxidation of isoprene & monoterpenes ($C_{10}$ BVOCs)

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \\
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \\
\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}
\]

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SOA from isoprene & monoterpenes (C\textsubscript{10} BVOCs)

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]
\[ \text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O} \]

*NO\textsubscript{3} is rapidly photolyzed and thus active primarily at night

BVOC lifetimes w.r.t. each oxidant

<table>
<thead>
<tr>
<th>BVOC</th>
<th>OH</th>
<th>O\textsubscript{3}</th>
<th>NO\textsubscript{3}</th>
<th>OH</th>
<th>O\textsubscript{3}</th>
<th>NO\textsubscript{3}</th>
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<td>1.4 hr</td>
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<td>2%\textsuperscript{K}</td>
<td>1%\textsuperscript{KL}</td>
<td>10%\textsuperscript{N,R}</td>
</tr>
<tr>
<td>α-pinene</td>
<td>2.7 hr</td>
<td>4.7 hr</td>
<td>5.4 min</td>
<td>8%\textsuperscript{E}</td>
<td>10%\textsuperscript{S}</td>
<td>0%\textsuperscript{F14}</td>
</tr>
<tr>
<td>β-pinene</td>
<td>1.9 hr</td>
<td>1.1 day</td>
<td>13 min</td>
<td>3%\textsuperscript{G}</td>
<td>20%\textsuperscript{vH}</td>
<td>50%\textsuperscript{F09}</td>
</tr>
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<td>40%\textsuperscript{F11} 170%\textsuperscript{B}</td>
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SOA yields (@ ~10 ug m\textsuperscript{-3})

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5x10\textsuperscript{8} #/cm\textsuperscript{3} = 20 ppt (Atkinson & Arey, 2003)
SOA from isoprene & monoterpenes (C_{10} BVOCs)

\[
\text{NO}_3 + \text{BVOCs} \rightarrow \text{SOA}
\]

**BVOC lifetimes w.r.t. each oxidant**

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<th>OH</th>
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**SOA yields (@ ~10 ug m^{-3})**

- Conditions may not be representative of the real atmosphere (walls, no background OA, other radicals)
- Typically limited to < a few hours of SOA aging

*NO_3* is rapidly photolyzed and thus active primarily at night

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References:

- Kroll, EST 2006
- Eddingsaas ACP 2012
- Griffin JGR 1999
- Yu JAC 1999
- Kleindienst, GRL 2006
- Shilling, ACP 2008
- von Hessberg, APC 2009
- Leungsakul ES&T 2009
- Ng et al, ACP 2008
- Rollins ACP 2009
- Fry ACP 2009
- Fry ACP 2011
- Fry EST 2014
- Boyd et al., EST 2017
Regional modeling & organonitrate aerosol observations show NO$_3$ oxidation is an important source of SOA.

- Adding NO$_3$ + BVOC SOA to a regional model increases surface OA in the southeastern US substantially (1-2 μg m$^{-3}$).

- AMS observations: organic nitrates 5-12% of total OA (5 μg m$^{-3}$ at SOAS)

=> Which BVOCs? Monoterpenes / isoprene?

Pye et al, ES&T 2015; Xu et al, ACP 2015
Can diurnal patterns in AMS factors give clues about SOA sources?

Data from SOAS ground site, Xu et al., PNAS 2015
Short story #1: Assess $\text{NO}_3 + \text{isoprene}$ SOA yield from aircraft measurements in regions of rapid $\text{NO}_3$ oxidation of isoprene: power plant plumes.
SENEX 2013: 21 research flights

Power plant plume transects during July 2, 2013 night flight

- Power plants are largest source of residual layer NO$_x$
- BVOC are titrated in narrow, concentrated plumes:

$$P_{NO_3} = k_{NO_2 + O_3}(T) \cdot [NO_2][O_3]$$

(Subset of flight)
Aircraft plume transects

Big differences in ammonium and sulfate aerosol produced in different plumes.
Screening plumes: Verify that aerosol increases were produced only by NO$_3$ + isoprene

(1) is all of the NO$_3$ reactivity in plumes due to reaction with isoprene? ✔ Based on observed isoprene: monoterpene ratio and known rate constants, yes.

(2) is all of the change in aerosol organic mass concentration during these plumes due to NO$_3$ + isoprene reactions?

(1) is all of the change in aerosol nitrate mass concentration due to NO$_3$ + isoprene reactions?
(2) is all of the change in **aerosol organic mass concentration**
during these plumes due to NO$_3$ + isoprene reactions?

- Organic:nitrate mass increase ratio in plumes is noisy, avg ~ 5
- What kind of isoprene organic nitrate molecular structure would have this Org:NO$_3$ ratio?

\[
\text{ONO}_2 \quad \text{HOO} \\
\text{ONO}_2 \quad \text{OOH}
\]

\[
\text{Org:NO}_3 = 1.6
\]

\[
\text{ONO}_2 \quad \text{HOO} \\
\text{ONO}_2 \quad \text{OOH}
\]

\[
\text{Org:NO}_3 = 2.7 \quad \Rightarrow \text{Would need 10 (!) more O’s on this molecule to get Org:NO}_3 \text{ to 5!}
\]

\[
\Rightarrow \text{Or, co-condensing organics? Loss of NO}_3 \text{ functional groups?}
\]
Screening plumes: Verify that aerosol increases were produced only by NO$_3$ + isoprene

(1) is all of the NO$_3$ reactivity in plumes due to reaction with isoprene? ✔ Based on observed isoprene: monoterpene ratio and known rate constants, yes.

(2) is all of the change in aerosol organic mass concentration during these plumes due to NO$_3$ + isoprene reactions? ✗ Based on very high Org:NO$_3$ ratios and correlation with total aerosol mass, likely other organics contribute

(1) is all of the change in aerosol nitrate mass concentration due to NO$_3$ + isoprene reactions?
(3) is all of the change in aerosol nitrate mass concentration due to NO₃ + isoprene reactions?

Previous studies report NO₂⁺:NO⁺ ratios for organic nitrates typically 2–3 times lower than for NH₄NO₃ (Fry et al., 2009, 2011; Bruns et al., 2010; Farmer et al., 2010; Liu et al., 2012); this can be used to apportion organic (pRONO2) vs. inorganic (NH₄NO₃) nitrate. **Conclusion: no sign of significant inorganic nitrate interference in plumes.**
Screening plumes: Verify that aerosol increases were produced only by NO₃ + isoprene

(1) is all of the NO₃ reactivity in plumes due to reaction with isoprene?

✔ Based on observed isoprene: monoterpene ratio and known rate constants, yes.

(2) is all of the change in aerosol organic mass concentration during these plumes due to NO₃ + isoprene reactions?

✗ Based on absurd Org:NO₃ ratios and correlation with aerosol mass, likely other organics contribute

(1) is all of the change in aerosol nitrate mass concentration due to NO₃ + isoprene reactions?

✔ Based on NO⁺:NO₂⁺ ratios, all increase is organic nitrate (& pRONO₂ is separable)

\[ Y_{SOA,mass} = \frac{(pRONO₂_{plume} \pm SD_{pRONO₂plume}) - (pRONO₂_{bkg} \pm SD_{pRONO₂bkg})}{-[isop_{plume} \pm SD_{isopplume}) - (isop_{bkg} \pm SD_{isopbkg})]} \times 3 \times \frac{329\text{ppt}}{\mu g \, m^{-3}} \]

3: nitrate mass + associated organics, assumed to be approximately double the nitrate mass.
Requires ~4 additional oxygens: e.g. a tri-hydroperoxynitrate
Observed SOA yields are large; higher at longest plume ages

<table>
<thead>
<tr>
<th>plume number</th>
<th>plume time (UTC)</th>
<th>SOA molar yield (fraction) [± SD]</th>
<th>SOA mass yield (fraction) [± SD]</th>
<th>plume age from O₃/NO₂ clock assuming S=1 (hours)</th>
<th>Likely NOx origin &amp; altitude (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7/2/13 2:18</td>
<td>0.09 [0.05]</td>
<td>0.25 [0.14]</td>
<td>2.5</td>
<td>Greene County @ 540 m</td>
</tr>
<tr>
<td>2</td>
<td>7/2/13 2:20</td>
<td>0.07</td>
<td>0.21</td>
<td>1.5</td>
<td>ibid</td>
</tr>
<tr>
<td>3</td>
<td>7/2/13 2:21</td>
<td>0.12 [0.10]</td>
<td>0.32 [0.27]</td>
<td>1.5</td>
<td>ibid</td>
</tr>
<tr>
<td>4</td>
<td>7/2/13 3:03</td>
<td>0.13</td>
<td>0.36</td>
<td>1.5</td>
<td>Gaston @ 720 m</td>
</tr>
<tr>
<td>5</td>
<td>7/2/13 3:55</td>
<td>0.06 [0.07]</td>
<td>0.17 [0.20]</td>
<td>1.4</td>
<td>Miller / Gorgas @ 690 m</td>
</tr>
<tr>
<td>6</td>
<td>7/2/13 4:34</td>
<td>0.05 [0.02]</td>
<td>0.15 [0.07]</td>
<td>2</td>
<td>ibid</td>
</tr>
<tr>
<td>7</td>
<td>7/2/13 4:37</td>
<td>0.10 [0.11]</td>
<td>0.26 [0.31]</td>
<td>5.5</td>
<td>ibid</td>
</tr>
<tr>
<td>8</td>
<td>7/2/13 4:39</td>
<td>0.16 [0.10]</td>
<td>0.45 [0.26]</td>
<td>5.8</td>
<td>Miller / Gorgas @ 1120 m</td>
</tr>
<tr>
<td>9</td>
<td>7/2/13 5:04</td>
<td>0.28 [0.14]</td>
<td>0.77 [0.39]</td>
<td>6.3</td>
<td>Gaston @ 1280 m</td>
</tr>
</tbody>
</table>

Chamber-based SOA mass yield estimates: 12-14% (Ng et al., 2008; Rollins et al., 2009)

Plume age estimates based on O₃/NO₂ ratio clock and model

=> What yield number *should* be used in models?
What isoprene products are likely contributing to SOA?

Likely 1\textsuperscript{st}-generation product: Based on ground contribution method (Pankow & Asher, 2008) $P_{\text{vap}}$, predicted C*: O:C elemental ratio (excluding NO$_3$):

\begin{align*}
\text{ONO}_2 \\
\text{ONOO} \quad 2.5 \times 10^4 \, \mu g \, m^{-3} \\
\text{ONO}_2 \\
\end{align*}

0.4

Possible 2\textsuperscript{nd}-generation products:

\begin{align*}
\text{OOH} \\
\text{ONO}_2 \quad 0.38 \, \mu g \, m^{-3} \\
\end{align*}

Or:

\begin{align*}
\text{OOH} \\
\text{ONO}_2 \quad 0.20 \, \mu g \, m^{-3} \\
\end{align*}

0.8

\textbf{This suggests that 1\textsuperscript{st} generation products cannot contribute, but 2\textsuperscript{nd}-gen can No oligomerization required} 1.2
Could NO$_3$ + isoprene products be a significant contributor at surface?

O:C elemental ratio (excluding NO$_3$):

- 0.4
- 0.8
- 1.2

Data from SOAS ground site
Xu et al., PNAS 2015
Could NO$_3$+isoprene products be a significant contributor to organic aerosol at the surface?

MO-OOA was 39% of total OA at SOAS

And it sure looks like an isoprene product

O:C elemental ratio (excluding NO$_3$):

- 0.4
- 0.8
- 1.2

Xu et al. speculated that LO-OOA factor was due to NO$_3$+ terpene products @ SOAS

Xu et al., PNAS 2015
Conclusions about NO$_3$ + isoprene SOA yields

- NO$_3$ + isoprene yields assessed from aircraft measurements increased with plume age, to as much as 10x (!) the typically assumed yield in models.
- This reaction may contribute substantially to an identified organic aerosol factor comprising 40% of total OA at the surface (measured at the SOAS ground site in central Alabama).
- In warm, rapidly industrializing regions of the world where isoprene emissions are large and NO$_x$ emissions are on the rise (e.g. parts of China, India), this SOA source may be increasing.
Plans for summer 2018 SAPHIR chamber NO$_3$ + isoprene SOA study

- Detailed investigation of NO$_3$ + isoprene reaction mechanism under atmospheric conditions
  - Compare O$_3$ vs NO$_3$
  - Compare initial RO$_2$ reactions: RO$_2$ vs. HO$_2$
  - With/without seed aerosol, varying pH?
- 30 July – 26 August 2018 @ Jülich, Germany
Short story #2: What about SOA produced from NO$_3$ + monoterpenes?

A puzzle about large differences in SOA yield for very similar looking monoterpene precursors

0% SOA yield vs. 50% SOA yield

α-pinene vs. Δ-carene

H-shifts auto-oxidation products (HOMs)

Fragmentation products

Isomerization products

Oxidant=NO$_3$

HO$_2$

RO$_2$

ROOH + O$_2$

ROOR + O$_2$

Q can be RO$_2$, HO$_2$, NO$_3$, NO...

Q'
Observation #1a: SOA mass yield for $O_3 + BVOC$ at varying $[NO_2]$ is suppressed by $NO_2$ **only** for $\alpha$-pinene

Draper et al., ACP 2015
Observation #1b: Product mass distributions measured by offline HPLC-ESI-MS differ at high m/z

Draper et al., ACP 2015; collaboration with Delphine Farmer and Yury Desyaterik (CSU)
**Observation #2: α-pinene vs. Δ-carene SOA yield difference is **NOT **affected by RO₂ reaction partner, inorganic seed**

<table>
<thead>
<tr>
<th>No.</th>
<th>Regime</th>
<th>SOA yield (AMS)</th>
<th>NO₃:Org</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>NO₃+RO₂</td>
<td>3%</td>
<td>0.08</td>
</tr>
<tr>
<td>14</td>
<td>RO₂+RO₂, seeded</td>
<td>1%</td>
<td>0.10</td>
</tr>
<tr>
<td>17</td>
<td>HO₂+RO₂</td>
<td>2%</td>
<td>0.17</td>
</tr>
<tr>
<td>11c</td>
<td>RO₂+RO₂</td>
<td>27%</td>
<td>0.09</td>
</tr>
<tr>
<td>13</td>
<td>NO₃+RO₂</td>
<td>35%</td>
<td>0.15</td>
</tr>
<tr>
<td>16</td>
<td>HO₂+RO₂, seeded</td>
<td>37%</td>
<td>0.12</td>
</tr>
<tr>
<td>18c</td>
<td>RO₂+RO₂, seeded</td>
<td>40%</td>
<td>0.06</td>
</tr>
<tr>
<td>19</td>
<td>HO₂+RO₂, seeded</td>
<td>25%</td>
<td>0.14</td>
</tr>
<tr>
<td>22c</td>
<td>RO₂+RO₂</td>
<td>104%</td>
<td>0.07</td>
</tr>
<tr>
<td>23</td>
<td>HO₂+RO₂</td>
<td>21%</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Observation #3: NO$_3$ + α-pinene under high [HO$_2$] shows low yield of ROOH “termination” channel, high yield of pinonaldehyde

=> Seems reasonable that this high-volatility favored channel would result in low SOA yield. But, why doesn’t Δ-carene similarly yield primarily caronaldehyde and thus have low yield?

Tran Nguyen, Becky Schwantes, Paul Wennberg @ CIT
Pawel Misztal & rest of the PTR-ToF-MS crew @ FIXCIT campaign
First attempts to calculate nitrooxy-RO₂ structures using Spartan

Δ-carene

α-pinene

_Hypothesis:_ Δ-carene nitrato-RO₂ can rapidly auto-oxidize to yield low-volatility products...

...while in α-pinene nitrato-RO₂, no H-abstraction is possible, because of structural constraints

_Could this be the reason for α-pinene’s anomalous behavior?_
Upping the computational game with the COPENHEL supergroup: Calculating reaction barriers for each RO₂’s options

1. The rates for all accessible H-shift reactions are below $10^{-4}$ s⁻¹ for both monoterpenes.

=> The peroxo radicals thus have lifetimes long enough to undergo bimolecular reactions, which occur on a timescale of ~ 0.01 and 100s
Upping the computational game with the COPENHEL supergroup: Calculating reaction barriers for each RO$_2$’s options

1. The rates for all accessible H-shift reactions are below $10^{-4}$ s$^{-1}$ for both monoterpenes.

2. However, the alkoxy-forming pathway is thermodynamically accessible for both monoterpenes.

=> What is the fate of these nitrooxy-alkoxy radicals (RO·) from $\alpha$-pinene and $\Delta$-carene?
Calculated bond scission reaction barriers for alkoxy radicals

Calculated reaction barriers in kcal mol\(^{-1}\) (zero-point corrected ωB97X-D/aug-cc-pVTZ electronic energy differences between the lowest-energy transition states and reactants)

Based on these different bond scission pathways, α-pinene will produce primarily pinonaldehyde...

Volatile => low SOA yield

...while most \( \Delta \)-carene will retain the nitrate group and may go on to later-generation H-shifts

\[ \text{Caronaldehyde} \]

\[ \text{\( \Delta^1 \)-carene} \]

\[ \text{R1a} \rightarrow \text{+NO}_3 \]

\[ \text{R1b} \rightarrow \text{+NO}_3 \]

\[ \text{R2} \rightarrow \text{+O}_2 \]

\[ \text{R3} \rightarrow \text{H-shifts} \]

\[ \text{R4} \rightarrow \text{Bimolecular} \]

\[ \text{R5a} \rightarrow \text{+NO}_2 \]

\[ \text{R5b} \rightarrow \text{+O}_2 \]

\[ \text{R6} \rightarrow \text{H-shifts} \]

\[ \text{H-shifts} \]

=> Successive H-shifts can produce highly oxidized molecules which contribute to high (org.nit-containing) SOA yield

Conclusions on molecular structure and \( \text{NO}_3^- + \text{monoterpenes} \) SOA

- Different preferred alkoxy scission pathways may explain huge SOA yield difference between \( \alpha \)-pinene and \( \Delta \)-carene

- Unfortunately, this means one can’t really lump monoterpenes in SOA mechanisms
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