DO YOU KNOW THE WAY TO SOA?

(1) WINTER ANTHROPOGENIC SOA    (2) SUMMER BIOGENIC SOA
(3) ANTHROPOGENIC EFFECTS ON BIOGENIC SOA

Joel Thornton
Department of Atmospheric Sciences
University of Washington

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joelt@uw.edu
OA CONTRIBUTION TO E. U.S. SURFACE PM2.5

The chart shows the PM$_{2.5}$ concentration (μg m$^{-3}$) for different years and seasons:
- **2007 Summer**: total PM$_{2.5}$ = 4.3 μg m$^{-3}$, with SO$_4^{2-}$ = 1.2, NO$_3^-$ = 0.3, NH$_4^+$ = 0.6, OA = 1.8, BC = 0.7, Other = 0.7.
- **2015 Summer**: total PM$_{2.5}$ = 2.7 μg m$^{-3}$, with SO$_4^{2-}$ = 1.2, NO$_3^-$ = 0.3, NH$_4^+$ = 0.6, OA = 1.8, BC = 0.7, Other = 0.7.
- **2007 Winter**: total PM$_{2.5}$ = 1.9 μg m$^{-3}$, with SO$_4^{2-}$ = 1.2, NO$_3^-$ = 0.3, NH$_4^+$ = 0.6, OA = 1.8, BC = 0.7, Other = 0.7.
- **2015 Winter**: total PM$_{2.5}$ = 1.9 μg m$^{-3}$, with SO$_4^{2-}$ = 1.2, NO$_3^-$ = 0.3, NH$_4^+$ = 0.6, OA = 1.8, BC = 0.7, Other = 0.7.
WHAT DRIVES WINTERTIME OA OVER EASTERN U.S.?

Implement SIMPLE SOA Scheme

AVOC co-emitted w/CO (80 g/kg)

AVOC + OH $\rightarrow$ ASOA

Shah et al GRL 2019

Hodzic & Jimenez 2011
WHAT DRIVES WINTERTIME OA OVER EASTERN U.S.?

- Net OA growth downwind of emissions due to anthropogenic SOA (ASOA) formation
- Winter SOA rate of growth remarkably similar to observed summer time values
- Simple scheme does quite well at reproducing near-surface SOA abundance and distribution

Shah et al GRL 2019
See also Schroeder et al JGR 2018
\[ \frac{d[SOA]_{ox}}{dt} = Y_{ox} k[VOC][Ox] - \left( \frac{1}{\tau} \right)[SOA_{ox}] - U \cdot \nabla[SOA_{ox}] \]
WHAT DRIVES SUMMERTIME OA IN THE SE U.S.?

Kim et al ACP 2015
SOURCE APPORTIONMENT FROM ON-LINE SOA COMPOSITION

a) gas-phase

b) particle-phase

Tofwerk HRTToF-CIMS

Lopez-Hilfiker et al AMT 2014

Monocarboxylic acids only
SOURCE APPORTIONMENT
COMPOSITION BASIS SETS

- >18 “basis set” HR mass spectra, $\chi_i$, from chamber expts
  - MT, Isop, SQT, aromatics, OH, $O_3$, NO$_3$, ...
  - >180 unique molecular compositions
  - Explain ~80% of detected OA mass in SOAS

- Field-derived spectra, $X(t)$, fit by linear combination of basis spectra $\chi_i$
  - $X(t) = \sum_i \alpha_i(t)\chi_i$
CHEMICAL PATHWAY APPORTIONMENT

MT + hv
OH/O₃/NO
~3.5 days

MT + OH
low NO

MT + O₃
low NO

O₃
low NOₓ

MT + dark

Biomass Burning
substituted aromatics

IEPOX
reactive uptake

MT-RO₂ + NO

Isoprene

dark O₃ + NO₂ (NO₃)
w/photo-oxidation

See also Haofei Zhang et al PNAS 2018
CHEMICAL PATHWAY APPORTIONMENT

- MT-RO₂ + NO
- Biomass Burning (substituted aromatics)
- IEPOX reactive uptake
- MT + hv OH/O₃/NO ~3.5 days
- MT + O₃ low NO
- MT + OH low NO
- O₃ low NOₓ
- dark O₃ + NO w/photo-oxidation
- Isoprene
  - Fires Primary (10%)
  - Anthropogenic Secondary (19%)
  - Isoprene Low NO (16%)
  - Monoterpenes High NO (12%)
  - Isoprene High NO (26%)
  - Anthropogenic Primary (9%)
  - Monoterpenes Low NO (8%)
“Typical” chamber experiments did not explain observed composition nor volatility

...requires coupled (simultaneous) oxidation over days timescales

Fresh (local) dynamic SOA mixed with aged/aging SOA
Simple, nearly chemistry-free SOA schemes capture wintertime OA evolution
- See also S. Pai and C. Heald’s work (ACPD)

Problems w/simple schemes: policy relevant questions related to trends and co-emitted pollutants (NO_x, SO_2, VCP, T, ...)

Possible Progress: winter focused campaigns allow isolation of anthropogenic VOC → SOA (much lower BVOC)
SUMMARY

- Dominant role for “synergistic” multi-day oxidation of monoterpenes dominates summertime SOA in rural SE US location
  - Clouds? High NOx isoprene?
  - Supports use of 2-D VBS type schemes with dynamic aging of both gas and particle components

- Possible Progress:
  - Observational network of online composition
  - Parameterizations for prompt/efficient MT SOA formation via autoxidation combined with aging
ANTHROPOGENIC PERTURBATIONS TO MT SOA

Primary OA

Absorptive partitioning

C-C bond fragmentation

MT SOA

MT + hv
OH/O_3/NO
~3.5 days

MT-RO_2 + NO

MT + OH
low NO

MT+O_3
low NO

O_3
low NO_x

dark O_3 + NO_x(NO_x)
w/photo-oxidation

Isoprene

Biomass Burning
substituted aromatics
IEPOX
reactive uptake

MT + dark

NO_x
ANTHROPOGENIC EFFECTS ON BIOGENIC SOAS

Pye et al, PNAS 2019
B-PINENE SOA AGING

OH scavenger added

$\Sigma$OA / AMS SO$_4$

normalized signal

desorb T (°C)

hours since start

0 5 10 15 20 25 30 35 40

nC = 8
nC = 10
nC = 13
nC = 16
nC = 17
nC = 18
nC = 19
ANTHROPOGENIC PERTURBATIONS TO MT SOA

- A fraction MT peroxy radicals undergo autoxidation

- Autoxidation promptly forms low volatility (SOA-forming) products

- Autoxidation potentially suppressed by NOx
  Praske, et al 2018
ANTHROPOGENIC PERTURBATIONS TO MT SOA

Pye et al, PNAS 2019
PREDICTED TRENDS IN MT AUTOXIDATION PRODUCTS
Recent work suggests ~20% of MT + OH reaction undergoes autoxidation at 0.3 to 3 s\(^{-1}\).

Y. Zhao et al 2018; L. Xu et al 2019

Equivalent to 0.3 to 1 ppb NO
AUTOXIDATION IS A MAJOR PATH TO MT SOA

- CMAQ and common explicit schemes do not reproduce SOA magnitude, volatility, nor oxidation extent without autoxidation.

<table>
<thead>
<tr>
<th>Model</th>
<th>$f_{\text{autox}}$</th>
<th>Yield$_{\text{SOA}}$</th>
<th>O:C</th>
<th>nC</th>
<th>C*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% by mole</td>
<td>% by mass</td>
<td>mol mol$^{-1}$</td>
<td>-</td>
<td>μg m$^{-3}$</td>
</tr>
<tr>
<td>MCM v3.3.1</td>
<td>0</td>
<td>&lt;1</td>
<td>0.59</td>
<td>8</td>
<td>104</td>
</tr>
<tr>
<td>Regional CTM</td>
<td>0</td>
<td>7</td>
<td>0.52</td>
<td>8</td>
<td>55</td>
</tr>
<tr>
<td>HOM mechanism</td>
<td>3.3</td>
<td>17</td>
<td>0.64</td>
<td>10</td>
<td>1.3</td>
</tr>
<tr>
<td>Observed</td>
<td>≥2.4</td>
<td>12 ± 4.6</td>
<td>0.68</td>
<td>9</td>
<td>0.08</td>
</tr>
</tbody>
</table>
ANTHROPOGENIC PERTURBATIONS TO MT SOA

Primary OA

MT SOA

NO$_x$

Absorptive partitioning

C-C bond fragmentation

Autoxidation suppression
THE CHALLENGE: PRECURSORS-PATHWAYS-VOLATILITY

\[
\frac{d[SOA]_{ox}}{dt} = Y_{ox}k[VOC][Ox] - \left(\frac{1}{\tau}\right)[SOA_{ox}] - U \cdot \nabla[SOA_{ox}]
\]

SOA Contribution \( \propto \frac{[C^V_i]}{C^*_i} \)
IEPOX SOA PATHWAYS AND FEEDBACKS
EVOLUTION OF IEPOX-SOA
AMS VS FIGAERO-CIMS

a) SOAS

b) BAECC (daytime only)
ANTHROPOGENIC SOURCES
Sulfate, NOx, organic molecules

BIODIC SOURCES
SOA precursors, e.g. Isoprene

Feedback effects
CLIMATE
Sensitivity to greenhouse gases
Radiative forcing

AEROSOL-CLOUD INTERACTIONS
AEROSOL-RADIATION INTERACTIONS

INTERACT
Secondary Organic Aerosols (SOAs)

SOA PROPERTIES
Semi-solid phase
Liquid phase
Volatility
Ambient T, RH

New particle formation
Growth/evaporation kinetics
Heterogeneous/multiphase chemistry

Lifetime
CCN number
Optical properties
Hygroscopicity

Laboratory studies
Modeling insights
Field studies
FIGAERO-IODIDE CIMS COMPARED TO AMS

slope=0.64  $R^2=0.8$

See, e.g., Lopez-Hilfiker et al AMT 2016
DATA SETS OF SIMULTANEOUS COMPOSITION & VOLATILITY

Biogenic Aerosols-Effects on Clouds and Climate (BAECC)
Hyytiälä, Finland spring/summer 2014
Boreal forest, mostly conifers

Southern Oxidant Aerosol Study (SOAS)
Centreville, AL in Summer 2013
Mixed broadleaf & conifers

Felipe Lopez-Hilfiker
Ben Lee
Emma D’Ambro
Claudia Mohr

SOAFFEE Chamber Expts
John Shilling (PNNL)
CHEMICAL PATHWAY APPORTIONMENT

AMS PMF
- Isoprene derived: 3%
- Biomass Burning
- MO-OOA
- LO-OOA: 73%

Hu et al, ACP 2016
Xu et al, PNAS 2014
BAECC (HYYTIÄLÄ) REACTIVITY

- BVOC + OH:
  - a-pinene: 39%
  - b-pinene: 9%
  - carene: 20%
  - camphene: 8%
  - limonene: 2%
  - isoprene: 2%

- BVOC + O3:
  - a-pinene: 18%
  - b-pinene: 0%
  - carene: 2%
  - camphene: 2%
  - limonene: 4%

- BVOC + NO3:
  - a-pinene: 78%
  - b-pinene: 4%
  - carene: 5%
  - camphene: 11%
  - limonene: 4%
  - isoprene: <1%
DISCUSSION: UNIQUENESS OF PATHWAY

- \(\alpha\)-pinene + OH
- \(\alpha\)-pinene + OH + L\_O\_3 + L\_NO\_x
- \(\alpha\)-pinene + OH + M\_O\_3 + M\_NO\_x
- \(\alpha\)-pinene + OH + H\_O\_3 + H\_NO\_x
- \(\alpha\)-pinene + OH + M\_O\_3
- \(\alpha\)-pinene + O\_3 (dark)
- \(\alpha\)-pinene + O\_3 + NO\_x (dark)
- Isoprene + OH + H\_NO\_x
- Isoprene + OH + L\_NO\_x
- IEPOX + aqueous acidic seed
- “BB” derived from residuals
DISCUSSION: UNIQUENESS OF “α-PINENE”

<table>
<thead>
<tr>
<th>Monoterpene</th>
<th>a-pinene</th>
<th>b-pinene</th>
<th>carene</th>
<th>limonene</th>
<th>camphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula:</td>
<td>$C_{10}H_{16}$</td>
<td>$C_{10}H_{16}$</td>
<td>$C_{10}H_{16}$</td>
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<td>$C_{10}H_{16}$</td>
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SOAS FIGAERO-CIMS FACTORIZATION

Day factor

Night factor 1

Night factor 2

Biomass burning

C_{7.4}H_{12.3}N_{0.9}O_{5.1}

C_{9.9}H_{15.2}N_{0.9}O_{7.8}

C_{8.5}H_{12.5}N_{0}O_{5.5}

C_{7}H_{10.5}N_{0}O_{6.7}
OXIDANTS/AGING/PEROXY RADICAL FATE

UV on

UV off

2xτ

O3 (ppb) NO2 (ppb)

OH (× 10^-6 cm^3)

NO (ppb)

α-p reactivity

RO2 fate

PINAL (ppt S^-1)

fraction α-p reacted

C10 H16 O5
C10 H18 O6
C10 H16 O6
C10 H16 O4
C8 H12 O5
C8 H12 O5
C8 H12 O5
C8 H12 O5
C8 H10 O5
C8 H10 O5
C7 H10 O5
C7 H10 O5
C7 H10 O5
C7 H10 O5
C7 H10 O5
C7 H10 O5
C10 H14 O6
C10 H14 O6
C10 H16 O4
C10 H16 O4
C10 H16 O4
C10 H16 O4
C10 H16 O4
C10 H16 O4

Red: OH
Green: O3
Blue: NO3
Dark blue: HO2
Turquoise: NO
Yellow: RO2
Purple: isom
DISCUSSION: AGING/VOLATILITY (SOAS)
DISCUSSION: AGING/VOLATILITY (HYYTIÄLÄ)

The graph shows the normalized signal as a function of temperature (°C) across different aging conditions. The conditions are as follows:

- Chamber, no aging
- Chamber + 6hr aging
- Chamber + 24hr aging
- Ambient

The signal is plotted on the y-axis, with temperature on the x-axis. The graph illustrates how the signal changes with temperature under different aging conditions.
SECONDARY ORGANIC AEROSOL (SOA) - IMPORTANCE

Spracklen et al ACP 2011
NITROGEN OXIDES AFFECT OH AND O₃
NITROGEN OXIDES AFFECT OH AND AUTOXIDATION
If autoxidation is important, SOA formation rates should be sensitive to local perturbations in oxidants.

Crounse et al JPC 2011
Ehn et al Nature 2014