Rethinking SOA growth and removal in 3D models based on explicit chemistry

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Objective:
• Develop new parameterizations that can capture the SOA production and solubility predicted by an explicit chemical mechanism (GECKO-A)
Secondary Organic Aerosols

- Dominance of organic aerosols (30-70%)
- Scattering (and absorbing?)
- Direct & indirect forcing on climate

-> formation mechanisms are complex and unconstrained
-> removal mechanisms rely mainly on aerosol wet deposition, others not quantified
How important is anthropogenically controlled SOA?

- **Spracklen et al., 2011**: Top-down using AMS & C\textsuperscript{14} obs
  - Production: 100 Tg yr\textsuperscript{-1} (anth. Controlled)
  - Direct forcing: -0.26 ± 0.15 Wm\textsuperscript{-2}
  - Indirect: -0.60 ± 0.24 Wm\textsuperscript{-2}

- **Jo et al., 2013**:
  - Production: 88 Tg yr\textsuperscript{-1}
  - Direct forcing: -0.28 Wm\textsuperscript{-2}

- **Carlton et al., 2010**: 50% of biogenic SOA in the USA is anthropogenically controlled

=> Larger effect than in Smith and Bond, [2013]

Organic Carbon Direct Forcing

No SOA in those runs!!
Inconsistent with the abundance of SOA
Explicit model GECKO-A suggests growth of anthropogenic SOA

- GECKO-A suggests a strong multiday growth for anthropogenics, which is not in 3D models.
- Need to re-evaluate the radiative impact of anthropogenic sources vs. preindustrial
What is in current 3D models (gas-phase)?

**Solubility – log(H)**

- **SOA**
- **SVOC<sub>i</sub>**
- **SVOC<sub>n</sub>**
- **VOC**
- **CO + CO<sub>2</sub>**

**Volatility log(C*), ug/m³**

- **Lifetime**: 5-15 days
- **?????????**
- **~ Weeks**

**2-products**

- **VOC**
- **+OH, O<sub>3</sub>**

**Volatility Basis Set**

- **with AGING (ARTIFICIAL)**
- **Made up to increase mass double counting!!!**

**Equation:**

\[ k = 10^{-11} \]
2-product vs. VBS in CAM-chem

Boundary layer SOA predicted from various approaches in CAM4

2-product model

<table>
<thead>
<tr>
<th>Burden</th>
<th>0.8 Tg</th>
<th>0.67 Tg</th>
<th>1.18 Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>30.2 Tg/year</td>
<td>30.3 Tg/year</td>
<td>67.1 Tg/year</td>
</tr>
<tr>
<td>Lifetime</td>
<td>9.7 days</td>
<td>8.1 days</td>
<td>6.4 days</td>
</tr>
</tbody>
</table>

⇒ Changes in SOA lifetime when the burden is increased

(courtesy of Yiqi Zheng, Yale)
2-product vs. VBS in CAM-chem

Comparison with surface AMS global data

- Current Models can adjust the mass to match SOA observations
- Future predictions of anthropogenically controlled SOA won’t be better constrained (courtesy of Pengfei Yu, CU)

Comparison with aircraft data (e.g. Texas-AQ)

- Current Models can adjust the mass to match SOA observations
- Future predictions of anthropogenically controlled SOA won’t be better constrained
Global model intercomparison study for OA

[Tsigaridis et al., ACPD]

=> Large variability in 3D models

=> Need to better constrain SOA production and removals
How do current parameterizations compare to explicit models?

GECKO-A (NCAR / CNRS, France) idealized runs:

1. Unconstrained SOA yields

- $\alpha$-pinene (low-NOx)

<table>
<thead>
<tr>
<th>Model</th>
<th>SOA (ng/m$^3$)</th>
<th>Time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GECKO-A full chemistry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VBS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VBS with ageing</td>
<td></td>
<td></td>
</tr>
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</table>

- Toluene (low-NOx)

<table>
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<tr>
<th>Model</th>
<th>SOA (ng/m$^3$)</th>
<th>Time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GECKO-A static fit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GECKO-A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Too Volatile oxidation products (will evaporate with Temp. and dilution)

<table>
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<th>Model</th>
<th>SOA (ng/m$^3$)</th>
<th>Time (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VBS (Lane et al. 2008)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VBS with ageing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GECKO-A</td>
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</tr>
</tbody>
</table>
Fitting a reduced mechanism to GECKO-A outputs

- Idealized simulation for α-pinene + OH

**Static Yields** -> parameterize GECKO overall yields for a given precursor

\[ \text{C}_{10}\text{H}_{16} + \text{OH} \rightarrow 0.13 \text{gas1} + 0.02 \text{gas2} + 0.01 \text{gas3} + 0.012 \text{gas4} + 0.07 \text{gas5} + 0.045 \text{gas6} \]

⇒ Easy to implement into 3D models, and should capture the regional SOA mass production suggested by GECKO-A
WRF-Chem simulations of surface SOA (June, 2010)

- VBS with ARTIFICIAL ageing of anth/biog
- GECKO – static fit

**Obs (IMPROVE sites)**

<table>
<thead>
<tr>
<th>Org. Carbon ($\mu g/m^3$)</th>
<th>10</th>
<th>8</th>
<th>6</th>
<th>4</th>
<th>2</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>model (WRF-Chem)</td>
<td></td>
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**Model Performance**

- **VBS**
  - $R^2 = 0.51$
  - NMB = 18%

- **GECKO**
  - $R^2 = 0.51$
  - NMB = 0.3%
GECKO-A vs. current parameterizations

WRF-Chem: SOA domain-averaged vertical profiles (June, 2010)

GECKO-A and VBS with ageing
- can provide similar mass,
- but proportions of anthropogenic and biogenic species are different
⇒ Will predict different future!
Condensable organic compounds are highly water soluble

[Hodzic et al. GRL submitted]

- Organic vapors dry and wet deposit depending on their solubility (Henry’s law coef.)
- Solubility is unknown for condensable organic vapors
- Crudely represented in 3D models (as HNO₃ H=10⁵ M/atm)
SOA removal mediated by dry & wet deposition of condensable vapors

Summer surface concentrations (VBS with ageing)

anthro. SOA

biog. SOA

Accumulated deposition

[Hodzic et al. GRL submitted]
Summary and ongoing work

Regional SOA growth & removal

- strong growth for anthropogenic precursors
- highly soluble oxidation products sensitive to dry and wet deposition

=> need to re-estimate the radiative impact of anthropogenic sources

Current parameterizations VBS vs. explicit modeling

- VBS with aging can be tuned to represent SOA observations however,
  ageing ARTIFICIAL not constrained by chamber experiments,
- GECKO-A predicts less volatile, and more soluble species than VBS

Fitting parameterizations to GECKO-A

- simple static fit for yields compares well with data, but needs more testing
  at both regional (WRF-chem) and global (CESM) scales.
- parameterization of the water solubility provides a constraint on the removal
Should we still worry about Organic Aerosols impact on climate?

No SOA in these runs!!

[Smith and Bond, 2013]
Should we still worry about Organic Aerosols impact on climate?

[Image: Global Aerosol Forcing (RCP4.5)]

[Carslaw et al. 2013]
How large is the anthropogenically controlled SOA?

Simple estimate from SOA - Ox Correlations

Slopes from 30 to 160 µg m\(^{-3}\)/ppm

~25 ppb O\(_3\) change (NH preindustrial to present):
- Slopes imply 0.75 to 4 µg m\(^{-3}\)
  ~ 0.3 - 2.0 Tg  (2 km PBL)
  ~ 20-145 Tg yr\(^{-1}\)

Other estimates:
- Jo et al., 2013:
  - Production: 88 Tg yr\(^{-1}\)
  - Direct forcing: -0.28 Wm\(^{-2}\)
- Spracklen et al., 2011: Top-down using AMS & C\(^{14}\) obs
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- Carlton et al., 2010: 50% of biogenic SOA in the USA is anthropogenically controlled
Static parameterization based on GECKO-A

- **α-pinene (low-NOx)**
- **Toluene (low-NOx)**
- **C12H26 n-alkane (low-NOx)**
- **Isoprene (low-NOx)**
How do current parameterizations compare to explicit models?

1. Unconstrained SOA yields

- **α-pinene (low-NOx)**
  - GECKO-A full chemistry
  - VBS
  - VBS with ageing

- **Toluene (low-NOx)**
  - GECKO-A
  - VBS
  - VBS with ageing

GECKO-A (NCAR / CNRS, France) idealized runs:

- VOC = 1ppt ; NOx (low) = 0.1 ppb
- OH = 2*10^6 molec./cc ; seed OA : 1μg/m^3

2. Too Volatile oxidation products

Observation (Thermodenuder)

Cappa and Jimenez, ACP, 2010