Improving the Representation of Secondary Organic Aerosol (SOA) in the MOZART-4 Global Chemical Transport Model

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Secondary organic aerosol (SOA) is formed through a series of oxidation reactions of VOCs followed by partitioning of products into particles.

A major component of fine particles (PM2.5) is organic aerosol (OA), a significant fraction of which is SOA.

Airborne particles pose serious health risks and have climate consequences.

Most global chemical transport models (CTMs) underestimate SOA compared to observation.

Outputs from global models are frequently used as boundary conditions for regional CTMs.

Improving representation of SOA in MOZART-4 will provide better estimates of SOA on global to regional scales.
MOZART-4 MODEL

- Model for Ozone and Related chemical Tracers, version 4 (MOZART-4) is an offline global chemical transport model.
- There are 85 gas-phase species, 12 bulk aerosol compounds, 39 photolysis and 157 gas-phase reactions in MOZART-4.
- The aerosol component of the model includes calculations of sulfate, black carbon, primary organic and secondary organic (SOA), ammonium nitrate and sea salt.
- SOA formation is based on two product (2p) model
SOA yield calculation: \[ Y_p = M_o \sum_i \left( \frac{\alpha_i K_{omi}}{1 + K_{omi}M_o} \right) \]

Where \( \alpha_i \) fractional yield of each \( S \) from reacted HC
\( K_{omi} \) partitioning coefficient
\( M_o \) total organic mass at a given time step

Fig. 1. Schematic of the two-product (2p) SOA model
(From Kroll and Seinfeld, 2008)
Steps to build and run MOZART-4

Step 1: Configuring system info
Gets system and directory info

Step 2: Preprocessing
Preprocesses MOZART chemistry input

Step 3: Building MOZART-4 executable
Extracts chemistry info, and compile to build system specific executable

Step 4: Running simulation
Modify name list file as desired, and run the model for different cases

Steps to update MOZART-4

Tagging appropriate parent VOC precursors in the gas-phase reactions to treat them in SOA calculations

Modifying mo_setsoa.F90 code to update two-product (2p) parameters and add new parent VOC species for SOA calculations

Fig. 2. Flow chart showing the steps in building and running MOZART-4
MODEL RUNS

- MOZART-4 was run for three cases: 1) Base-case: original model with normalized SOA parameters, 2) Case A: updated with two-product volatility basis set (2p-VBS) parameters, and 3) Case B: updated with 2p-VBS parameters and additional new parent VOCs
- Global domain with 2.8°x2.8° grid-cells, 28 layers extending up to ~2 hPa (dimension: 64 x 124 x 28)
- Global anthropogenic emissions from precursors of ozone and their effects in the troposphere (POET) emissions inventory, biogenic emissions from on-line calculations by MEGAN emissions model, fire emissions from global fire emissions database (GFED)
- Meteorology from the NCAR reanalysis of the NCEP forecast for the year 2006
Table 1. List of original and newly added parent VOCs contributing to SOA mass with updated 2p-VBS parameters used in MOZART-4

<table>
<thead>
<tr>
<th>Status</th>
<th>Model parent VOC</th>
<th>SPRC 99</th>
<th>Oxidant</th>
<th>$\alpha_1$</th>
<th>$K_{om1}$</th>
<th>$\alpha_2$</th>
<th>$K_{om2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>C$<em>{10}$H$</em>{16}$</td>
<td>TERP</td>
<td>O3 or OH</td>
<td>0.289</td>
<td>0.008</td>
<td>0.086</td>
<td>0.205</td>
</tr>
<tr>
<td>Original</td>
<td>TOLUENE</td>
<td>ARO1+ARO2</td>
<td>OH</td>
<td>0.325</td>
<td>0.008</td>
<td>0.124</td>
<td>0.146</td>
</tr>
<tr>
<td>Original</td>
<td>BIGALK</td>
<td>ALK3+ALK4+ALK5</td>
<td>OH</td>
<td>0.100</td>
<td>0.150</td>
<td>0.047</td>
<td>0.080</td>
</tr>
<tr>
<td>Added</td>
<td>ISOP</td>
<td>ISOPRENE</td>
<td>OH</td>
<td>0.178</td>
<td>0.011</td>
<td>0.022</td>
<td>2.106</td>
</tr>
<tr>
<td>Added</td>
<td>BIGENE</td>
<td>OLE2</td>
<td>OH</td>
<td>0.144</td>
<td>0.006</td>
<td>0.022</td>
<td>0.185</td>
</tr>
<tr>
<td>Added</td>
<td>C$_3$H$_6$</td>
<td>OLE1</td>
<td>OH</td>
<td>0.078</td>
<td>0.005</td>
<td>0.006</td>
<td>0.167</td>
</tr>
</tbody>
</table>
Fig. 3. Global distributions of monthly-average emission rates (mg m\(^{-2}\) day\(^{-1}\)) for (a) monoterpenes (C\(_{10}\)H\(_{16}\)), and (b) isoprene (C\(_{5}\)H\(_{8}\)).

Global emissions for 2006

(i) Isoprene: 462 Tg

(ii) Monoterpenes: 89 Tg
RESULTS

Fig. 4. Global distributions of simulated monthly-average SOA surface concentrations (µg m\(^{-3}\)) (top: Base-case) and relative increase from base-case (bottom: Case A) for March, June, September and December of 2006.
Fig. 5. Global distributions of predicted monthly-average SOA surface concentrations (µg m⁻³) (top: base-case) and relative increase from base-case (bottom: Case B) for March, June, September and December of 2006.
Fig. 6. Vertical distributions of annual-average SOA concentrations over different regions of the world. Open diamonds represent base-case, open squares represent Case A, and open circles represent Case B.
Table 2. Regionally-averaged annual SOA concentrations at surface predicted for 2006

<table>
<thead>
<tr>
<th>Region</th>
<th>Base-case</th>
<th>Case A</th>
<th>Case B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada (50-70N, 235-300E)</td>
<td>0.06±0.04</td>
<td>0.08±0.04</td>
<td>0.12±0.07</td>
</tr>
<tr>
<td>USA (25-50N, 235-300E)</td>
<td>0.08±0.05</td>
<td>0.13±0.10</td>
<td>0.27±0.19</td>
</tr>
<tr>
<td>Europe (30-70N, 10W-30E)</td>
<td>0.09±0.06</td>
<td>0.20±0.16</td>
<td>0.31±0.22</td>
</tr>
<tr>
<td>North Asia (45-70N, 60-150E)</td>
<td>0.05±0.04</td>
<td>0.07±0.05</td>
<td>0.12±0.07</td>
</tr>
<tr>
<td>Southeast Asia (10-45N, 60-125E)</td>
<td>0.09±0.11</td>
<td>0.16±0.18</td>
<td>0.42±0.45</td>
</tr>
<tr>
<td>Indonesia (10S-10N, 90-150E)</td>
<td>0.20±0.27</td>
<td>0.23±0.30</td>
<td>0.84±0.84</td>
</tr>
<tr>
<td>North Africa (0-30N, 20W-60E)</td>
<td>0.06±0.10</td>
<td>0.09±0.12</td>
<td>0.27±0.36</td>
</tr>
<tr>
<td>South Africa (40S-Eq, 0-60E)</td>
<td>0.04±0.06</td>
<td>0.05±0.08</td>
<td>0.22±0.27</td>
</tr>
<tr>
<td>South America (30S-Eq, 270-330E)</td>
<td>0.22±0.43</td>
<td>0.24±0.45</td>
<td>0.59±0.81</td>
</tr>
<tr>
<td>Australia (45-10S, 290-310E)</td>
<td>0.06±0.06</td>
<td>0.07±0.08</td>
<td>0.38±0.33</td>
</tr>
</tbody>
</table>
Fig. 7. Distributions of predicted aerosol optical depth (AOD) (top: base-case) and relative increase from base-case (bottom: Case B)
How does the updated MOZART-4 output compare to other models and observation?

- The amount of observational data for global SOA is essentially nonexistent, since SOA is largely not a measurable component of total aerosol. Most of the reported data have been calculated based on EC/OC and OC/OM ratios from measured fine particulate mass.
- Comparison with other model output is also difficult because of the differences in the types of chemical transport model, chemical mechanisms, treatment of parent VOCs contributing to SOA, estimation techniques for SOA, and sources of emissions inventories.
- Example comparison: over China, SOA concentrations of 0.05 – 1.0 µg m⁻³ (this study) vs. 0.4 – 2.5 µg m⁻³ (Jiang et al., 2012).
- Current study predicted free tropospheric (2-6km) SOA max over the NW pacific of ~0.08 µg m⁻³ vs ~4.6 µg m⁻³ measured during the ACE-Asia study in 2001 (Heald et al. 2008).
SUMMARY

- The base-case simulation predicts annual average surface SOA of 0.22±0.43 µg m⁻³ in South America, 0.20±0.27 mg m⁻³ in Indonesia, 0.08±0.05 µg m⁻³ in the USA, and 0.09±0.06 µg m⁻³ in Europe.
- Case A: updating the existing SOA parameters with 2p-VBS shows increases by ~8%, ~11%, ~62%, and ~110% from the base-case in South America, Indonesia, USA, and Europe, respectively.
- Case B: updating the parameters and adding new VOC parent species shows even more dramatic increase in annual average SOA for above regions. SOA increases by ~200-400% from the base-case.
- Updating the existing MOZART-4 model increases SOA estimates from the base-case, but still under-estimates from observation.
- On-going work includes update to the SOA module of CESM, which will replace the current SOA module in MOZART-4 in the future.
Additional Slides
Overview of Relevant Gas-Phase Chemistry

"Ox"

Day: OH, O₃ (HO₂, NOₓ)
- Anthropogenic precursors: react w/OH
- Biogenic precursors
  - Isoprene reacts w/OH
  - Monoterpenes and sesquiterpenes react w/OH+O₃
- Then...branching based on NOₓ concentrations

Night: O₃, NO₃
- Typically anthropogenic SOA precursors (benzene, xylene, toluene) react slowly with NO₃
- Biogenic precursors react w/NO₃
  - Isoprene, on order of reaction w/OH
  - Reactions w/α-,β-pinene particularly fast

Modified from Presto et al., 2005, ES&T
Overview of SOA Model Approaches: Two-Product (2p) and Volatility Basis Set (VBS)

α-Pinene + OH (first generation)

α-Pinene + OH (lumped compounds)

2 products (2p)

Products tracked = 2 x N

Fit chamber data to obtain $\alpha_{1,2}$ and $C^*_{1,2}$ values

volatility basis set (VBS)

Products tracked = $j$ or $j x N$

bins 1 to $j$ (usually 4)

Fix $C^*_i$, fit chamber data to obtain $\alpha_i$ values

Sources: Pinho et al., J. Atmos. Chem.; Odum et al., ES&T; Donahue et al., ES&T