Simulating SOA Across the United States – Sensitivity Analyses Using the Community Multiscale Air Quality (CMAQ) Model

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Overview

• SOA treatment in CMAQ model
• CMAQ results – 2003 annual simulation
• Tracer-based estimates of SOA from isoprene, monoterpenes, sesquiterpenes, and aromatics
• Model evaluation of source-specific SOA contributions
• Sensitivity analyses using the CMAQ model
  – Sesquiterpene emissions
  – SOA density
  – Isoprene contributions to in-cloud SOA
  – SOA/SOC ratios
• Summary and Future Directions
SOA Treatment in CMAQ Model

• Edney et al. (2007) recommended most important SOA precursors & pathways, based on peer-reviewed literature.
• Summary of SOA treatment:
  – Pankow-Odum model: semi-volatile (SV) products partition to organic PM phase
    • Monoterpene oxidation $\rightarrow$ 2 SV products
    • Sesquiterpene oxidation $\rightarrow$ 1 SV product (Griffin et al., 1999 daylight expts)
  • Isoprene oxidation $\rightarrow$ 2 SV products (Kroll et al., 2006 low-NOx expts)
  • Long-chain alkane oxidation $\rightarrow$ 1 SV product (Strader et al., 1999)
  • Aromatic oxidation $\rightarrow$ 6 SV & 3 non-volatile products
    – 3 precursors: high-yield, low-yield, and benzene
    – RO2 + NO $\rightarrow$ 2 SV products (Ng et al., 2007 & Henze et al., 2008)
    – RO2 + HO2 $\rightarrow$ 1 non-volatile product
  – ROG-specific $\Delta H_{vap}$ values for $c_{sat}^*(Temp)$ (Offenberg et al., 2006)
  – ROG-specific SOA/SOC ratios (Kleindienst et al., 2007)
  – Acidic conditions: SV isoprene products $\rightarrow$ non-vol. product (Surratt et al., 2007)
  – In-cloud SOA formation from GLY & MGLY + OH (Carlton et al., 2008)
  – All SV products $\rightarrow$ non-vol. oligomers in a 20h $\frac{1}{2}$ life (Kalberer et al., 2004)
• Above treatment will be in the public release of CMAQ v4.7 next month.
CMAQ Results – 2003 Annual Average

CMAQ v4.6 with updated SOA treatment
- SAPRC99 gas-phase chemistry
- AERO4 modal aerosol module
Meteorological inputs from MM5/MCIP
Emissions:
- Biogenics from BEIS 3.13 + sesquiterpenes
- 2003 fires and point sources
- 2002 NEI for other sources
Boundary conditions: estimated from global model
Domain: 36 km grid spacing, 14 vertical layers
CMAQ Results – Seasonal Cycle

Key features in Southeast

• Summer peak due to
  – Biogenic emissions peak (yellow + green + dark green)
  – Cloud SOC (light blue) requires OH

* Converted all results from SOA to SOC. Hereafter, all units are μgC m⁻³.
CMAQ Results – Seasonal Cycle

Research Triangle Park, NC

- Previous CMAQ evaluations for carbonaceous PM:
  - OC, EC (numerous surface sites)
  - WSOC, $^{14}$C (intensive campaigns)
  - Molecular markers for POC

- None of these measurements permit a direct assessment of the model predictions of different classes of SOC
Tracer-Based Estimates of SOC

Tracer-based method for estimating source contributions to ambient SOC

• Lab Experiments
  – Smog chamber irradiations of numerous VOC/NOx mixtures
  – Identified and quantified unique tracer compounds (e.g., methyl tetrols) using advanced GC/MS methods.
  – Computed tracer/SOC ratios for each SOA precursor (# tracers = 3 isop, 9 mono., 1 sesq., 1 arom.)

• Field Measurements
  – Collected 33 PM$_{2.5}$ samples in RTP throughout 2003 (2 – 5 day duration)
  – Quantified the same tracer compounds that were found in the chamber studies.
  – Estimated ambient SOC contribution from each VOC precursor, using the tracer/SOC ratios.

• See Kleindienst et al. (Atmos. Environ., 41: 8288-8300, 2007) for details.

Greatest source of uncertainty:
- Are the tracer/SOC ratios measured in the chamber equal to those in the atmosphere?

Approach:
- Accept the tracer estimates at face value until better information becomes available.
Model Evaluation for 4 SOC Classes

Tracer-Based Estimates

CMAQ Model Results

- Model results are consistently low (31 out of 33 samples), especially during summer months
- Explore the cause, by examining various model parameters
Model Evaluation for 4 SOC Classes

CMAQ Model Results [μgC m⁻³]

Tracer-Based Estimates [μgC m⁻³]
Model Evaluation for Sesquiterpene SOC

- Model bias is most pronounced during summer (underprediction > factor of 3)
- What’s the dominant cause? We can safely rule out the following:
  - Systematic meteorological error
  - SESQ + O₃ reaction rate constant
  - Stoichiometric yield of SV product
- A lower c_{sat} or a higher ΔH_{vap} would help, but no chamber data support this.
- Emission rates of sesquiterpenes [μg gdw⁻¹ hr⁻¹] are highly uncertain.
  - Initially, we used 0.3 for loblolly pine and 0.1 for all other plant types.
  - Replaced 0.1 with MEGAN values: 0.175 (broadleaf); 0.108 (needleleaf); 0.055 (shrubs); 0.204 (grass/crop) based on Sakulyanontvittaya et al. (2008)
- Repeated simulation (Aug.15 – Sep. 4)
Sensitivity #1: SESQ Emissions
Sesquiterpene SOC (18-day average)

SOC\textsubscript{SESQ} increases by ~3x in central states and Midwest. Increase is ~2x across southeast. In RTP, average SOC\textsubscript{SESQ} concentration increases by 76%, from 0.21 to 0.36 \(\mu\text{gC m}^{-3}\).

Relative increase in SOC\textsubscript{SESQ} concentration (76%) exceeds the emissions increase in RTP (59%).
Model Evaluation for Sesquiterpene SOC

CMAQ Model Results $[\mu gC\ m^{-3}]$

Tracer-Based Estimates $[\mu gC\ m^{-3}]$

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For illustrative purposes, let’s assume the average change during the sensitivity test period is representative of the remainder of the year.
Model Evaluation for 4 SOC Classes

Sensitivity Run #1

CMAQ Model Results [μgC m⁻³]

Tracer-Based Estimates [μgC m⁻³]

Monoterpene SOC

+8%

Sesquiterpene SOC

+76%

Isoprene SOC

+3%

Aromatic SOC

+1%

U.S. EPA Office of Research & Development, Atmospheric Modeling Division
Sensitivity #2: SOA Density

When SOA yields are reported, the SMPS-based particle volume is typically converted to mass by assuming a fixed density.

Griffin et al., (1999)

Kroll et al., (2006)

Ng et al., (2007)
Sensitivity #2: SOA Density

An average of values in the recent literature (Bahreini et al. 2005; Alfarra et al. 2006; Ng et al. 2007; Kostenidou et al. 2007; Offenberg et al., 2007) places the density of monoterpene and sesquiterpene SOA at 1.3 g cm$^{-3}$.

Repeat simulation (Aug. 15 – Sep. 4)
Sensitivity #2: SOA Density

Sensitivity Run #1

Revised SOA Density

Monoterpane SOC

Sesquiterpene SOC
Model Evaluation for 4 SOC Classes

Sensitivity Run #2

CMAQ Model Results [µgC m\(^{-3}\)]

Tracer-Based Estimates [µgC m\(^{-3}\)]

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Model Evaluation for Isoprene SOC

- Model bias is largest during summer (underprediction > 3x), and quite substantial during spring & fall (> 2x)
- We’re already using the highest SOC_{isop} yields reported in the literature (low-NOX conditions of Kroll et al., 2006)
- Recent studies indicate that isoprene tracers (methyltetrols & 2-methylglyceric acid) may be formed by pathways other than ISOP + OH → SV products
- In CMAQ, SOA is formed in clouds from GLY & MGLY. ~70% of those aldehydes come from isoprene.
  - Add 0.7×SOC_{cld} to modeled SOC_{isop}
Model Evaluation for Isoprene SOC

- Model results now fall within factor of 2 of most tracer estimates, but are still low during summer months. (median values: 0.31 vs. 0.57 μgC m⁻³)
- For SOC_{isop}, we’ve set SOA/SOC = 2.5 based on an average of multiple experiments by Kleindienst et al. (2007). Several of those experiments were done in the presence of SO₂.
  - Without SO₂, SOA/SOC = 1.6
  - With SO₂, SOA/SOC = 2.7
- SOA yields reported by Kroll et al. (2006) were obtained without SO₂. By using a large SOA/SOC, the model may be producing too little SOC.
- Repeated simulation (Aug.15 – Sep. 4)
Sens #3: Isoprene SOA/SOC Ratio

Isoprene SOC (+0.7 SOC$_{\text{cld}}$)

SOC$_{\text{ISOP}}$ increases by 18% in RTP.
Model Evaluation for 4 SOC Classes

Sensitivity Run #3

CMAQ Model Results [μgC m⁻³]

Tracer-Based Estimates [μgC m⁻³]
Model Evaluation for Aromatic SOC

- Aromatic SOC from CMAQ model is consistently lower than tracer-based estimates.
  - Almost a factor of 6 during summer
  - Almost a factor of 4 year round
- We cannot explain this difference by changing model parameters in any justifiable way.
- Aromatic tracer is highly oxidized: 2,3-Dihydroxy-4-oxopentanoic acid tracer/SOC ratio is quite low (0.0079)
- Perhaps this tracer requires more time to form (chamber residence time = 6 h) so its atmospheric concentrations are elevated…
Summary & Future Directions

• Much can be learned by comparing CMAQ model results with tracer-based estimates of SOC classes.
• Gap between model and measurements can be reduced by considering
  – sesquiterpene emission rates reported recently.
  – SOA density measured in recent chamber expts.
  – in-cloud formation of isoprene SOA.
  – SOA/SOC measured in recent chamber expts.
• Additional research is needed to understand the model biases for aromatic and isoprene SOC.

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