Modeling Carbonaceous Fine PM in CMAQ: Current Model Performance & Future Plans

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Overview

• CMAQ aerosol module
• Current model performance (P. Bhave)
  ▪ Total Carbon, OC, & EC
  ▪ POA tracers and $^{14}$C
• Future Plans (A. Carlton)
  ▪ EPA laboratory & field studies
  ▪ SOA module updates
CMAQ Aerosol Module Description

- Tri-modal size distribution
- Gas/particle interactions treated for fine modes only
- OC separated from the inorganic aqueous phase

COARSE MODE

SVOCs

Aromatics

Monoterpenes

Na\(^+\), Cl\(^-\), SO\(_4^{2-}\)

Soil, Other

2 FINE MODES

EC

HNO\(_3\)

NH\(_3\)

H\(_2\)SO\(_4\)

NH\(_4^+\)

SO\(_4^{2-}\)

Na\(^+\)

Cl\(^-\)

HCl

H\(_2\)O

H\(_2\)O

POA

SOA\(_a\)

SOA\(_b\)

Other
**Current CMAQ Model Performance**

- Goal: maximize the use of ambient data to evaluate and improve CMAQ predictions
- Measurements used to date
  - Total Carbon, OC, & EC
  - POA source-specific tracers
  - Radiocarbon ($^{14}$C)
  - SOA source-specific tracers
Across eastern U.S., CMAQ underpredicts OC & TC at most sites by ~1 μgC m^-3 during summer factor of ~2 or more at many sites.

Model Evaluation – OC/EC Ratio

Legend:
CMAQ results = solid line; empirical estimates = dashed line

$\text{OC}_{\text{sec}}$ is underestimated in the Southeast during summer
$\text{OC}_{\text{sec}}$ is overestimated in the west-coast states

*** Next, probe specific source contributions – take advantage of detailed summertime measurements collected in the Southeast.

Model Eval. – POA tracers (Jul’99)

Radiocarbon Measurements ($^{14}$C)

- Technique takes advantage of fact that $^{14}$C isotope is absent in fossil fuels
- PM$_{2.5}$ samples collected at Nashville on June 21 – July 13, 1999 were analyzed for $^{14}$C

Model Eval. – Fossil-Fuel Carbon

Excluding July 4\textsuperscript{th} influence, 
MB = -0.6 \( \mu \)g/m\textsuperscript{3} 

MB = Mean Bias
Model Eval. – Contemporary Carbon

Excluding July 4th influence,
MB = -2.3 μg/m³

MB = Mean Bias
Model Evaluation – Recap.

- In Southeast during summer,
  - TC is underestimated by ~40%
  - OC/EC ratio analyses indicate SOA underestimation by factor of 2
  - POA from biomass combustion and vehicle exhaust show no bias on average
  - Based on $^{14}$C data, most of missing carbon is from contemporary sources

- **Hypothesis**: Model bias is dominated by missing sources of biogenic SOA.
EPA Laboratory & Field Studies

- Investigators: Edney, Kleindienst, Offenberg, Lewandowski, and Jaoui

- Approach: develop a tracer-based method for estimating source contributions to ambient SOA
  
  - Laboratory 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/SOA ratios for each VOC precursor.

  - Field Studies
    - Collected PM$_{2.5}$ samples at a number of sites. Quantified the same tracer compounds that were found in the chamber studies. Estimated ambient SOA contribution from each VOC precursor, using the tracer/SOA ratios.
Ambient Tracer-Based Estimates
Res. Tri. Park, NC 2003

Summer sampling purposefully conducted during high-pollution episodes

Observations [µgC m\(^{-3}\)]
CMAQ Results (RTP, 2003)

Missing sources of SOA

RESEARCH & DEVELOPMENT
Building a scientific foundation for sound environmental decisions
Biogenic SOA driven by NO$_3$ in CMAQ

CMAQ biogenic SOA = monoterpane + \[
\begin{aligned}
&\text{OH} \\
&\text{O}_3 \\
&\text{NO}_3
\end{aligned}
\]
SOA Updates in next CMAQ release

• Objectives
  ▪ Include all major sources of SOA identified in field samples
  ▪ Include all major processes that are supported by laboratory studies (both EPA and extramural)

• Constraints
  ▪ Underlying data should be in peer-reviewed literature
  ▪ Regulatory applications prohibit use of computationally-intensive chemical mechanisms (e.g., MCM)

• Preview of CMAQ model revisions
  ▪ Update $\Delta H_{\text{vap}}$ based on lab studies
  ▪ Remove SOA from olefins, cresol
  ▪ Address NOx regimes for SOA from alkanes and aromatics
  ▪ Add SOA from isoprene (2 products)
  ▪ Add SOA from sesquiterpenes (1 product)
    • Add sesquiterpenes to BEIS
  ▪ Isoprene yields will vary with inorganic PM “acidity”
  ▪ Allow polymerization of aromatic SOA
  ▪ In-cloud SOA formation is under investigation

• Revised model will be tested extensively against field data!

under development using a box model

Implemented in CMAQ
Enhanced Aqueous Chemistry

• New aerosol species added to CMAQ, AORGC
• 2 Reactions added to aqueous chemistry
  • Glyoxal and methylglyoxal reactions with •OH
    • Gas-to-drop partitioning of aldehydes and •OH
  • DORGC = $\alpha \cdot DGLY + \alpha \cdot DMGLY$
    • Where DGLY = fraction of GLY reacted
• Yield based on laboratory experiments and box modeling. ORGC includes likely SOA contributors (e.g., oxalic acid and larger compounds)
• MGLY yields assumed to be same as GLY

Preliminary Aqueous Results

Increased surface layer PM$_{2.5}$ concentrations have air quality implications

Note: Assumed cloud SOA yield of 4%

Total carbon = organic carbon + elemental carbon
Development of Rosenbrock Solver

• Developing a generalized solver
  • Allows for simultaneous calculation of
    • partitioning, equilibrium, oxidation reactions
  • Photolysis calls from the aqueous phase
    • $\text{H}_2\text{O}_2 \rightarrow 2 \text{OH}$
  • Expand aqueous mechanism with organic reactions
Disclaimer

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