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

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In partnership with U.S. EPA, National Exposure Research Laboratory

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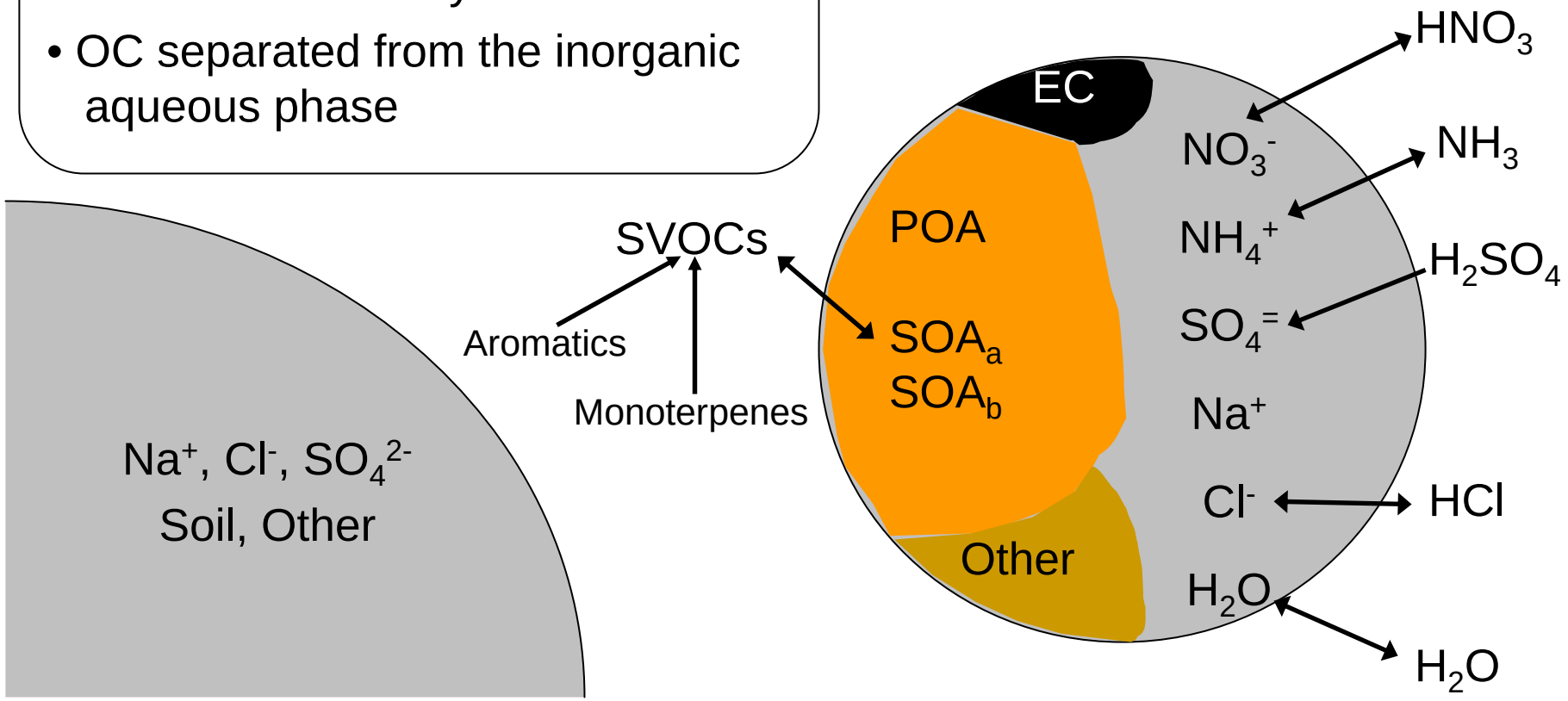
Overview

- 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

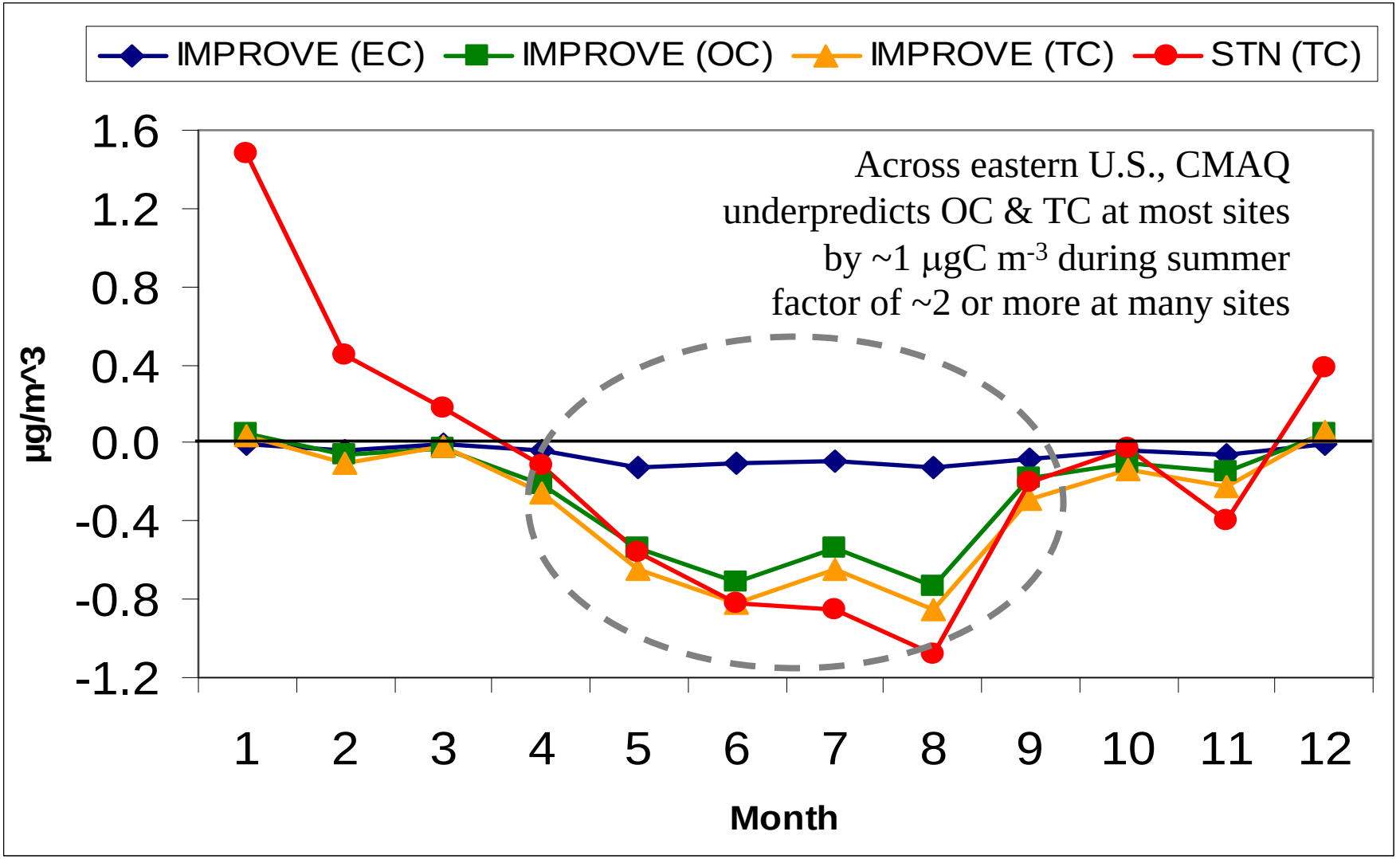


COARSE MODE **2 FINE MODES**

Current CMAQ Model Performance

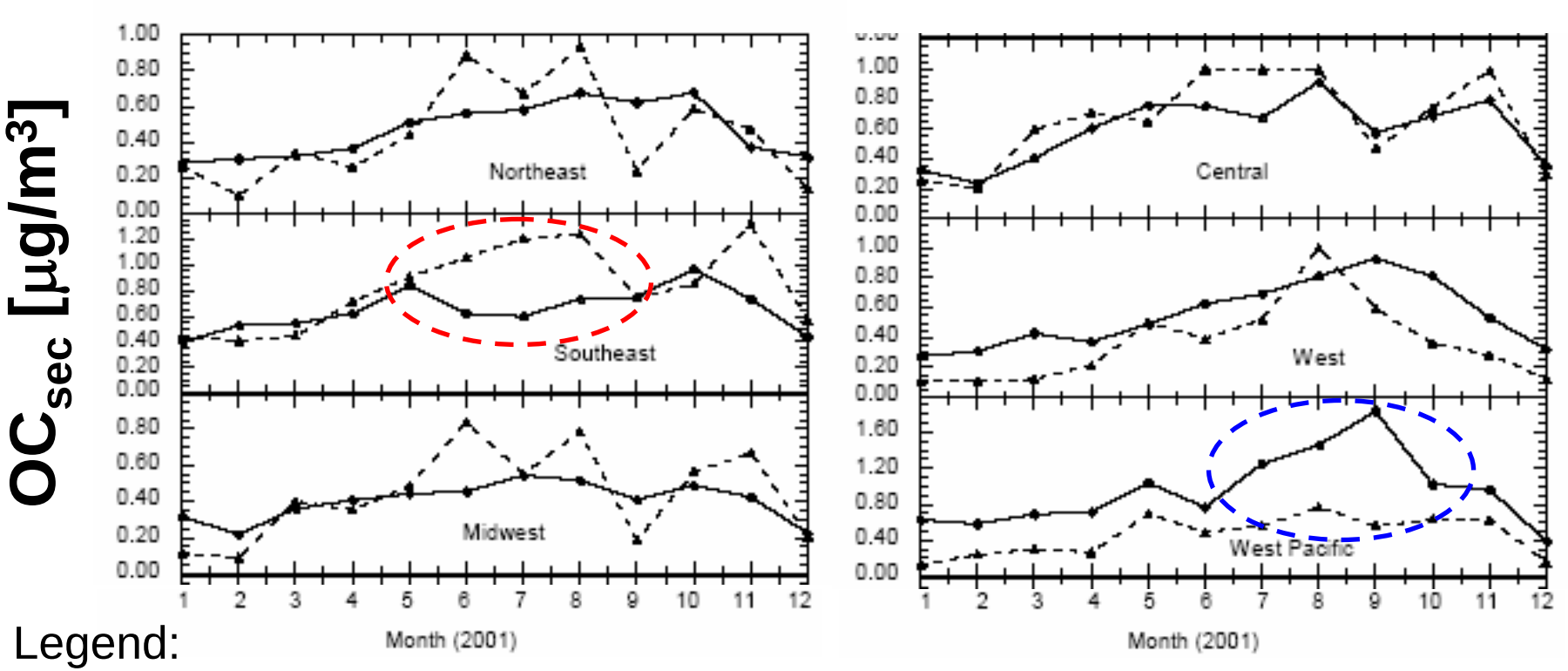
- Goal: maximize the use of ambient data to evaluate and improve CMAQ predictions
- Measurements used to date
  - Total Carbon, OC, & EC
  - POA source-specific tracers
  - Radiocarbon (^{14}C)
  - SOA source-specific tracers

Model Evaluation – OC & EC



Values shown are median absolute bias across eastern U.S sites. Ref: K.W. Appel, et al. (2007), *Atmos. Environ.* in review.

Model Evaluation – OC/EC Ratio



Legend:

CMAQ results = solid line; empirical estimates = dashed line

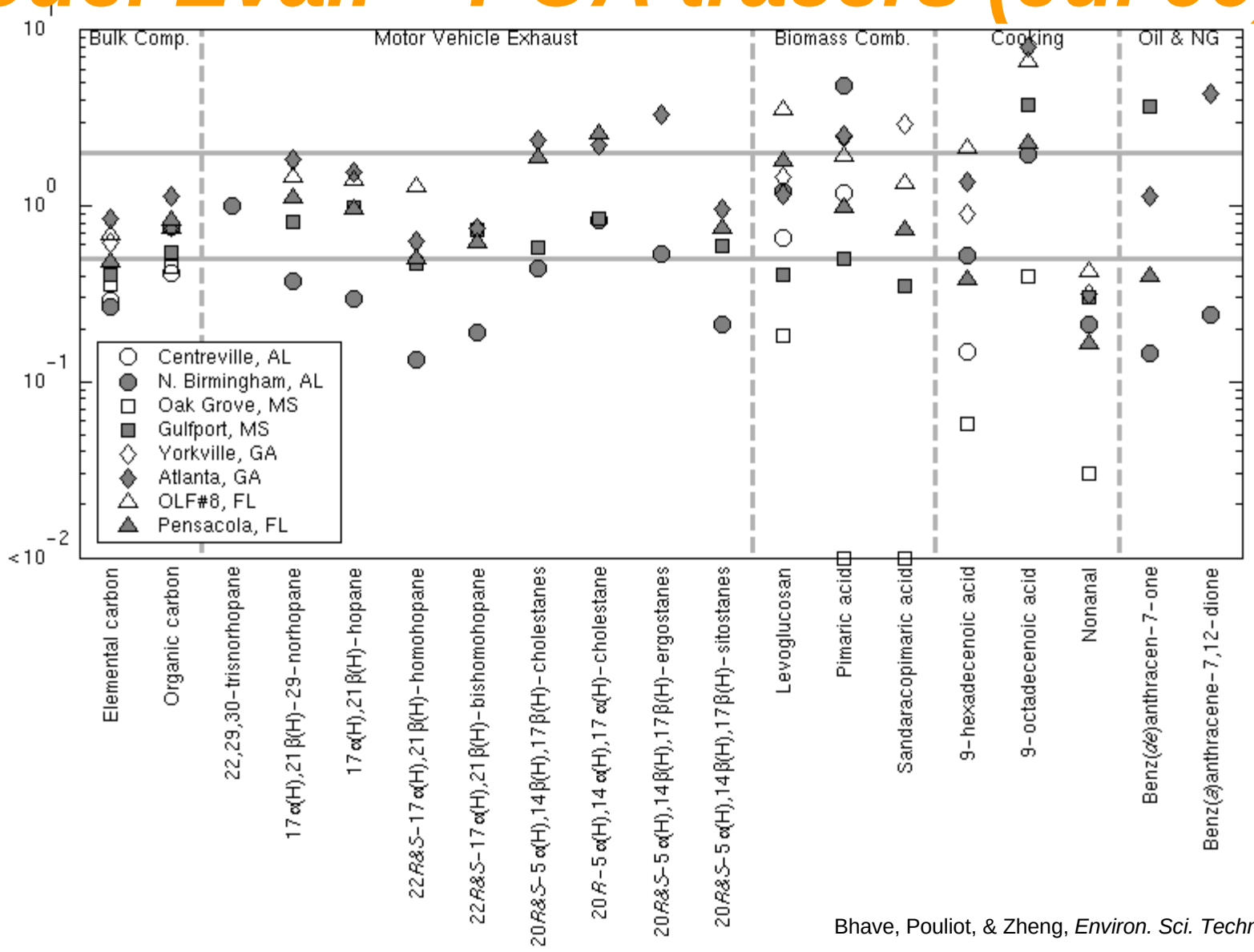
OC_{sec} is underestimated in the Southeast during summer

OC_{sec} is overestimated in the west-coast states

Yu, Bhave, Dennis, & Mathur, *Environ. Sci. Technol.* (2007)

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

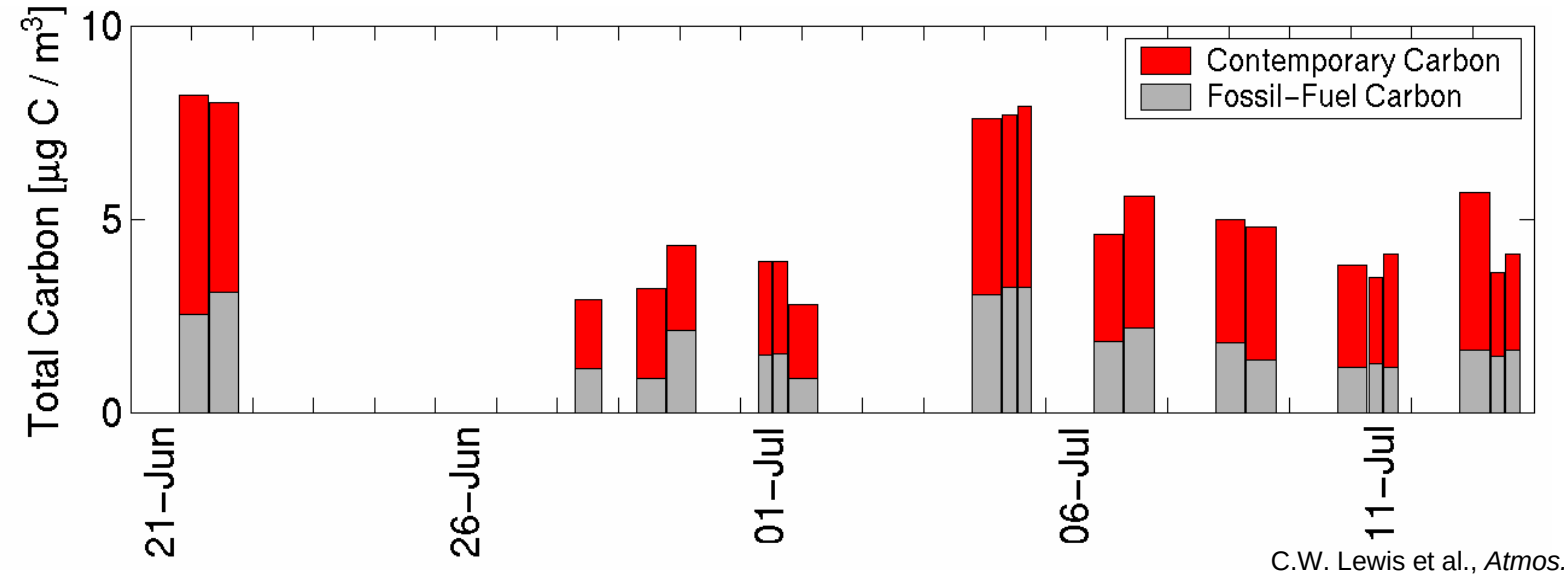
Model Eval. – POA tracers (Jul'99)



Bhave, Pouliot, & Zheng, *Environ. Sci. Technol.* (2007)

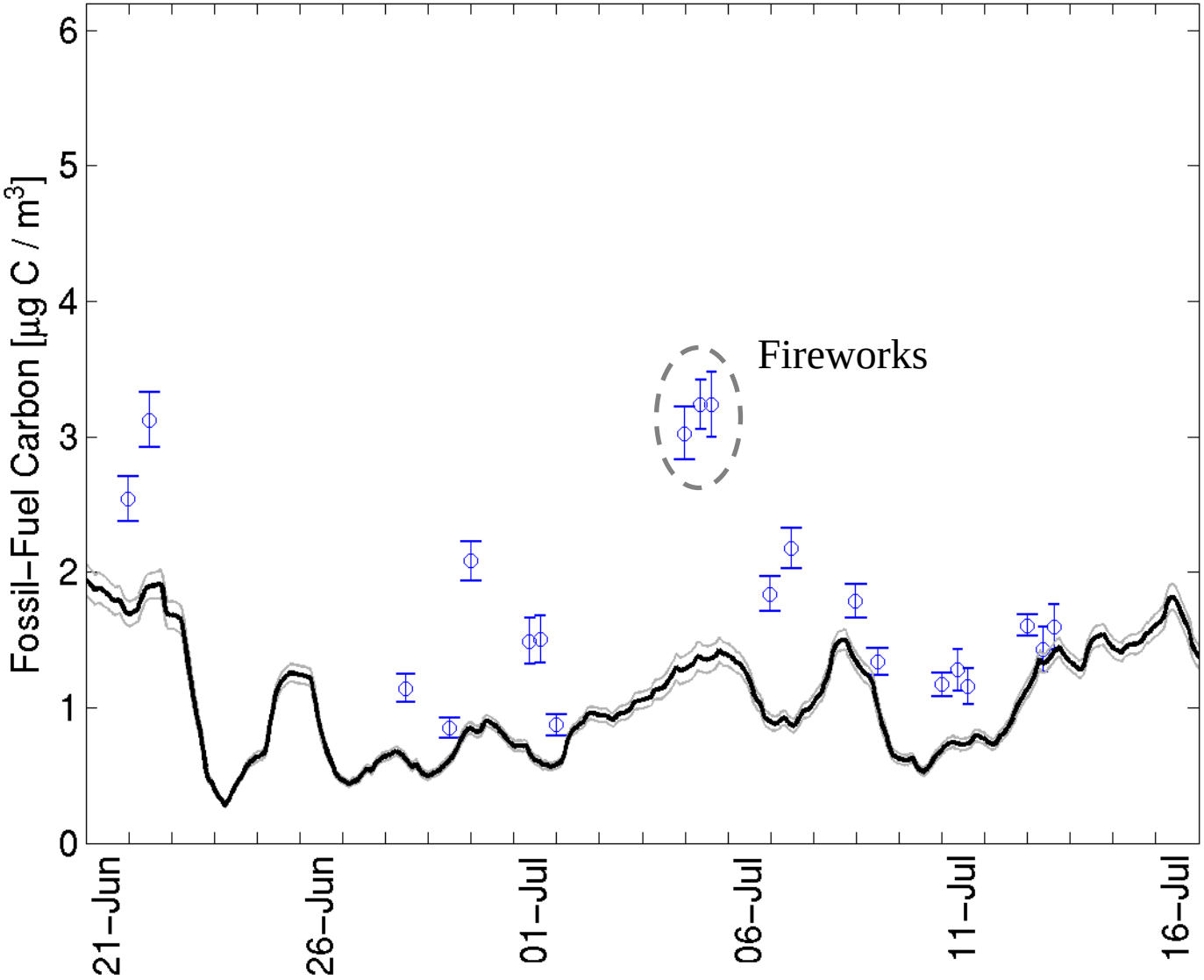
Radiocarbon Measurements (^{14}C)

- 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



C.W. Lewis et al., *Atmos. Environ.* (2004)

Model Eval. – Fossil-Fuel Carbon



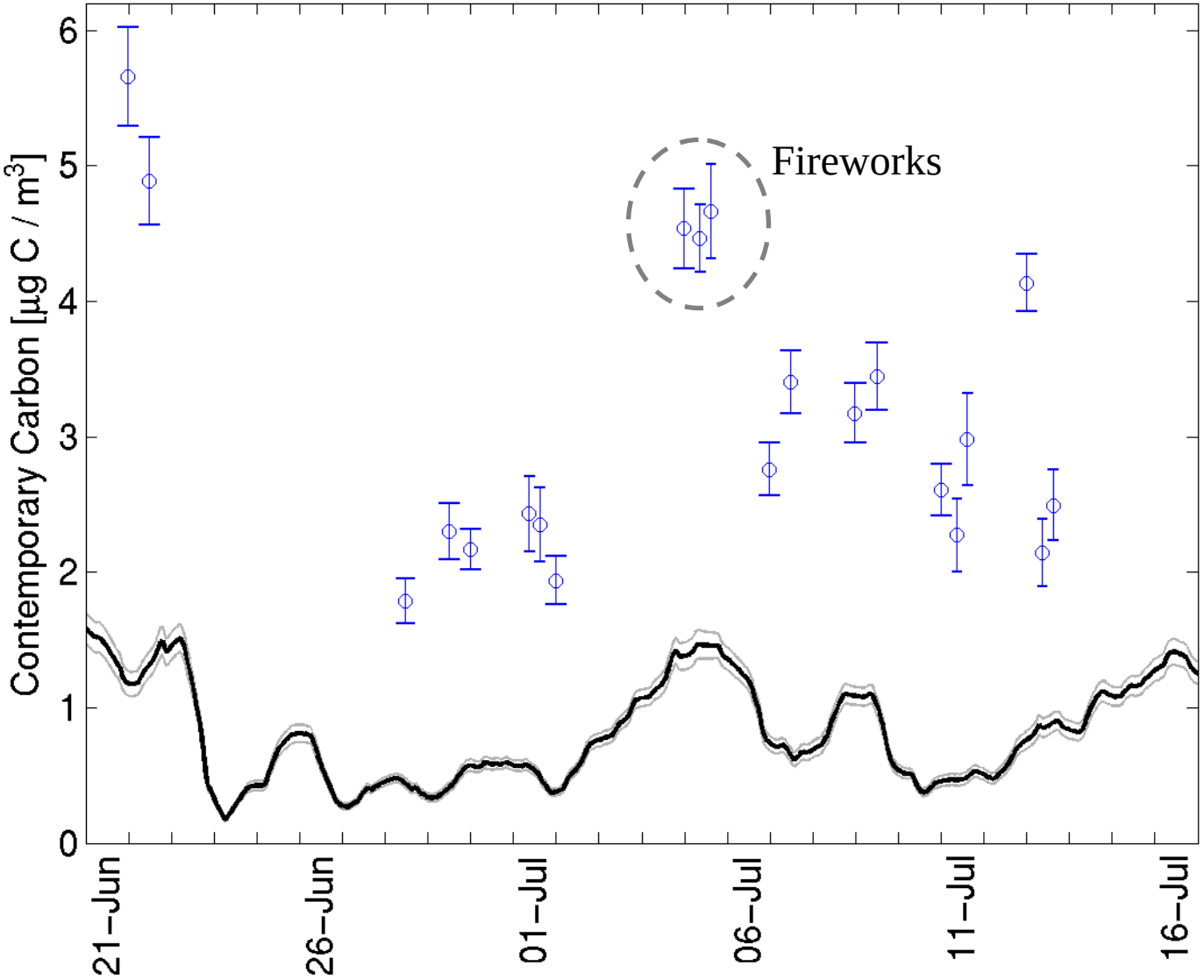
MSP sampler

CMAQ 24h-avg

Excluding July 4th influence,
MB = -0.6 µg/m3

MB = Mean Bias

Model Eval. – Contemporary Carbon



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

MB = Mean Bias

Model Evaluation – Recap.

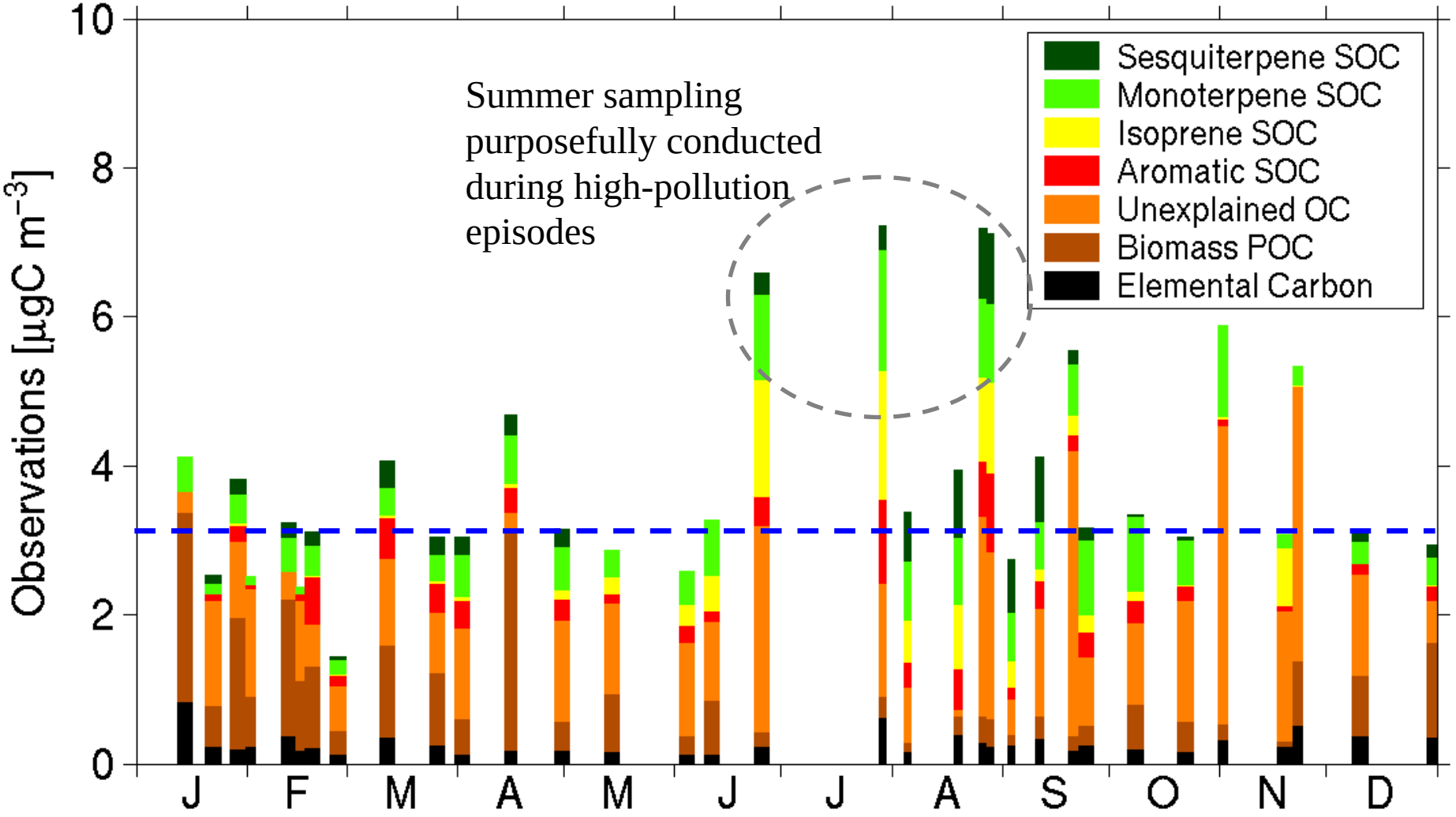
- In Southeast during summer,
  - TC is underestimated by ~40%
  - OC/EC ratio analyses indicate SOA underestimation by factor of 2
  - POA from biomass combustion and vehicle exhaust show no bias on average
  - Based on ^{14}C data, most of missing carbon is from contemporary sources
- *Hypothesis*: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

EPA Laboratory & Field Studies

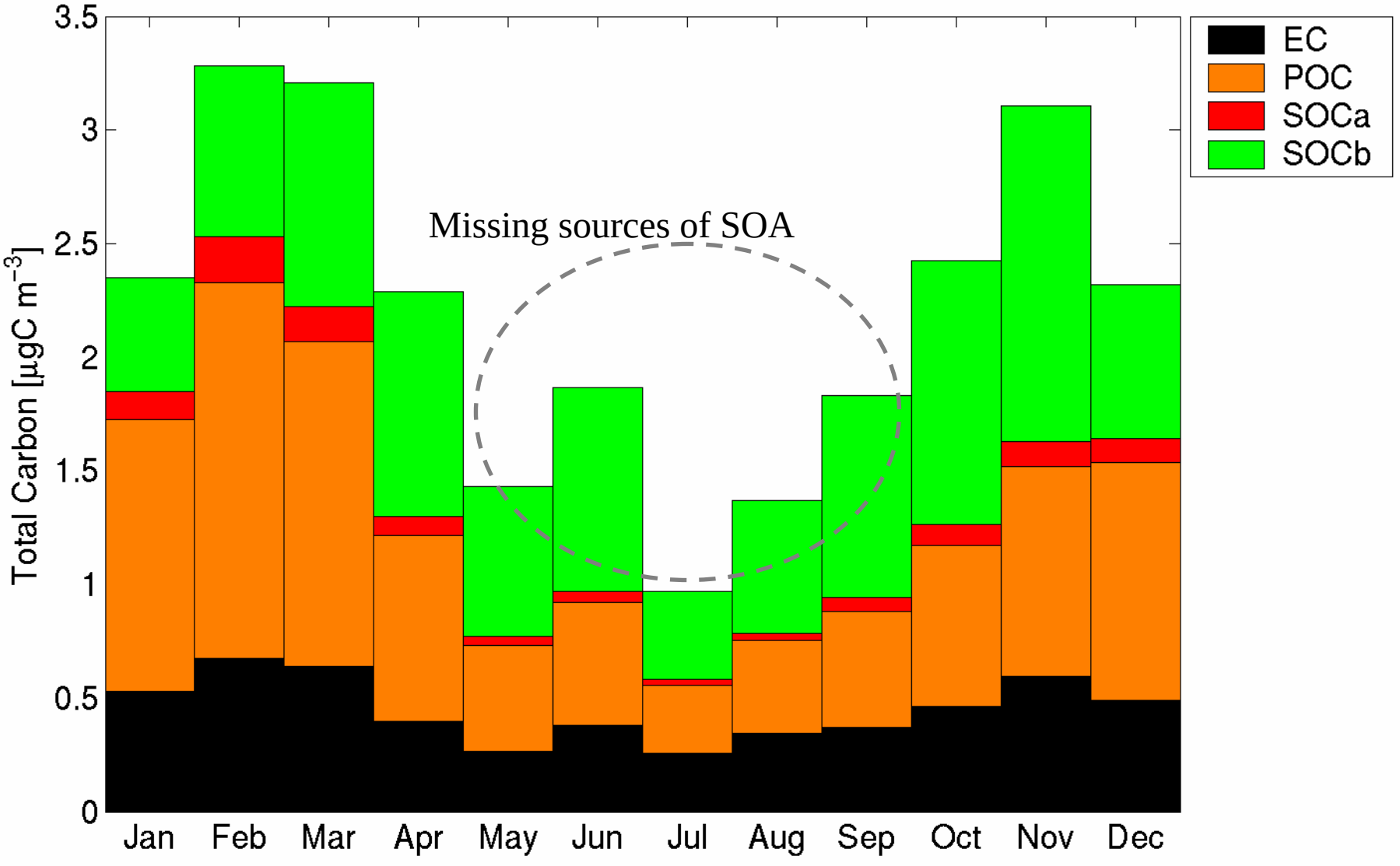
- Investigators: Edney, Kleindienst, Offenberg, Lewandowski, and Jaoui
- *Approach:* develop a tracer-based method for estimating source contributions to ambient SOA
  - Laboratory Experiments
    - Smog chamber irradiations of numerous VOC/NOx mixtures. Identified and quantified unique tracer compounds (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

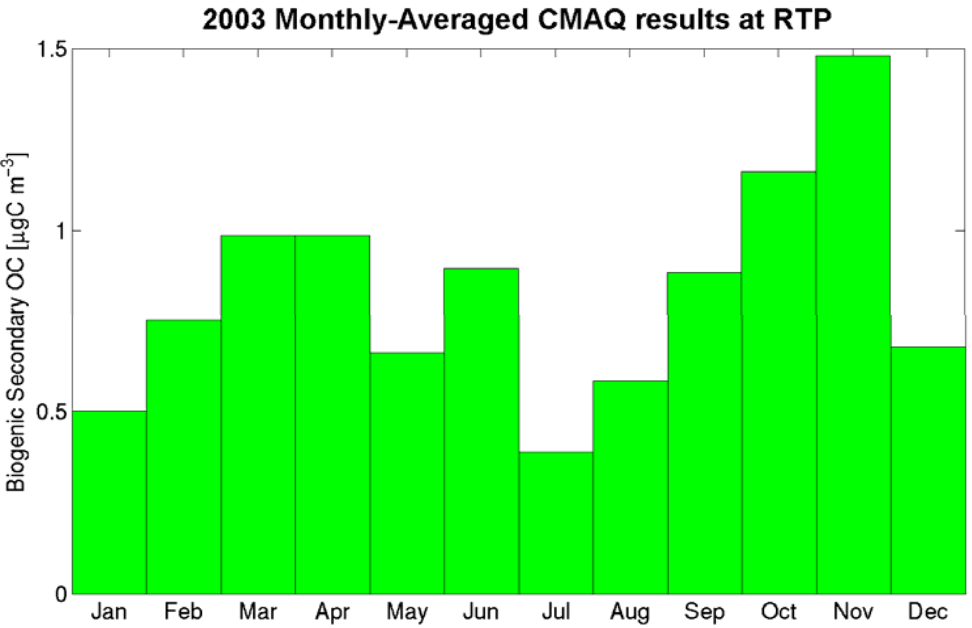


CMAQ Results (RTP, 2003)

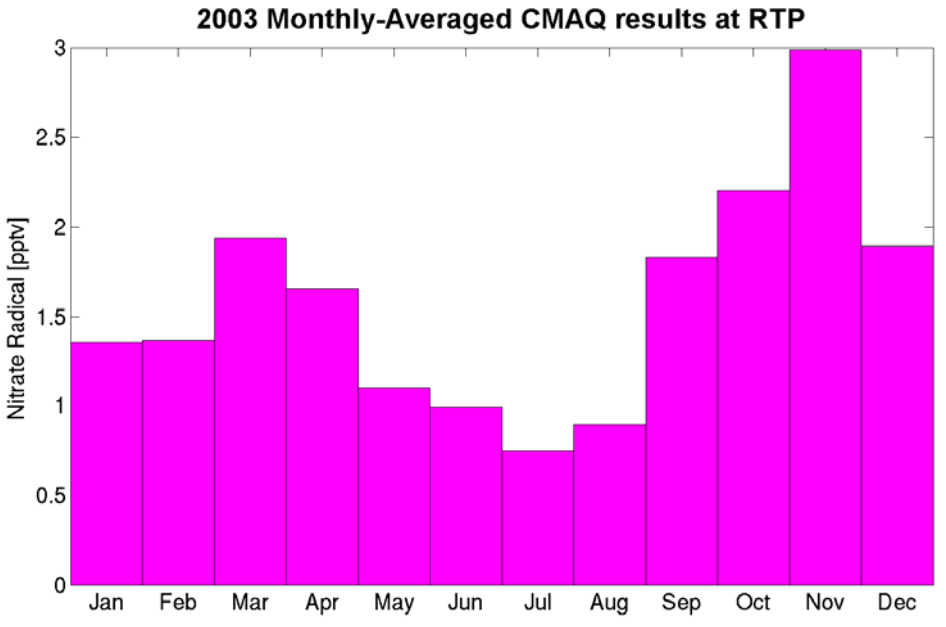


Biogenic SOA driven by NO_3 in CMAQ

Biogenic SOA



Nitrate Radical



$$\text{CMAQ biogenic SOA} = \text{monoterpene} + \begin{cases} OH \\ O_3 \\ NO_3 \end{cases}$$

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 ΔH_{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

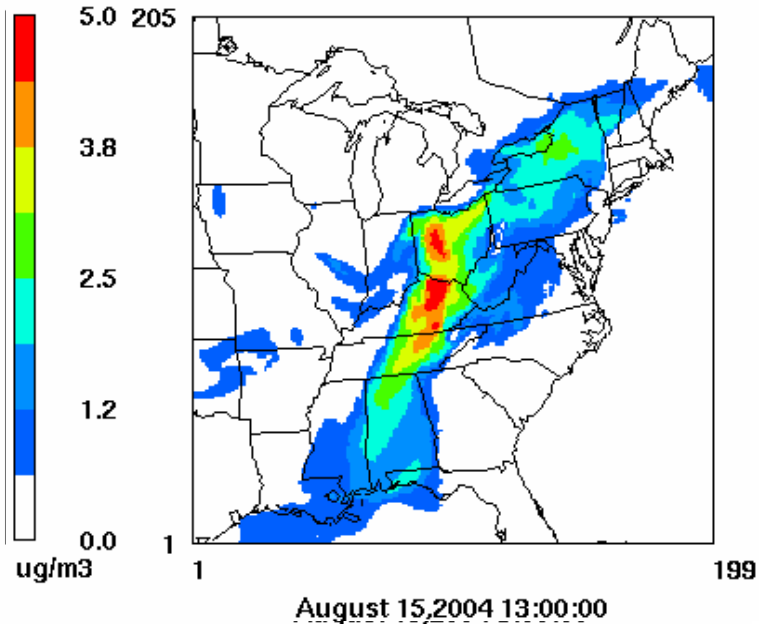
Enhanced Aqueous Chemistry

- 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 = α * DGLY + α * 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

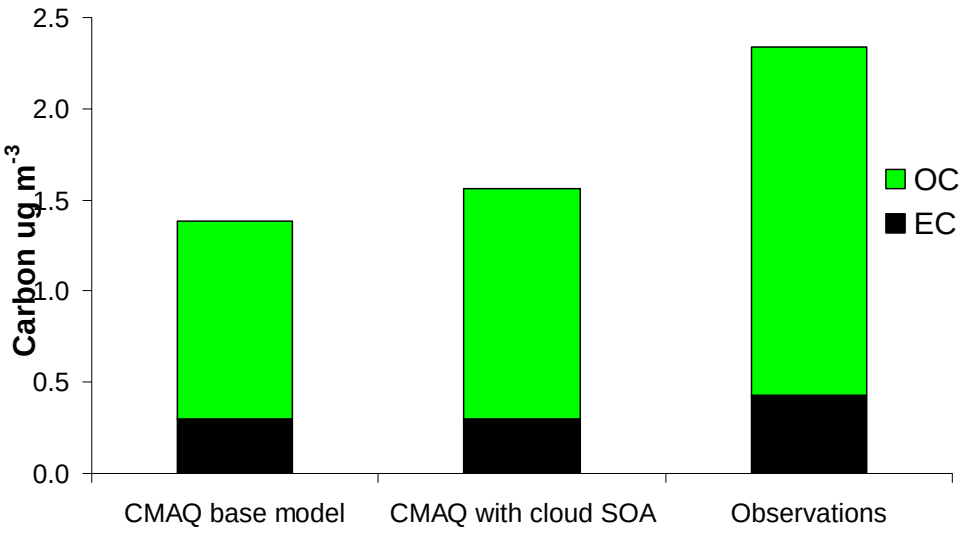
Carlton, Turpin, et al., Atmos. Environ. (2007)

Preliminary Aqueous Results

Surface Layer Concentrations of Cloud-Produced SOA



Total Carbon (OC + EC) Comparison



August 2004 IMPROVE comparison

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, equilbrium, oxidation reactions
  - Photolysis calls from the aqueous phase
    - $H_2O_2 \rightarrow 2\ OH$
  - Expand aqueous mechanism with organic reactions

Disclaimer

The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their views or policies.