United States Environmental Protection Agency

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

Prakash Bhave, Sergey Napelenok, George Pouliot, Ann Marie Carlton, Golam Sarwar

International Conference on Carbonaceous Particles in the Atmosphere
Berkeley, California
August 12 – 14, 2008

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 → 2 SV products (Griffin et al., 1999 daylight expts)
    - Sesquiterpene oxidation → 1 SV product (Griffin et al., 1999 daylight expts)
    - Isoprene oxidation → 2 SV products (Kroll et al., 2006 low-NOx expts)
    - Long-chain alkane oxidation → 1 SV product (Strader et al., 1999)
    - Aromatic oxidation → 6 SV & 3 non-volatile products (Ng et al., 2007 & Henze et al., 2008)
      - 3 precursors: high-yield, low-yield, and benzene
      - RO2 + NO → 2 SV products
      - RO2 + HO2 → 1 non-volatile product
  - ROG-specific ΔH_{vap} values for c_{sat}*(Temp) (Offenberg et al., 2006)
  - ROG-specific SOA/SOC ratios (Kleindienst et al., 2007)
  - Acidic conditions: SV isoprene products → non-vol. product (Surratt et al., 2007)
  - In-cloud SOA formation from GLY & MGLY + OH (Carlton et al., 2008)
  - All SV products → non-vol. oligomers in a 20h ½ life (Kalberer et al., 2004)
- Above treatment will be in the public release of CMAQ v4.7 next month.

CMAQ Results – 2003 Annual Average

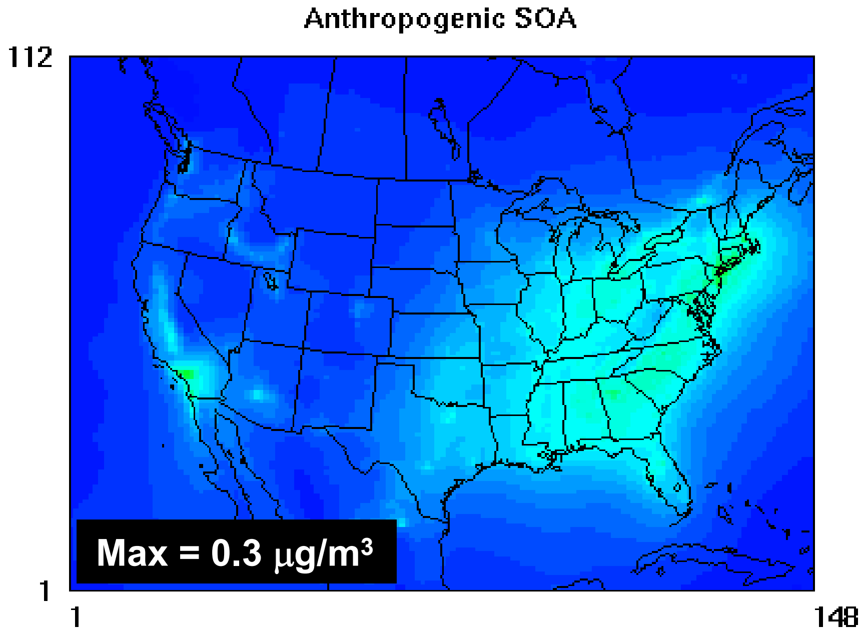
CMAQ v4.6 with updated SOA treatment
- SAPRC99 gas-phase chemistry
- AERO4 modal aerosol module

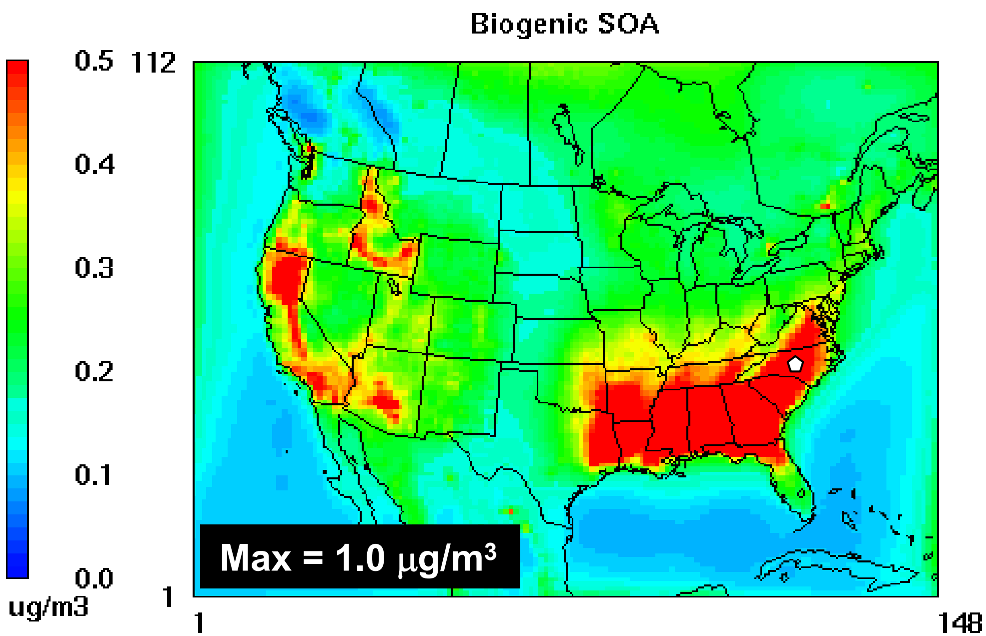
Meteorological inputs from MM5/MCIP

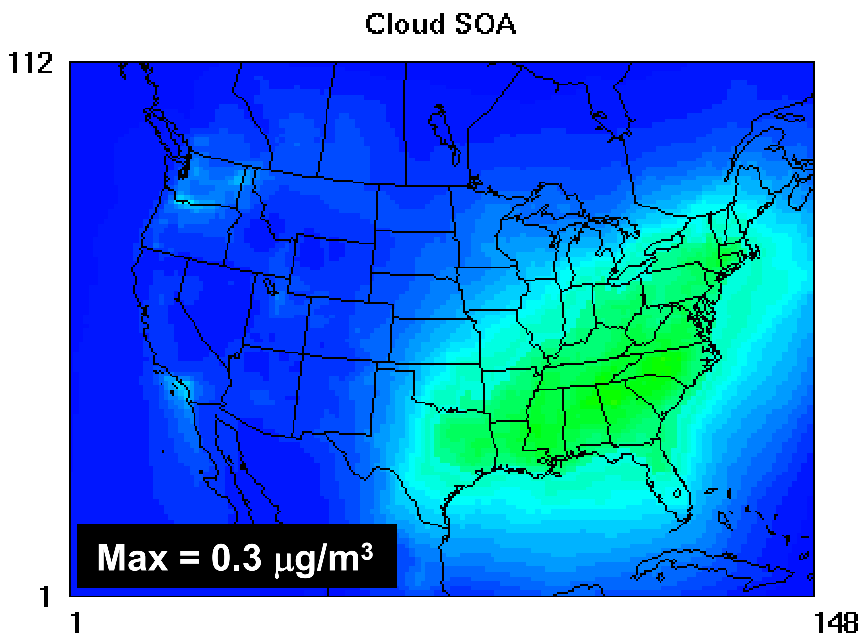
Emissions:
- Biogenics from BEIS 3.13 + sesquiterpenes
- 2003 fires and point sources
- 2002 NEI for other sources

Boundary conditions: estimated from global model

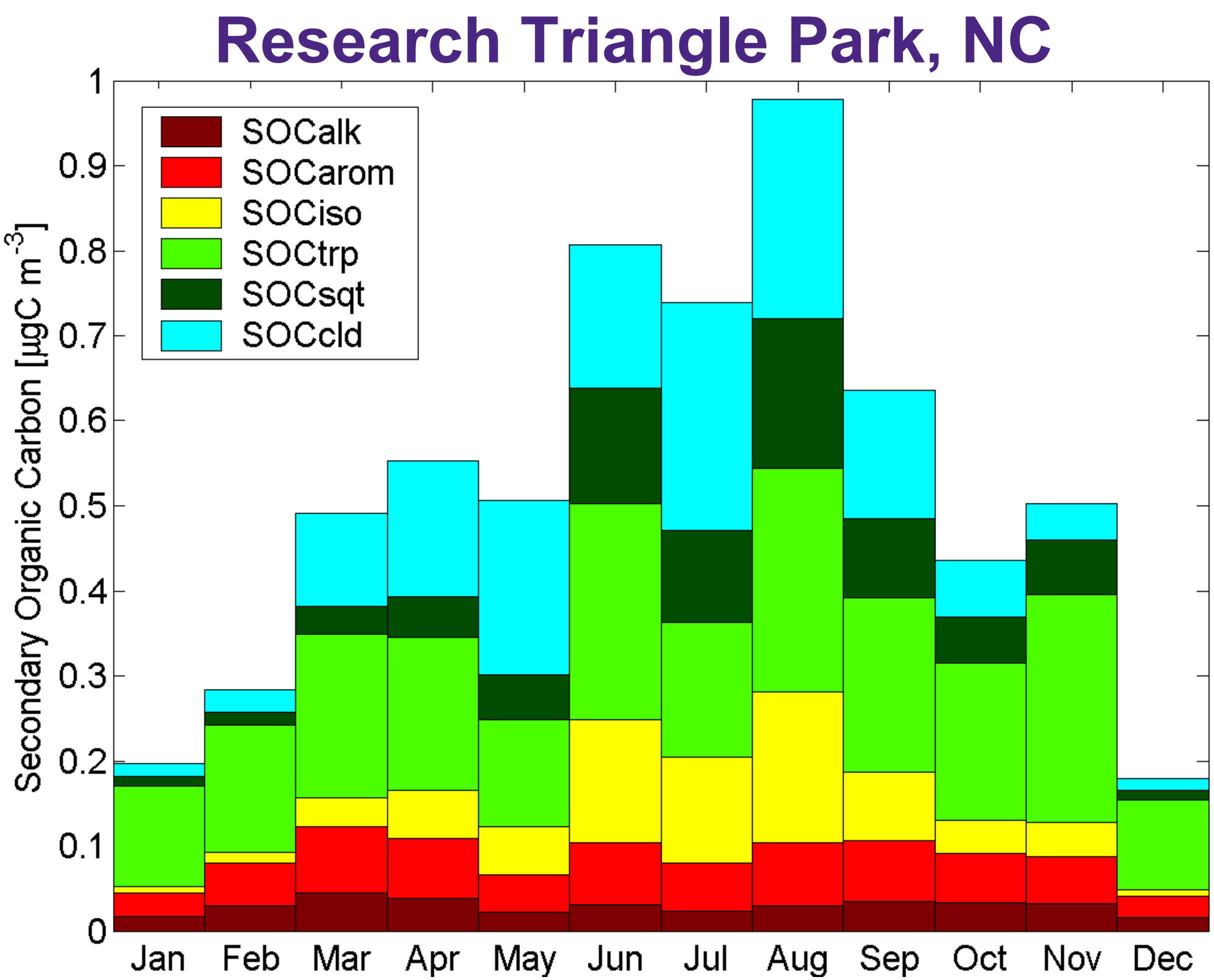
Domain: 36 km grid spacing, 14 vertical layers







CMAQ Results – Seasonal Cycle

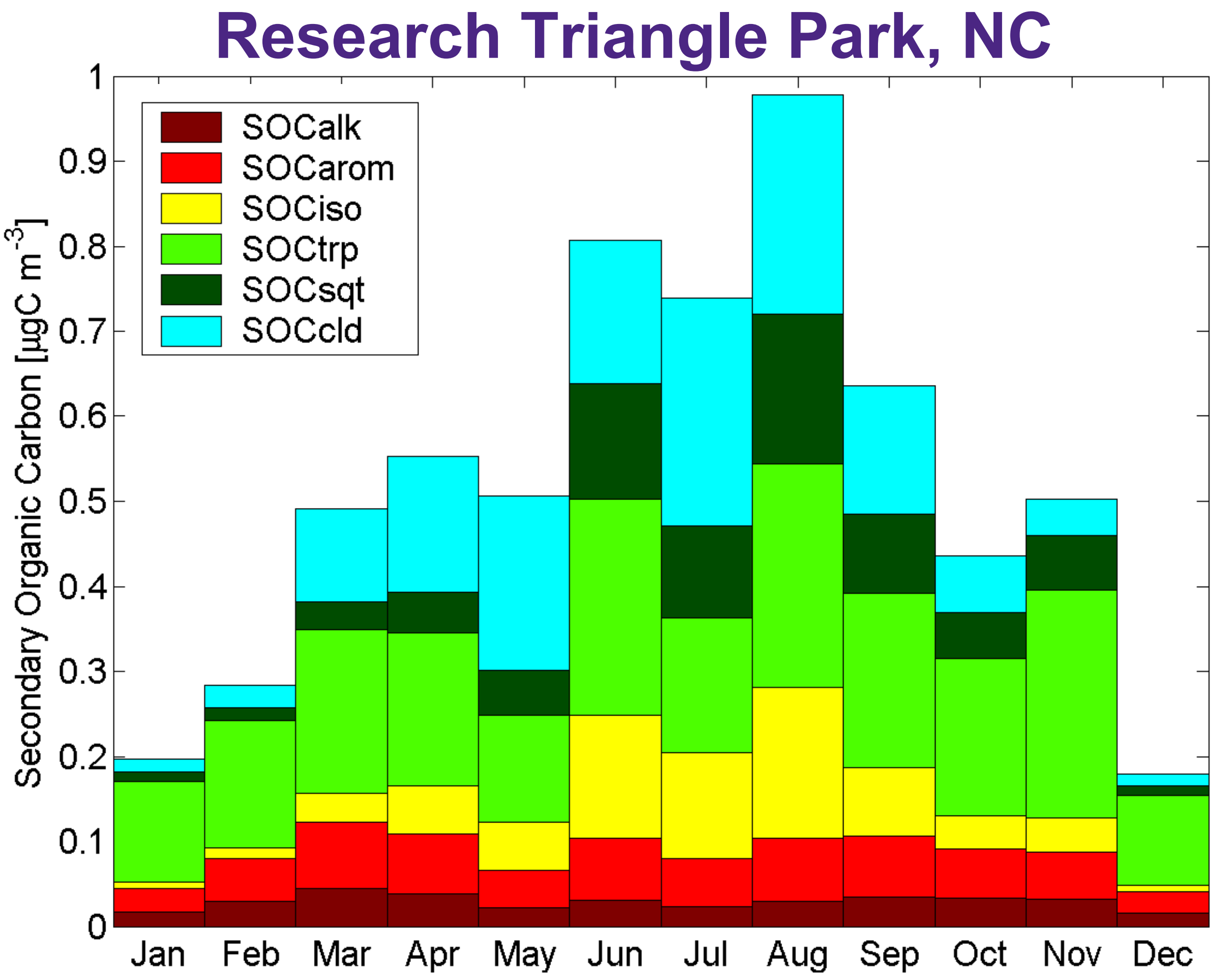


<u>Key features in Southeast</u>

- 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

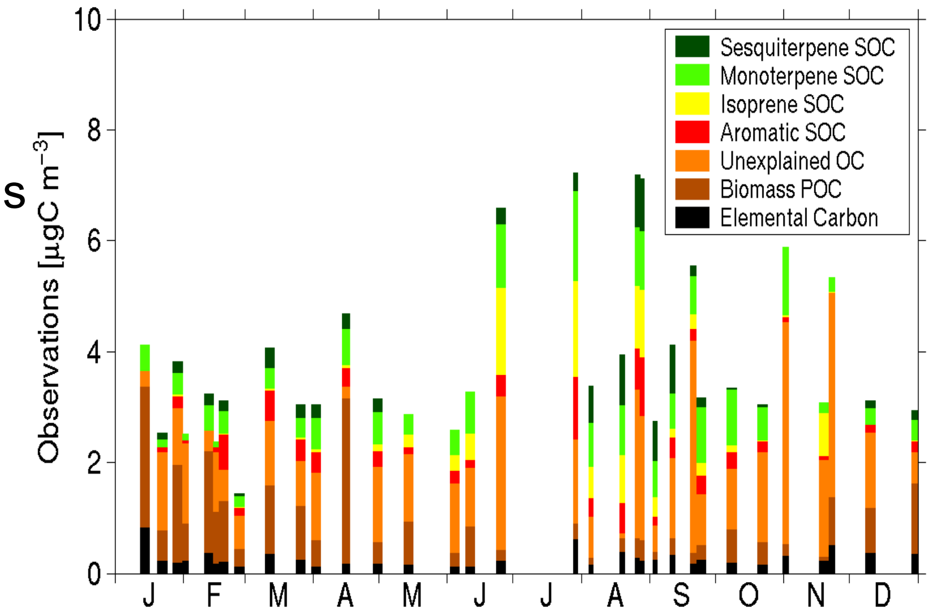


- Previous CMAQ evaluations for carbonaceous PM:
  - OC, EC (numerous surface sites)
  - WSOC, ^{14}C (intensive campaigns)
  - Molecular markers for POC
- None of these measurements permit a direct assessment of the model predictions of different classes of SOC

Tracer-Based Estimates of SOC

<u>Tracer-based method for estimating source contributions to ambient SOC</u>

- 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.
  - <u>Estimated</u> 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:

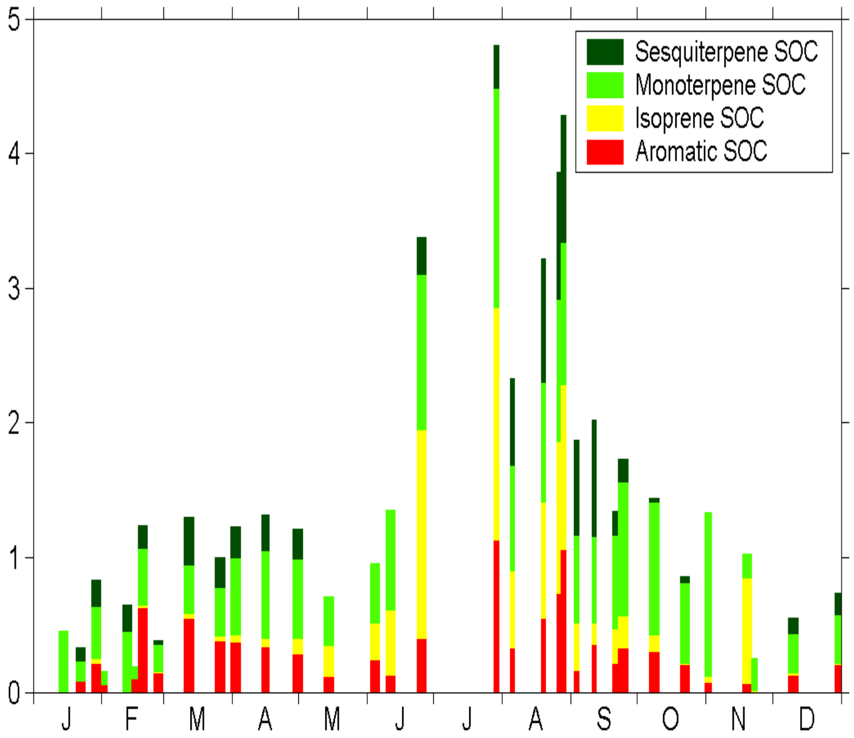
- Are the tracer/SOC ratios measured in the chamber equal to those in the atmosphere?

Approach:

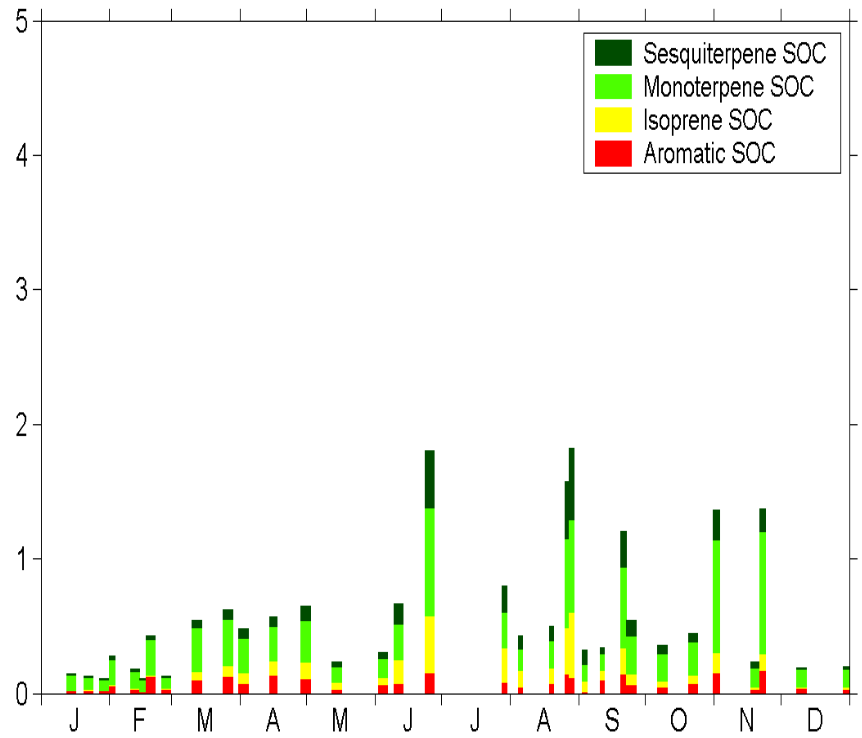
- Accept the tracer estimates at face value until better information becomes available.

Model Evaluation for 4 SOC Classes

Tracer-Based Estimates

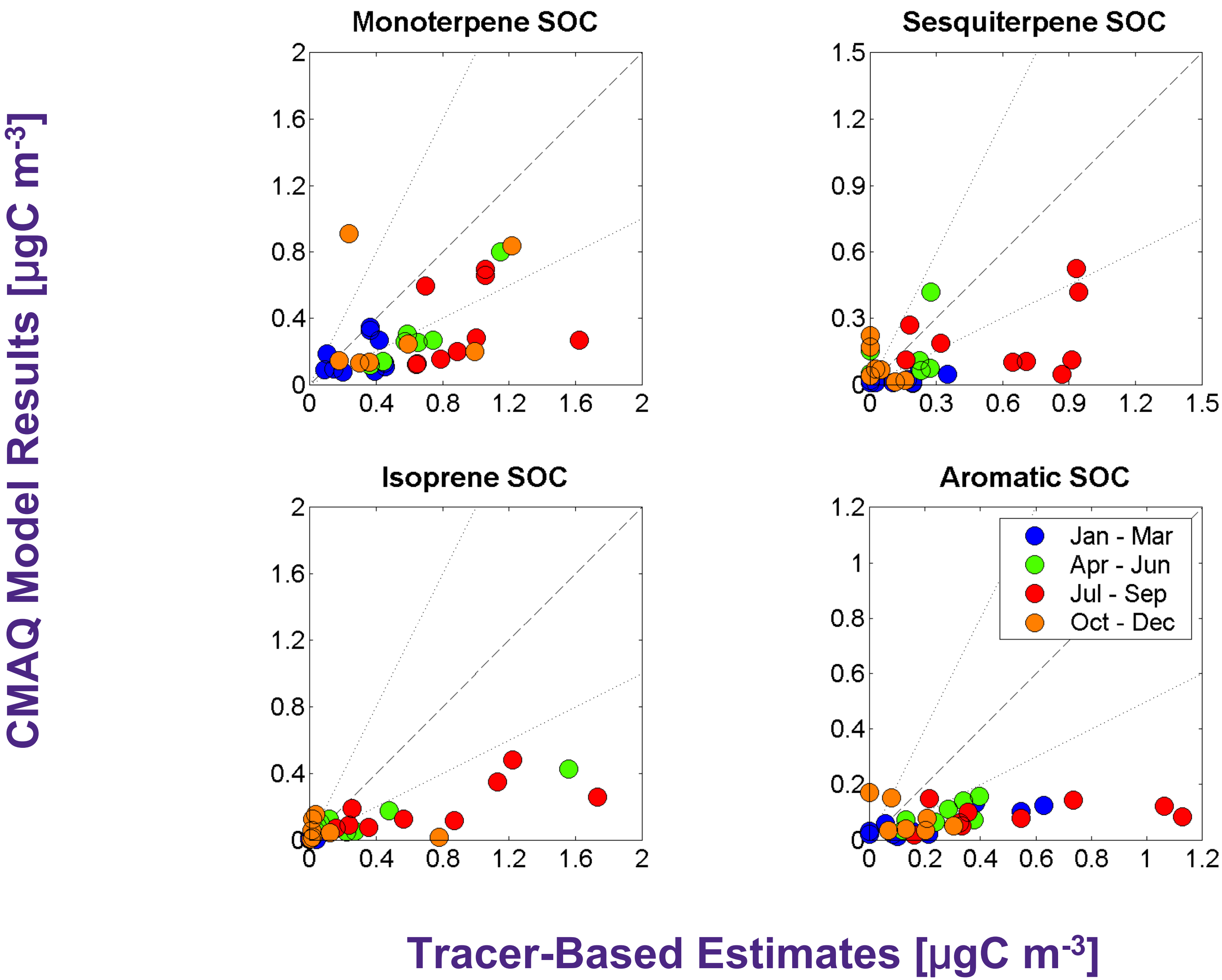


CMAQ Model Results



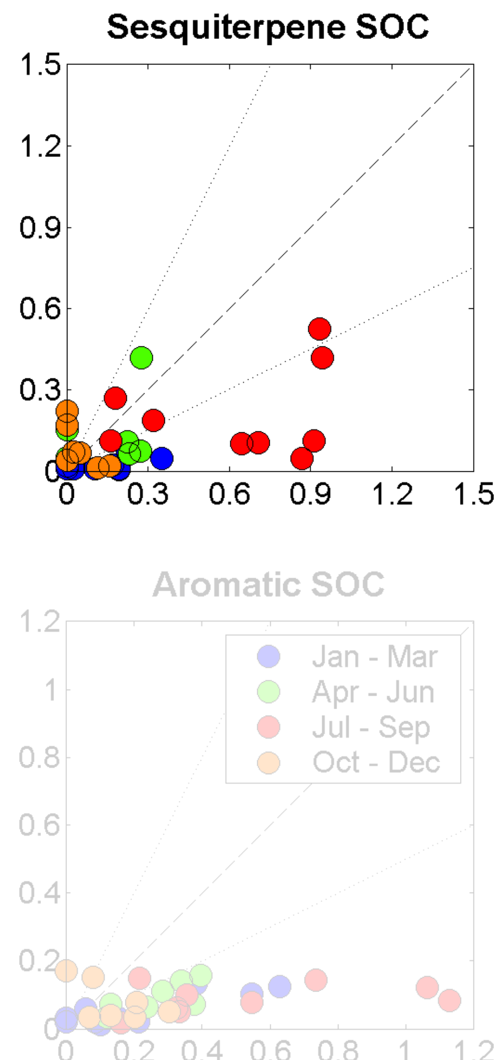
- Model results are consistently low (31 out of 33 samples), especially during summer months
- Explore the cause, by examining various model parameters

Model Evaluation for 4 SOC Classes

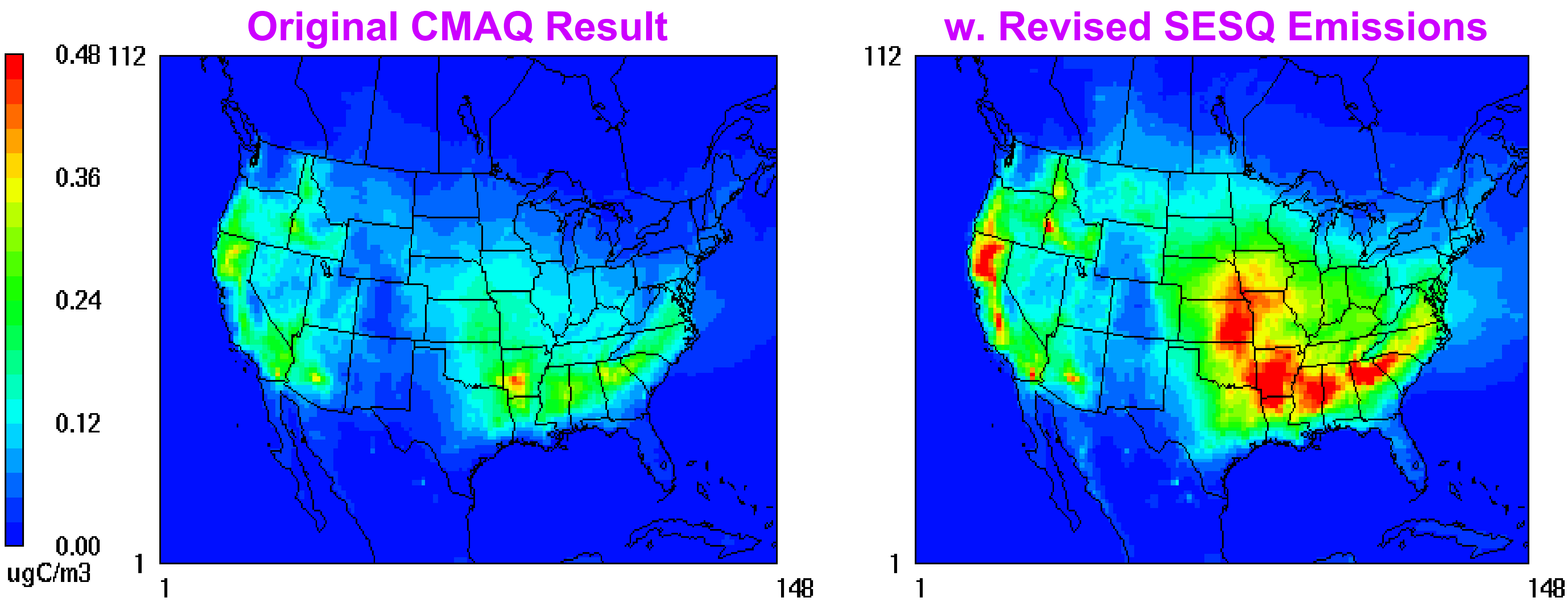


Model Evaluation for Sesquiterpene SOC

- 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 + O_3 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)



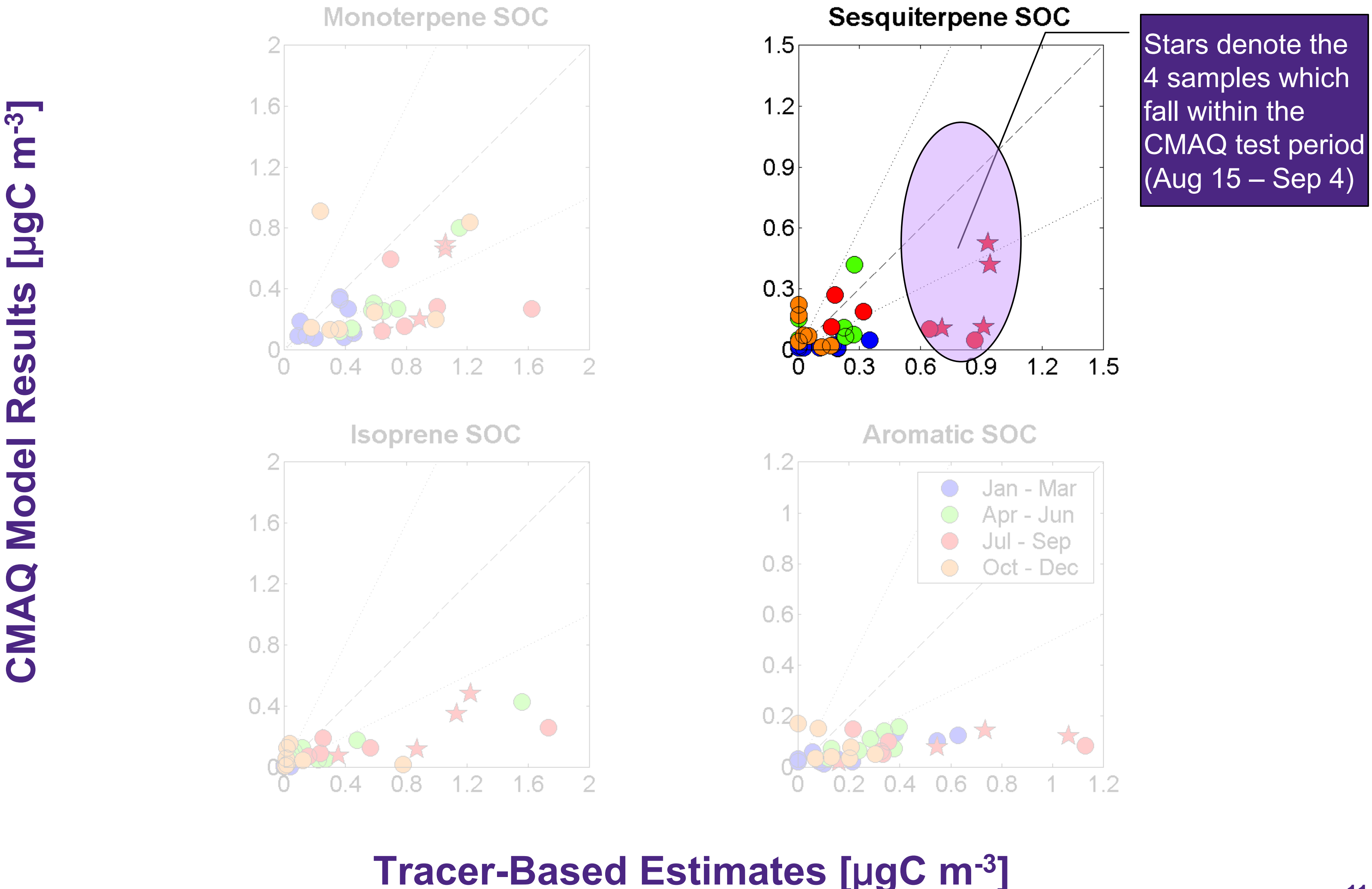
Sensitivity #1: SESQ Emissions
Sesquiterpene SOC (18-day average)



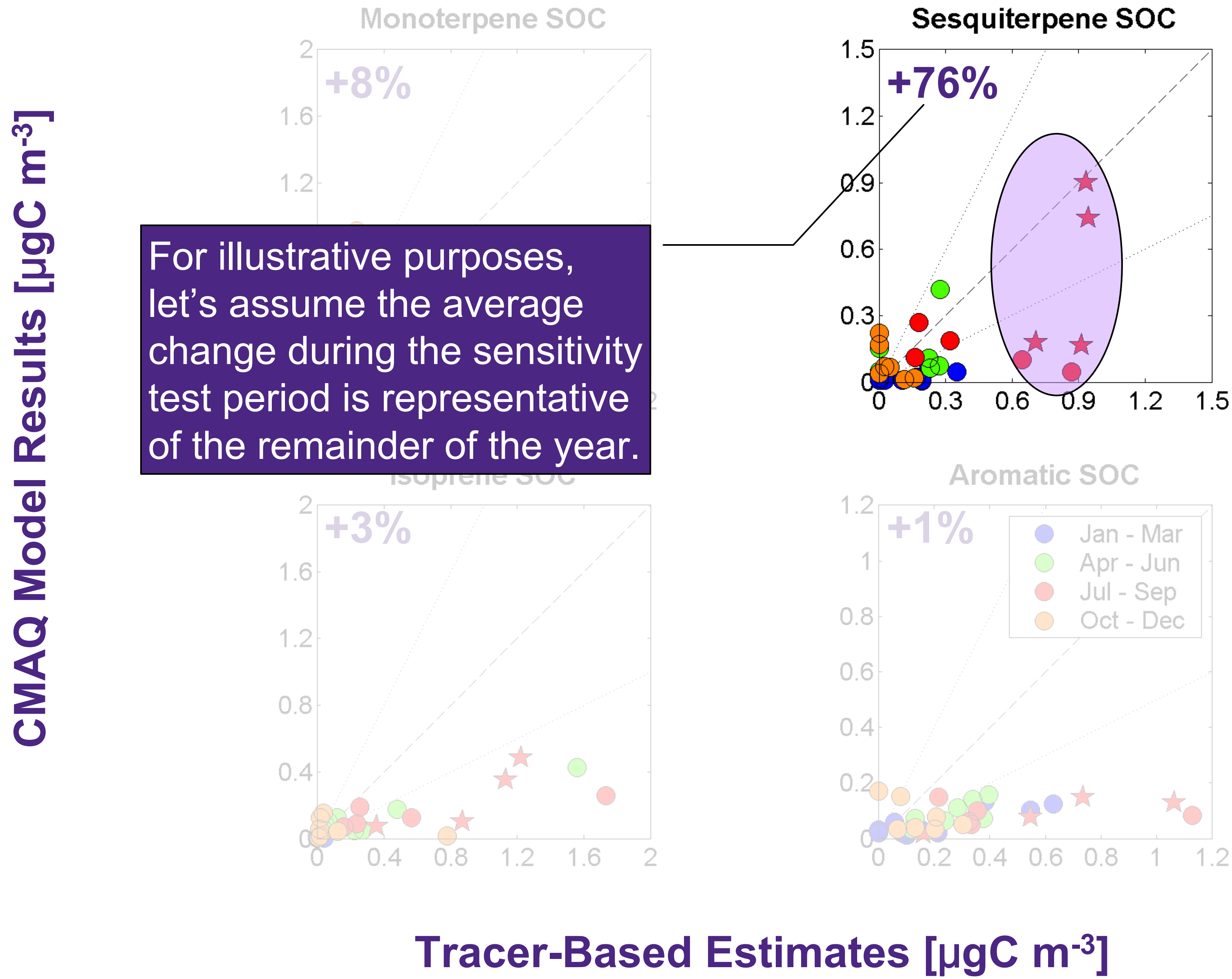
SOC_{SESQ} increases by ~3x in central states and Midwest. Increase is ~2x across southeast.
In RTP, average SOC_{SESQ} concentration increases by 76%, from 0.21 to 0.36 μgC m^{-3}.

Relative increase in SOC_{SESQ} concentration (76%) exceeds the emissions increase in RTP (59%)

Model Evaluation for Sesquiterpene SOC

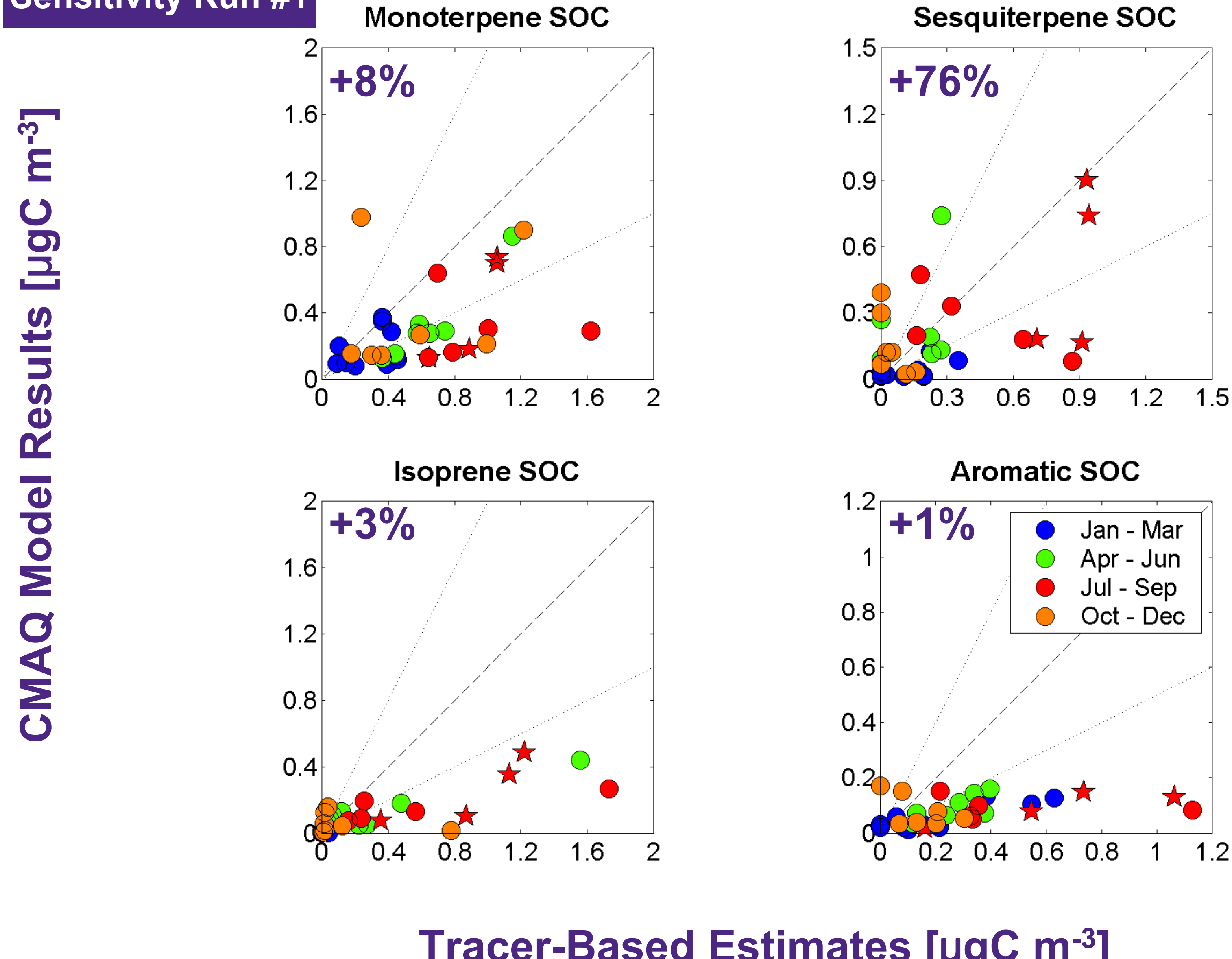


Model Evaluation for Sesquiterpene SOC



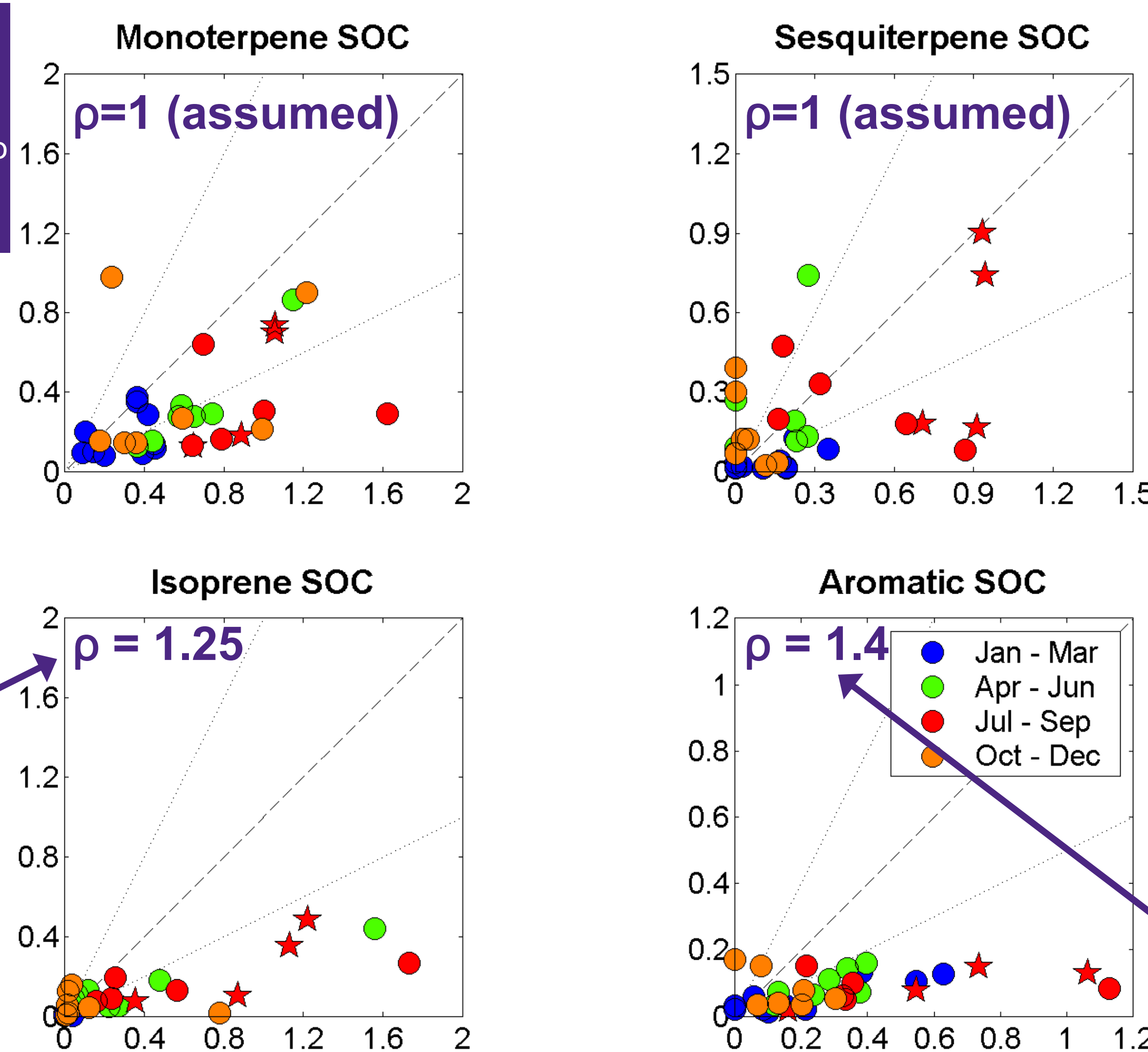
Model Evaluation for 4 SOC Classes

Sensitivity Run #1



Sensitivity #2: SOA Density

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

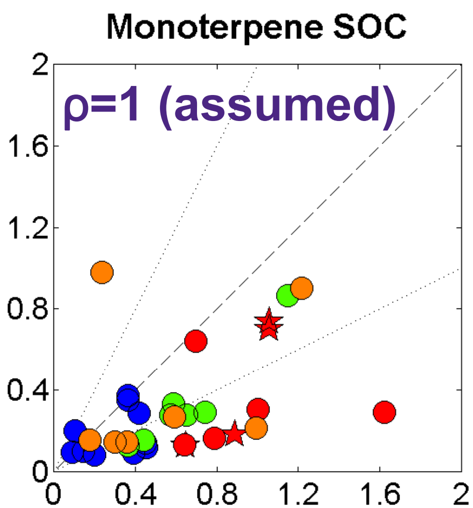


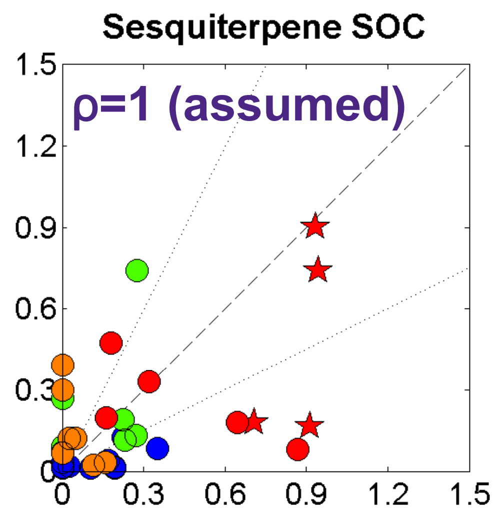
Griffin et al., (1999)

Kroll et al., (2006)

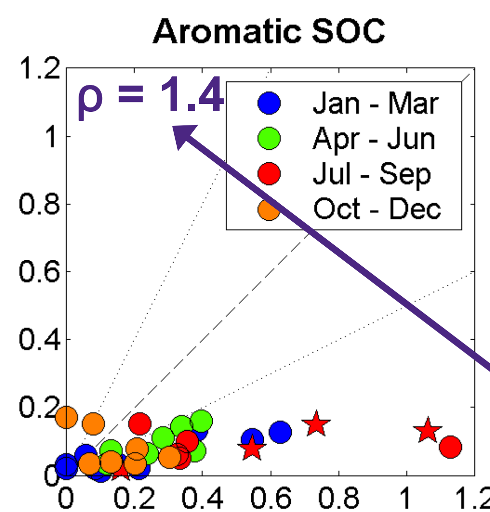
Ng et al., (2007)

Sensitivity #2: SOA Density





Griffin et al., (1999)

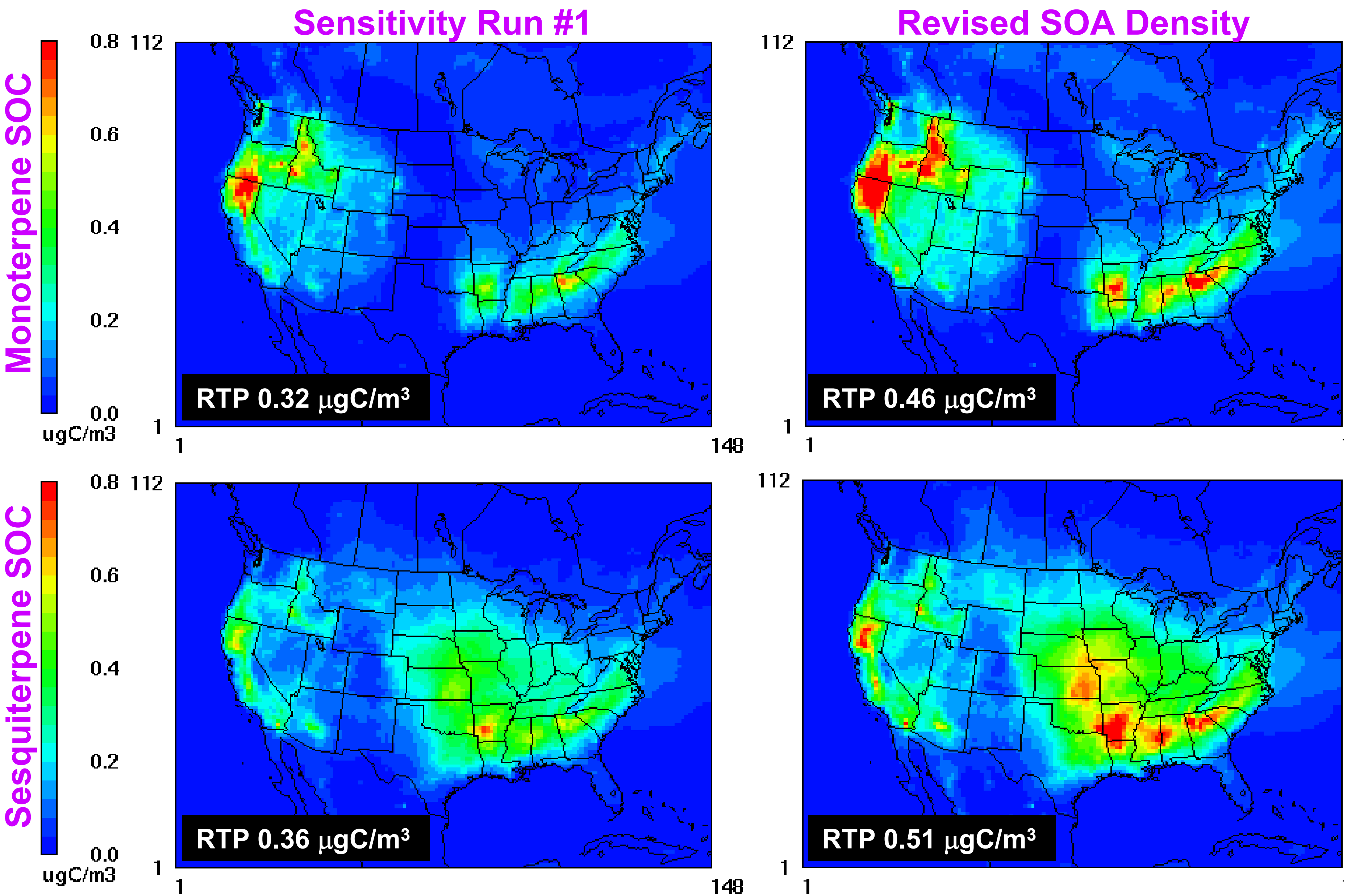


Ng et al., (2007)

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}.

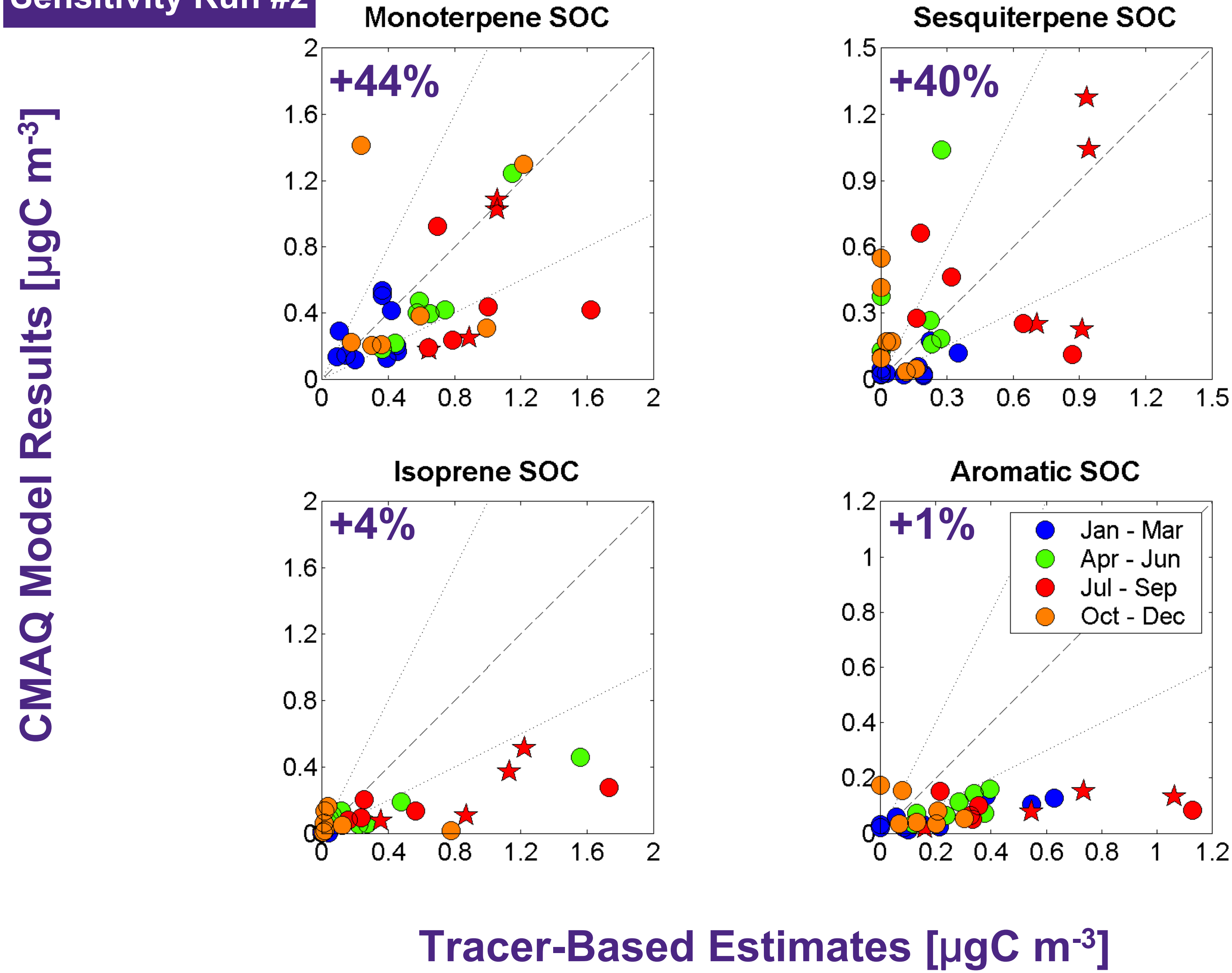
Repeat simulation (Aug. 15 – Sep. 4)

Sensitivity #2: SOA Density

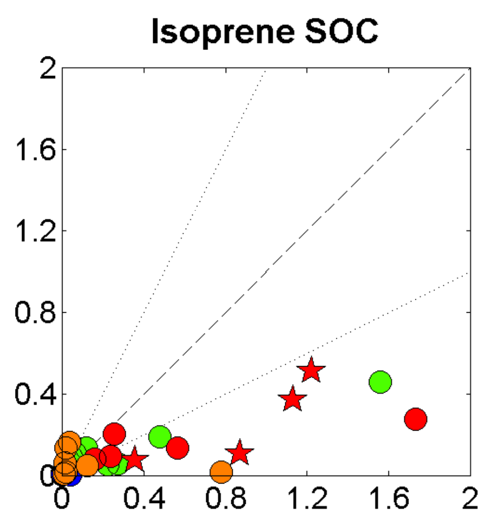


Model Evaluation for 4 SOC Classes

Sensitivity Run #2

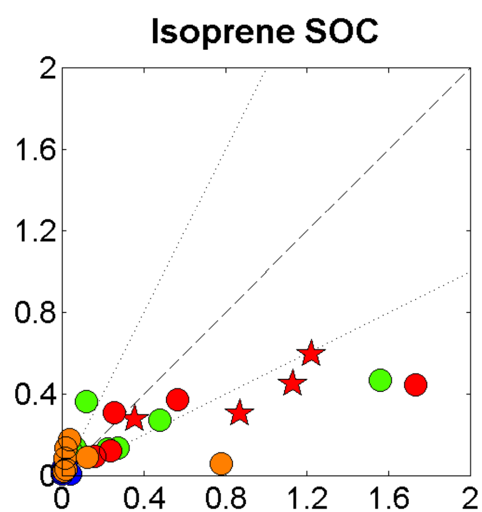


Model Evaluation for Isoprene SOC



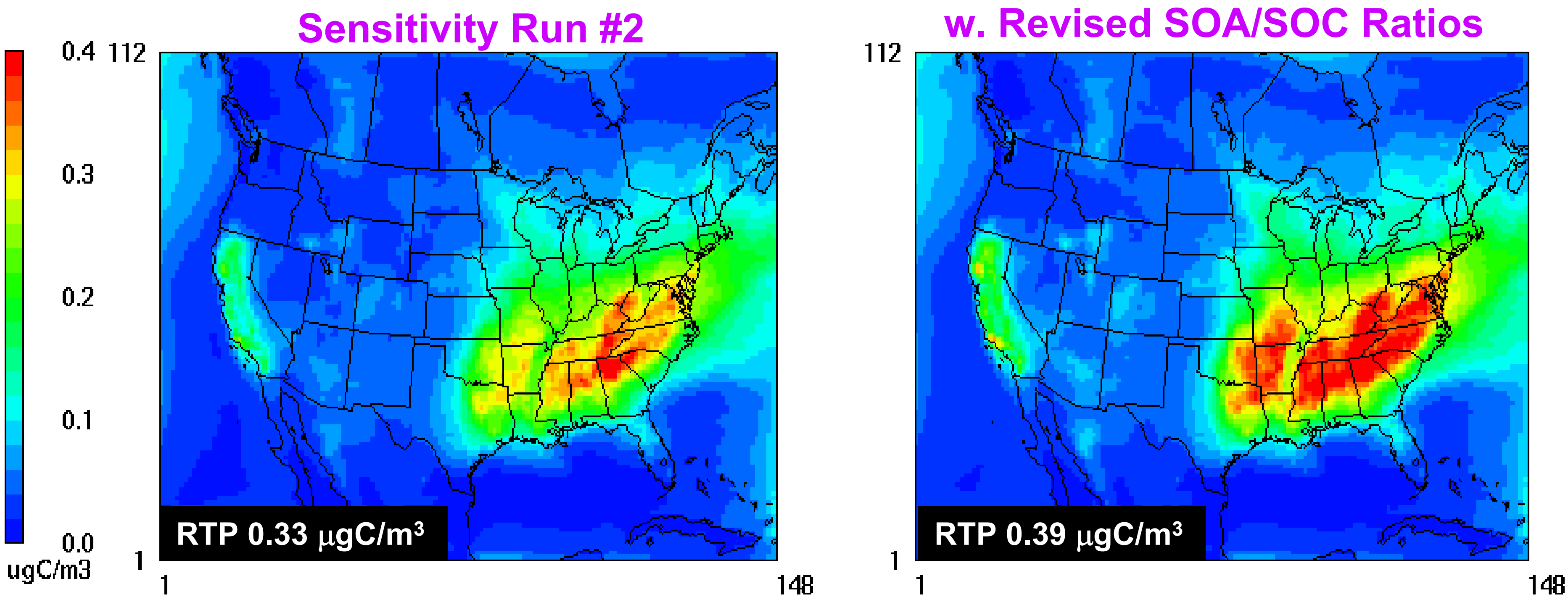
- Model bias is largest during summer (underprediction > 3x), and quite substantial during spring & fall (> 2x)
- We're already using the highest SOC_{isop} yields reported in the literature (low-NO_X conditions of Kroll et al., 2006)
- Recent studies indicate that isoprene tracers (methyltetrols & 2-methylglyceric 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 $0.7 \times SOC_{cld}$ 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 SO_2.
  - Without SO_2, SOA/SOC = 1.6
  - With SO_2, SOA/SOC = 2.7
- SOA yields reported by Kroll et al. (2006) were obtained without SO_2. By using a large SOA/SOC, the model may be producing too little SOC.
- Repeated simulation (Aug.15 – Sep. 4)

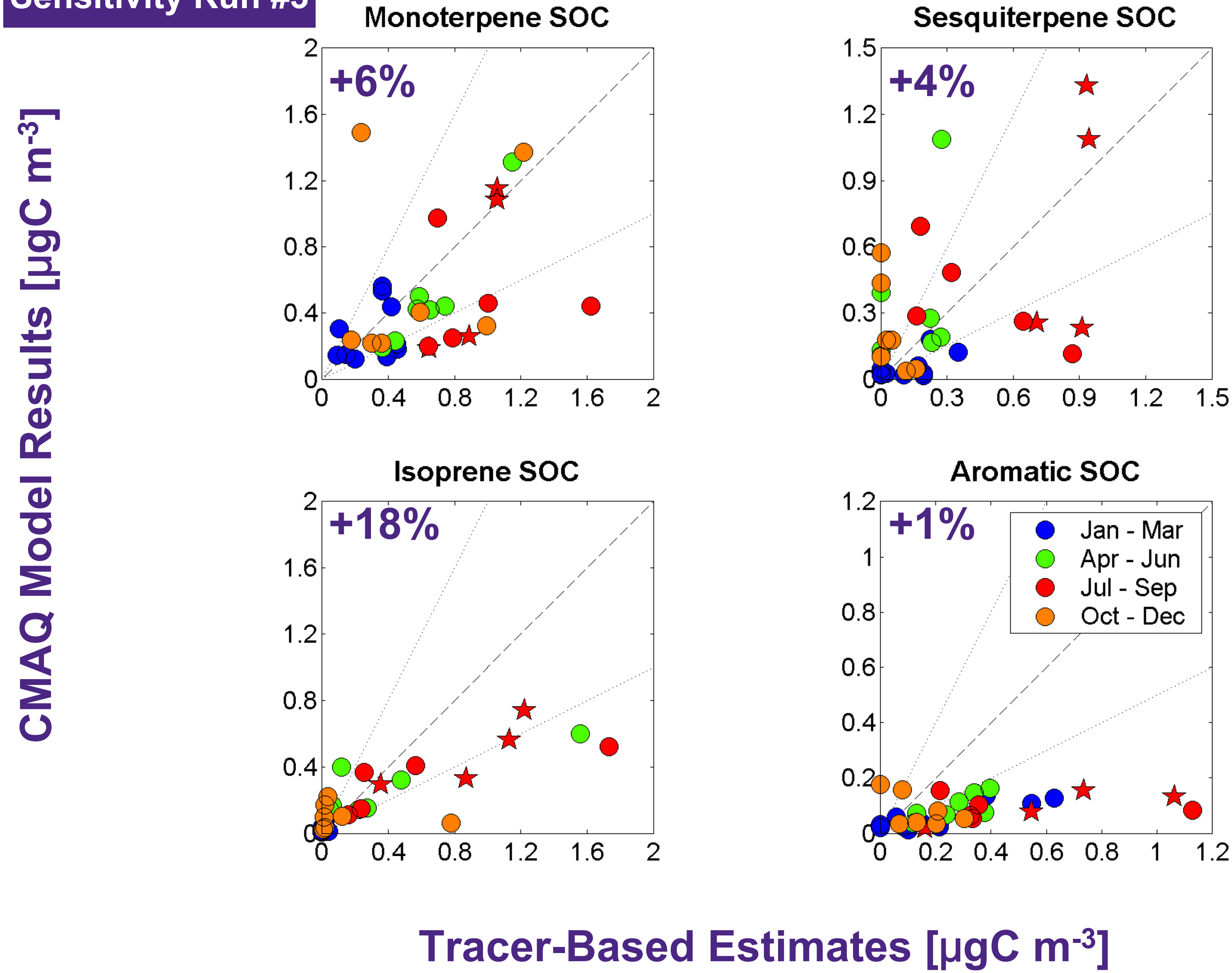
Sens #3: Isoprene SOA/SOC Ratio
Isoprene SOC (+0.7 SOC_{cld})



SOC_{ISOP} increases by 18% in RTP.

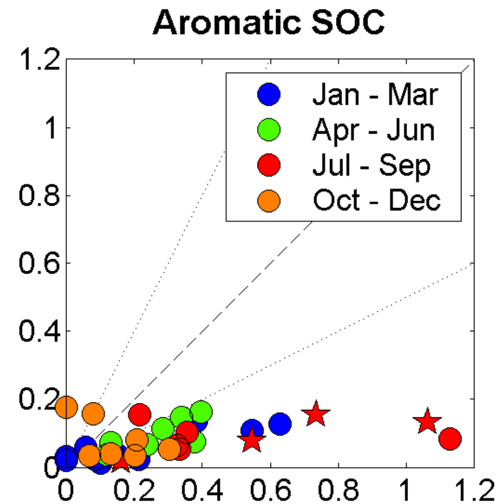
Model Evaluation for 4 SOC Classes

Sensitivity Run #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.

Acknowledgements

- Tad Kleindienst, Ed Edney, John Offenberg, Michael Lewandowski, Mohammed Jaoui (HEASD)
- Chris Nolte, Rob Pinder, Rohit Mathur (AMD)
- Nancy Hwang, Ruen Tang (CSC)