

US EPA ARCHIVE DOCUMENT

# Source-Oriented Chemical Transport Model for Primary and Secondary Organic Aerosol

Mike Kleeman

Civil and Environmental Engineering  
UC Davis

Rob Griffin,

EOS/Earth Sciences  
University of New Hampshire

Simon Clegg

University of East Anglia

June 2007



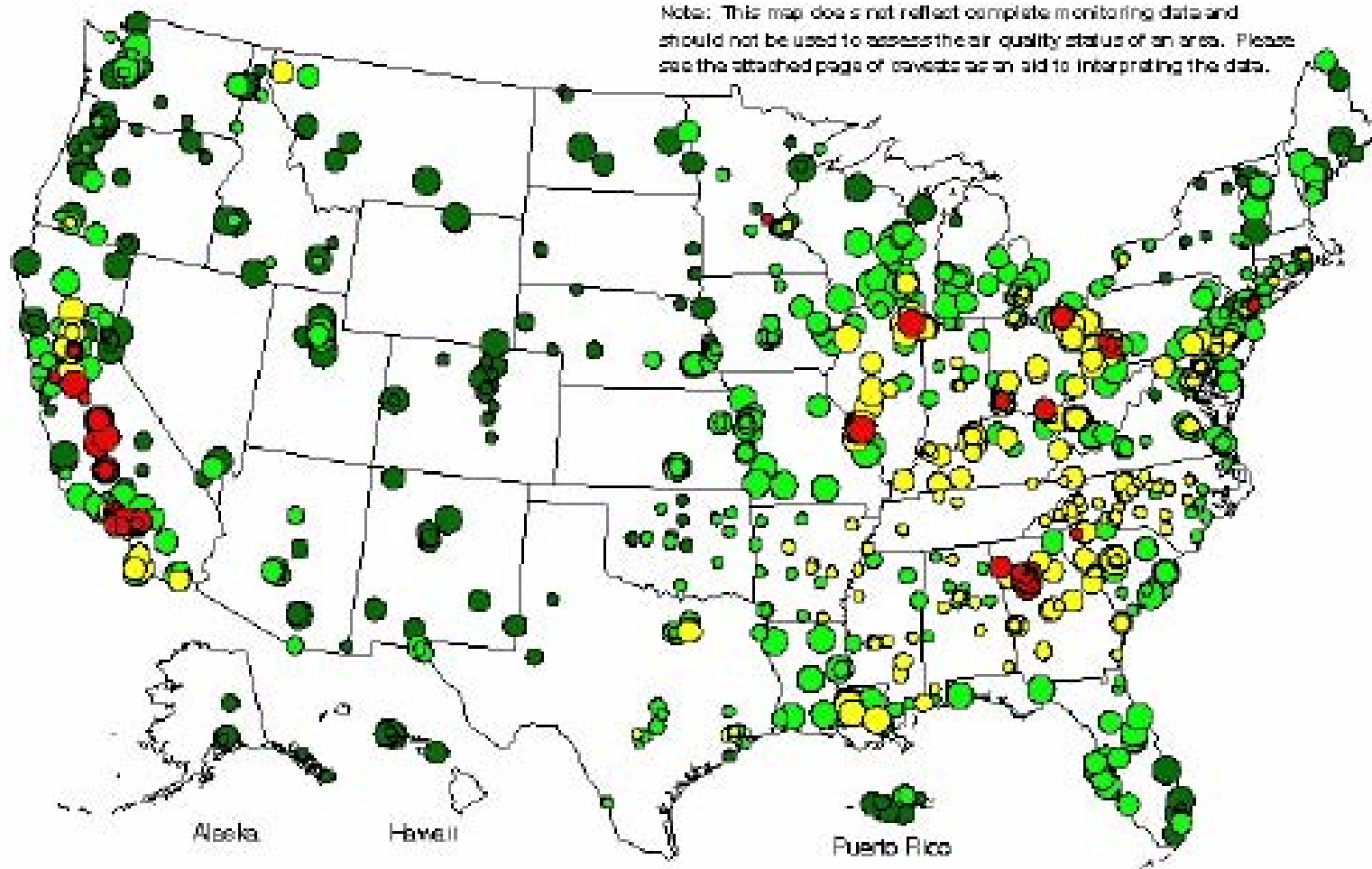
This research is funded by

U.S. EPA - Science To Achieve  
Results (STAR) Program

Grant # **RD831082**



Note: This map does not reflect complete monitoring data and should not be used to assess the air quality status of an area. Please see the attached page of reports as an aid to interpreting the data.



Data Completeness

- less ○ < 4 quarters
- ↑ □ one or more quarters with < 11 samples
- All quarters with at least 11 samples
- more ○ All quarters 75% or more complete

Concentration (ug/m3)

- > 20
- 15- 20
- 10- 15
- 0- 10

Figure 1. 1999 annual mean  $PM_{2.5}$  concentrations (calculated as the mean of each quarterly mean).

Source: U.S. EPA AIRS data base, July 12, 2000.

# Unique Tracers For Source Apportionment of Particulate Carbon

Unique Tracer	Source	Comment
Levoglucosan Methoxyphenols Betulin Juvabione, Dehydrojuvabion Dehydroabietic acid	General Wood Combustion General Wood Combustion Paper Birch Balsam Fir Conifers	Emissions rate depends on combustion conditions.
Hopanes and Steranes	Lubricating oil in Gasoline-and Diesel powered engines	Does not distinguish between gasoline and diesel vehicles.
Isoprenoids and Tricyclic Terpanes	Gasoline-powered Motor Vehicle Exhaust	Trace amounts present in diesel vehicle exhaust.
C31 Hopanes Divanillyl 1,2-divanillylethane	Coal	
Cholesterol Acyl Monoglycerides	Grilling/Charring Meat	Emission rate depends on the cooking method: charbroiling or frying.
1,6-anhydro-2-acetamido-2-deoxyglucose	Grilling/Charring Crustacean Seafood	
High molecular weight, odd carbon number n-alkanes	Leaf Abrasion	
Iso- and anteiso-alkanes	Tobacco Smoke	

# Key Questions:

- Are tracers modified in the atmosphere?
  - Effect of oxidants
  - Aqueous processing
- How do we distinguish between sources that do not have unique tracers?
- How do we quantify secondary organic aerosol (SOA)?
- How can we reduce the cost of source apportionment?

# Project Objectives

- Predict the formation of secondary organic aerosol using a state-of-the-science chemical transport model
- Identify improvements to secondary organic aerosol prediction algorithms
- Determine regional source contributions to primary organic aerosol and secondary organic aerosol using a source-oriented approach

# Summary of Project Accomplishments

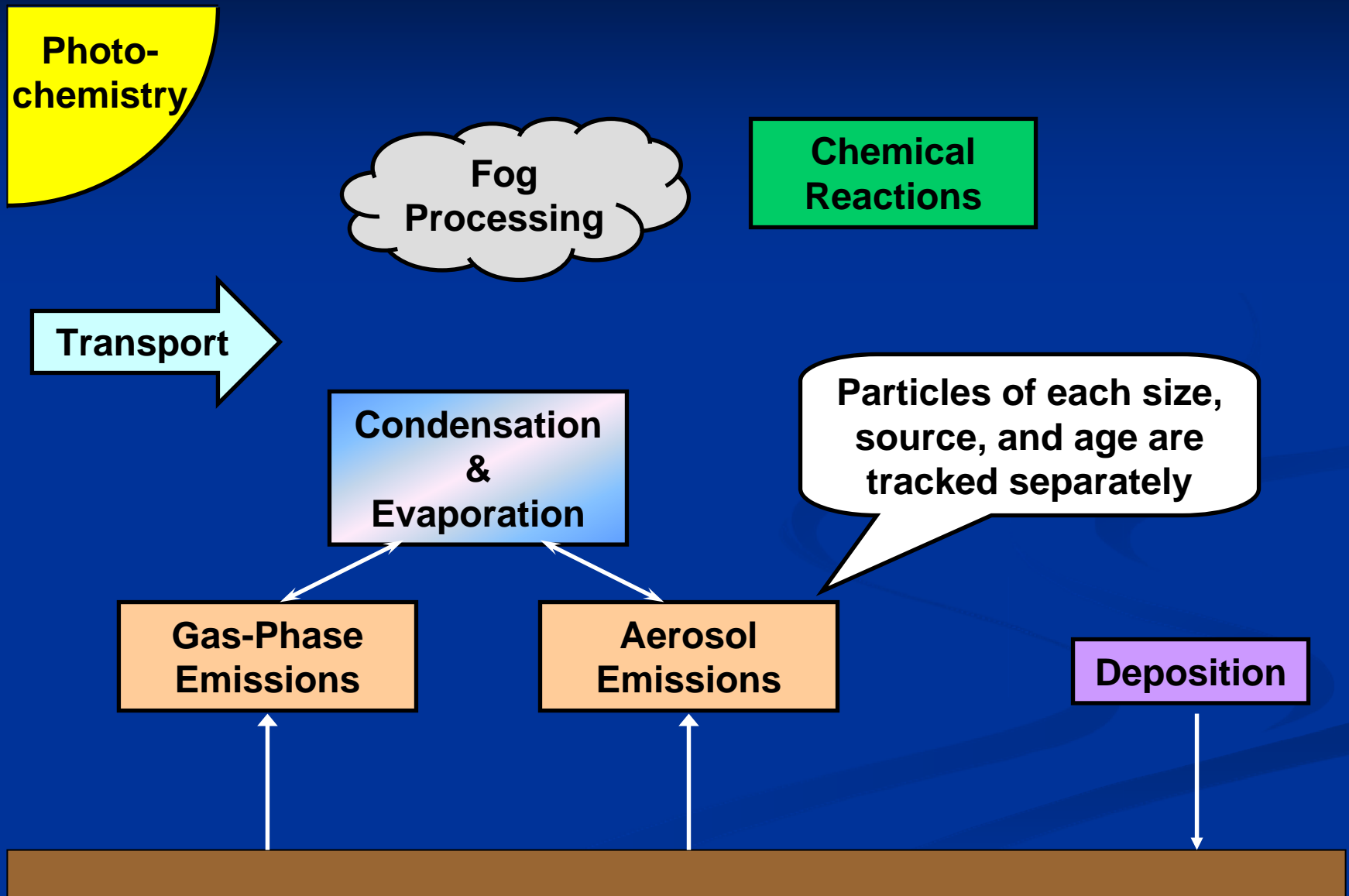
1. R.J. Griffin, D. Dabdub, and J.H. Seinfeld, Development and initial evaluation of a dynamic species-resolved model for gas-phase chemistry and size-resolved gas/particle partitioning associated with secondary organic aerosol formation, *J. Geophys. Res.*, 110: D5, 2005.
2. J. Chen and R.J. Griffin\*, Modeling secondary organic aerosol formation from oxidation of  $\alpha$ -pinene,  $\beta$ -pinene, and d-limonene, *Atmospheric Environment*, 39: 7731-7744, 2005.
3. T. Held, Q. Ying, M.J. Kleeman, J.J. Schauer, M.P. Fraser, A comparison of the UCD/CIT air quality model and the CMB source-receptor model for primary airborne particulate matter, *Atmospheric Environment*, 39: 2281-2297, 2005. (supported jointly by EPA project #RD831082 and CARB project #2000 – 05PM).
4. Q. Ying, T. Held, M.J. Kleeman, Source contributions to the regional distribution of secondary particulate matter in California, *Atmospheric Environment*, 40: 736-752, 2006. (supported jointly by EPA project #RD831082 and CARB project #2000 – 05PM).
5. S. Vutukuru, R.J. Griffin, and D. Dabdub, Simulation and analysis of secondary organic aerosol dynamics in the South Coast Air Basin of California, *J. Geophys. Res.*, 111, D10S12, doi: 10.1029/2005JD006139, 2006.
6. J. Chen, H. Mao, R.W. Talbot, and R.J. Griffin, Application of the CACM and MPMPO modules using the CMAQ model for the Eastern United States, *J. Geophys. Res.*, 111, D23S25, doi: 10.1029/2006JD007603, 2006.
7. Q. Ying, M.P. Fraser, J. Chen, R.J. Griffin and M.J. Kleeman. Verification of a source-oriented externally mixed air quality model during a severe photochemical smog episode. *Atmospheric Environment* (7): 1521-1538 MAR 2007.
8. M.J. Kleeman, Q. Ying, M.J. Mysliwiec, R.J. Griffin and J. Chen. Source apportionment of secondary organic aerosol during a severe photochemical smog episode. *Atmospheric Environment* 41, 576-591, 2007.
9. S.L. Clegg, M.J. Kleeman, R.J. Griffin, and J.H. Seinfeld. Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model. I. Treatment of inorganic electrolytes and organic compounds in the condensed phase, and the results of an atmospheric simulation. *Atmospheric Chemistry and Physics Discussions*, submitted for publication, 2007.
10. S.L. Clegg, M.J. Kleeman, R.J. Griffin, and J.H. Seinfeld. Effects of uncertainties in the thermodynamic properties of aerosol components in an air quality model. II. Predictions of pure component vapour pressures of organic compounds. *Atmospheric Chemistry and Physics Discussions*, submitted for publication, 2007.

# Source-Oriented Model for Primary and Secondary Organic Aerosol

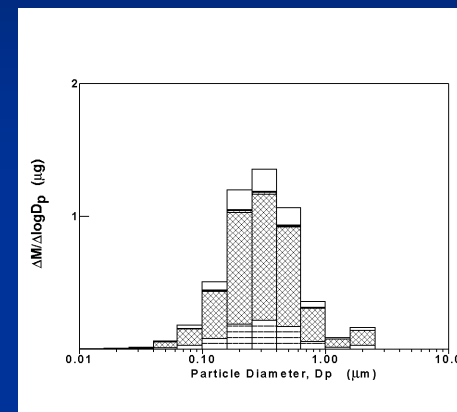
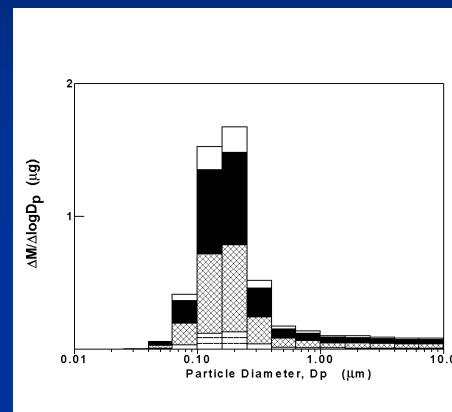
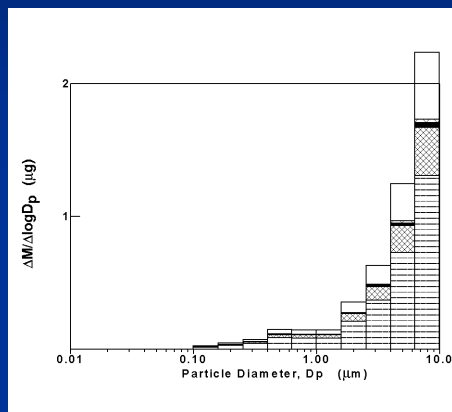
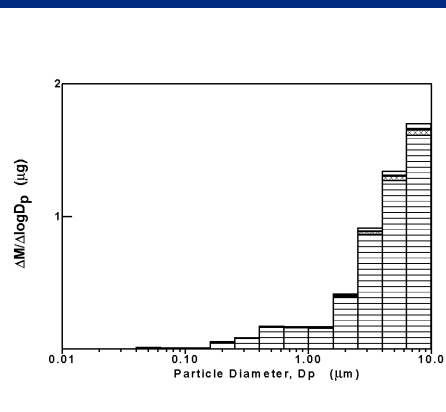
- Track the primary and secondary organic species through a mathematical simulation of emissions, transport, chemical reaction, phase-change, and deposition.
- Keep particles emitted from different sources separate
  - Realistic simulation of atmospheric processing for organic species
  - Source apportionment tool



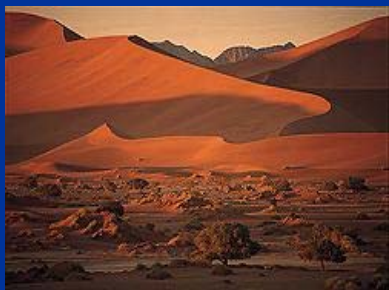
# Air Quality Model



# The Source Oriented External Mixture Model Tracks Particles Separately in the Atmosphere



Crustal Material Other than Paved Road Dust



Paved Road Dust



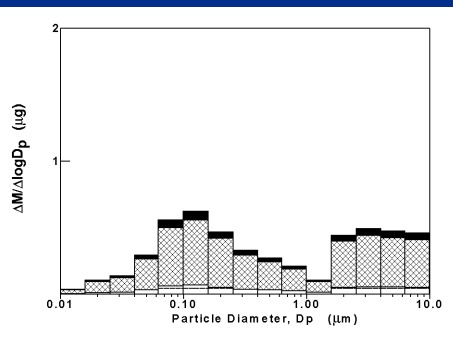
Diesel Engines



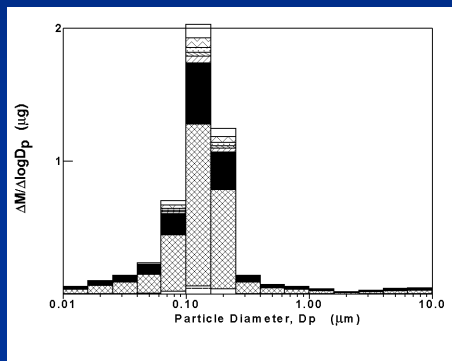
Meat Cooking



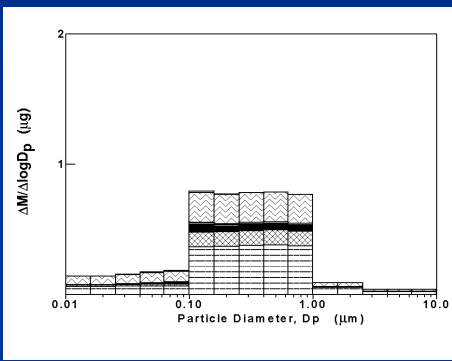
# The Source Oriented External Mixture Model Tracks Particles Separately in the Atmosphere



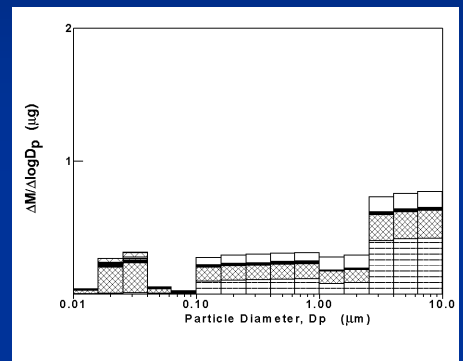
Non-cat Gas Engines



Cat Gas Engines



Acidic Industrial





# Atmospheric Transformation Processes

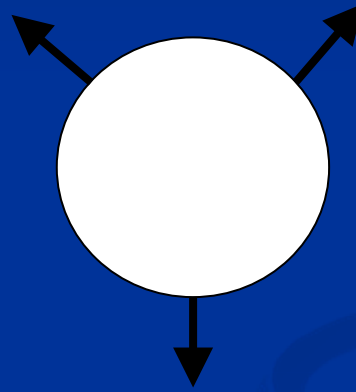
## Fog Chemistry:

- based on model of Jacob et al. (1989)
- 58 active chemical species
- 177 kinetic reactions
- 29 equilibrium relationships

## Secondary Organics:

- based on model of Griffin et al. (2005)

- kinetic gas - particle exchange
- temperature dependence for vapor pressure
- activity coefficient calculations



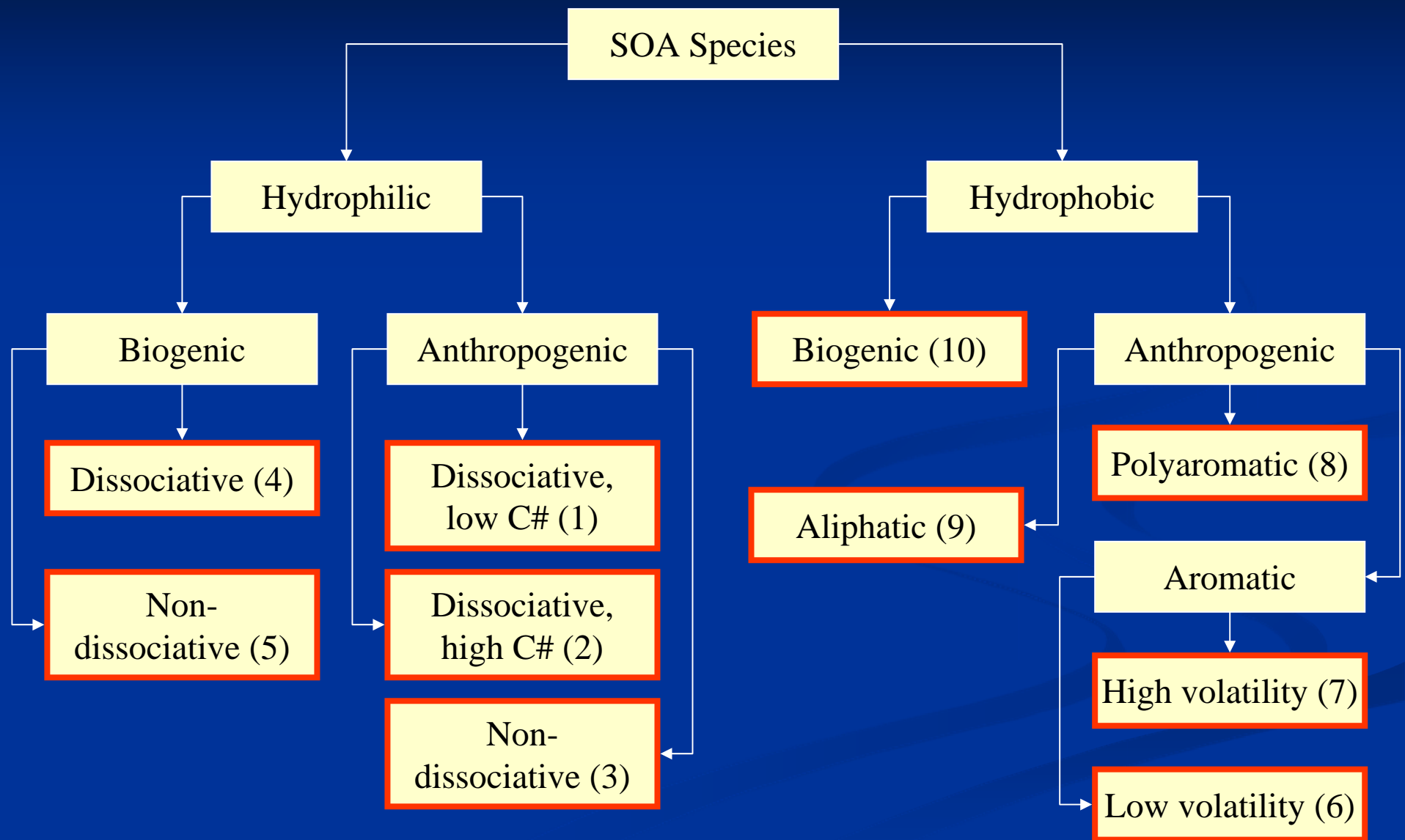
## Small Aerosol Water Content:

- based on AIM model of Wexler et al. (1991)
- kinetic exchange between gas and particle phase
- particle phase species in equilibrium with one another

# Improvements for SOA Model

- Improvements to gas-phase chemical mechanism describing production of semi-volatile species
- Partitioning into aqueous and organic particle phases
- Activity coefficient calculations for organics

# Original SOA Surrogate Species Classifications

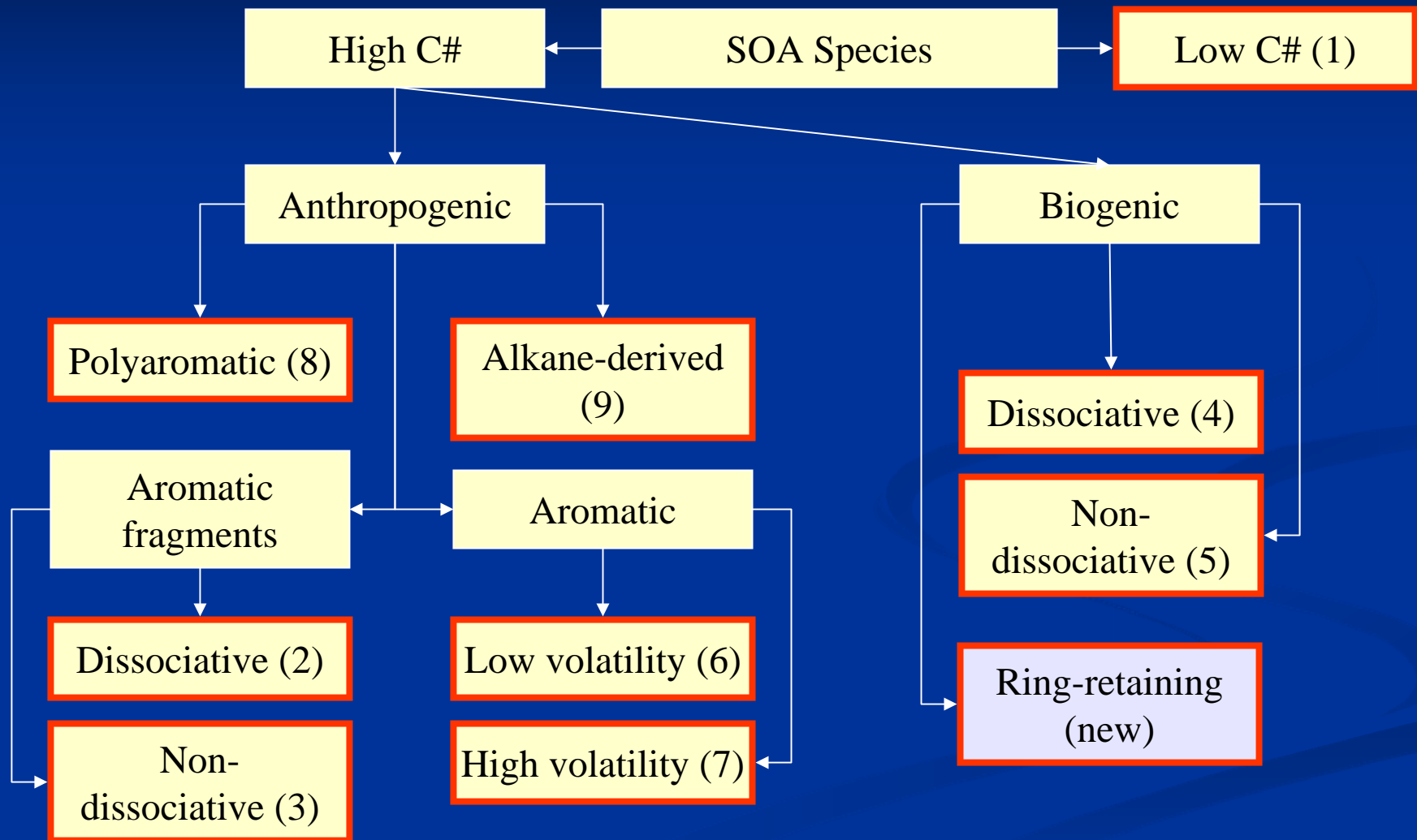


# SOA Model Adaptations

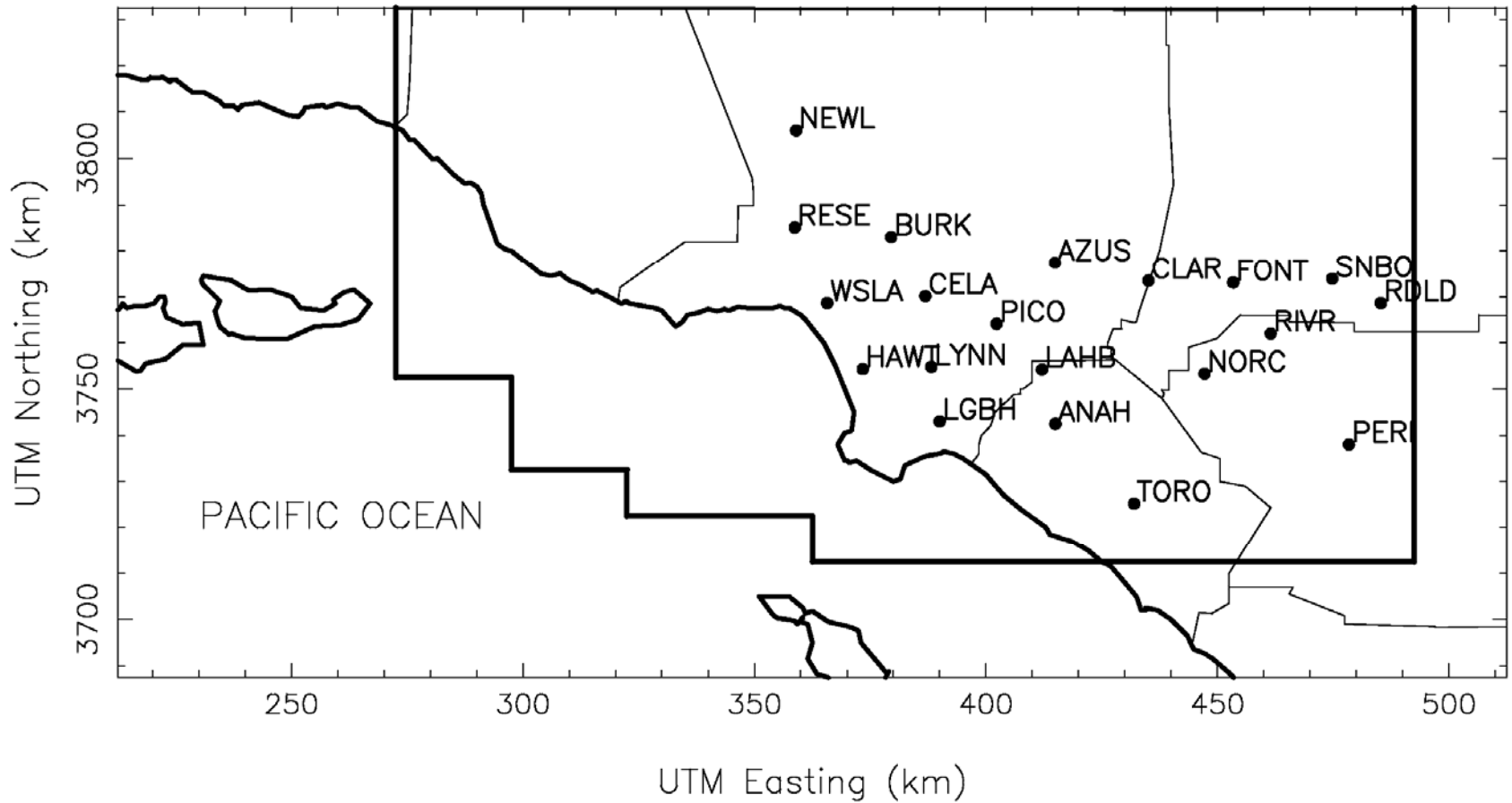
- Chemical changes (stoichiometry and kinetics) to better match observed product distribution, to provide a distinction between high- and low-SOA-yield compounds, and to better match temporal behavior of SOA formation in chambers
- Vapor pressures recalculated using structure activity relationships
- Certain very reactive species are no longer included in partitioning calculations
- NET: Expected decrease in SOA formation, more in-line with other methods based on chamber parameterizations



# New SOA Surrogate Species Classifications

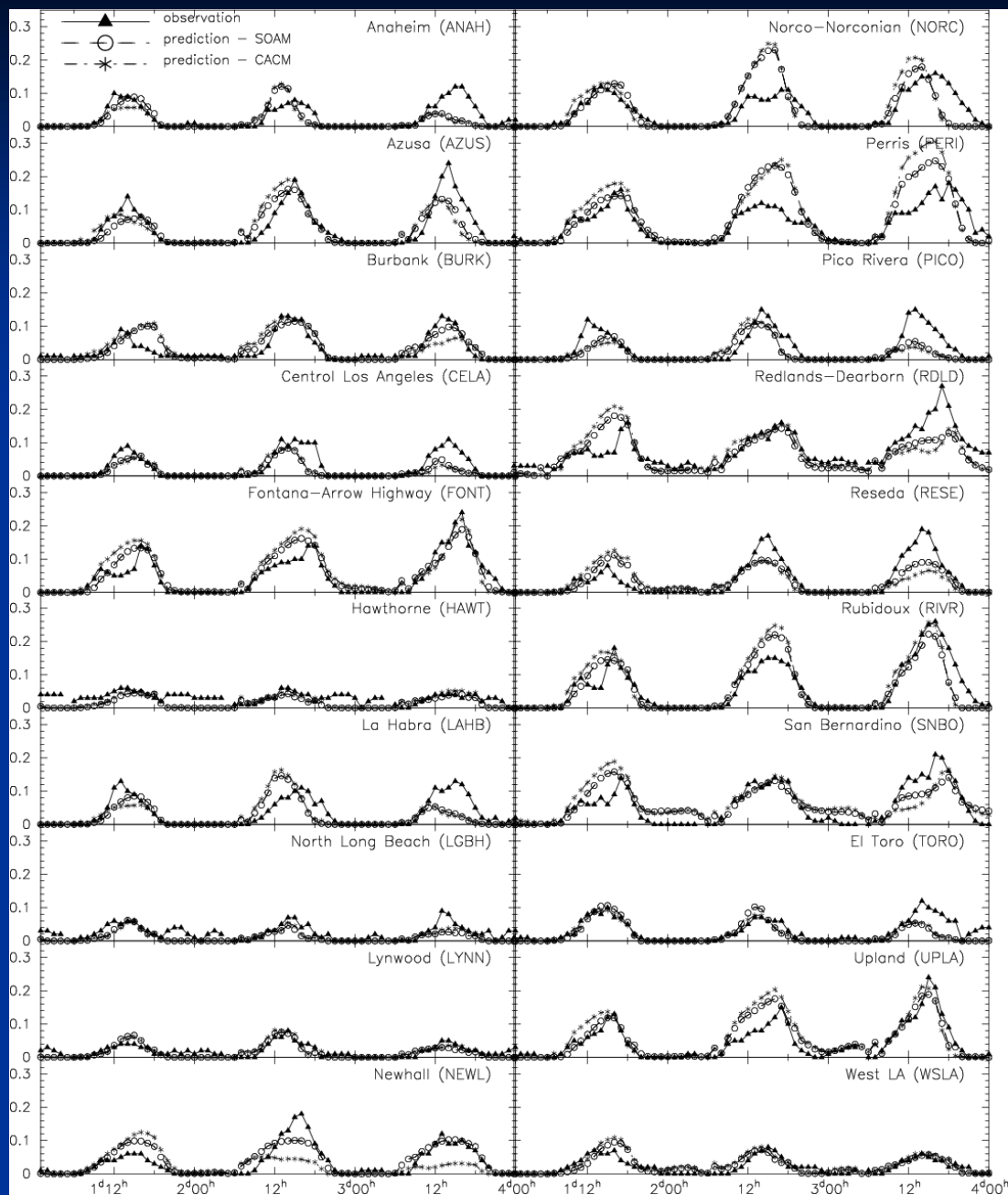


# September 7-9, 1993 SoCAB Study Domain



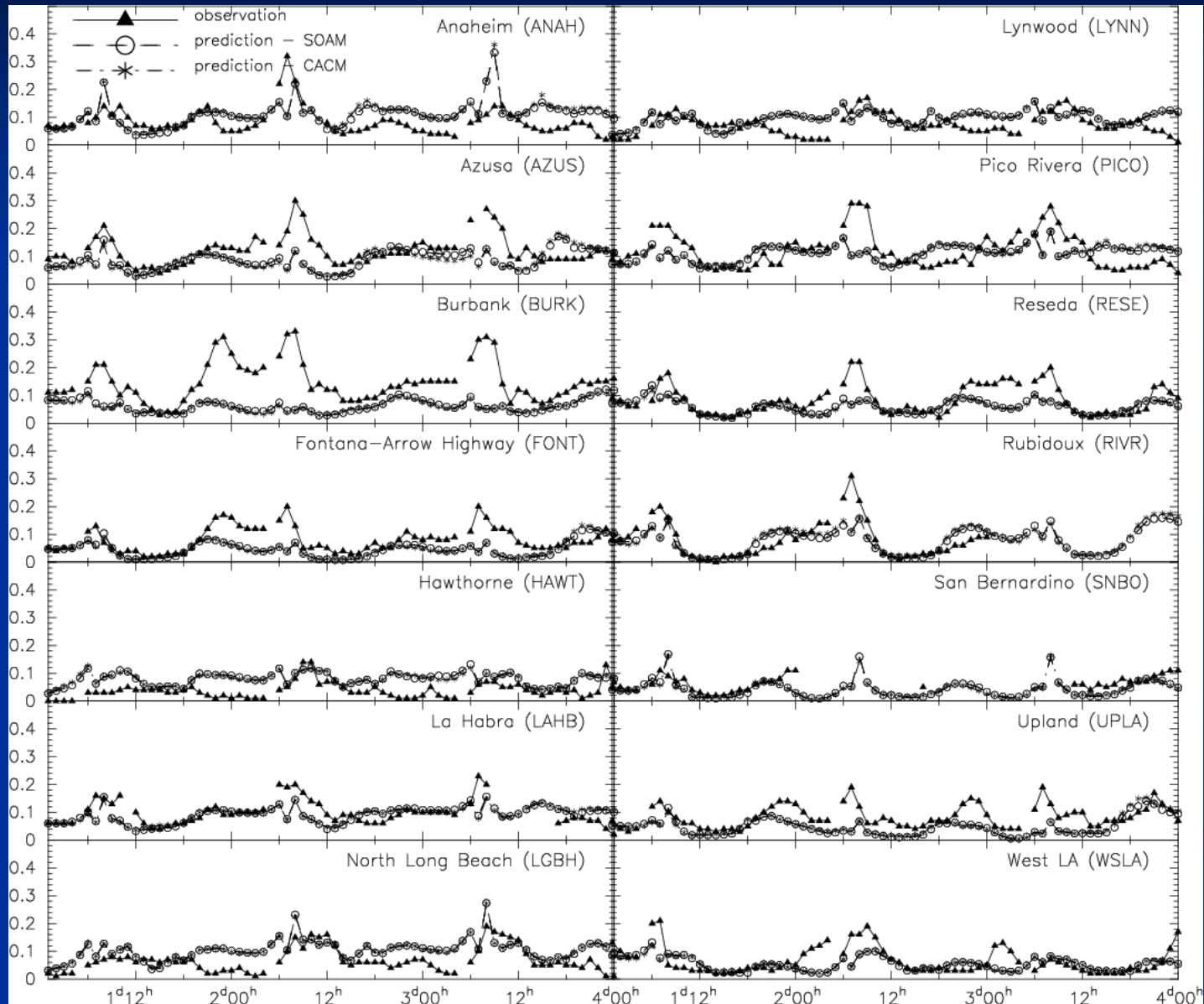
# Model Performance for Ozone

Ozone (ppm)



# Model Performance for NOx

NOx (ppm)



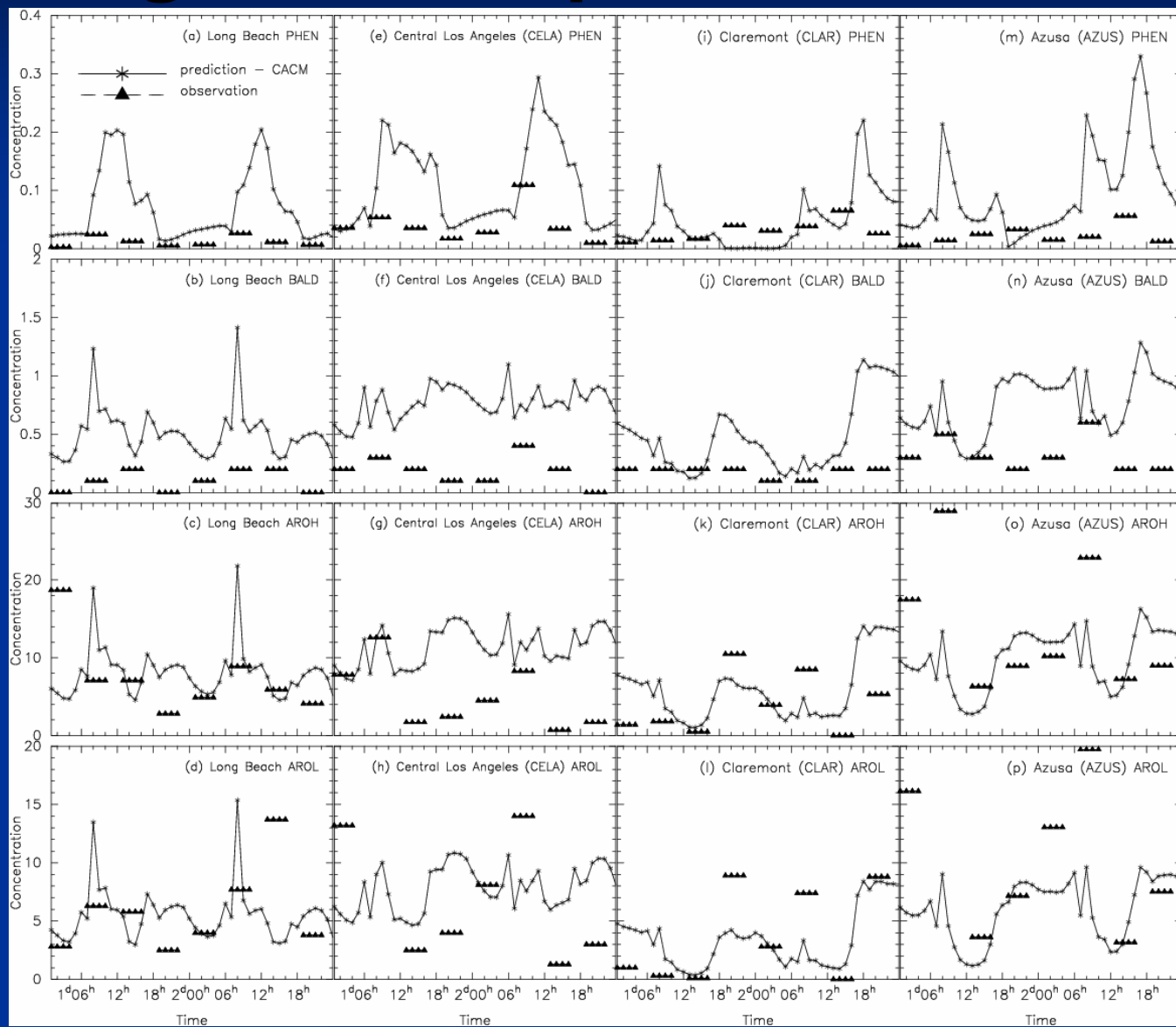
# Model Performance for Individual Organic Compound Classes

PHEN  
(ppm)

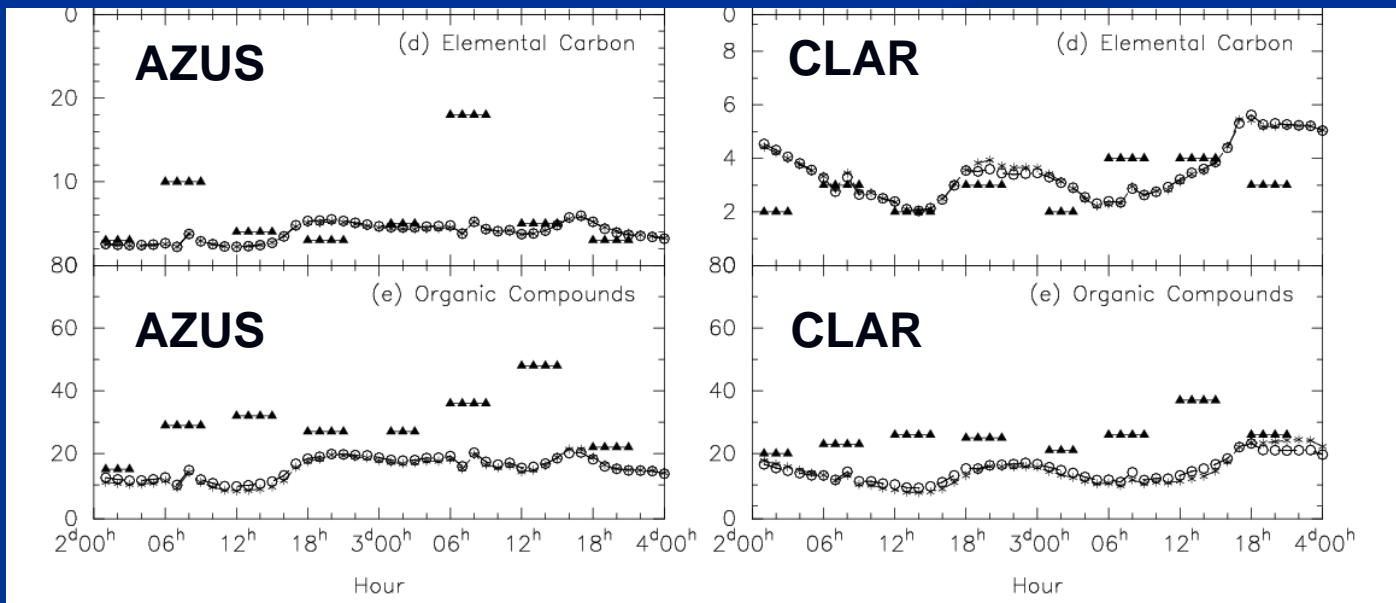
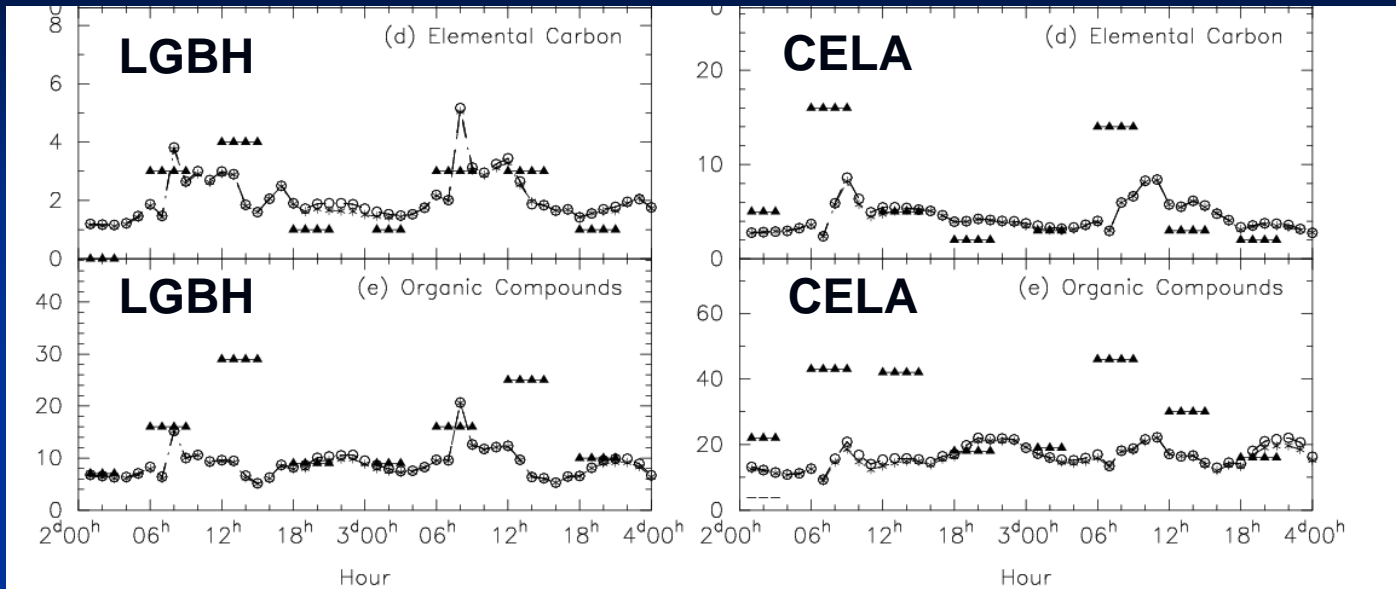
BALD  
(ppm)

AROH  
(ppm)

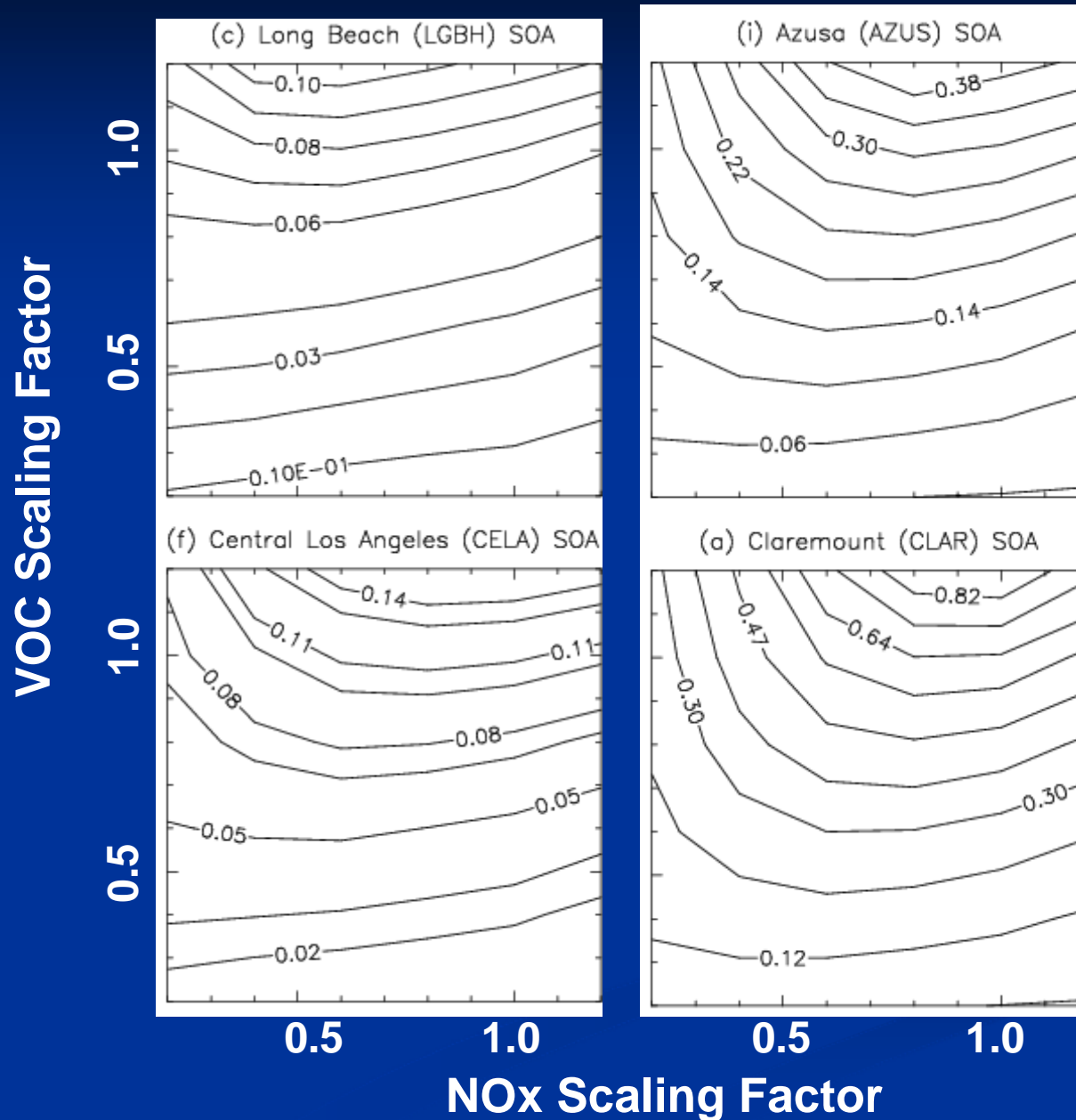
AROL  
(ppm)



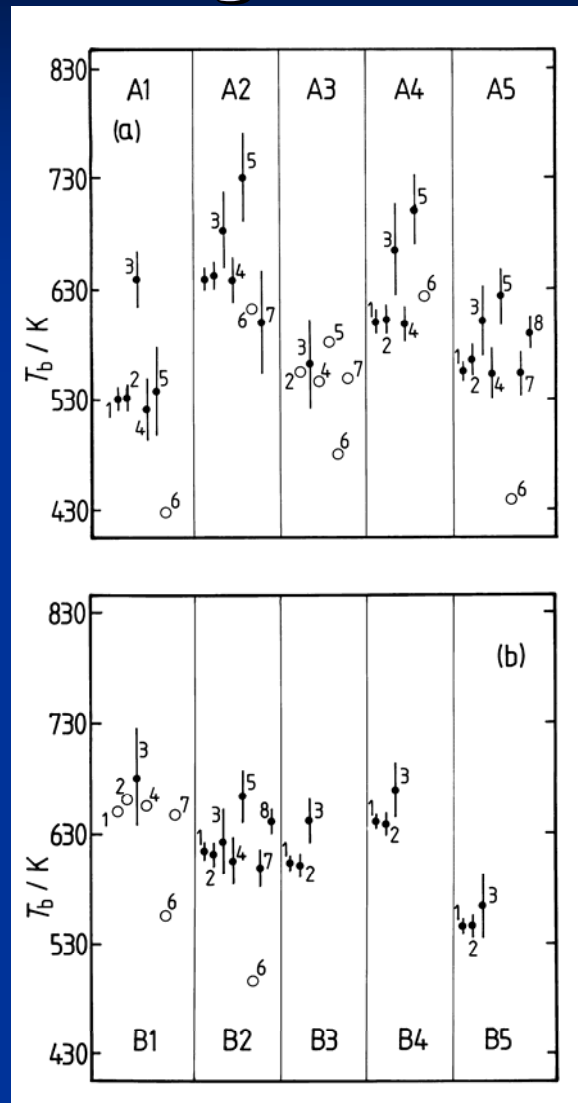
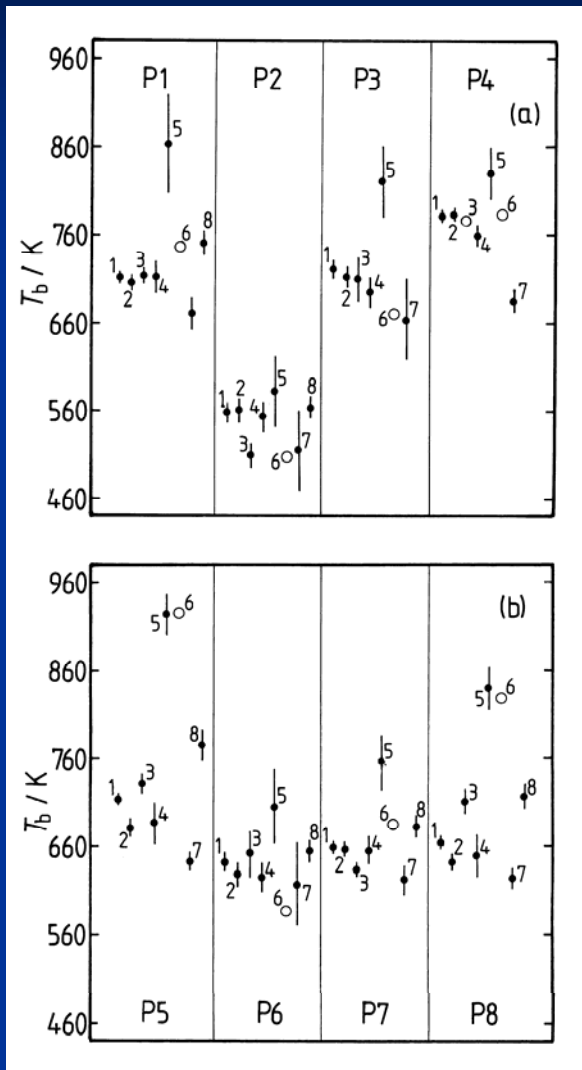
# Model Performance for Carbonaceous Aerosol



# Sensitivity of SOA to VOC Emissions



# Estimated Boiling Points For Surrogate Compounds Using Different Methods



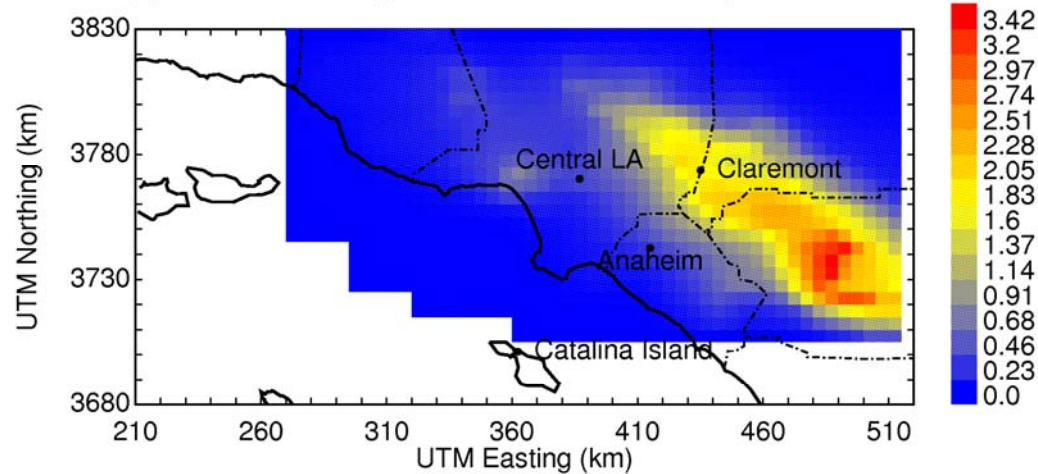
## METHODS:

- 1 – Nannoolal et al. (2004);
- 2 – Cordes and Rarey (2002);
- 3 – Kolovanov and Petrauskas (undated), and ACDLabs software v8.0 (Advanced Chemistry Development Inc., 2004);
- 4 - Stein and Brown (1994);
- 5 – Joback and Reid (1987);
- 6 – Wen and Qiang (2002a,b);
- 7 – Constantinou and Gani (1994);
- 8 - Marrero-Morejon and Pardillo-Fontdevila (1999).

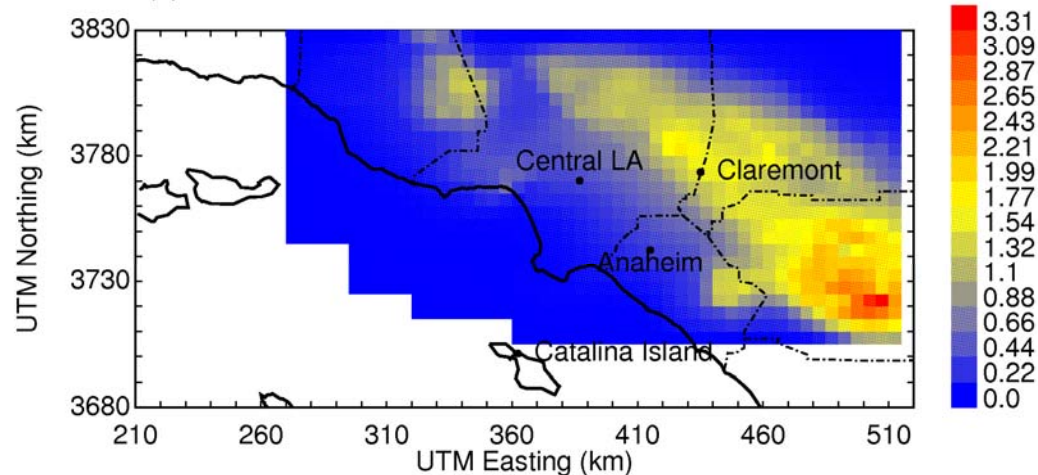


# Effect of Boiling Point Uncertainty on Predicted SOA

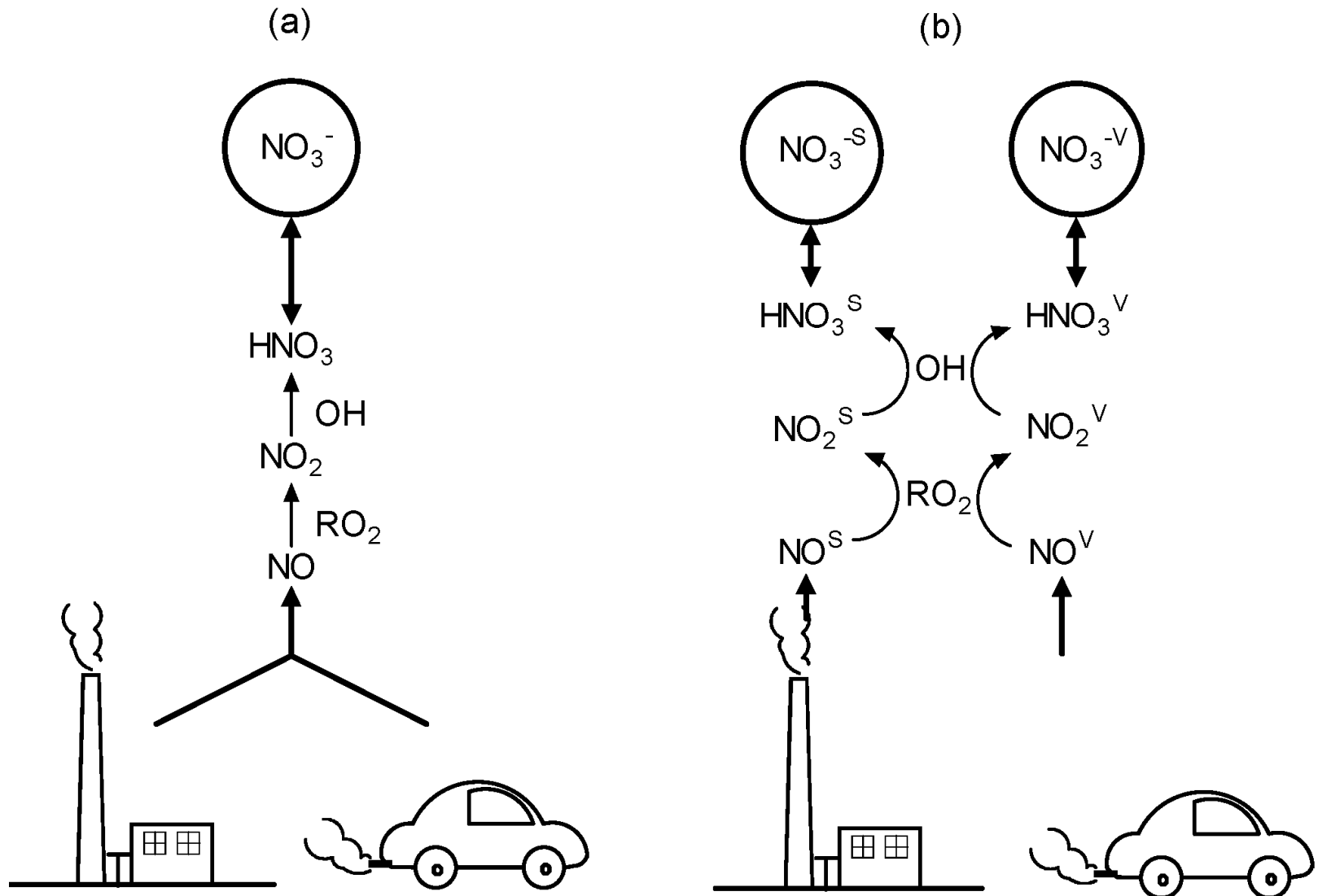
(a) Predicted 24hr-Avg SOA Concentrations on September 9, 1993



(b) Predicted Increase in SOA Concentrations Due to Lower Tb



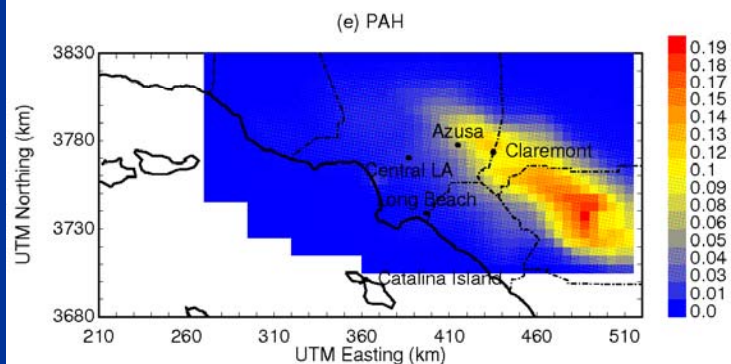
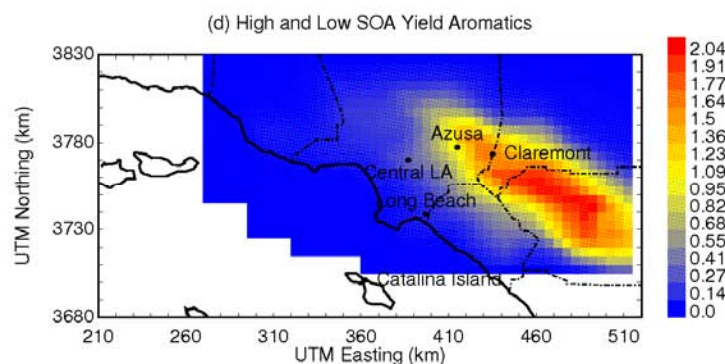
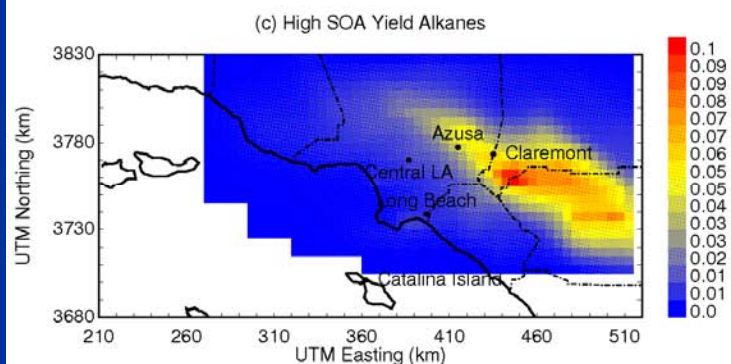
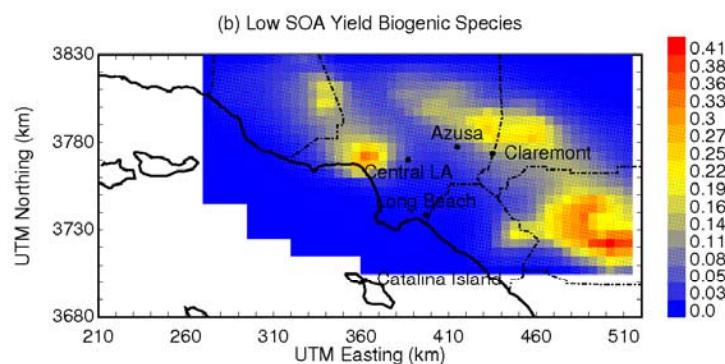
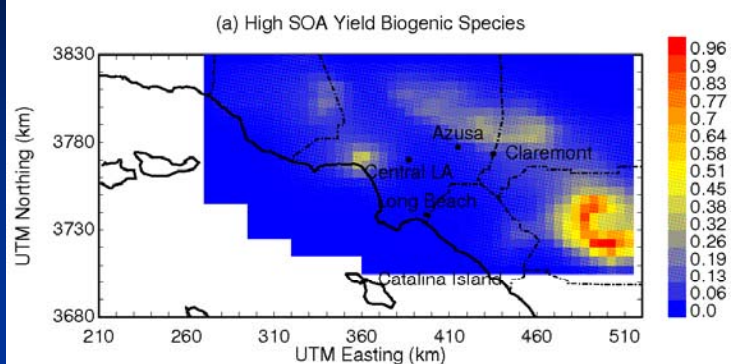
# Source Apportionment of Secondary Particulate Matter



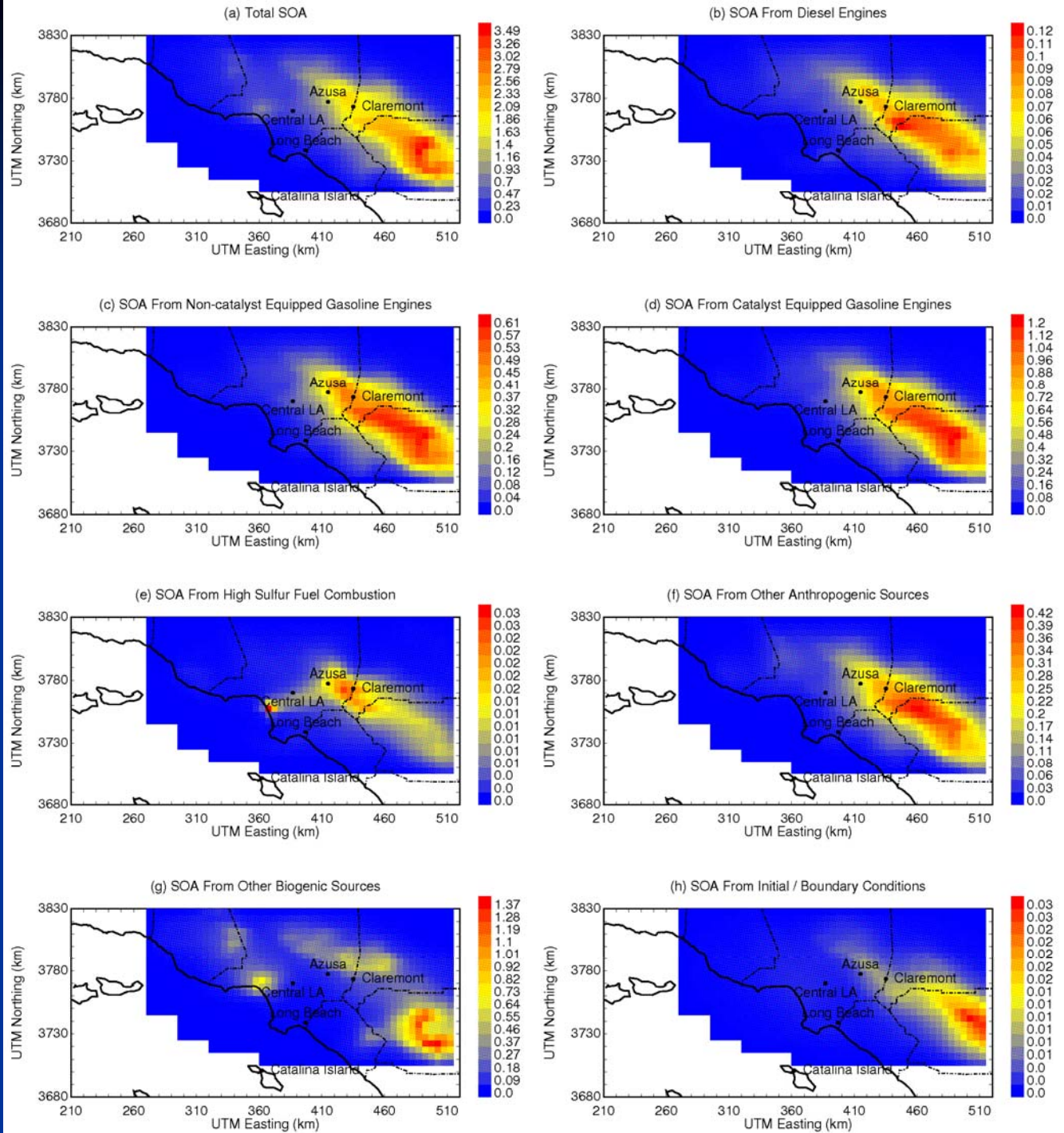




# SOA Concentrations By Precursor Family

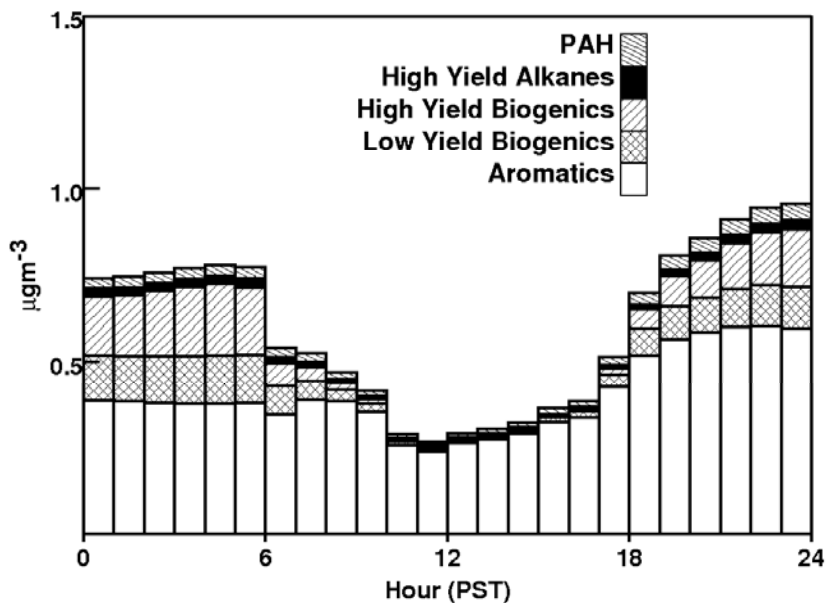


# Source Contributions to SOA

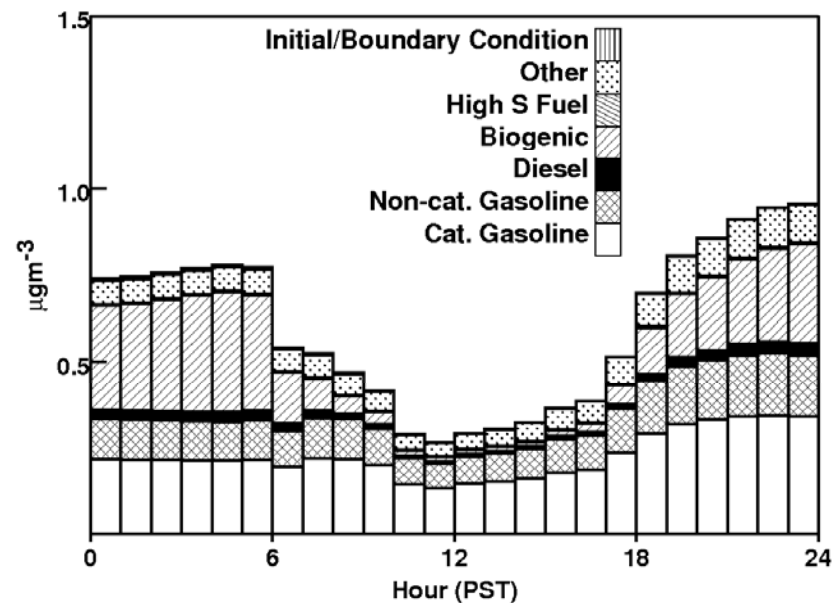


# Diurnal Variation of SOA Source Contributions

(a) SOA Speciation



(b) SOA Source Apportionment



# Conclusions

- SOA calculations currently under-predict OC concentrations during typical air pollution episodes in California
  - Incorrect parameterization of surrogate compounds
  - Missing entire formation pathways (oligomer formation)
- Known sources of SOA in central Los Angeles are dominated by transportation
  - Catalyst and non-catalyst equipped gasoline engines



# Conclusions

- Biogenic sources make a surprisingly significant contribution to SOA in at the north and south ends of the SoCAB
  - Water soluble material
  - Highest concentrations at night
- Source-oriented methodology can be applied anywhere a chemical transport model is used

# Acknowledgements

- US Environmental Protection Agency Science To Achieve Results Grant # RD831082
- San Joaquin Valleywide Air Pollution Study Agency
- California Air Resources Board (Karen Magliano, Ajith Kaduwela, Vernon Hughes)
- Chevron
- Tony Held, Qi Ying, and Jin Lu