



# **Sources and Atmospheric Transformations of Organic Aerosols**

---

**Allen Robinson**

**Center for Atmospheric Particle Studies  
Carnegie Mellon University**

**Presented at the Regional Air Quality Workshop  
Hosted by LADCO, Rosemont, IL October 15-16, 2008.**

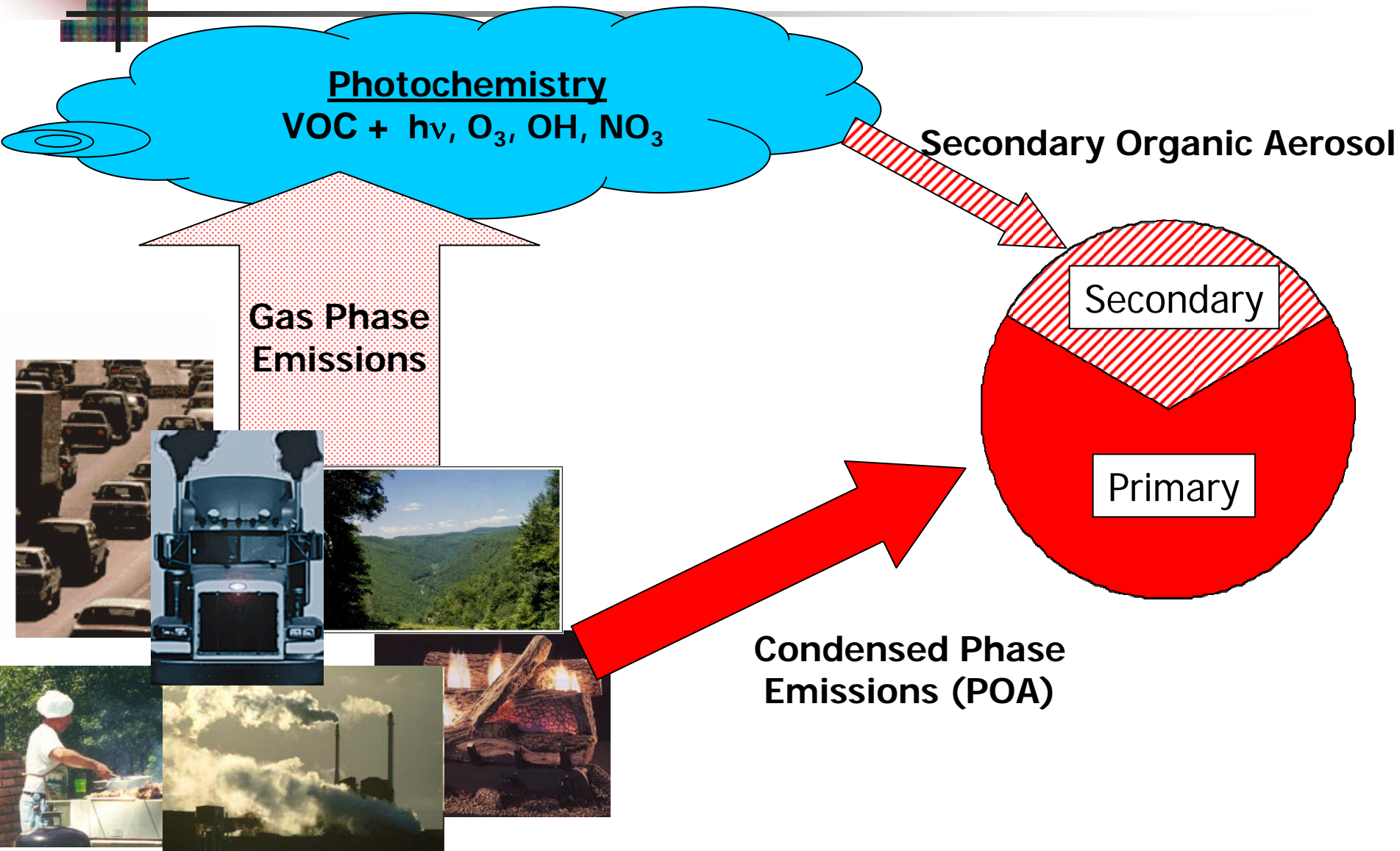


# Outline

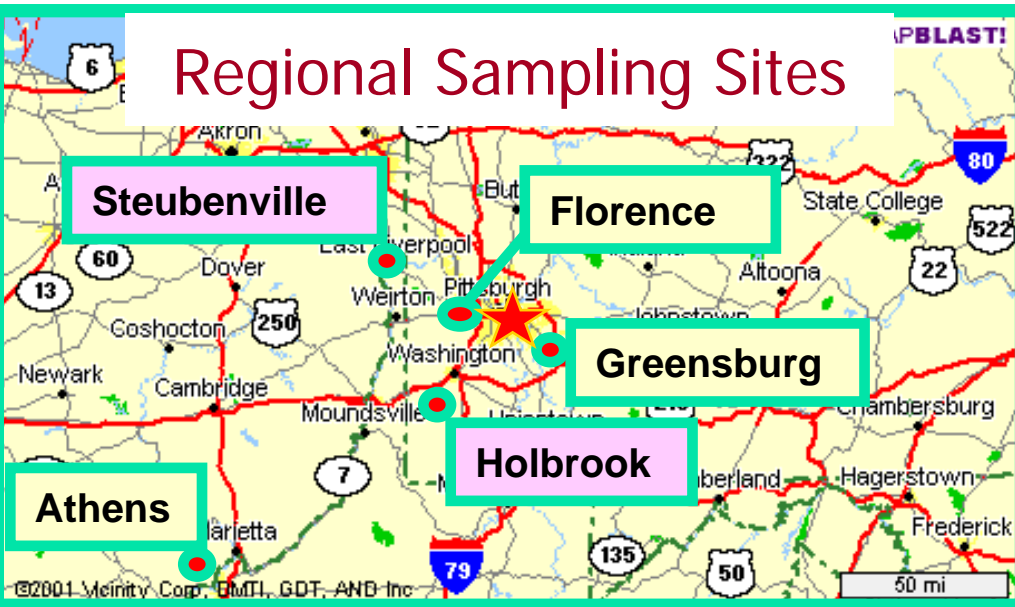
---

- Source of organic PM
  - Regional versus local
  - Primary versus secondary
  - Chemical Transport Modeling
  - Rethinking organic aerosols
- TAG: Hourly measurements of molecular markers

# Sources of Organic Aerosol (OA)



# Pittsburgh Air Quality Study (PAQS)



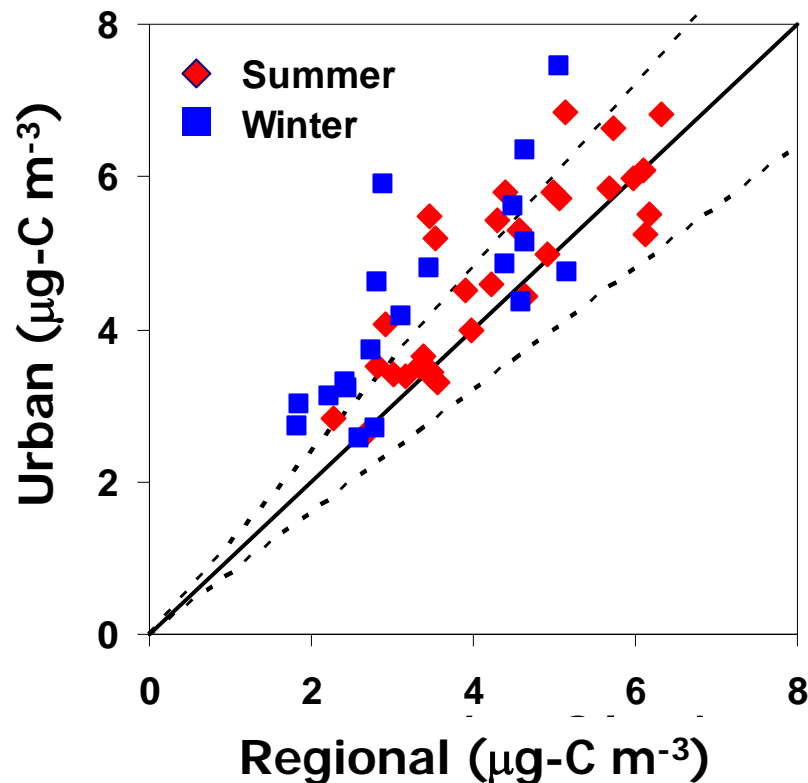
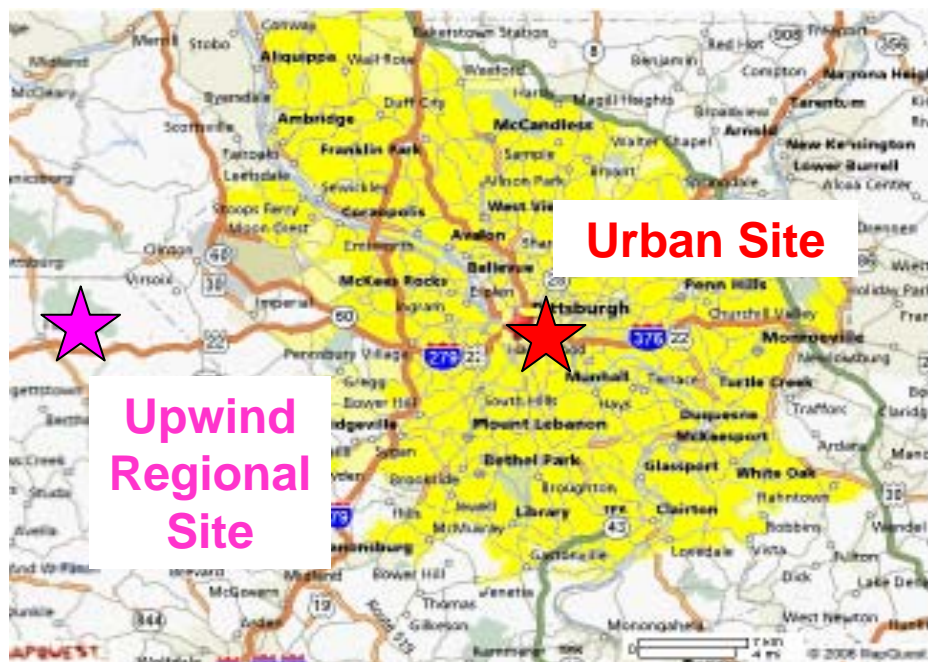
- July 2001 – August 2002
- 20 research groups

- Field measurements
- Source characterization
- Modeling
- Instrument development



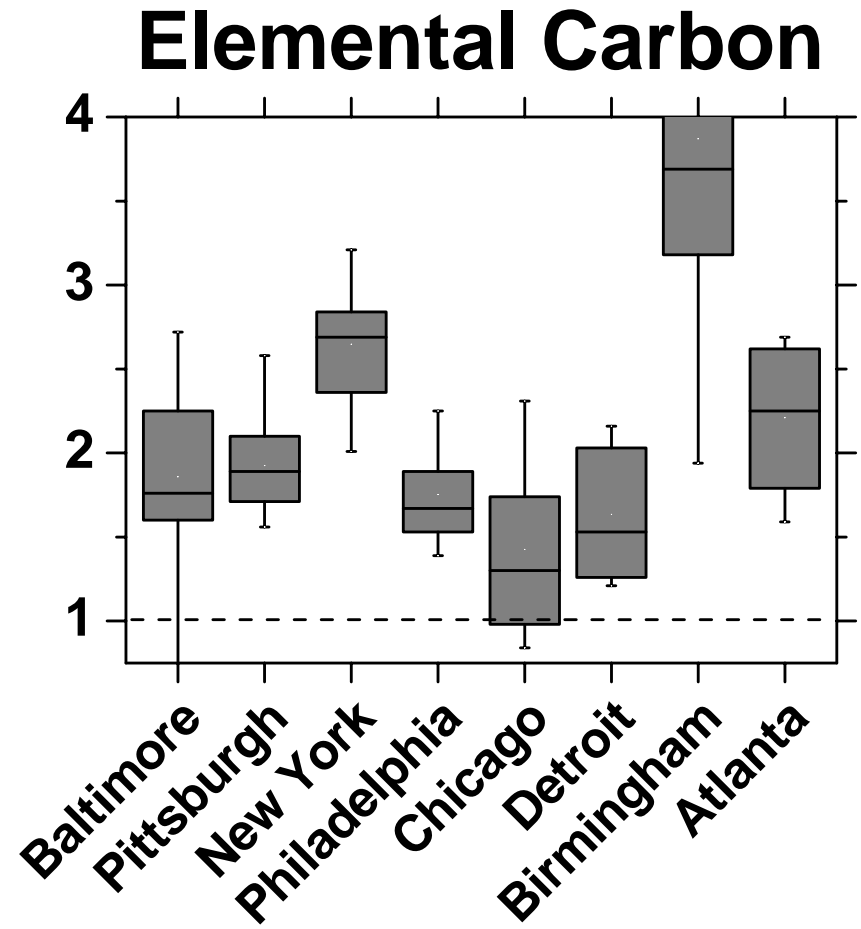
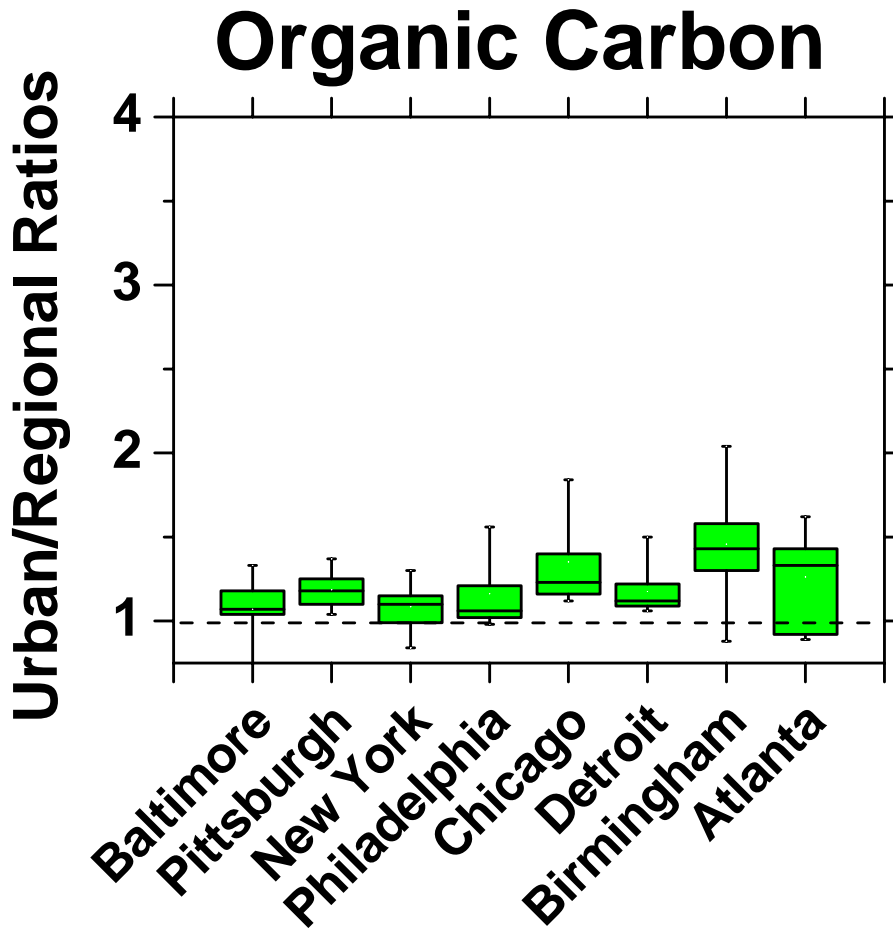
# What is role of regional transport?

Map of Pittsburgh Metropolitan Area

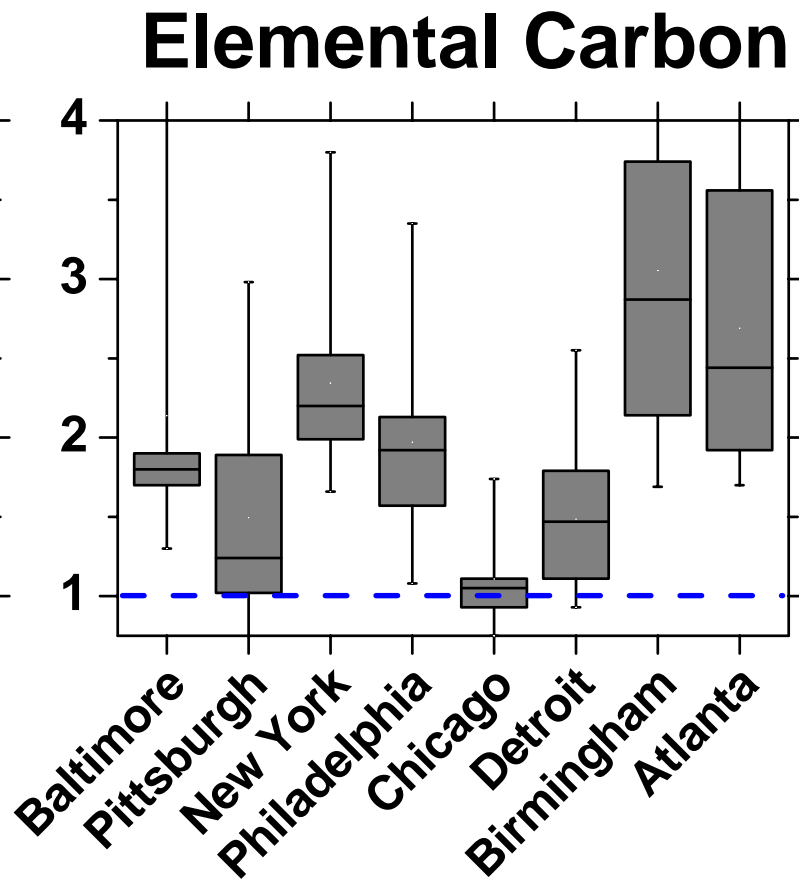
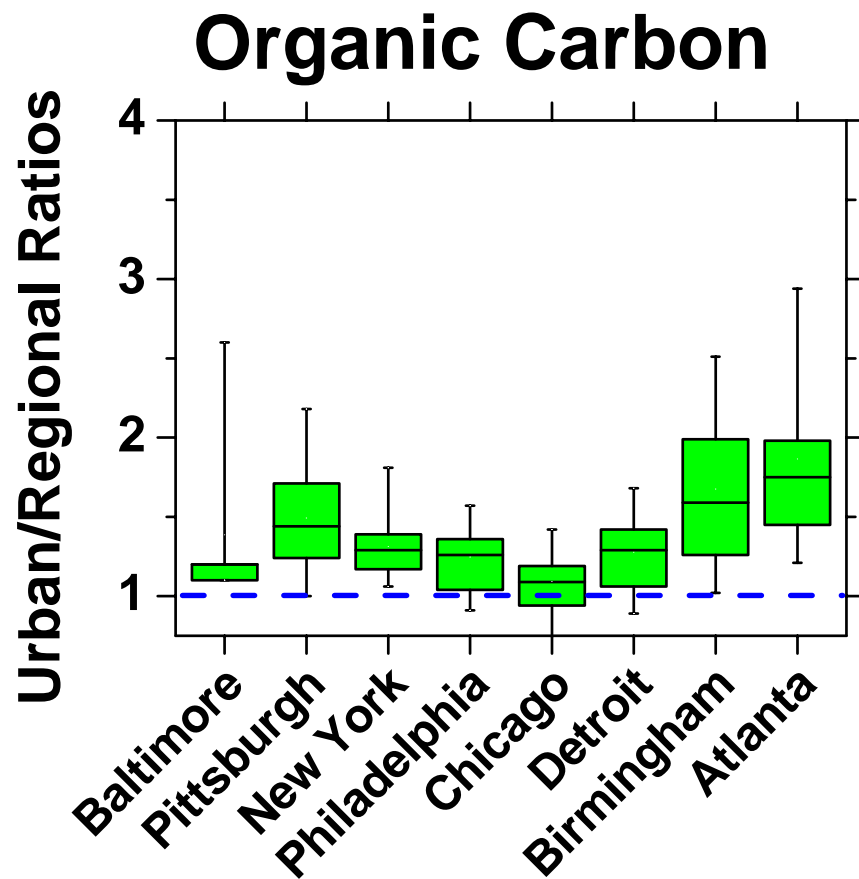


80% of OA in Pittsburgh arrives via regional transport

# Summertime Spatial Patterns of Carbonaceous PM<sub>2.5</sub>

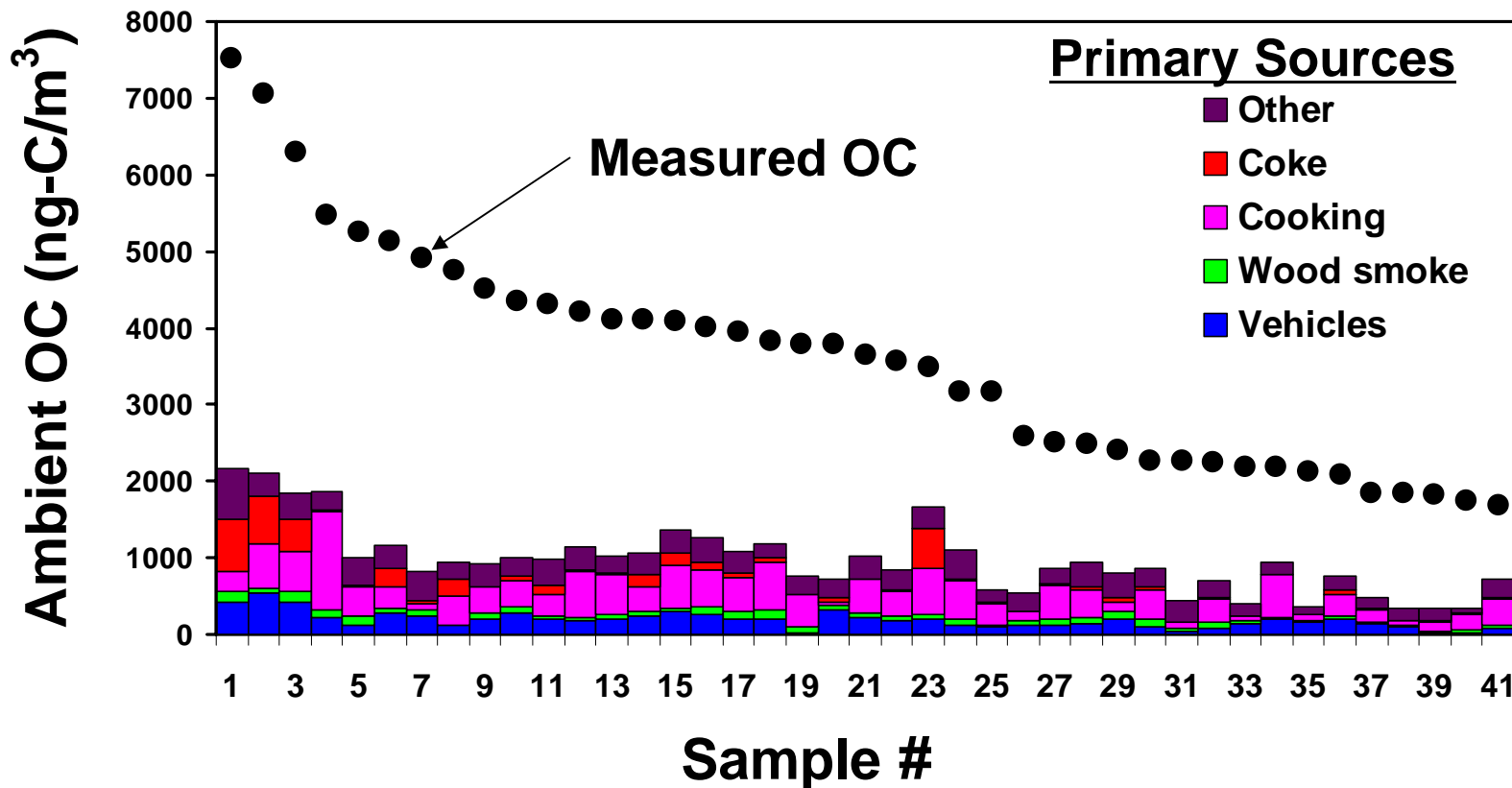


# Wintertime spatial patterns in carbonaceous PM<sub>2.5</sub>



# How important are primary emissions?

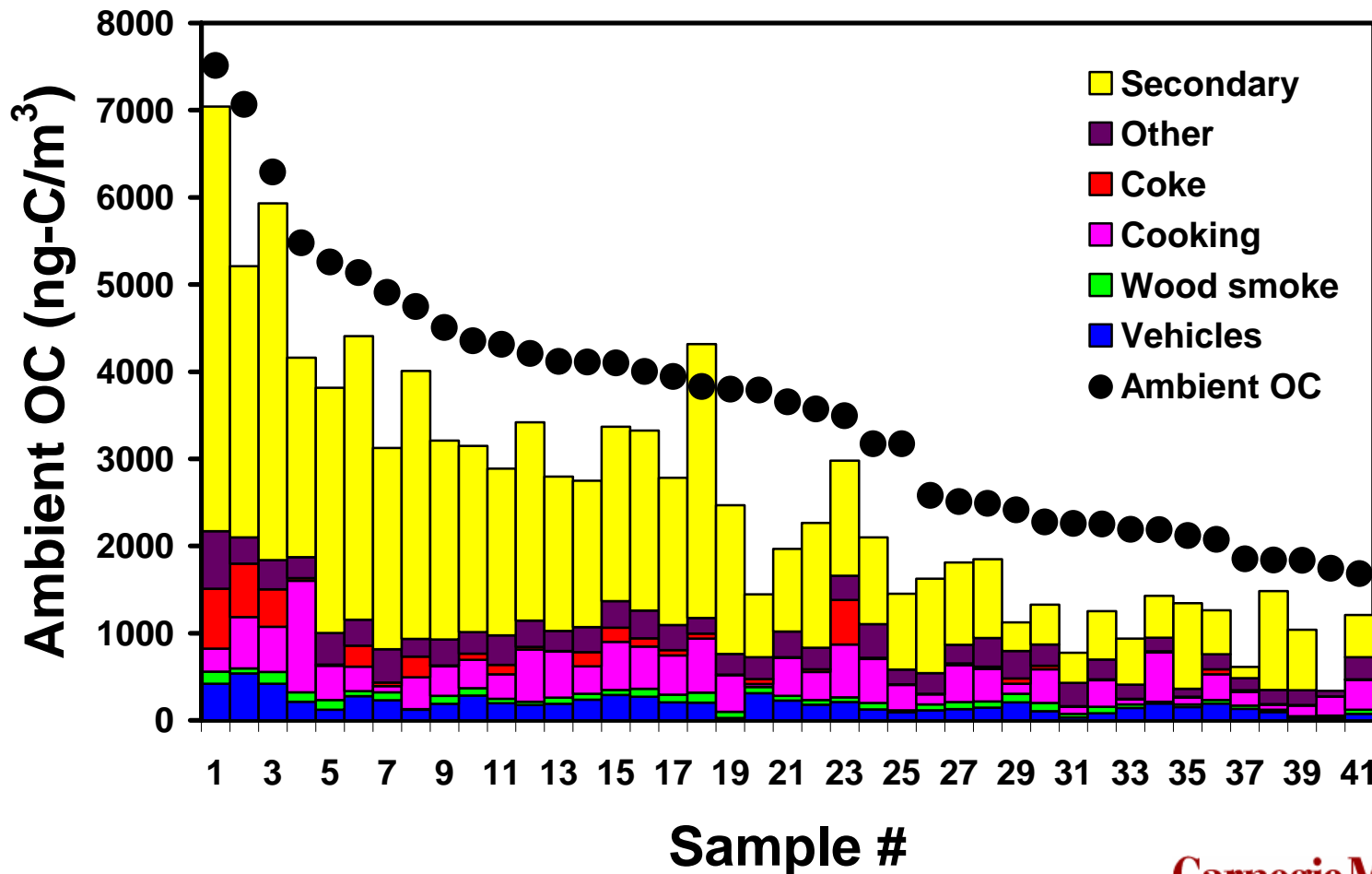
CMB analysis of Summer 2001 & 2002 molecular marker data from Pittsburgh



(Subramanian et al. AE 2007)

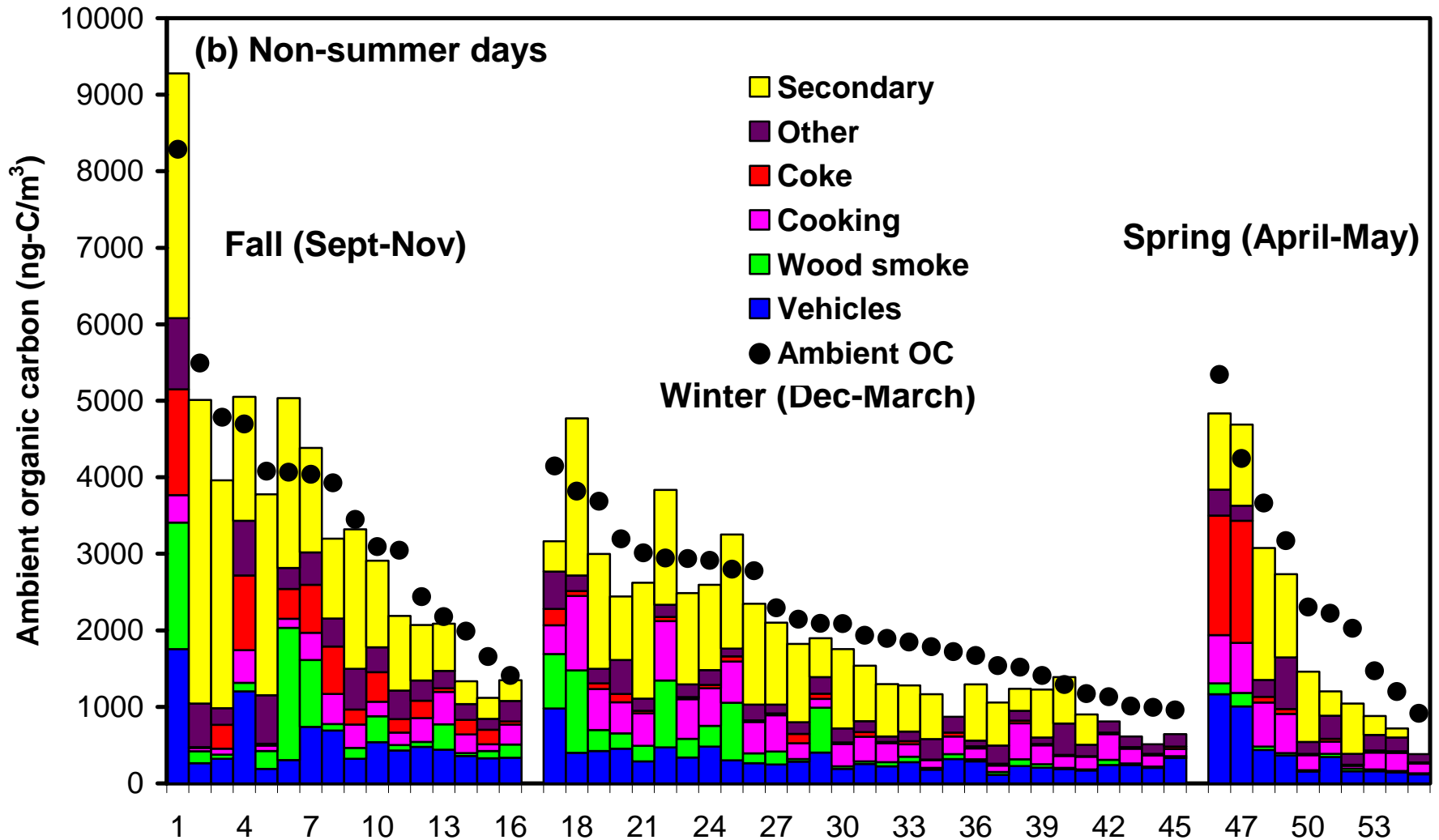
# SOA estimate explains most of missing OC mass

Summer CMB analysis with SOC estimate added



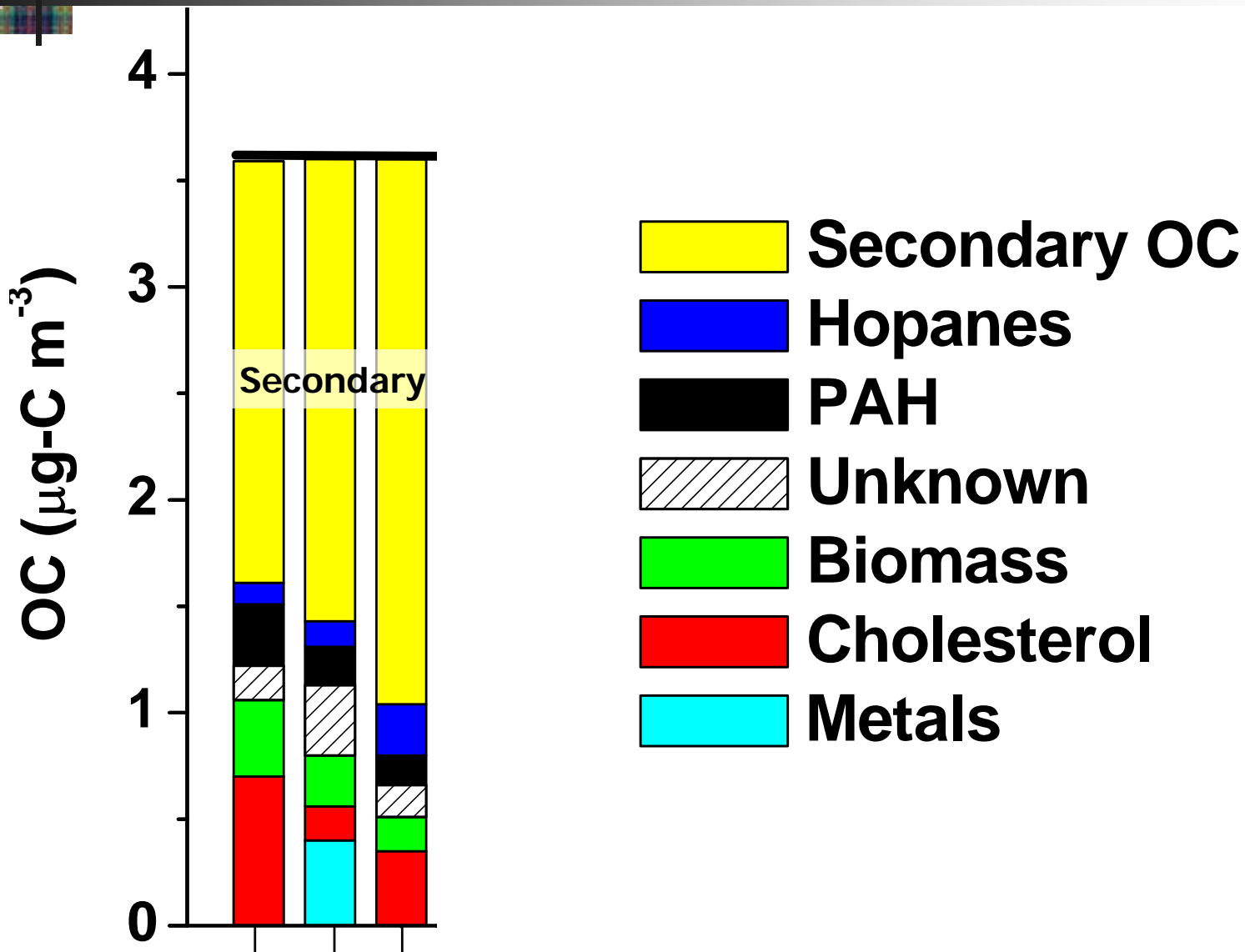
(Subramanian et al. AE 2007)

# SOA contributes less in other seasons



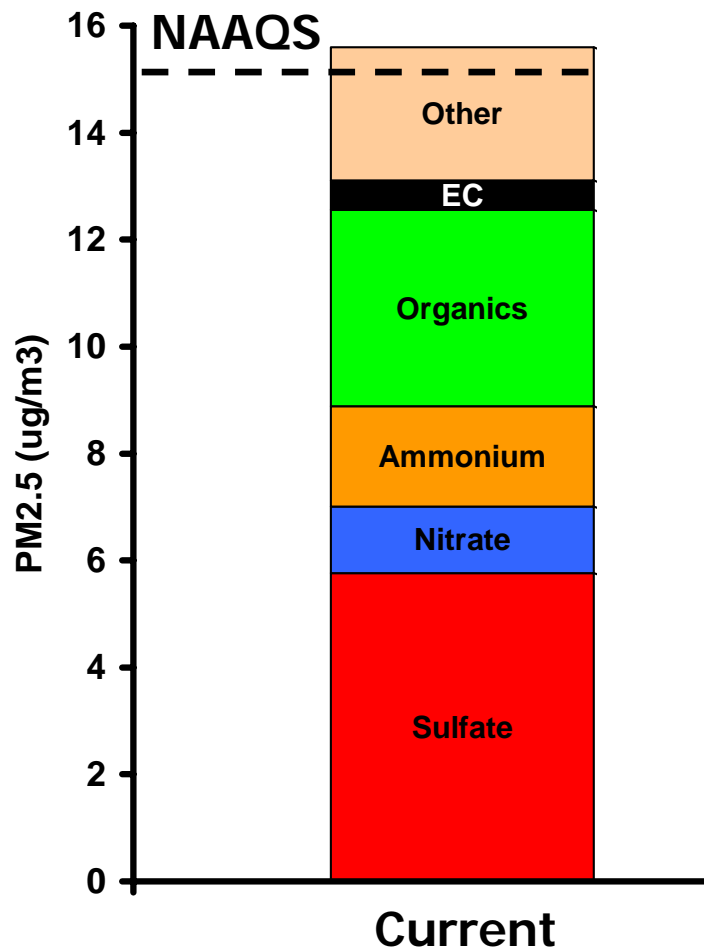
(Subramanian et al. AE 2007)

# Multiple receptor models predict secondary dominant in summer

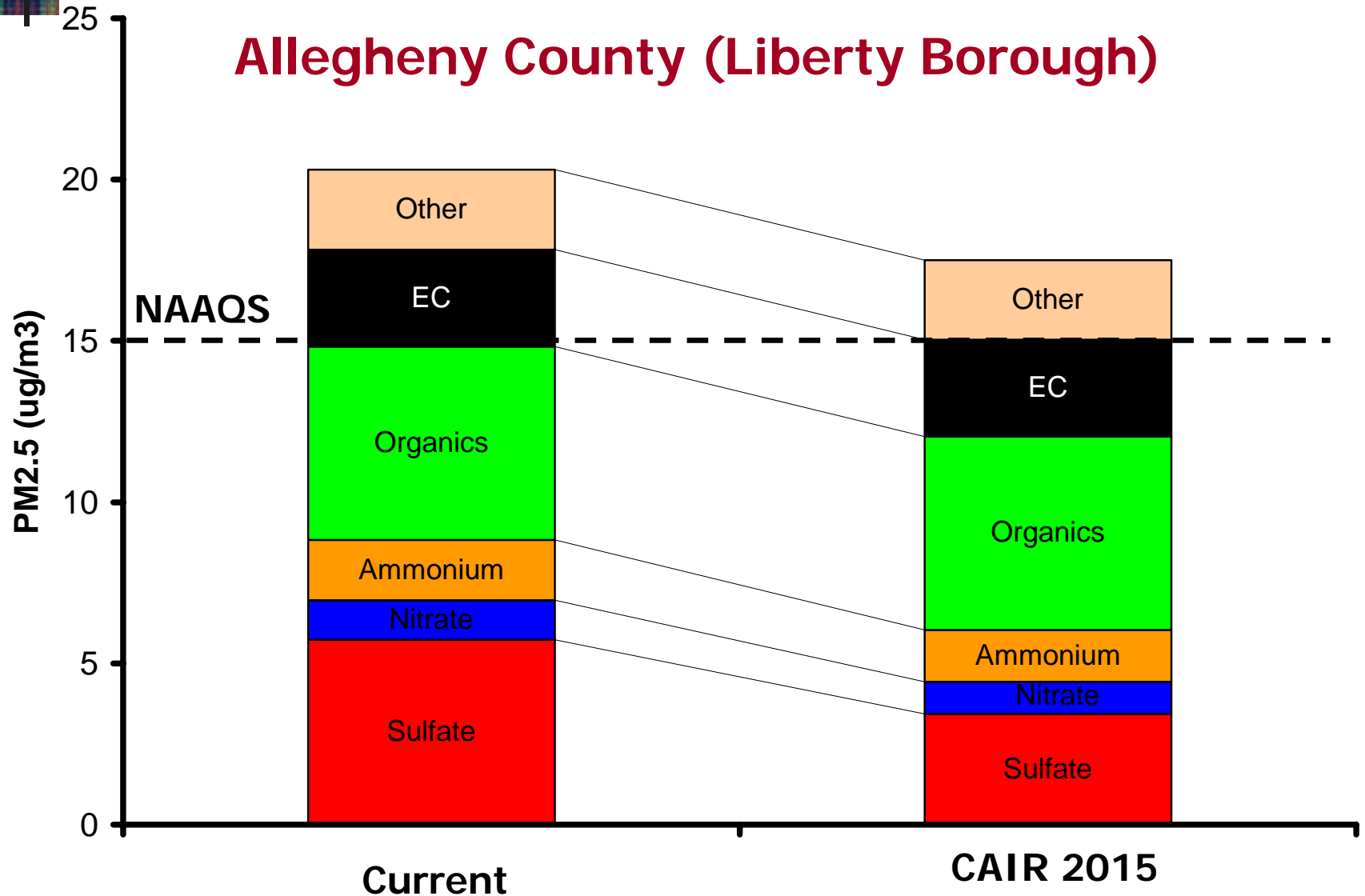


# Do we need to control organics?

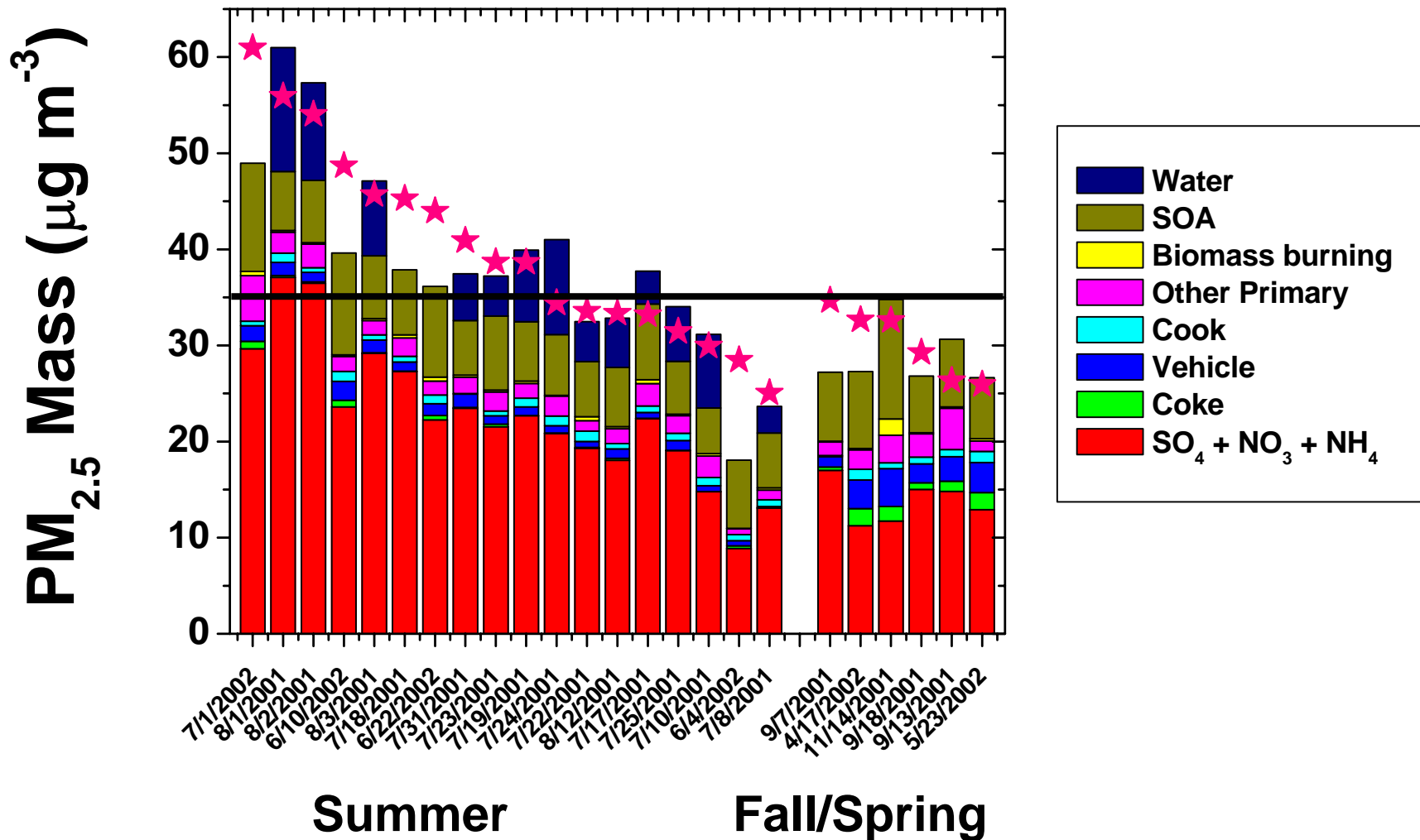
## Allegheny County



# Do we need to control organics?



# Pittsburgh PM<sub>2.5</sub> mass balance on high concentration days



(Subramanian et al. AE 2007)



# What is the source of this SOA?

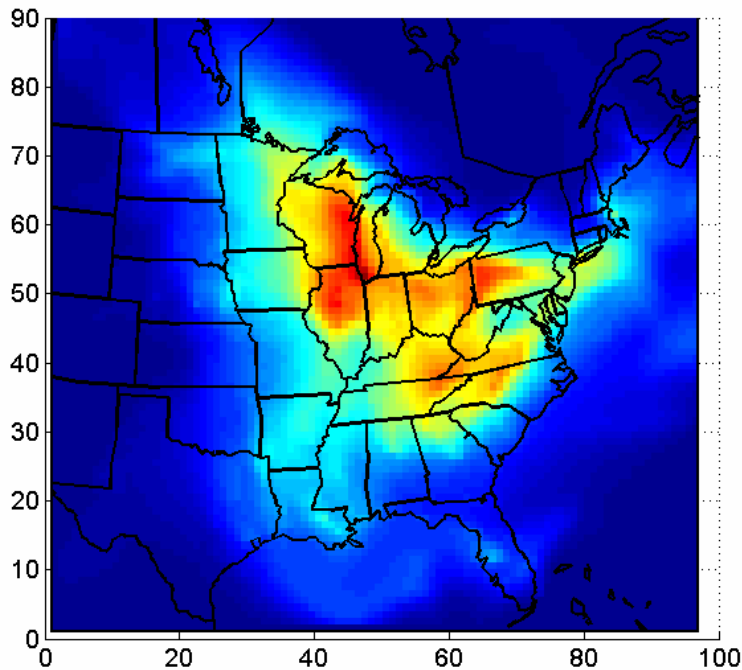
---

- Anthropogenic
  - Light aromatics
- Biogenics
  - Monoterpenes
  - Isoprene
- Other??

**Traditional Precursors**

# PMCAMx Chemical Transport Model (CTM) for source-oriented modeling

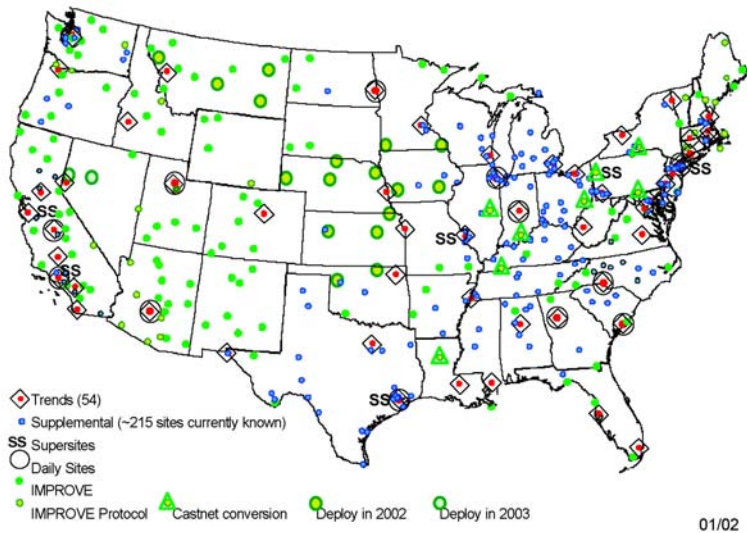
## Modeling Domain



- Photochemical transport model: PMCAMx+
- Grid
  - 36x36 km grid
  - 14 levels up to 6 km
- Aerosol
  - 10 size sections
  - 13 species
- LADCO Base E Inventory
  - NEI 1999 V2
  - Update activity data for power plants from CEM
  - Mobile6 for vehicles
- Meteorology
  - MM5

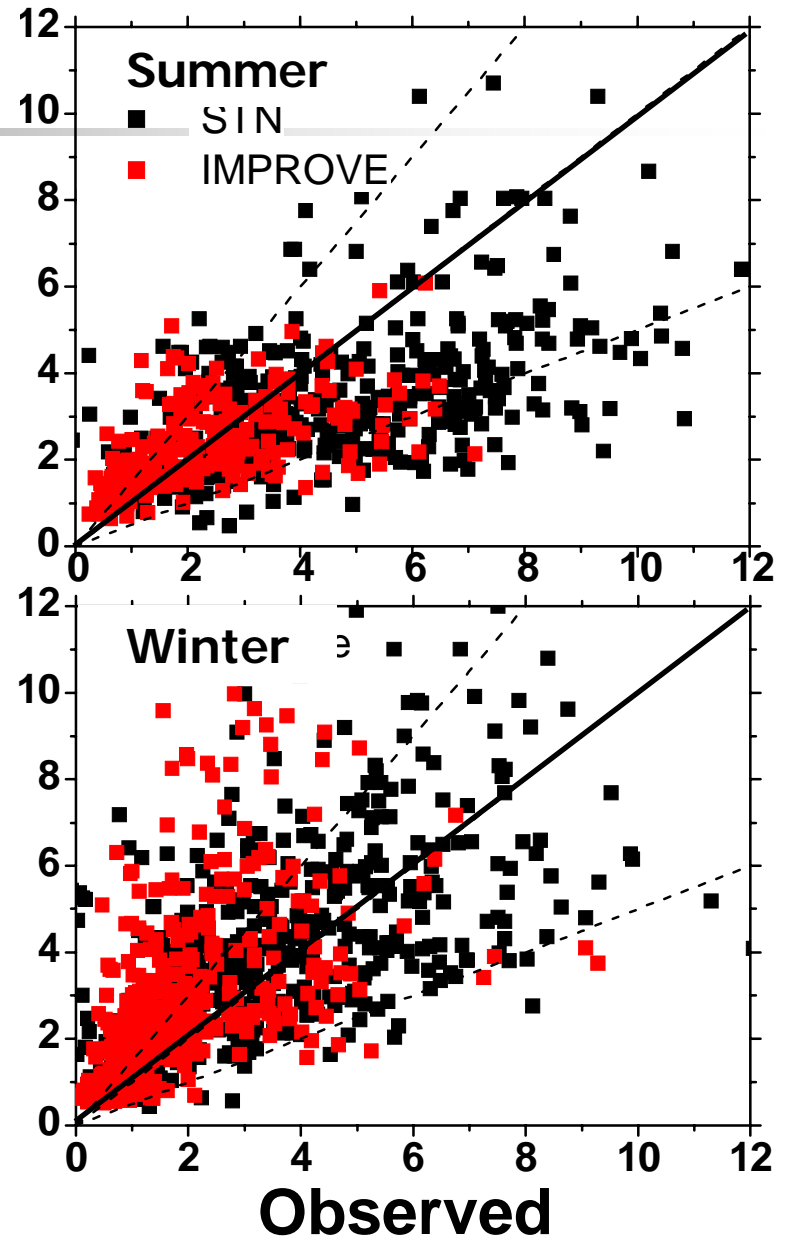
# Model Evaluation

## STN & IMPROVE Sites



**IMPROVE: as reported (blank corrected)**  
**STN: Corrected for handling blank (~ 1ug/m<sup>3</sup>)**

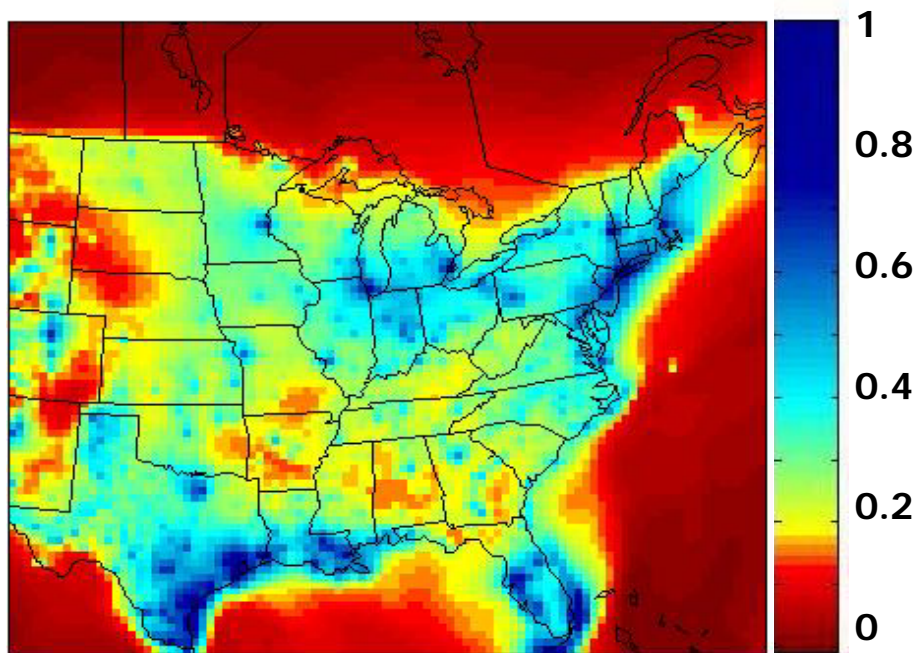
Predicted



(Karydis et al. JGR 2007; Shrivastava et al. JGR 2008)

# Predicted Primary-Secondary Split

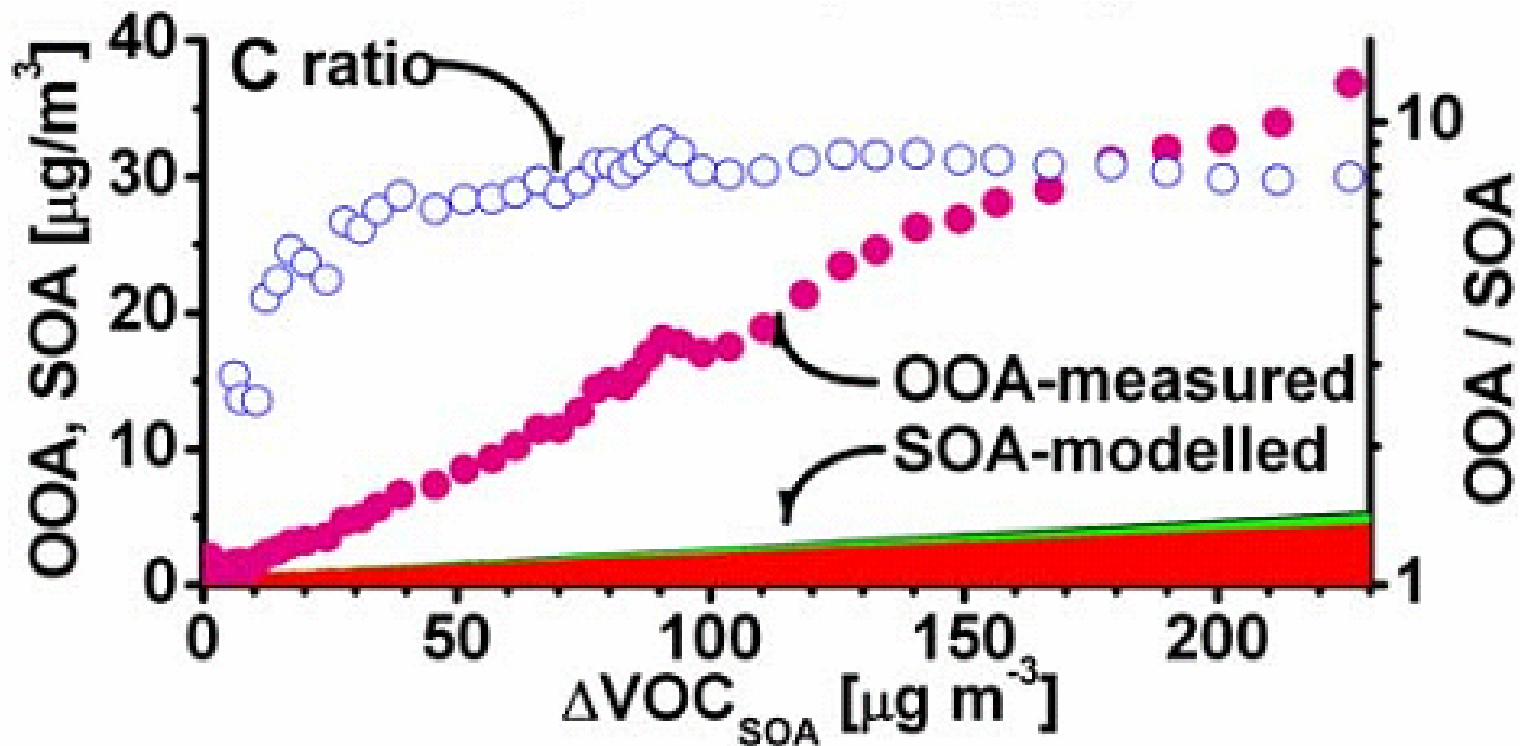
Summertime predictions  
of a CTM



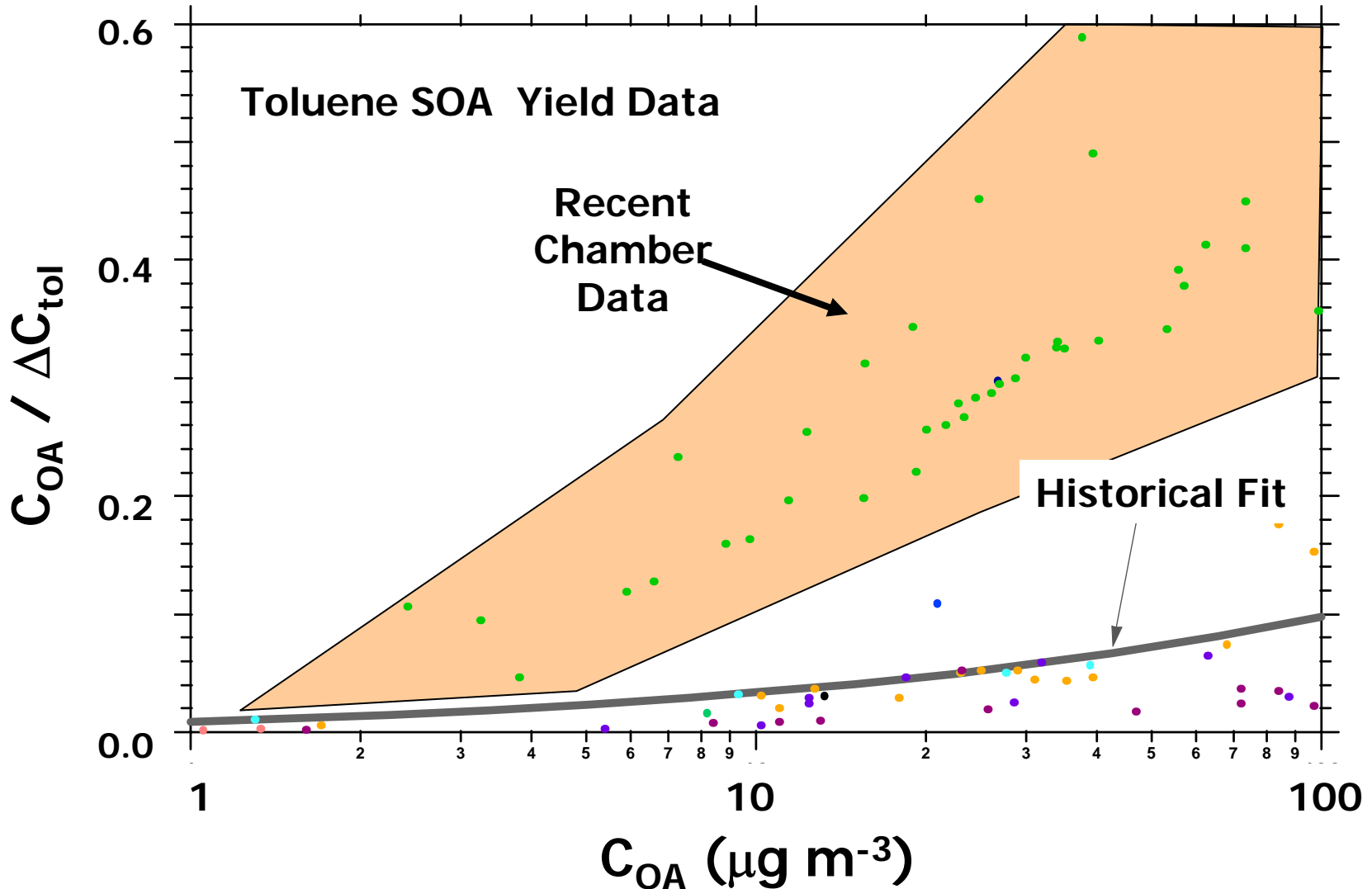
Traditional POA  
Total OA

# Large unexplained SOA formation in urban areas

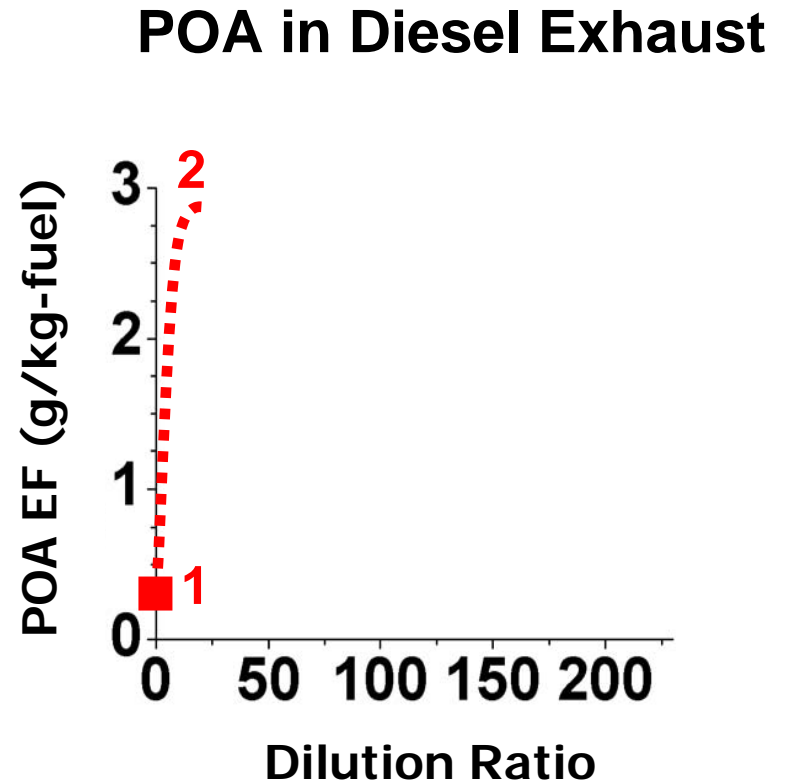
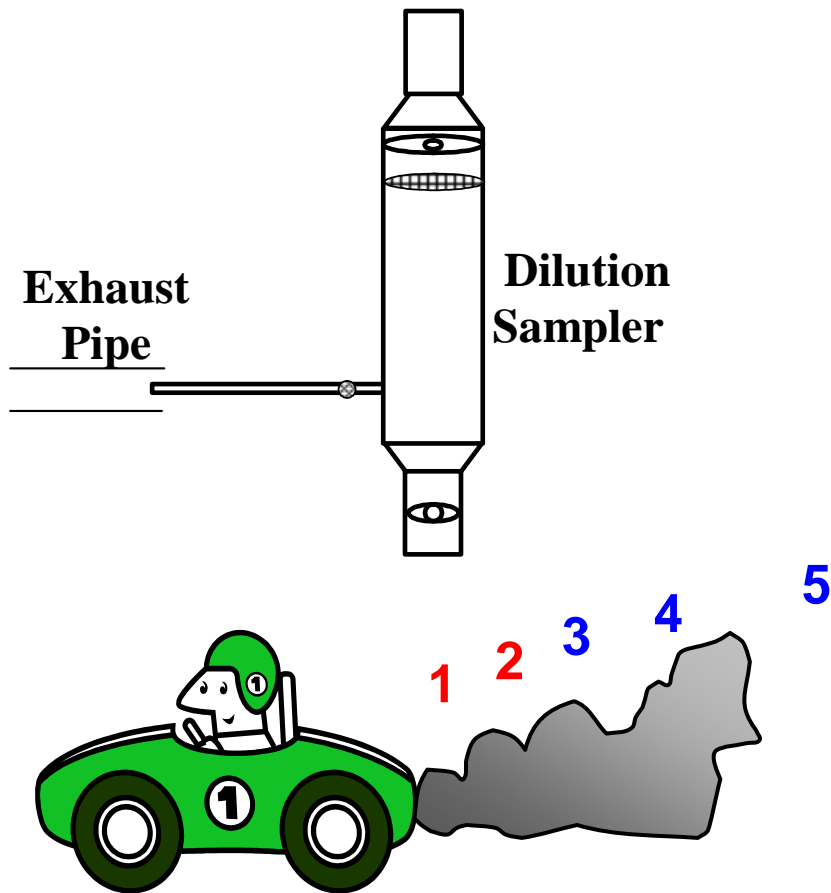
## MEXICO CITY



# Yields for traditional precursors are uncertain and rising!



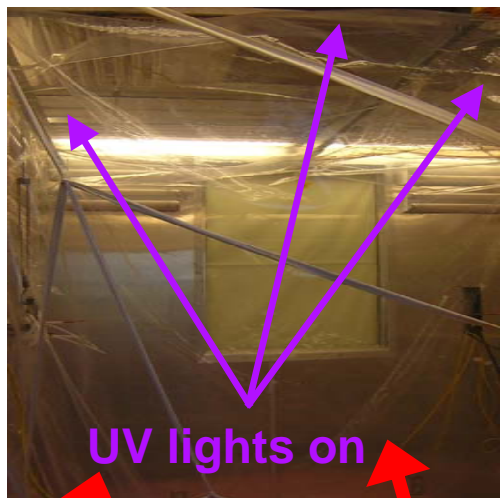
# Primary organic aerosol is semivolatile



Hildeman et al. AST 1989  
Lipsky and Robinson ES&T 2006

# Unexplained SOA production

CMU Smog Chamber



UV lights on

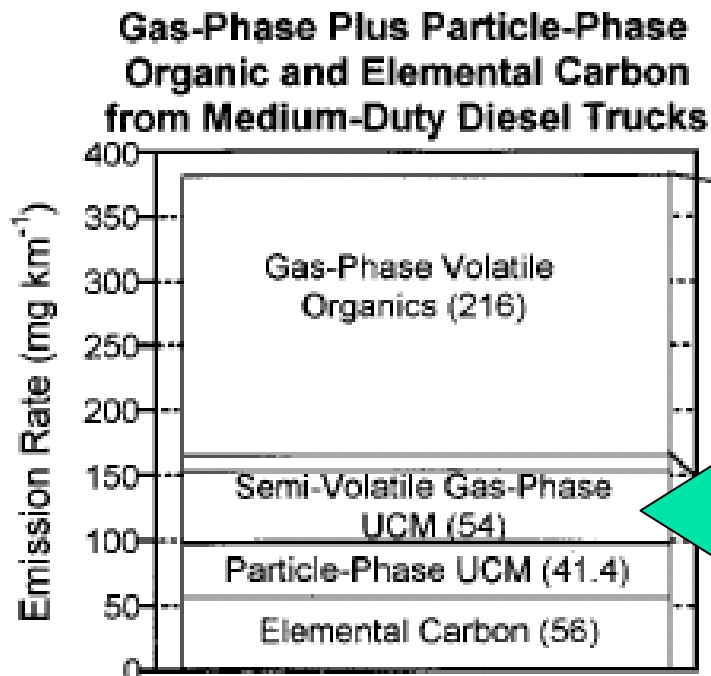


Diesel Engine

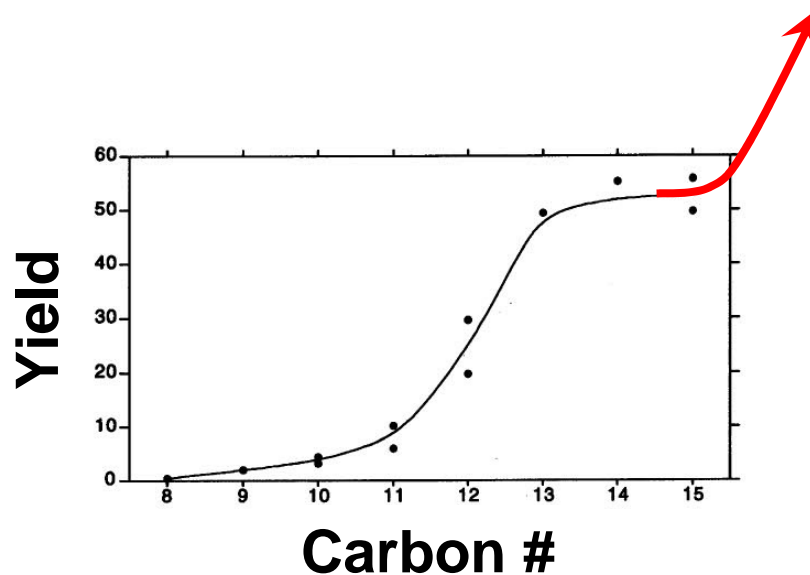


Wood Stove

# Non-traditional SOA precursors



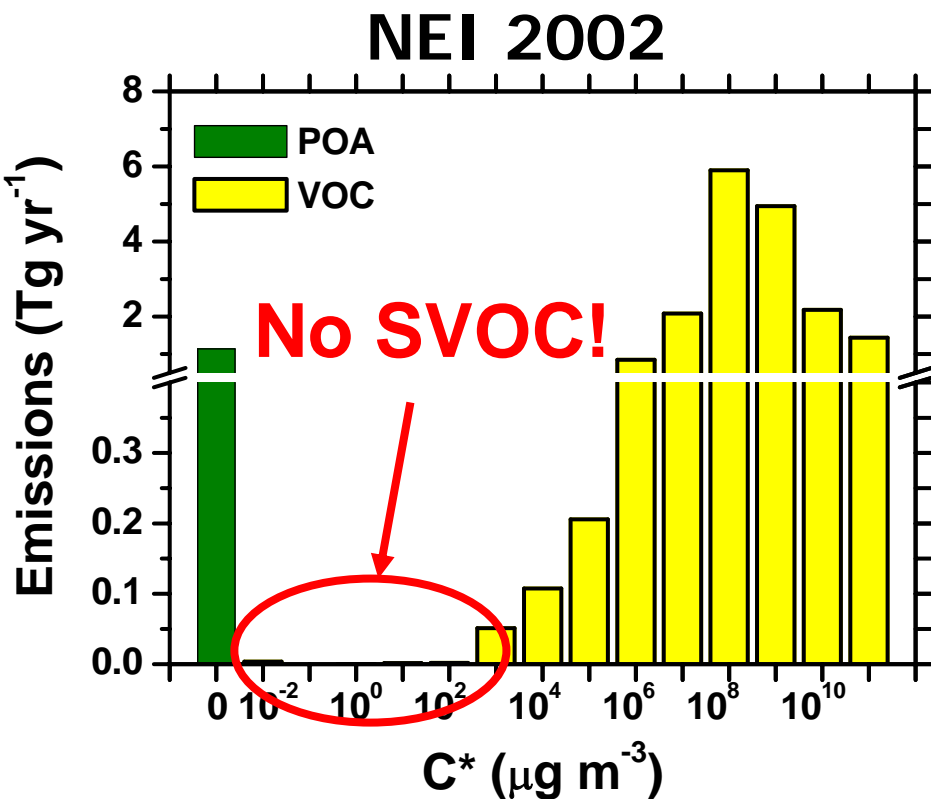
(Schauer et al. EST 1999)



(Lim et al. EST 2005)

**SVOC Vapors**

# No SVOCs in inventories





# Conclusions (1)

---

- Sources of OA
  - Regional with a few hotspots
  - Secondary dominated
  - Nontraditional precursors
- Problems with current static conceptual model for OA

# **T**hermal Desorption **A**erosol **G**C-MS (TAG)



Automated hourly measurement of less-polar semivolatile organics

- **Sample collection - inertial impaction**
- **Sample isolation - thermal desorption (heated to 300°C)**
- **Analyte separation and identification – GC/MS**

(Williams et al. AS&T 2006)

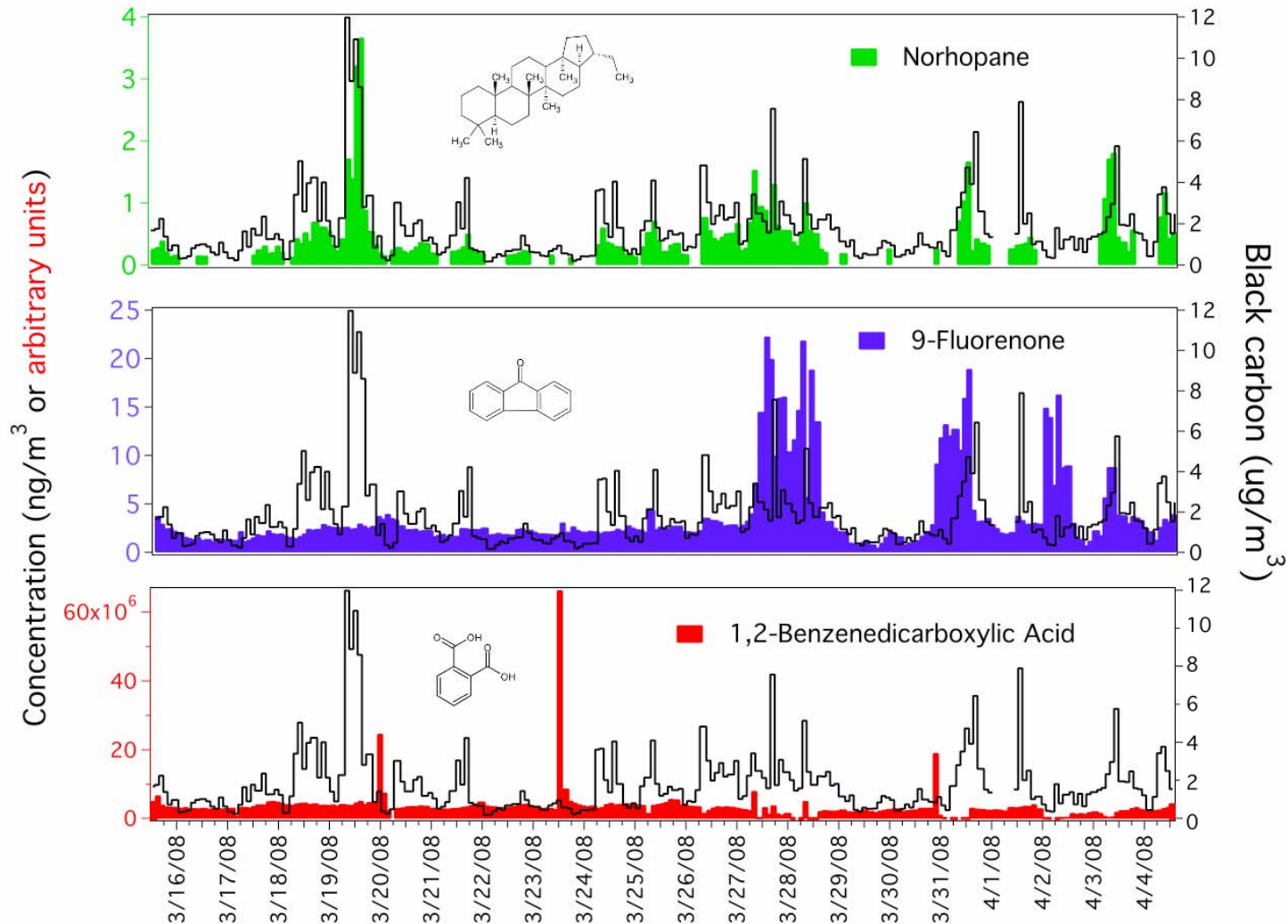
# TAG in Downtown Pittsburgh



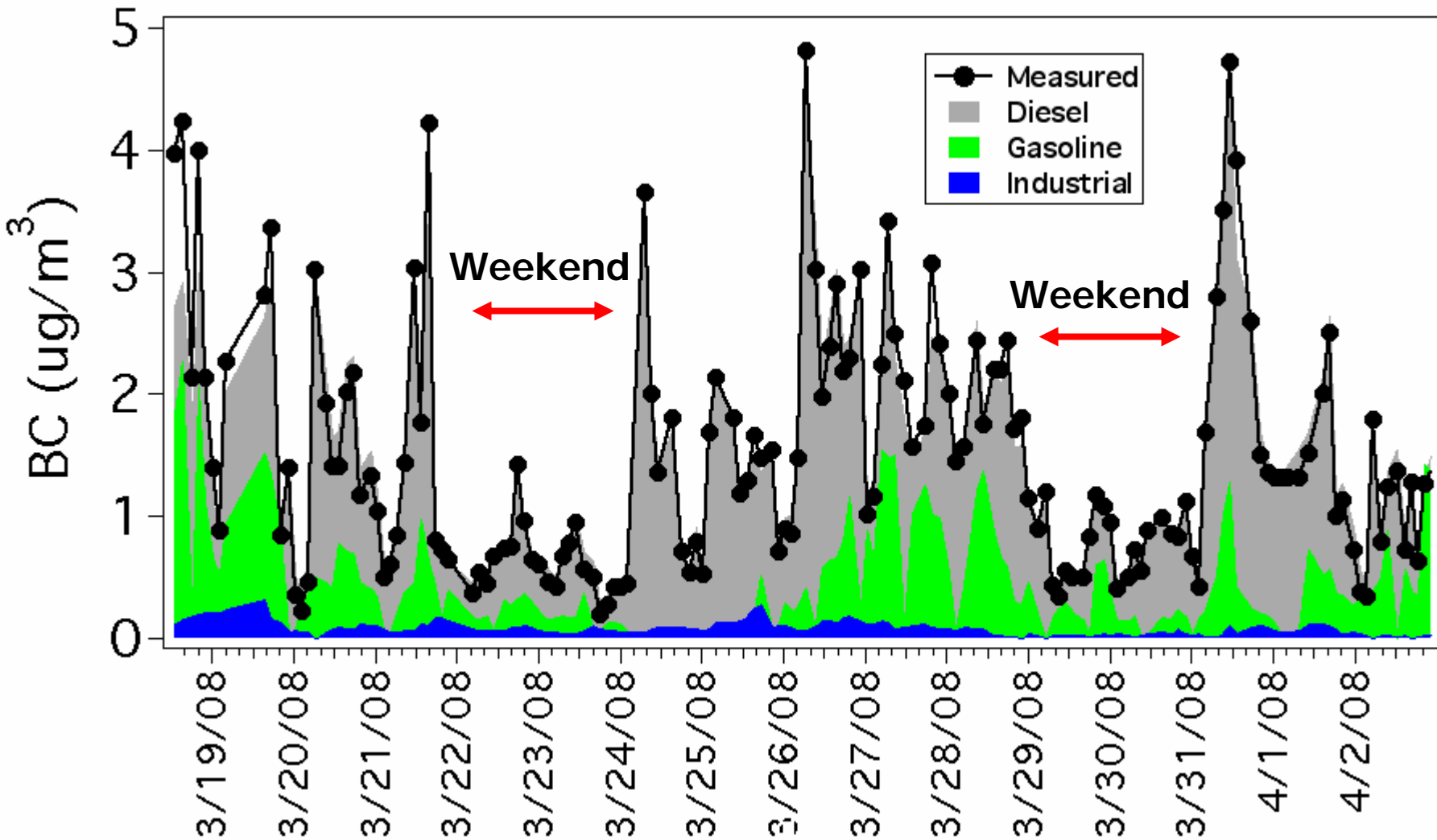
## Collocated instruments

- *in situ* GC-MS for hourly VOCs
- Feb - May 2008
- Aethalometer for black carbon

# Temporal patterns for molecular markers from different sources



# PMF Appportionment of EC



# Acknowledgements

## Center for Atmospheric Particle Studies



- **Carnegie Mellon**
  - R. Subramanian, Emily Weitkamp
  - Neil Donahue
- **Others:**
  - W. Rogge, A. Bernardo-Bricker
- **Funding**
  - EPA
  - DOE
  - NSF



# Questions

---

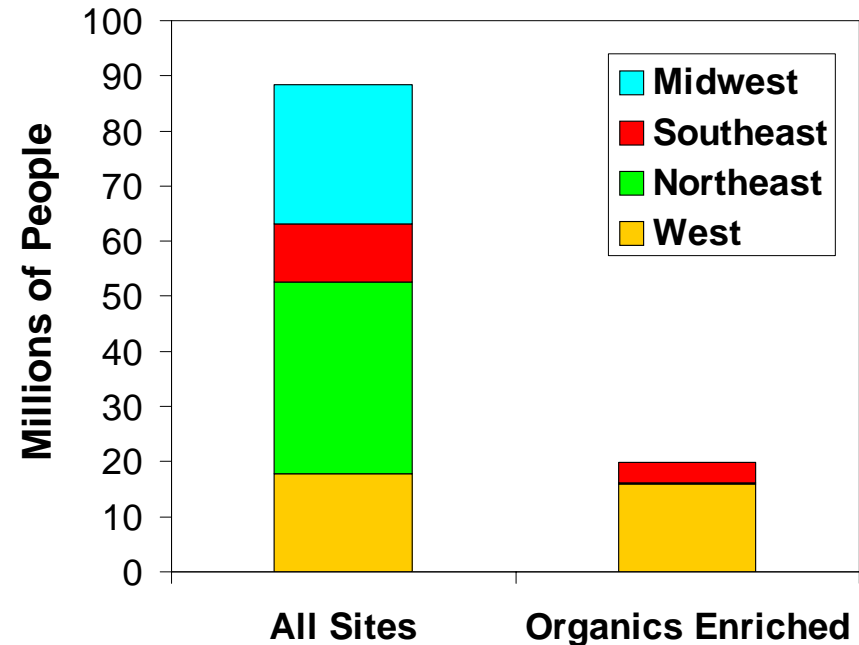
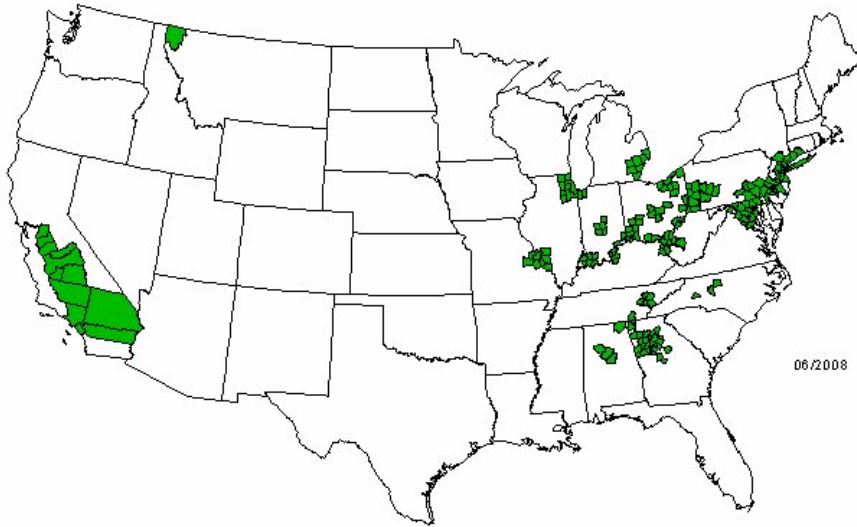
# Lots of sources of organic aerosols



# PM<sub>2.5</sub> annual standard violations

~ 90 Million people live in PM<sub>2.5</sub> non-attainment areas

## Map of non-attainment areas



Map from <http://www.epa.gov/oar/oaqps/greenbk/mappm25.html>