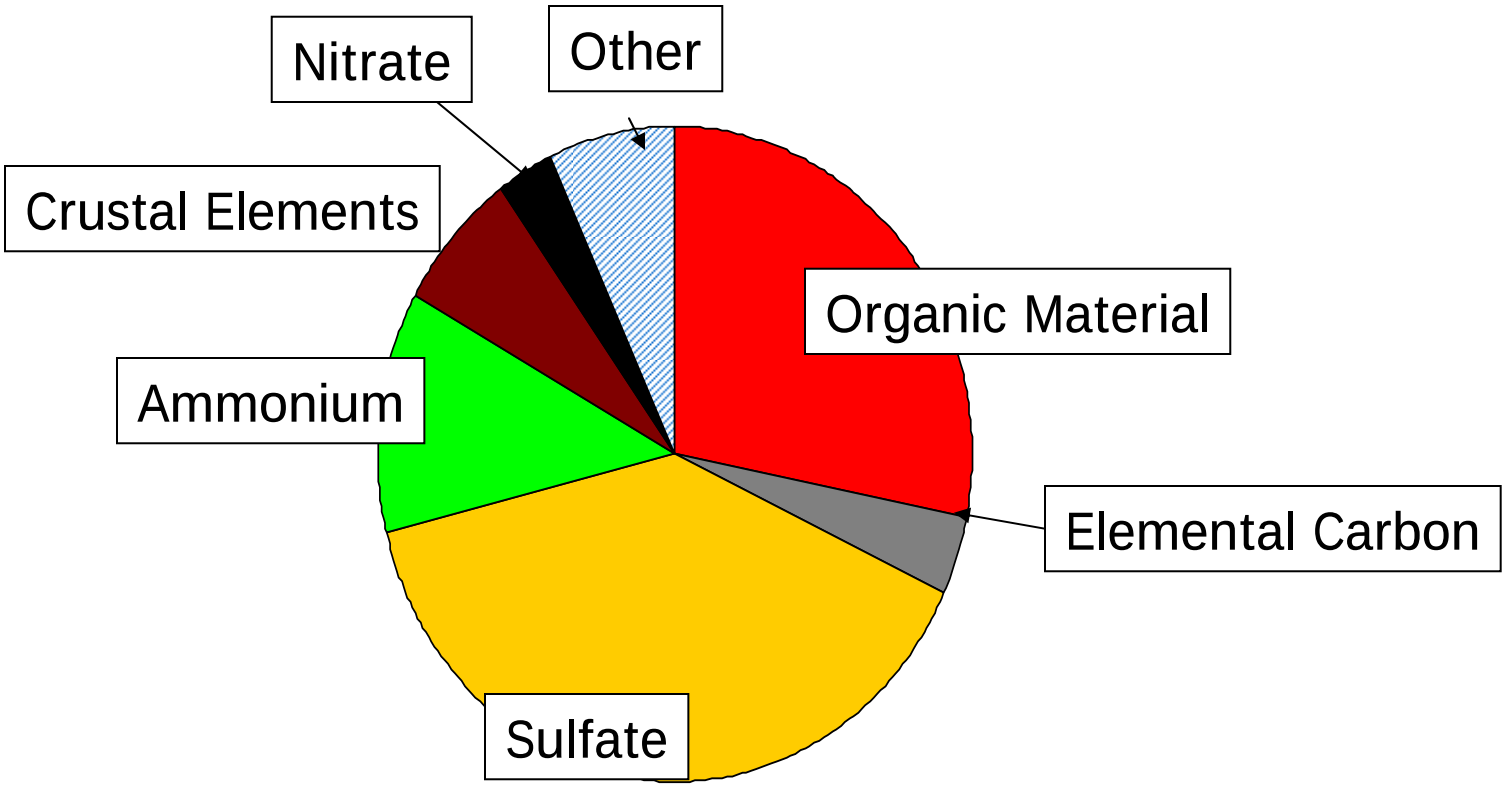
A Revised Framework for Treating Primary Organic Aerosol Emissions in Inventories and Models

Allen Robinson, Andrew Grieshop, Manish Shrivastava,
Neil Donahue, Timothy Lane, Spyros Pandis

Center for Atmospheric Particle Studies
Carnegie Mellon University

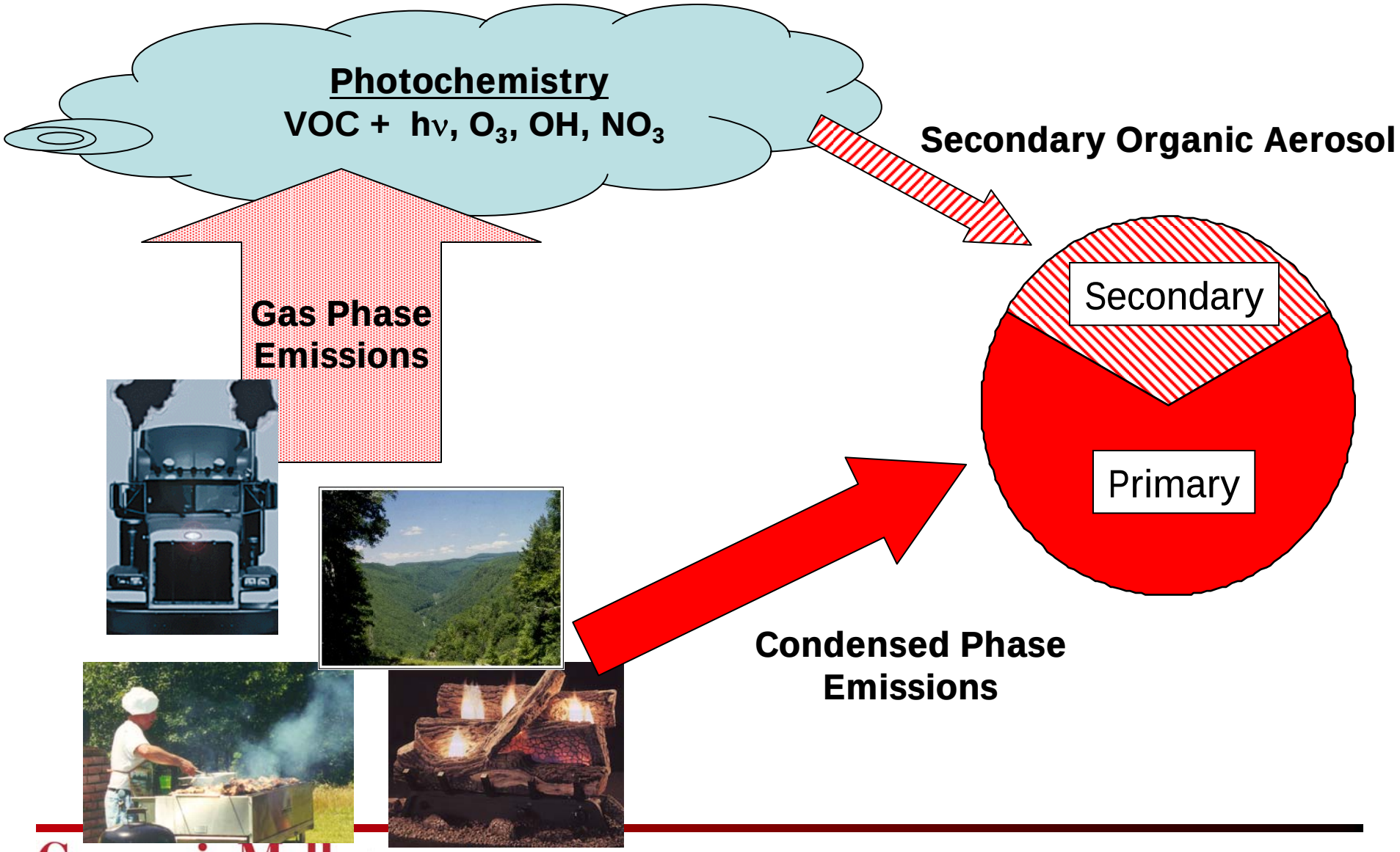
Presented at the 16th Annual International Emissions Inventory Conference
Raleigh, North Carolina, May 14-17, 2007

Fine Particulate Matter Composition



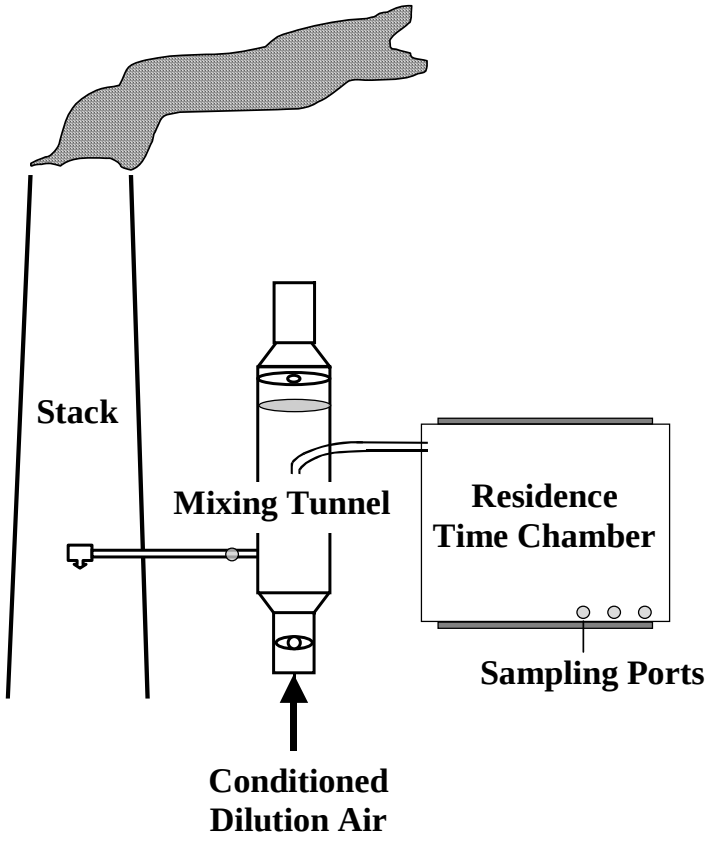
Pittsburgh July 2001, 20.1 ug/m^3

Sources of Organic Aerosol (OA)

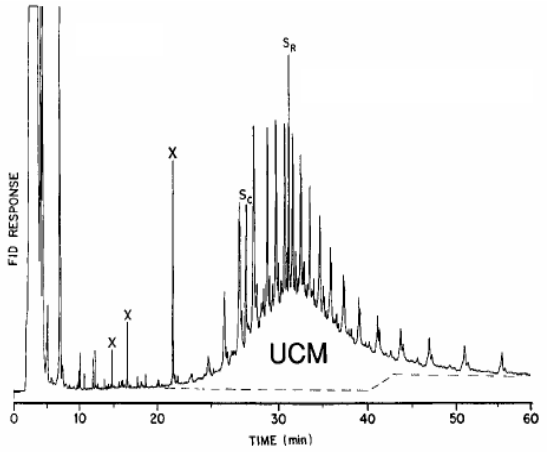


What is primary organic aerosol?

Measure with dilution sampler



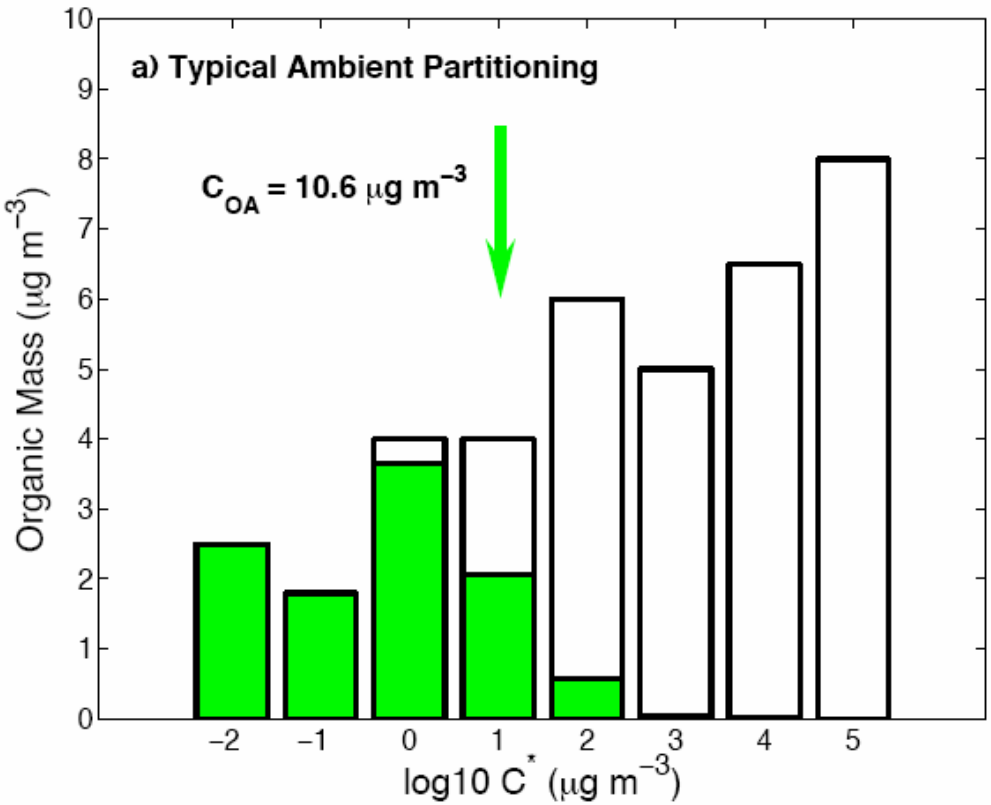
GC/FID of extracted filter sample



- Broad range of compounds
- ~ 10% Resolved
- ~ 90% Unresolved Complex Mixture (UCM)
  - branched compounds
  - cyclic compounds

Hildemann et al.

Gas-Particle Partitioning and the Volatility Distribution



Partitioning Theory:

- Raoult's Law
  - $P_i = \gamma_i P_{sat,i}(T) y_i$
- C* or Partitioning Coefficient

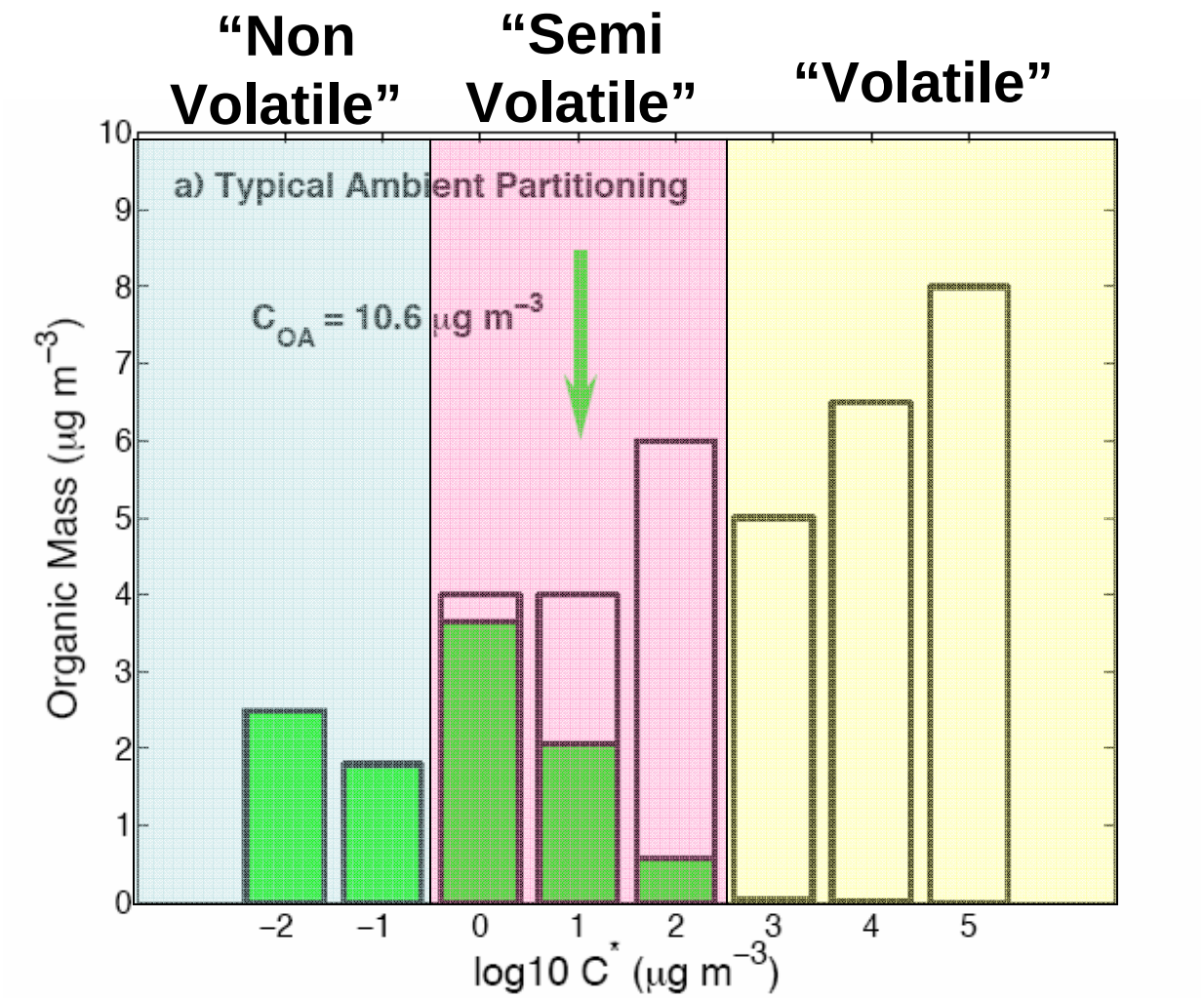
$$X_{p,i} = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

$$C_{OA} = \sum X_{p,i} C_i$$

Donahue et al. ES&T 2006

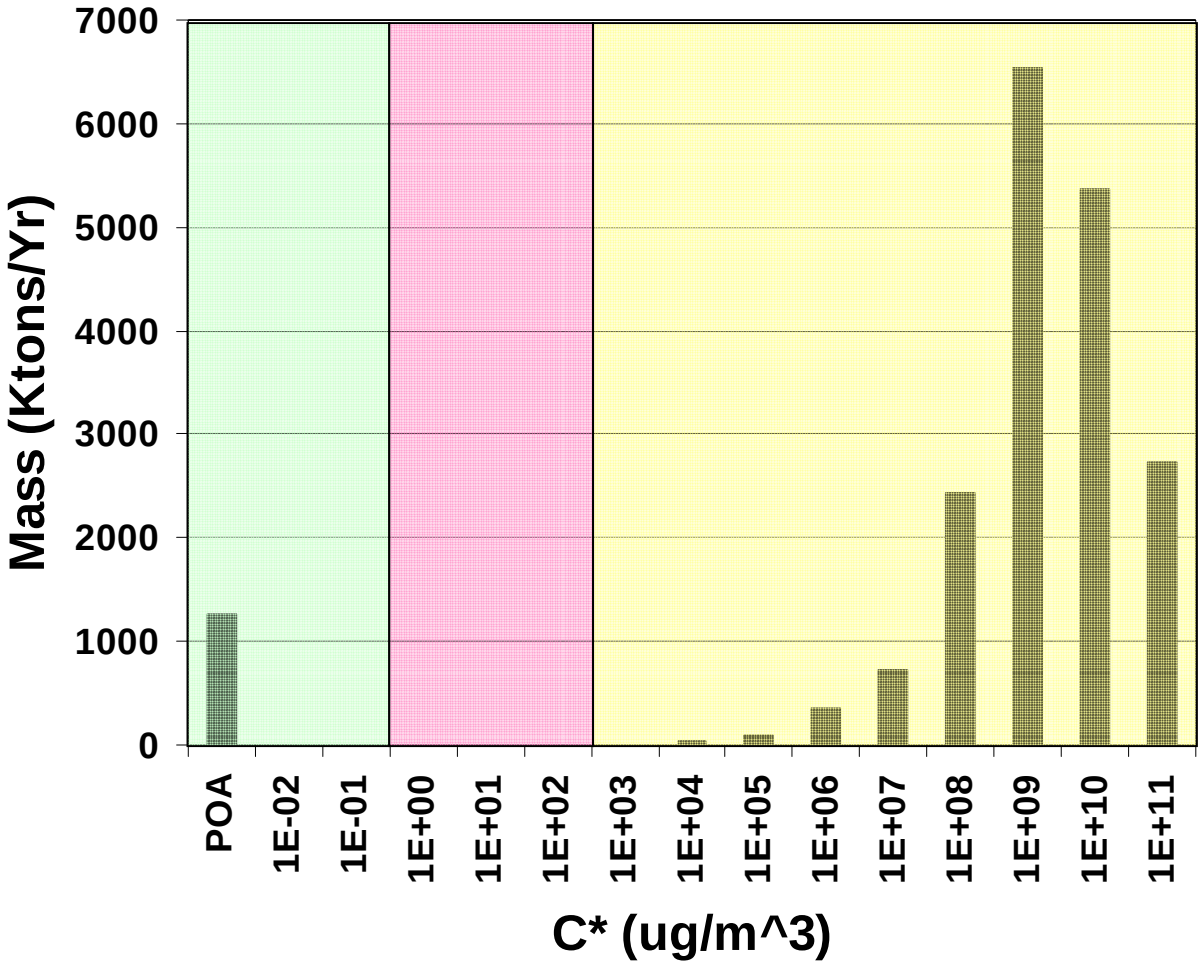
Pankow AE 1987 & 1994

Volatility Distribution



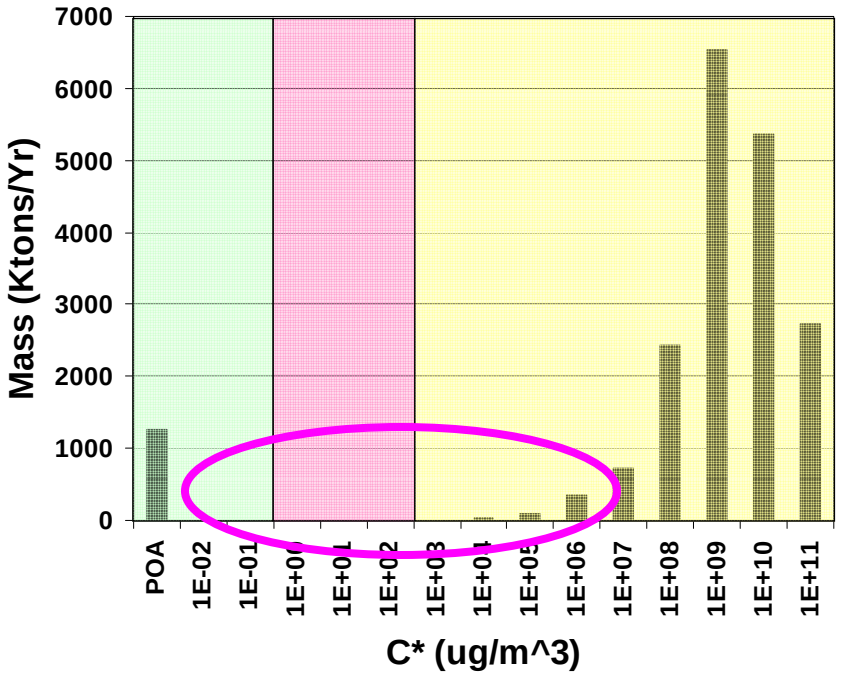
Donahue et al. ES&T 2006

Volatility distribution of NEI 2002

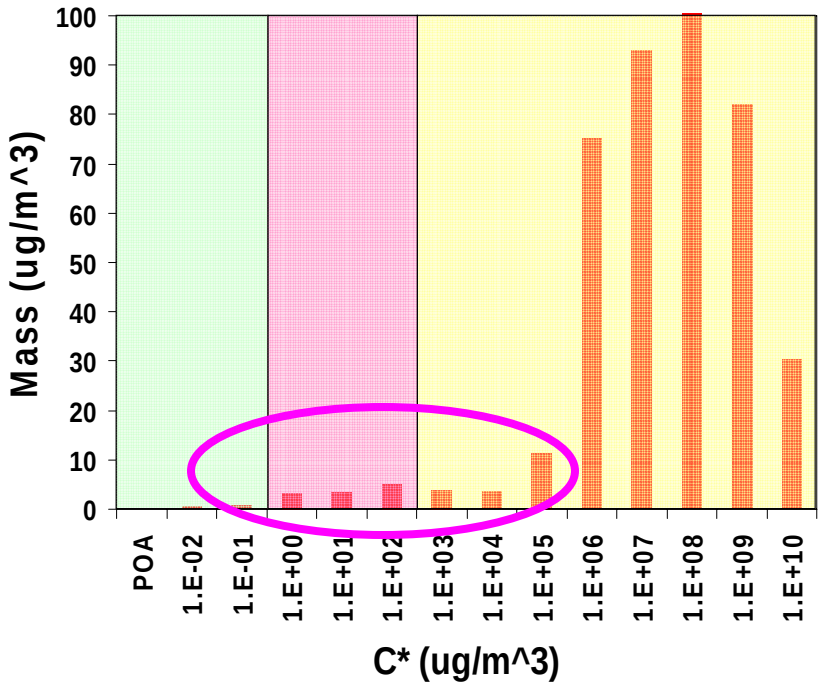


Comparing NEI and ambient data

NEI

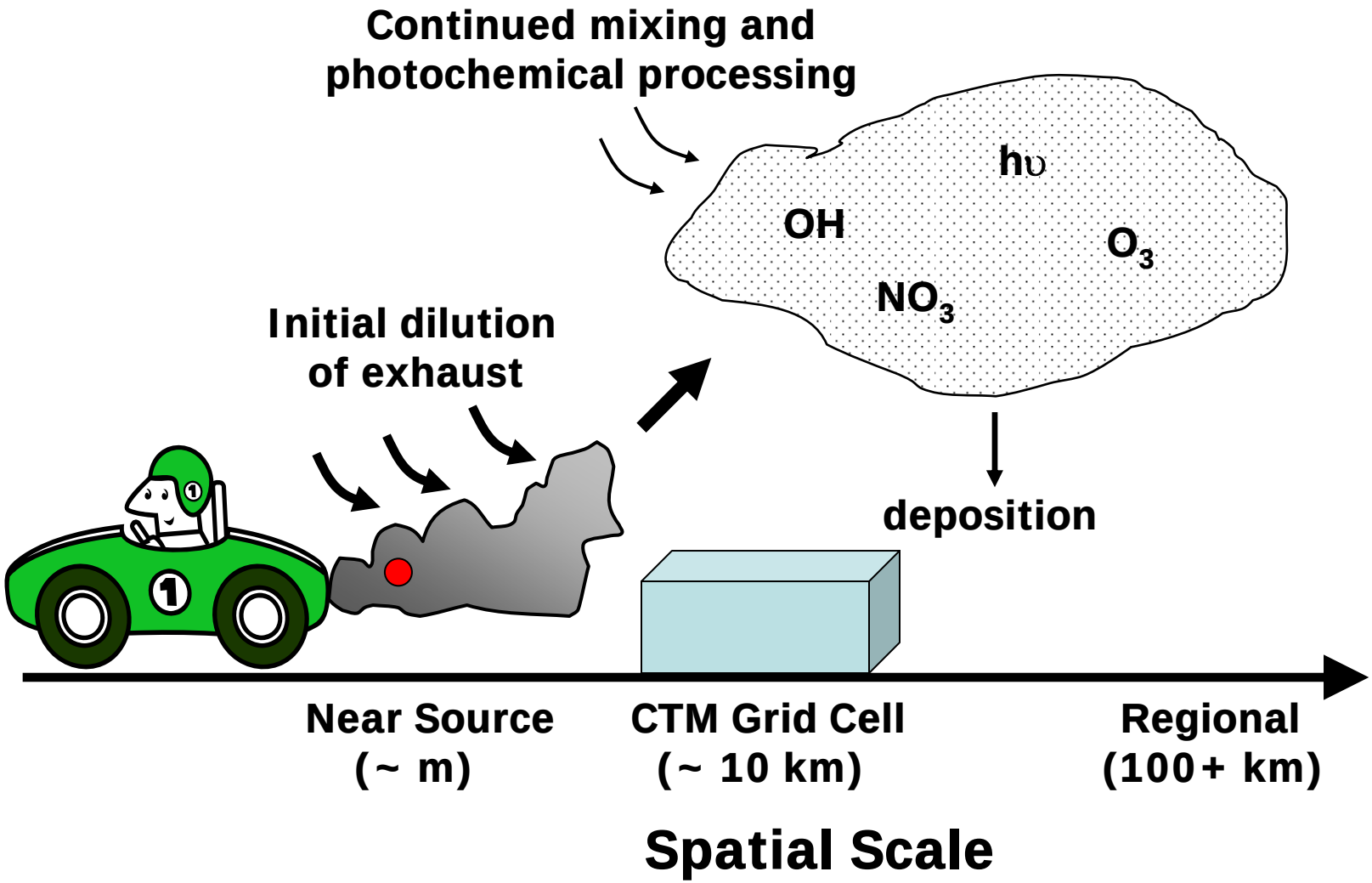


Los Angeles

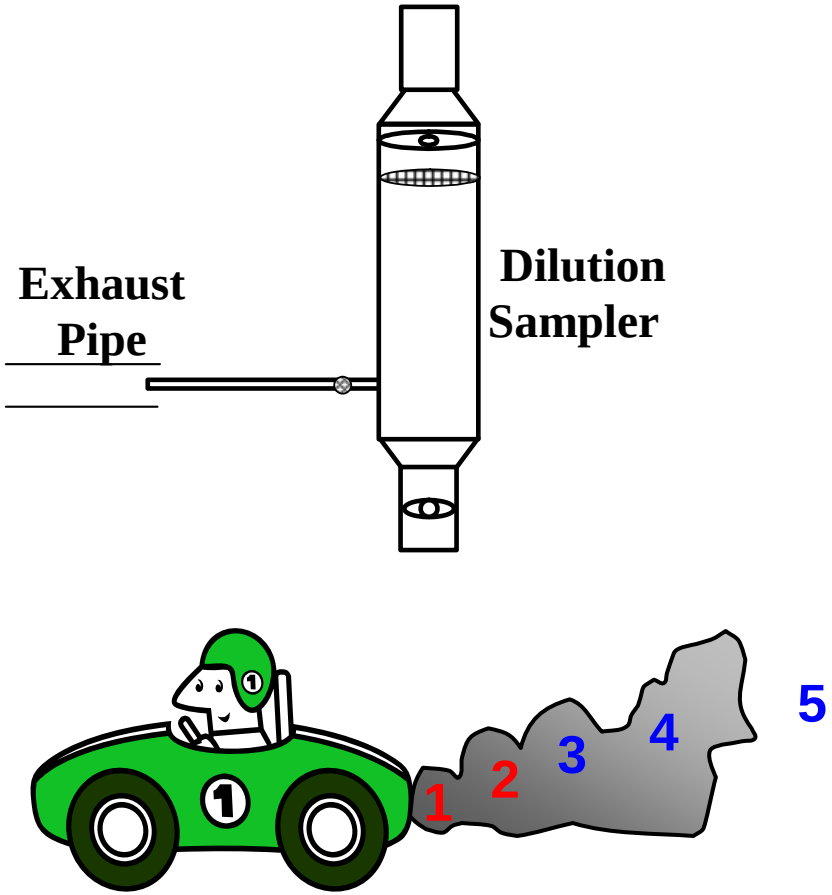


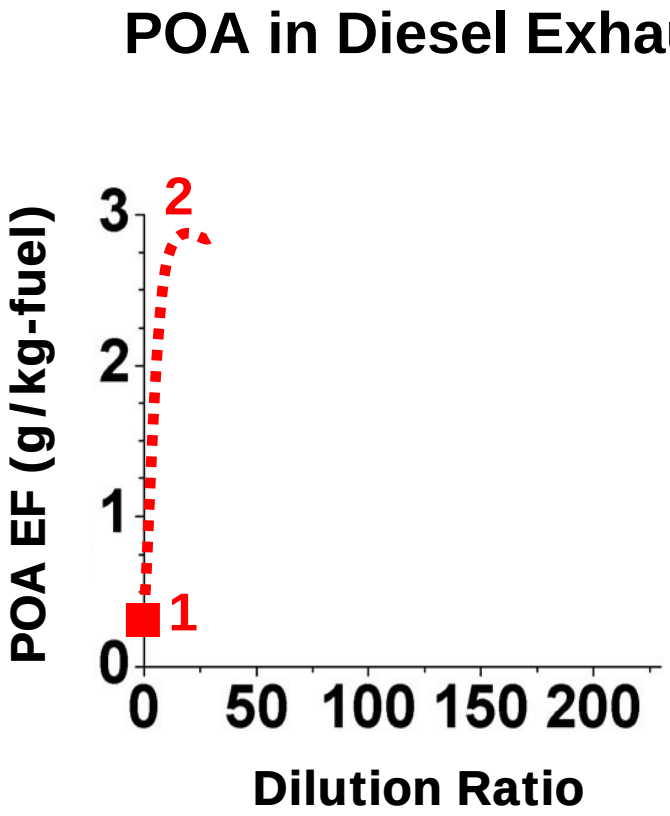
LA data from Fraser et al. ES&T 1996, 1997

How do primary emissions evolve after leaving the tail pipe?



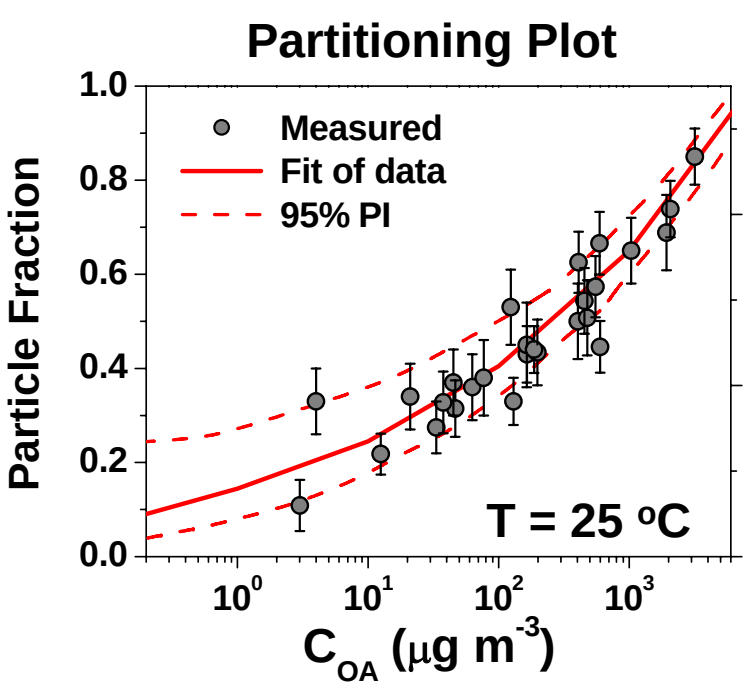
Gas-particle partitioning of primary emissions in near field

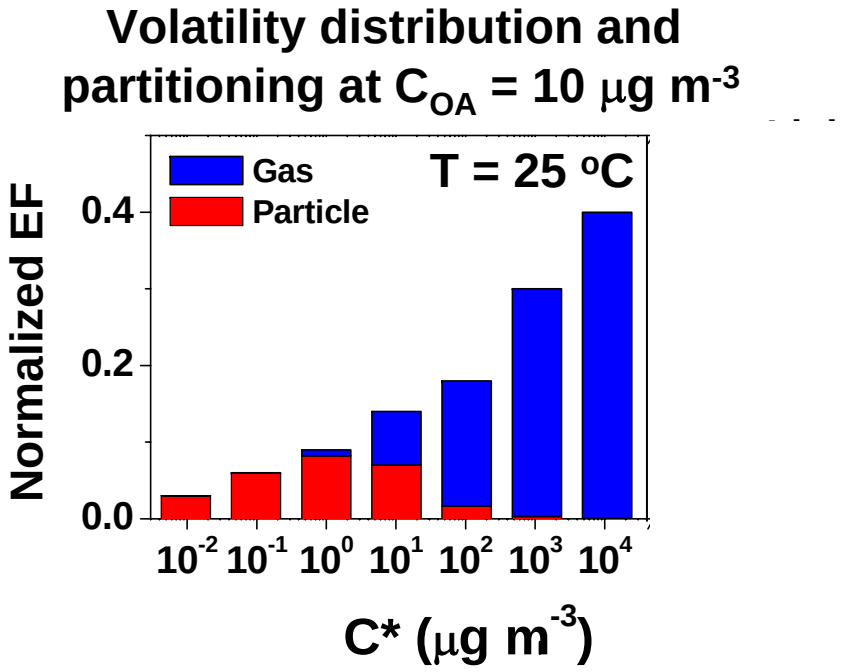




Hildeman et al. AST 1989
Lipsky and Robinson ES&T 2006

Volatility distribution of diesel exhaust



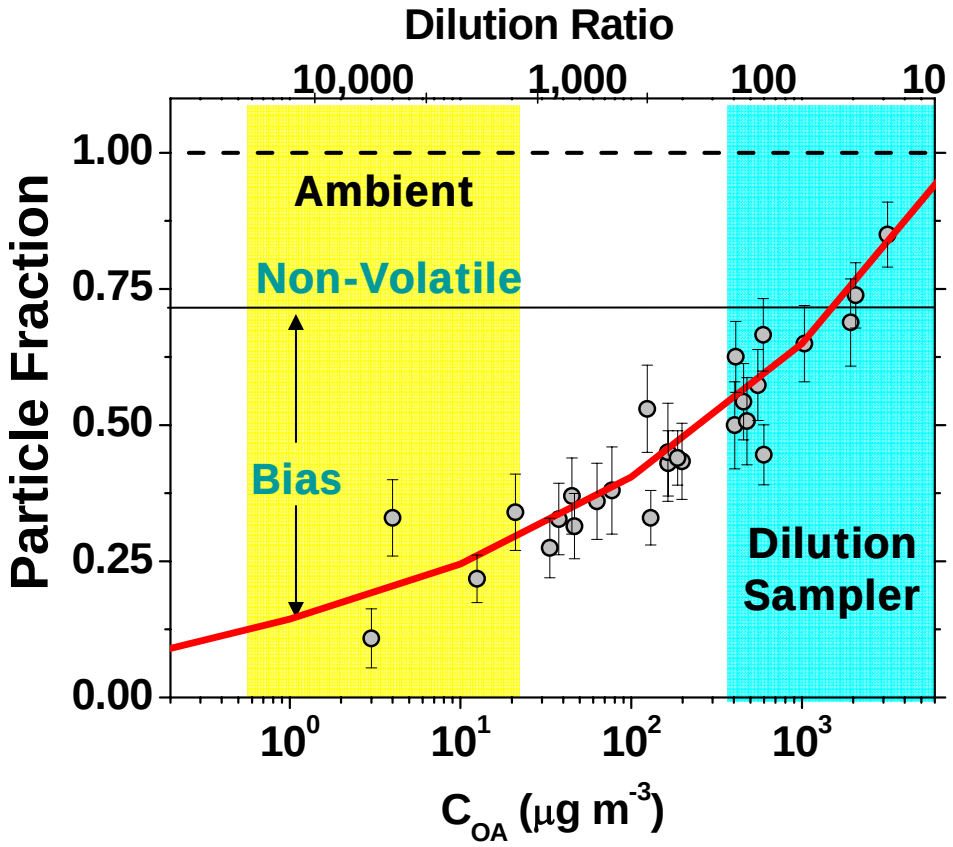


$$X_p = \sum_{i=1}^{n} f_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

$$X_p = \frac{f_1}{1+\frac{1}{C_{OA}}} + \frac{f_2}{1+\frac{10}{C_{OA}}} + \cdots + \frac{f_5}{1+\frac{10^4}{C_{OA}}}$$

Shrivastava et al. ES&T 2006
Robinson et al. Science 2007

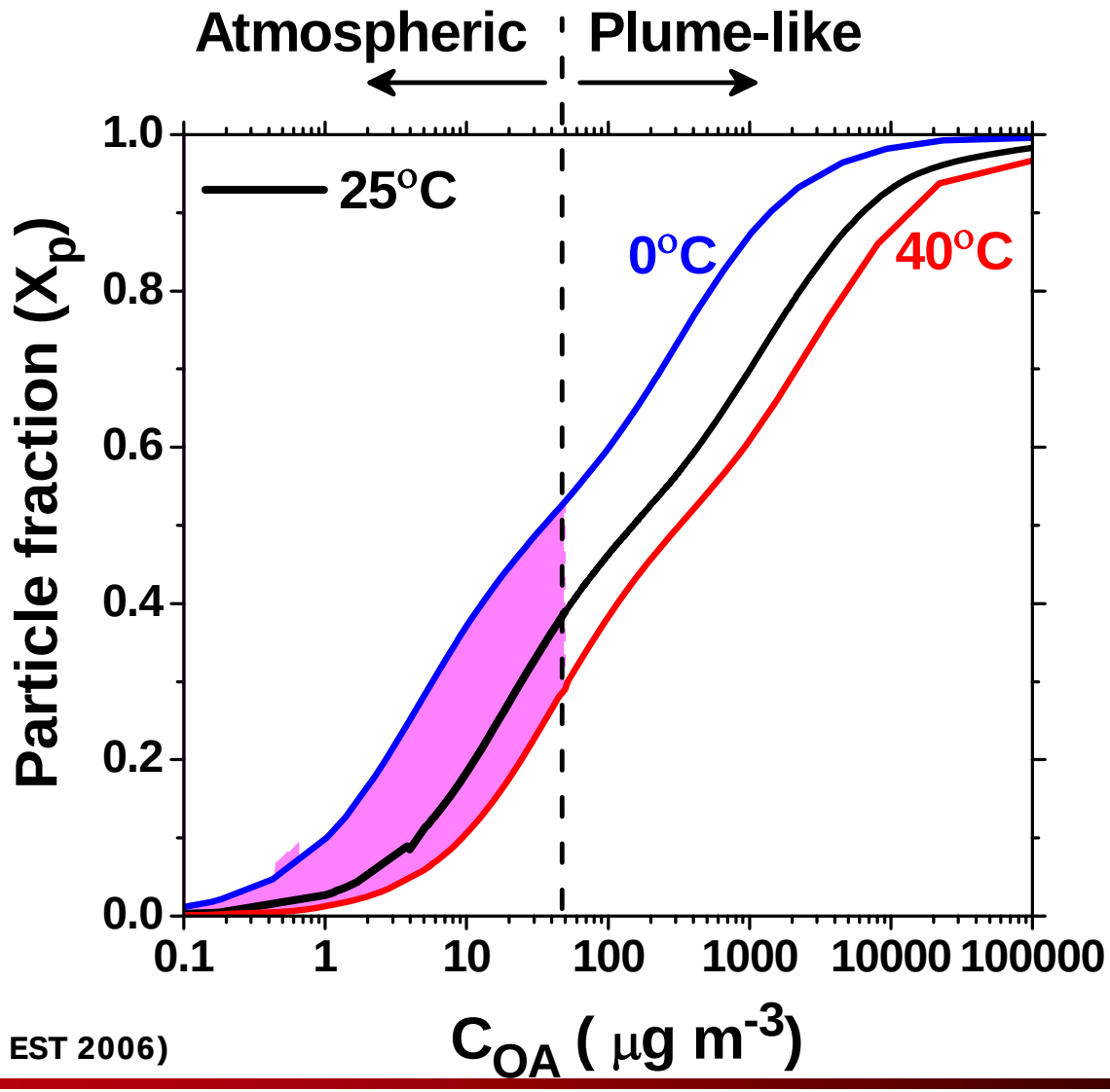
POA emission factors may be biased high



POA emissions for high emitting sources may be biased by a factor of 5!

Shrivastava et al. EST 2006.

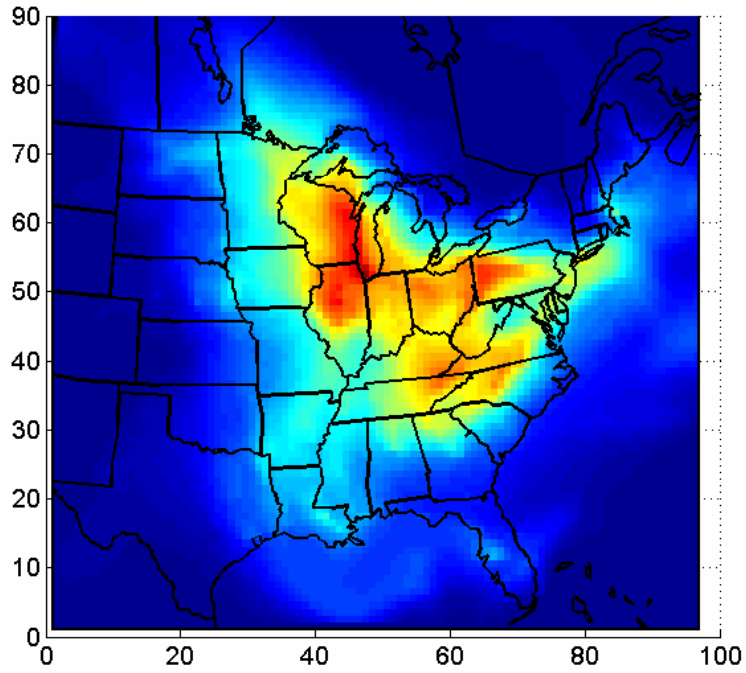
Cannot represent emissions with a single, static emission factor



(Shrivastava et al. EST 2006)

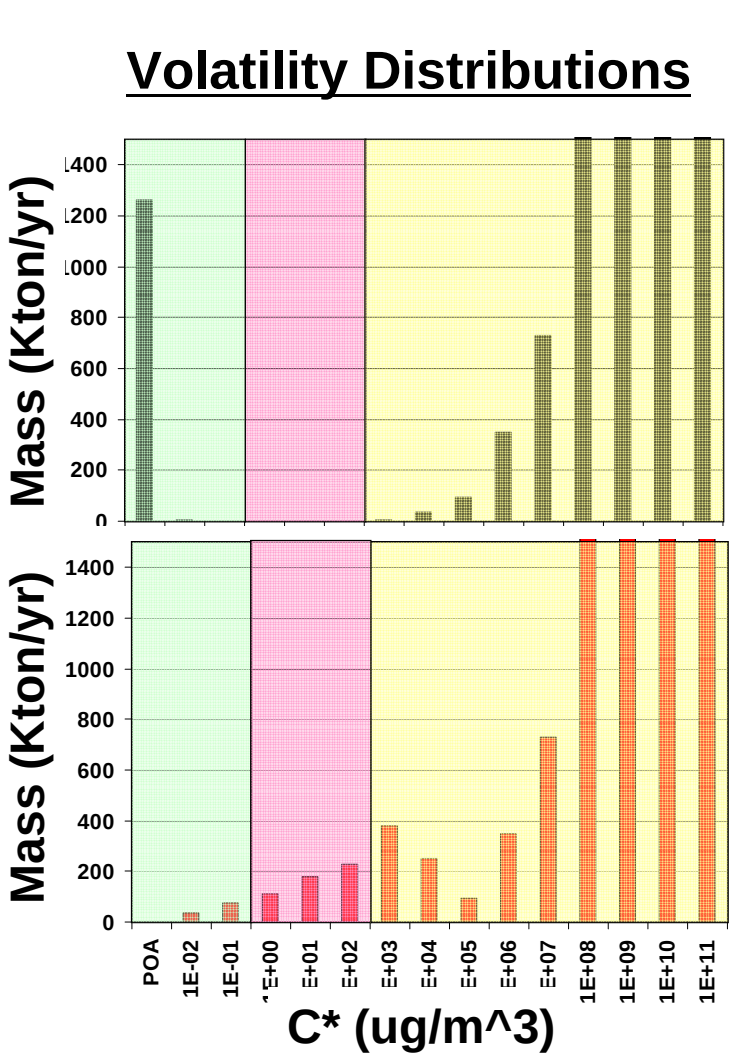
Simulating Organic Aerosols in Eastern US with a Chemical Transport Model

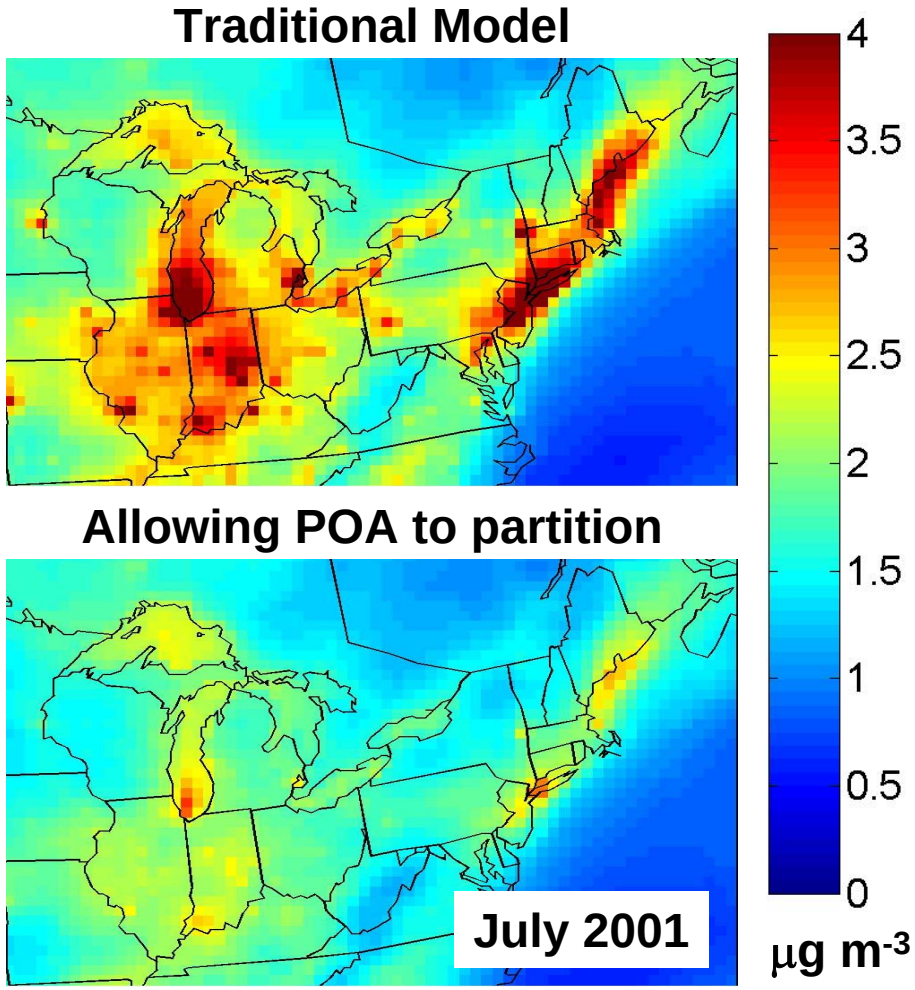
Modeling Domain



- **PMCAMx+**
  - 36x36 km grid
  - MM5
  - July 12-28, 2001
- **LADCO Base E Inventory**
  - NEI 1999 V2
- **Modifications**
  - Apply diesel volatility distribution to all primary emissions
  - Partitioning of primary emissions

Evaporation dramatically reduces regional POA





Robinson et al. Science 2007.

Photochemical aging of diesel exhaust

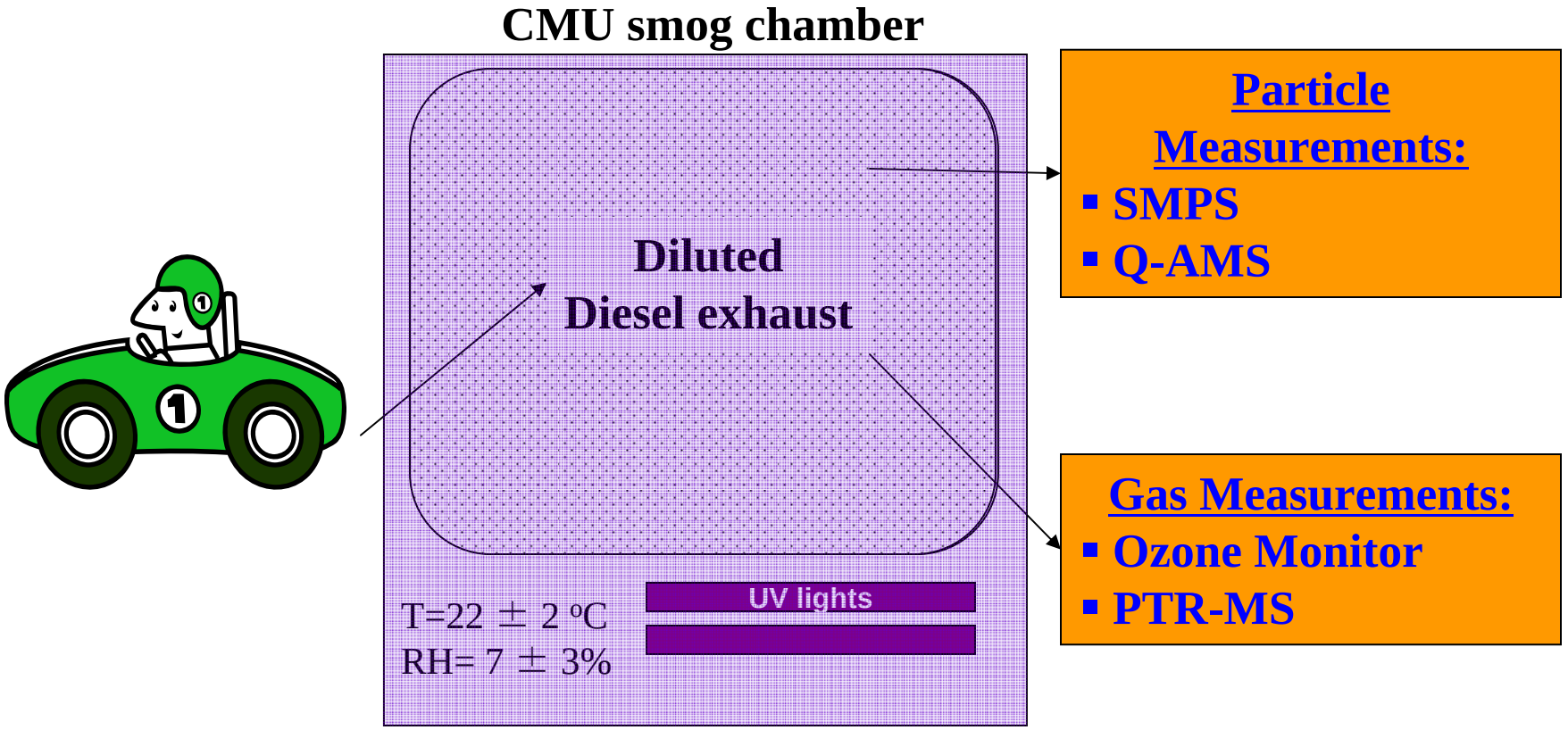
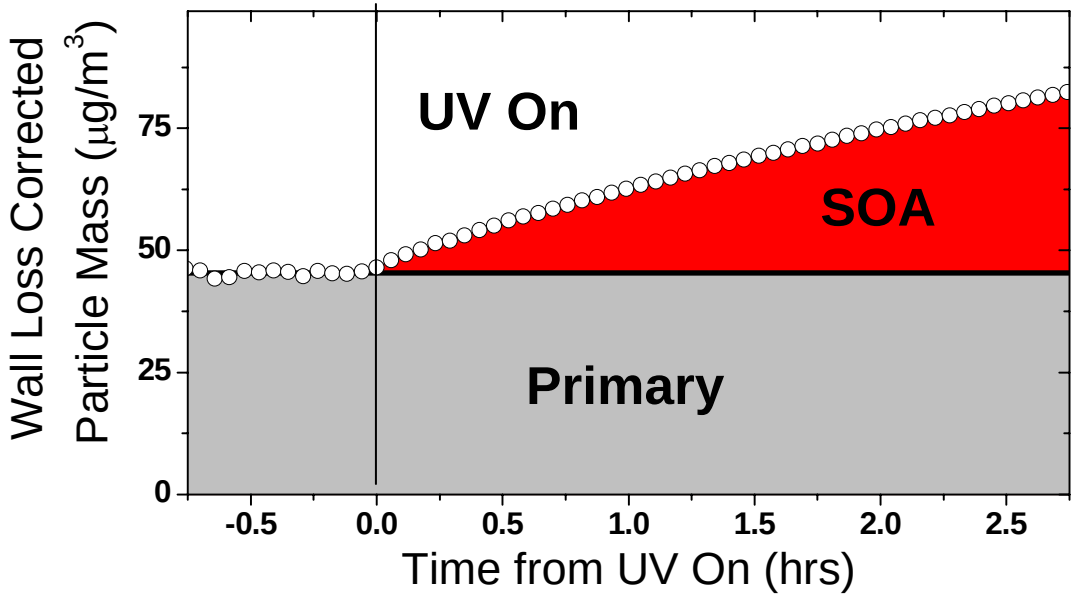
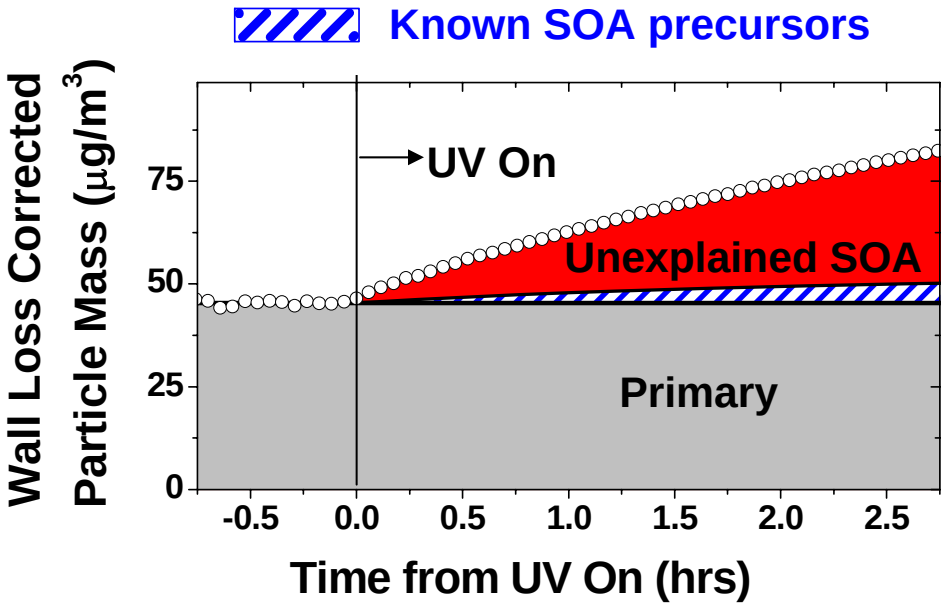


Photo-oxidation creates significant amounts of SOA



Robinson et al. Science 2007.

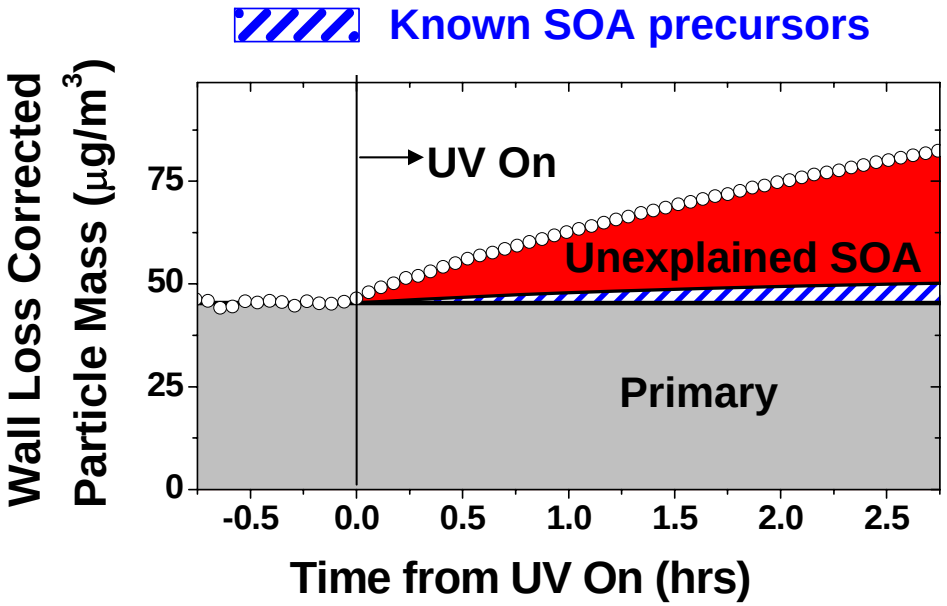
What is contribution of known SOA precursors?

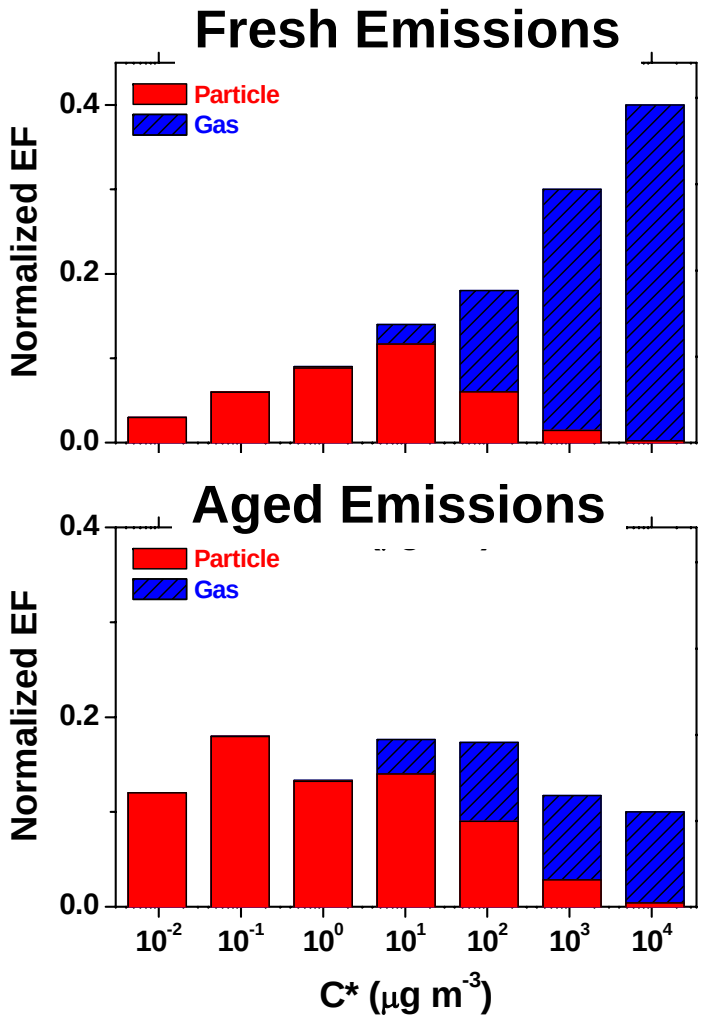


- SOAM II **(Koo et al. 2003)**
- 58 precursors
  - **Measured Aromatics**
  - **Estimates for other species**
- Assume ideal solution
- Wall losses

Robinson et al. Science 2007.

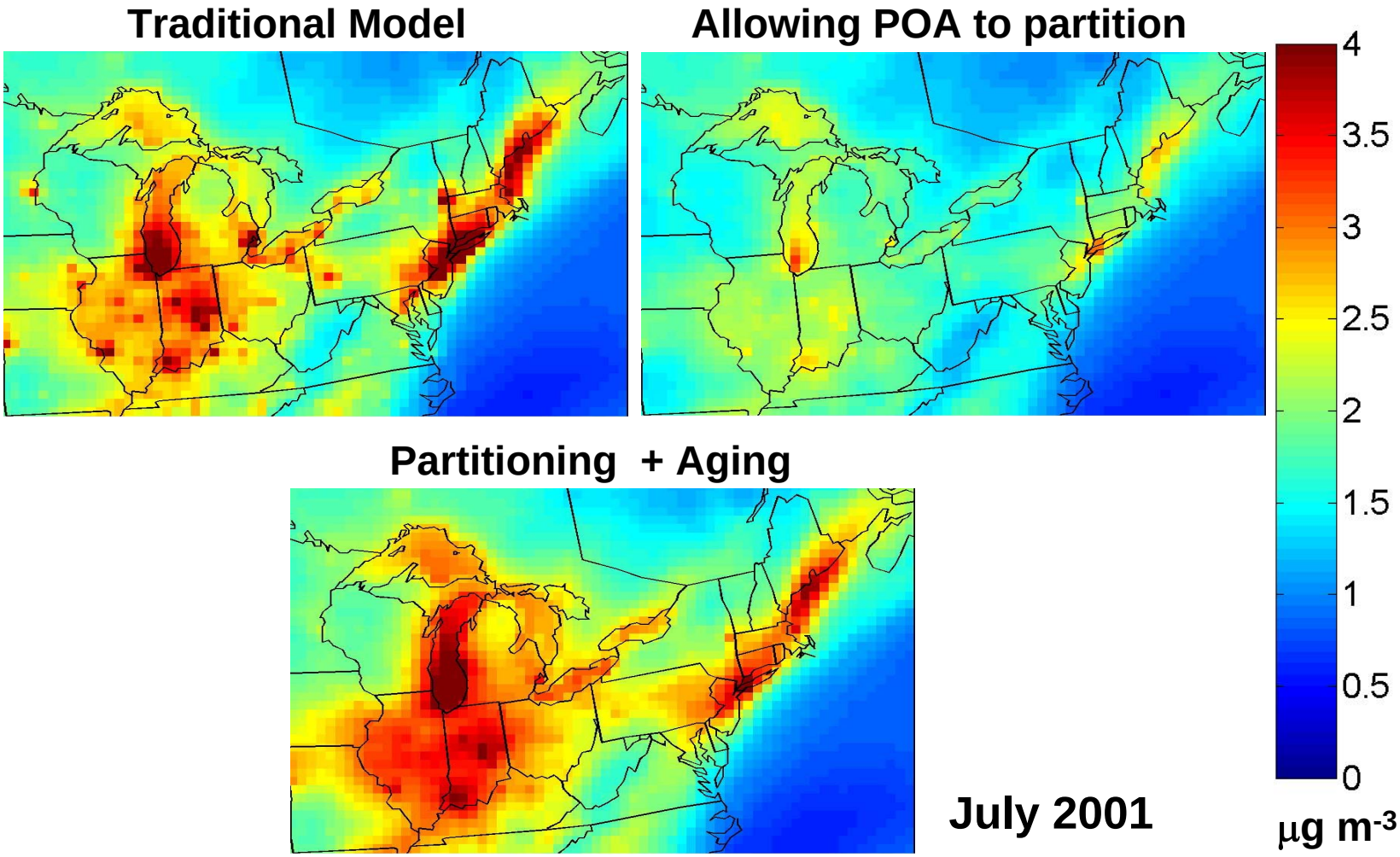
Aging of low volatility vapors source of unexplained SOA





Robinson et al. Science 2007.

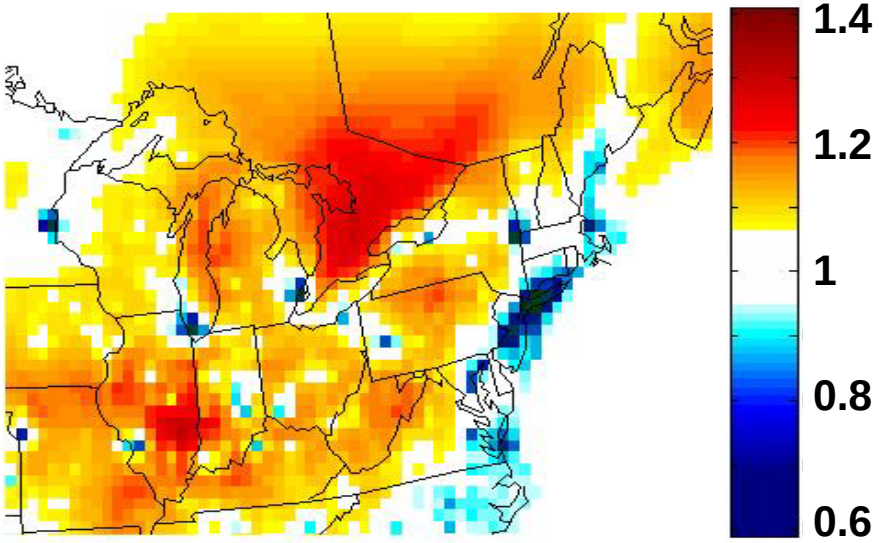
Predicted Summertime Organic Aerosol



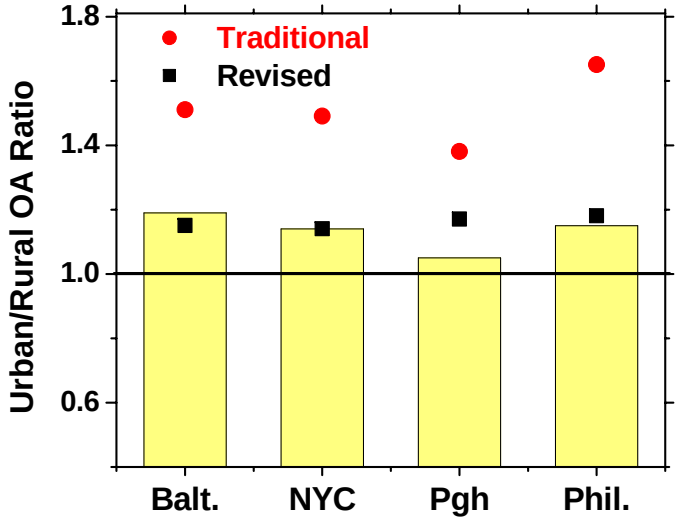
Robinson et al. Science 2007.

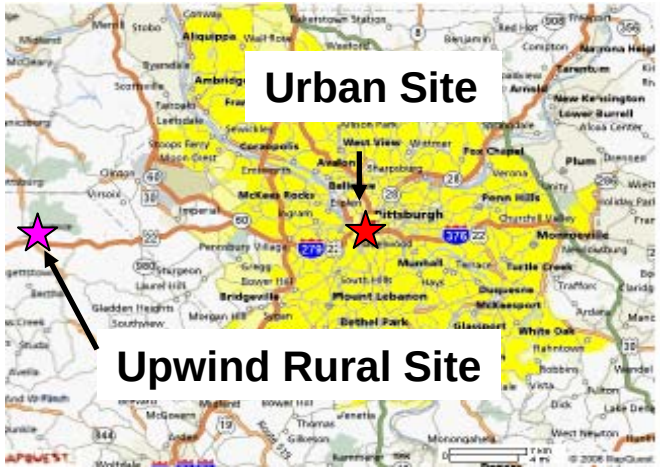
Revised model predicts a more regional aerosol

Ratio of Revised-to-Traditional Model Predicted OA levels



Model-Measurement Comparison

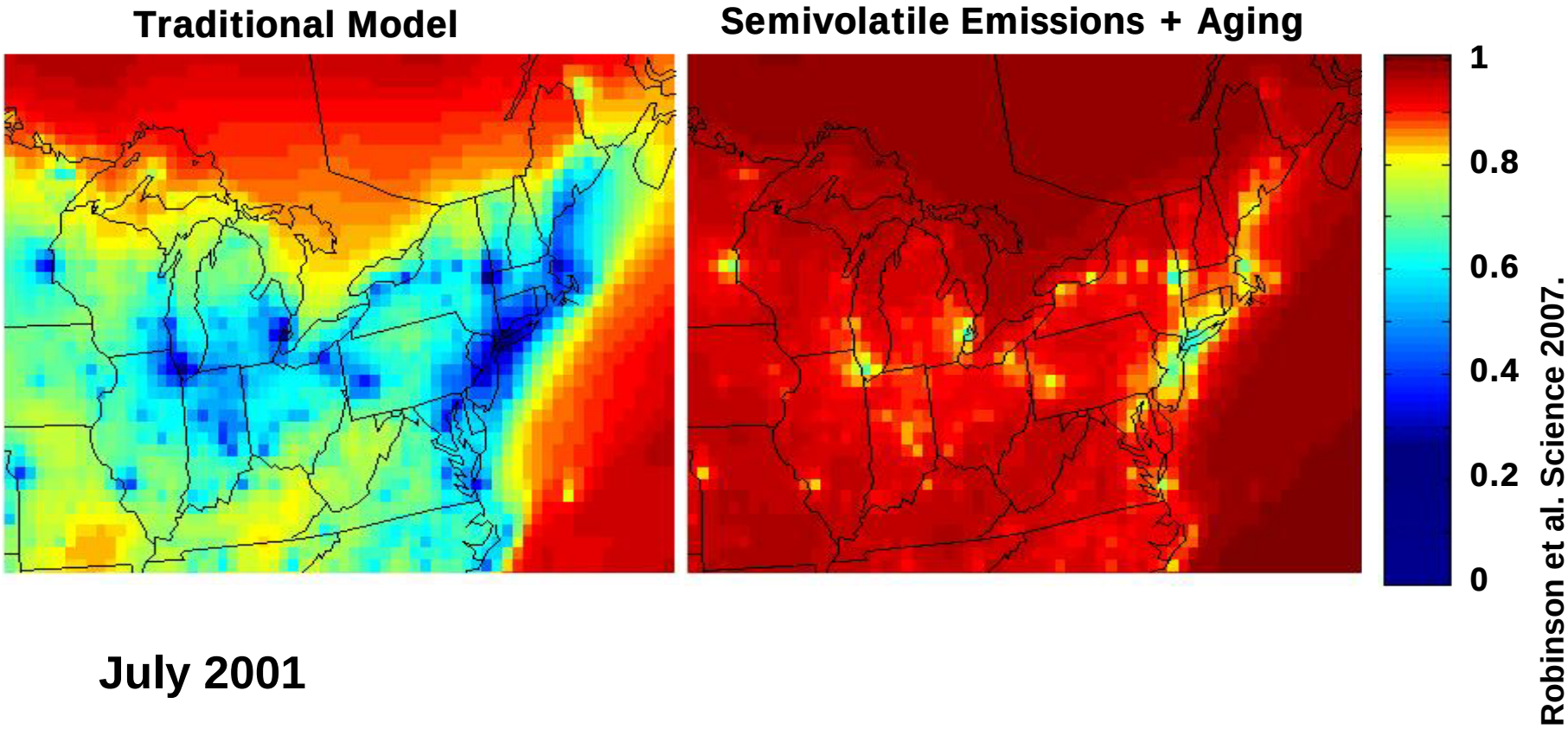




Robinson et al. Science 2007.

Dramatic shift in primary-secondary split

Predicted fractional contribution of SOA to total OA concentration



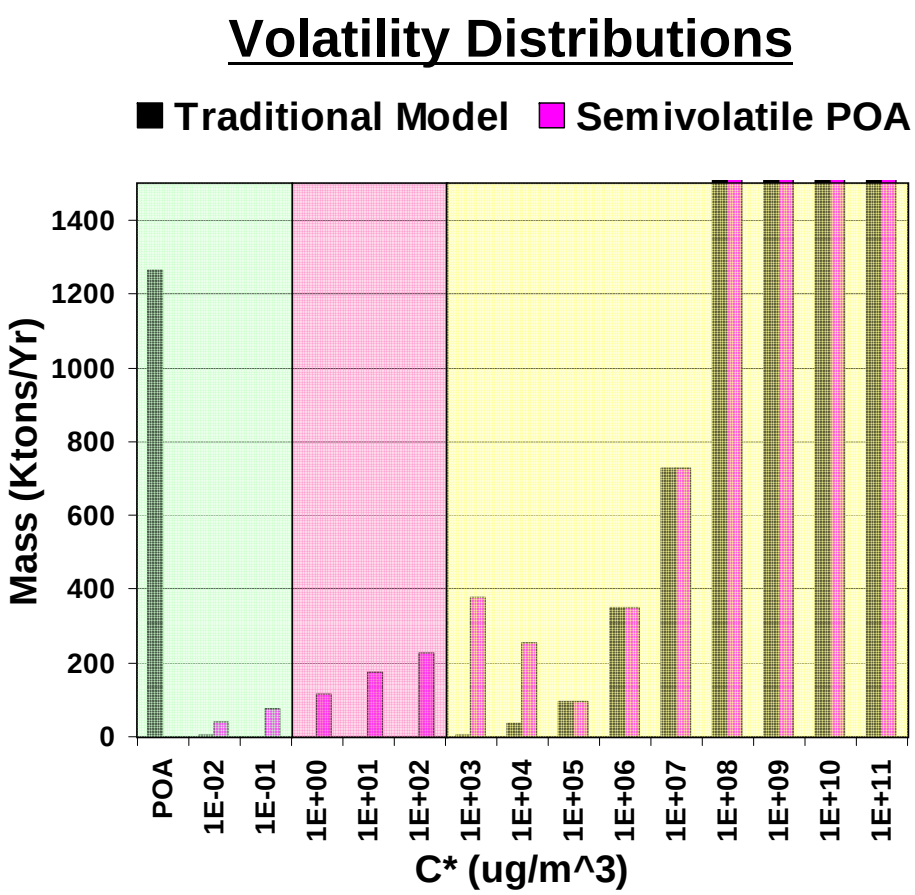
Conclusions

- **Revised conceptual model for treating primary emissions**
  - **Gas-particle partitioning of semivolatile organics**
  - **Photochemical aging of semivolatile emissions**
- **Implications for regional OA**
  - **Reduce POA**
  - **Increase SOA**
  - **Developing control strategies?**
- **Implications for emission inventory**
  - **Represent emissions using volatility distribution**
  - **Include all low-volatility organics**

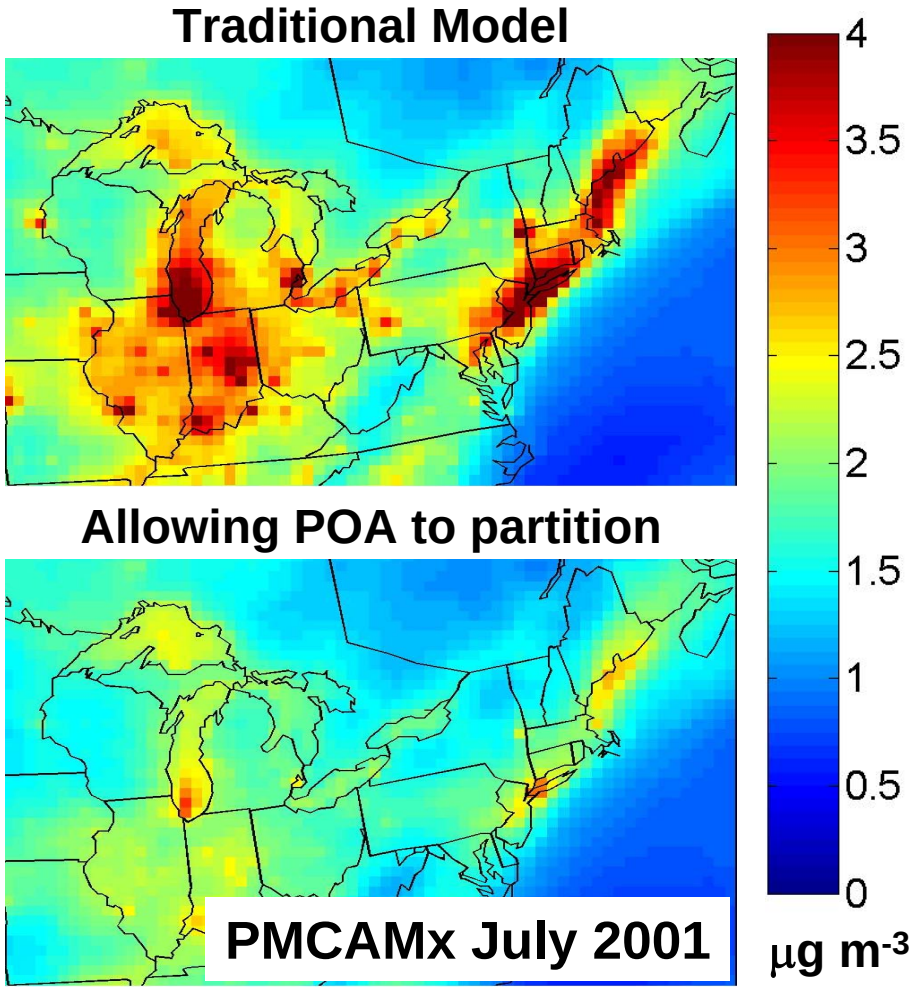
Acknowledgments

- Funding US EPA through the STAR Program

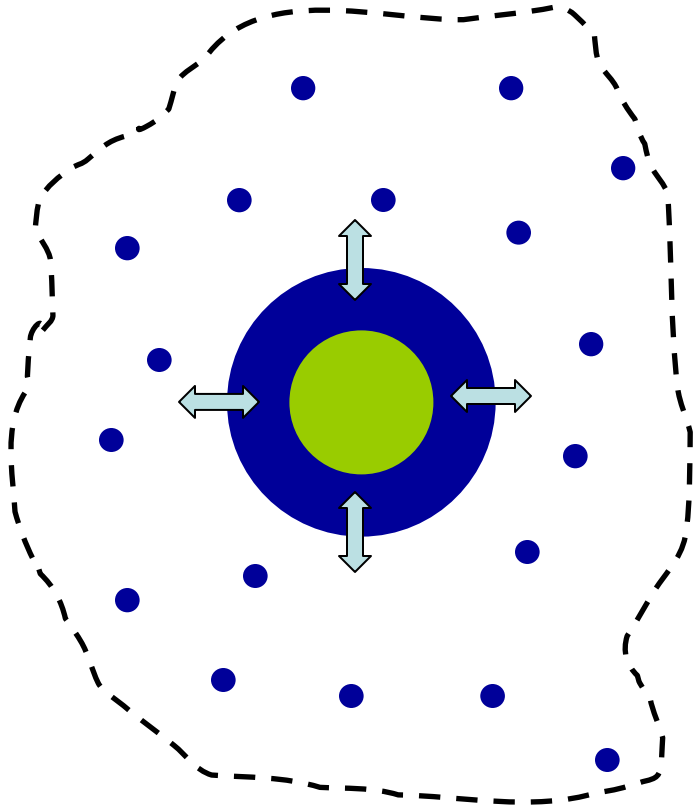
Evaporation dramatically reduces regional POA



Robinson et al. Science 2007.



Gas-particle partitioning of semivolatile organics



Semi-volatile Organics

Non-volatile material

Partitioning Theory:

- Raoult's Law
  - $P_i = \gamma_i P_{sat,i}(T) y_i$
- C* or Partitioning Coefficient

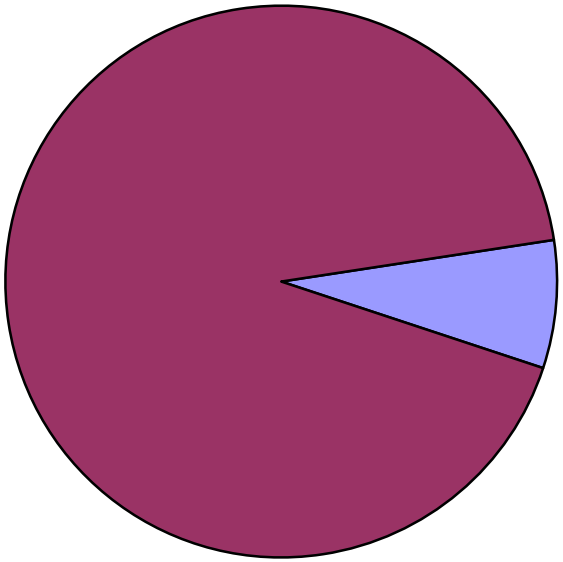
$$X_{p,i} = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

  - 0.1 ug/m^3 < C* < 1000 ug/m^3

(Pankow AE 1987, 1994)

Gases Dominate Organic Emissions

Anthropogenic VOC
~ 15,000 Kton/year



POC
~ 1,200 Kton/year

NEI 2002