US EPA ARCHIVE DOCUMENT

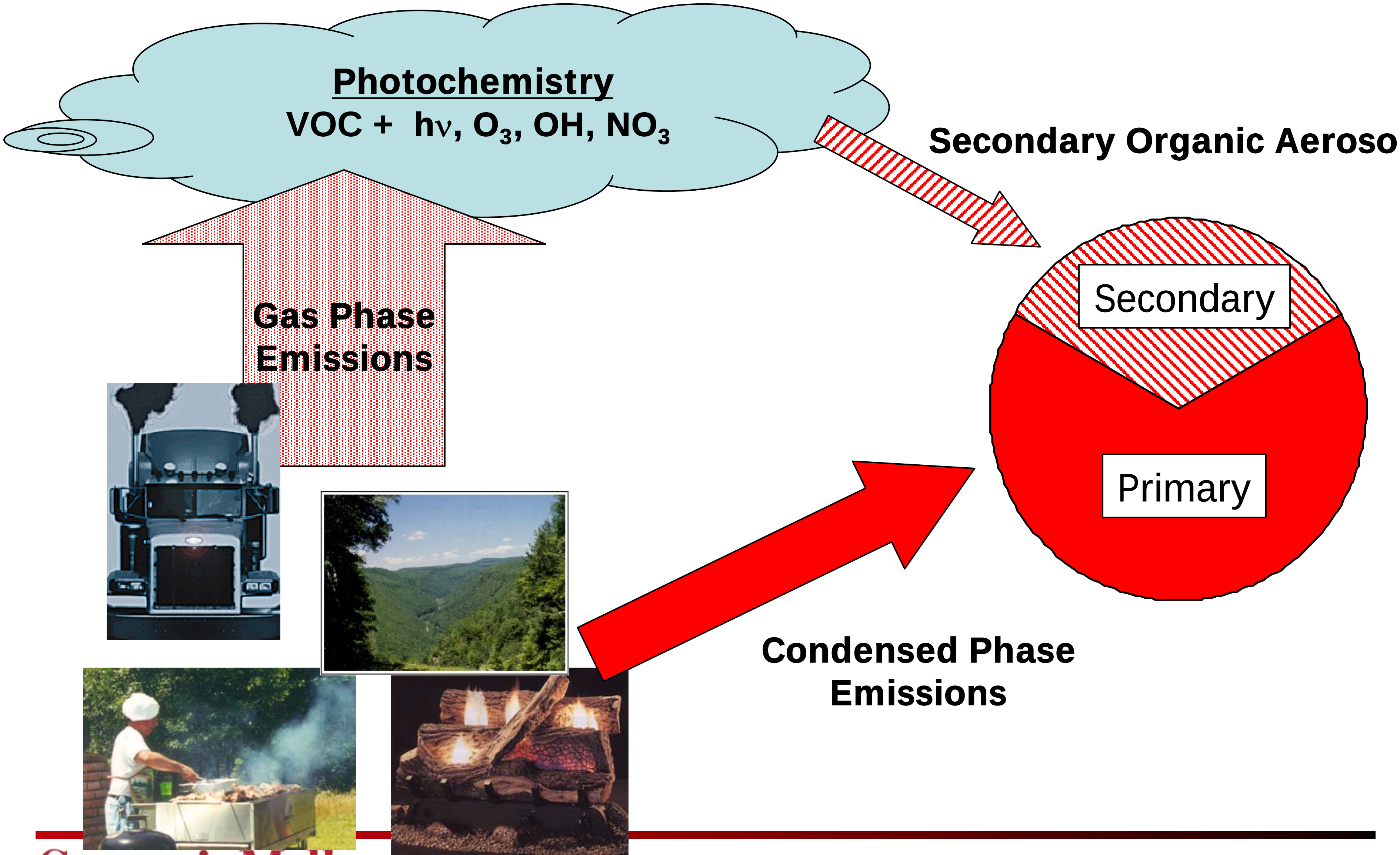
Source-Apportionment of Primary Organic Carbon in the Eastern United States Combining Receptor-Models, Chemical Transport Models, and Laboratory Oxidation Experiments

Allen Robinson

Center for Atmospheric Particle Studies
Carnegie Mellon University

Presented at the EPA Atmospheric Science Progress Review Meeting, Research Triangle Park, North Carolina, June 21-22, 2007

Sources of Organic Aerosol (OA)

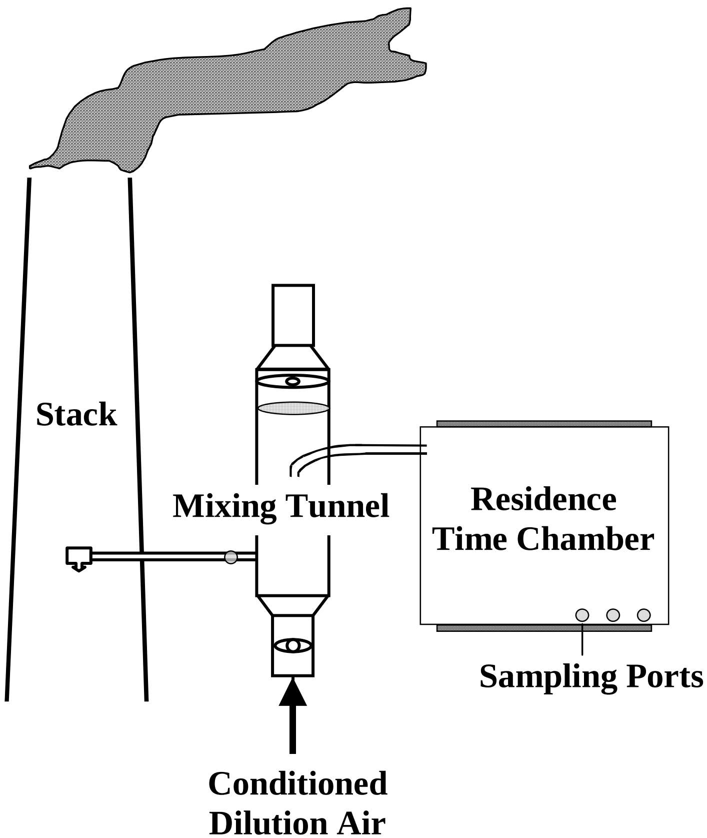


Current conceptual model for organic aerosol

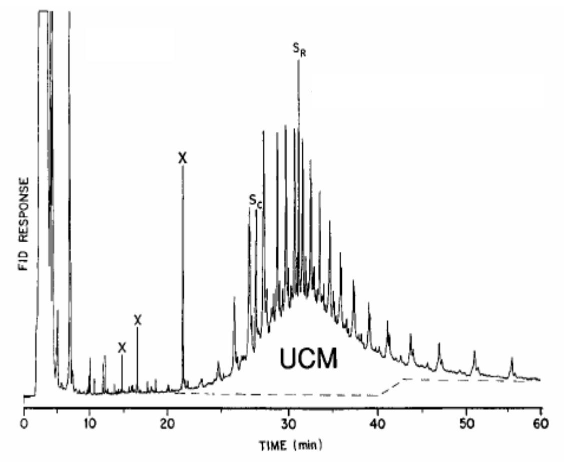
- Primary organic aerosol
  - **Non-volatile**
  - **Non-reactive**
- Secondary organic aerosol
  - **High flux, but very volatile precursors**
    - **Light aromatics**
    - **Monoterpenes**
  - **Absorptive partitioning of non-reactive condensable products**

What is primary organic aerosol?

Measure with dilution sampler



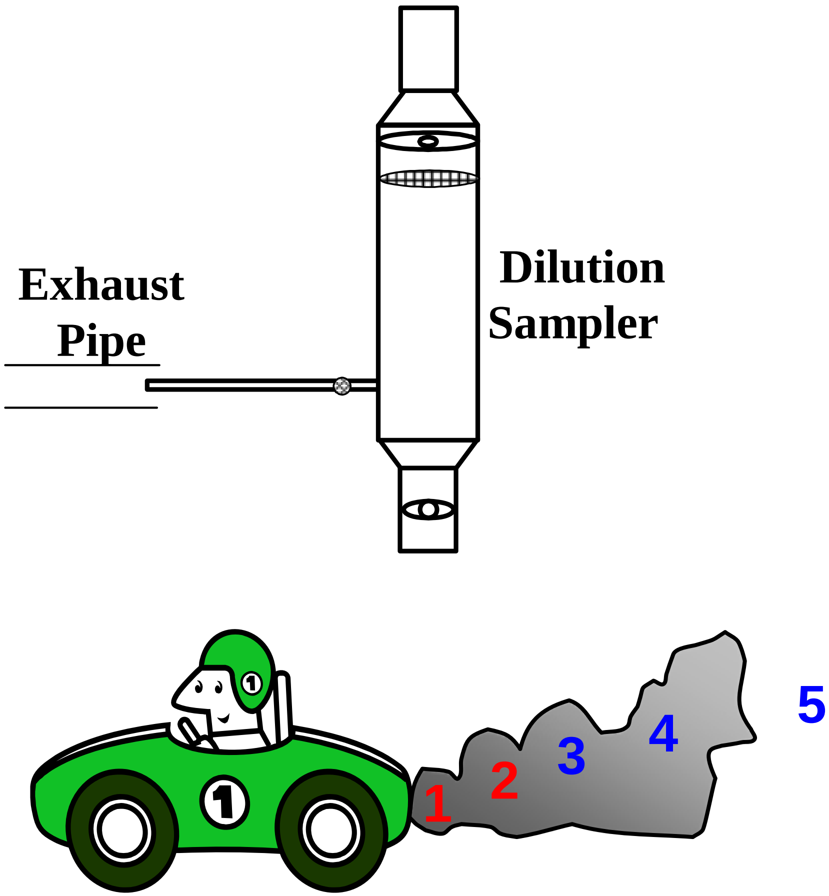
GC/FID of extracted filter sample



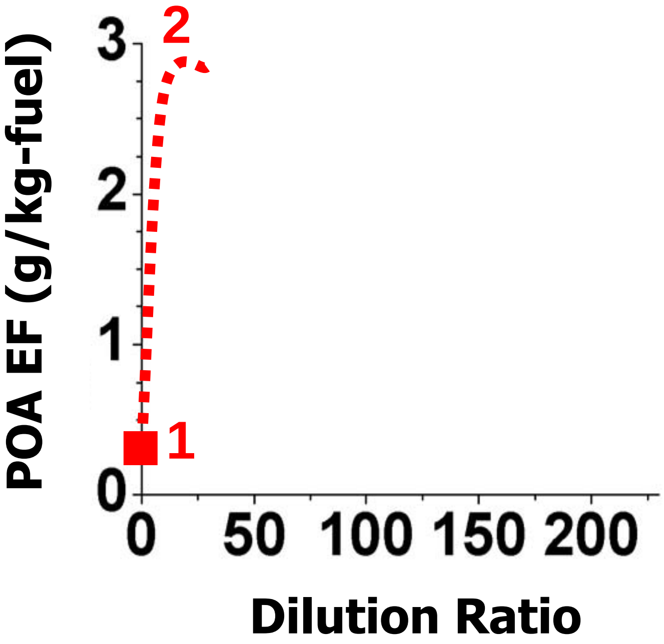
- Broad range of compounds
- ~ 10% Resolved
- ~ 90% Unresolved Complex Mixture (UCM)
  - branched compounds
  - cyclic compounds

Hildemann et al. AS&T 1989, EST 1991

Gas-particle partitioning of primary emissions with dilution



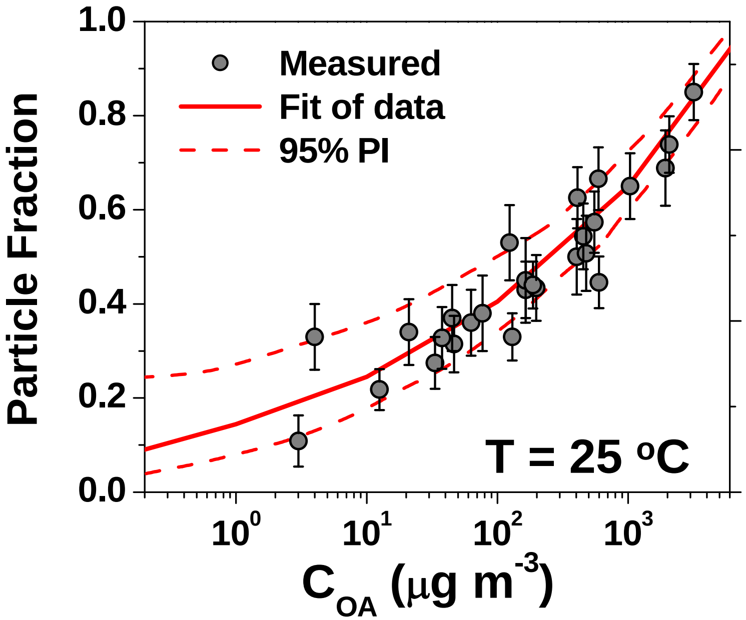
POA in Diesel Exhaust



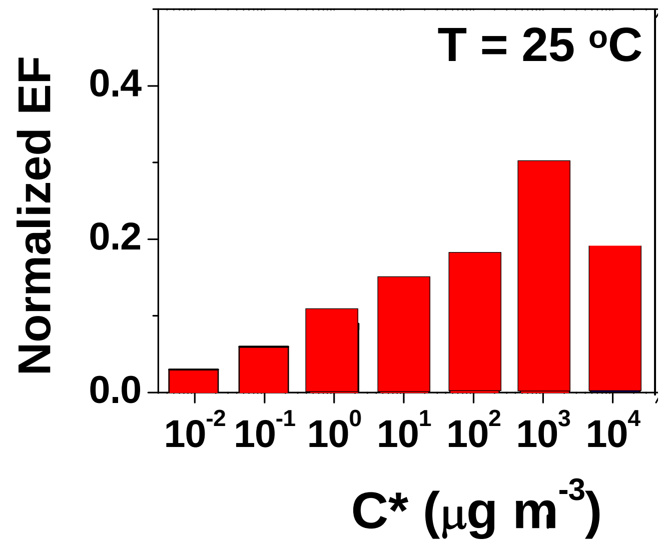
Hildeman et al. AST 1989
Lipsky and Robinson ES&T 2006

Volatility distribution of diesel exhaust

Partitioning Plot



Volatility distribution

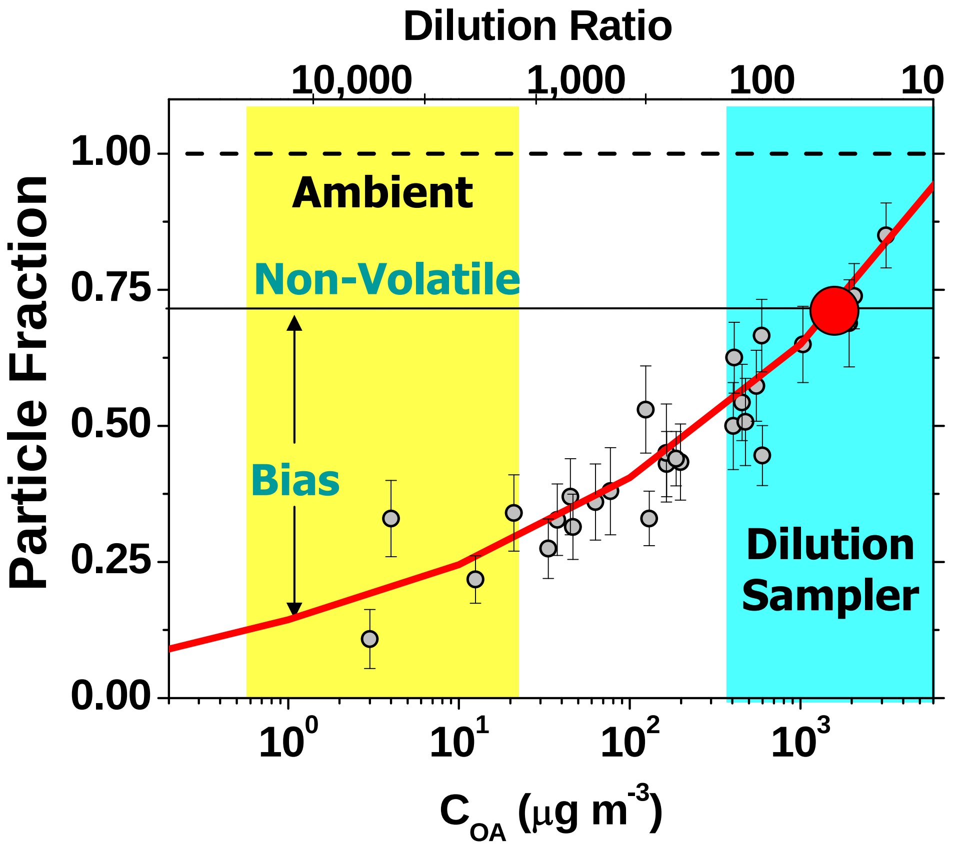


$$X_p = \sum_{i=1}^{n} f_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

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

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

Traditional POA emission factors biased high

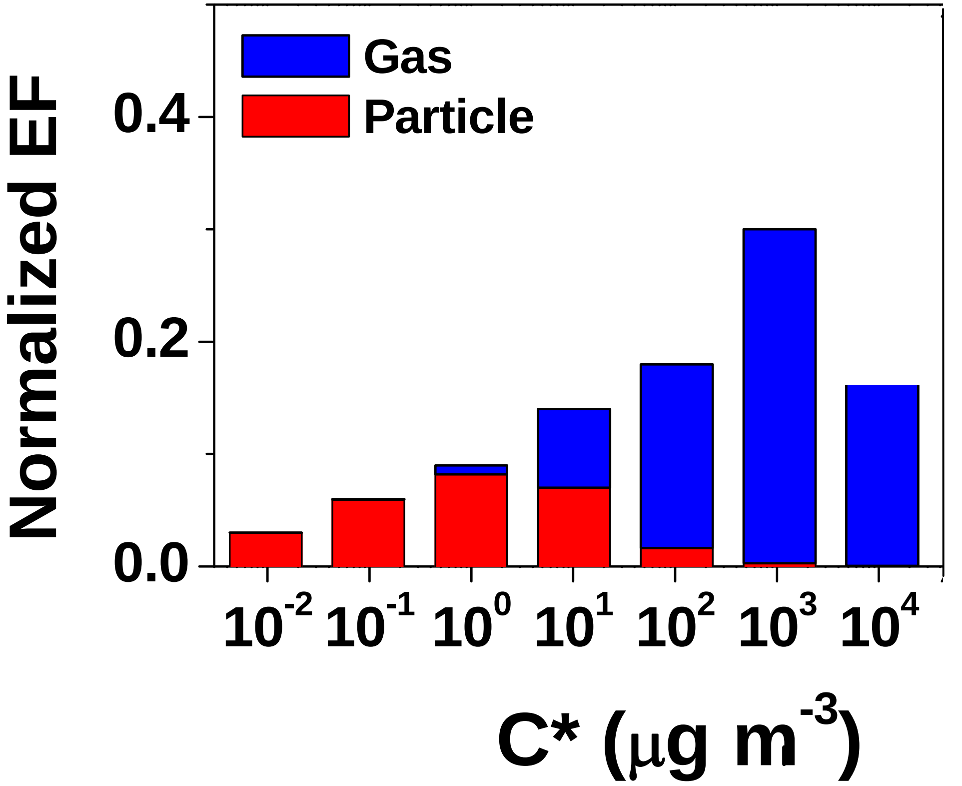


POA emissions for high emitting sources may be biased by a factor of 5!

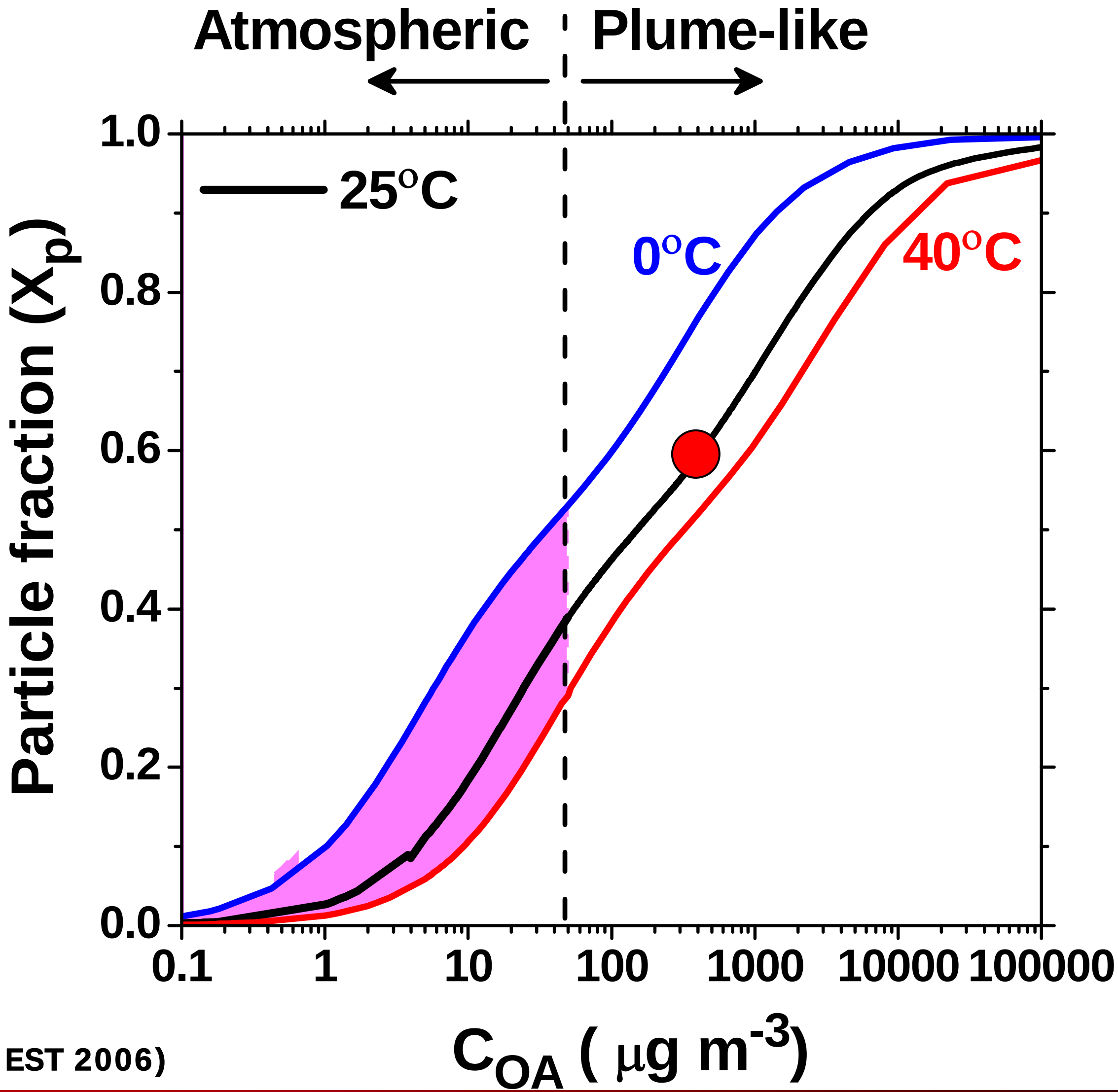
Shrivastava et al. EST 2006.

“Large” Amounts of Low Volatility Organic Vapors

Predicted Gas-Particle Partitioning at T = 298 K, 10 μg/m^{-3} of OA



POA varies with atmospheric conditions



(Shrivastava et al. EST 2006)

Photochemical aging of diesel exhaust

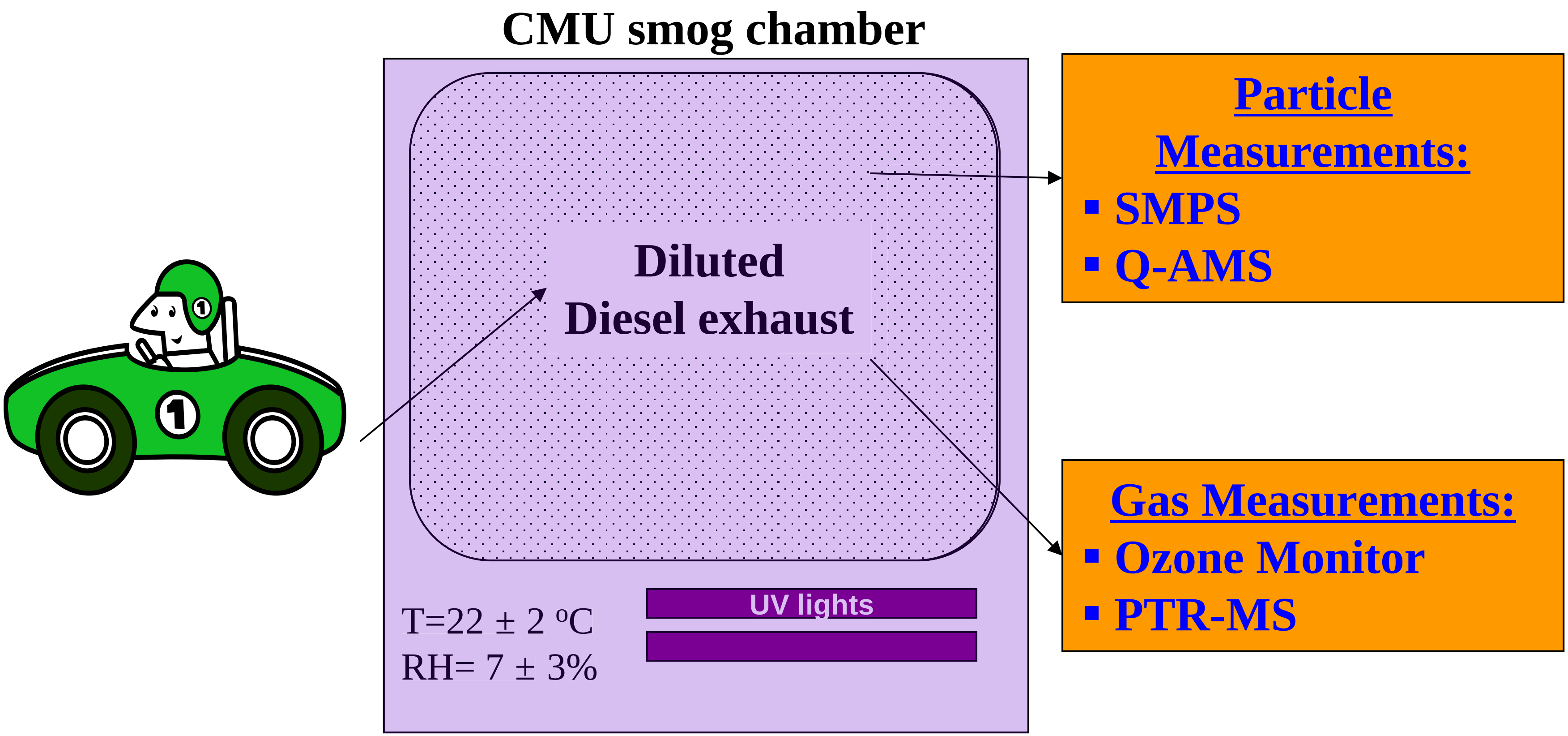
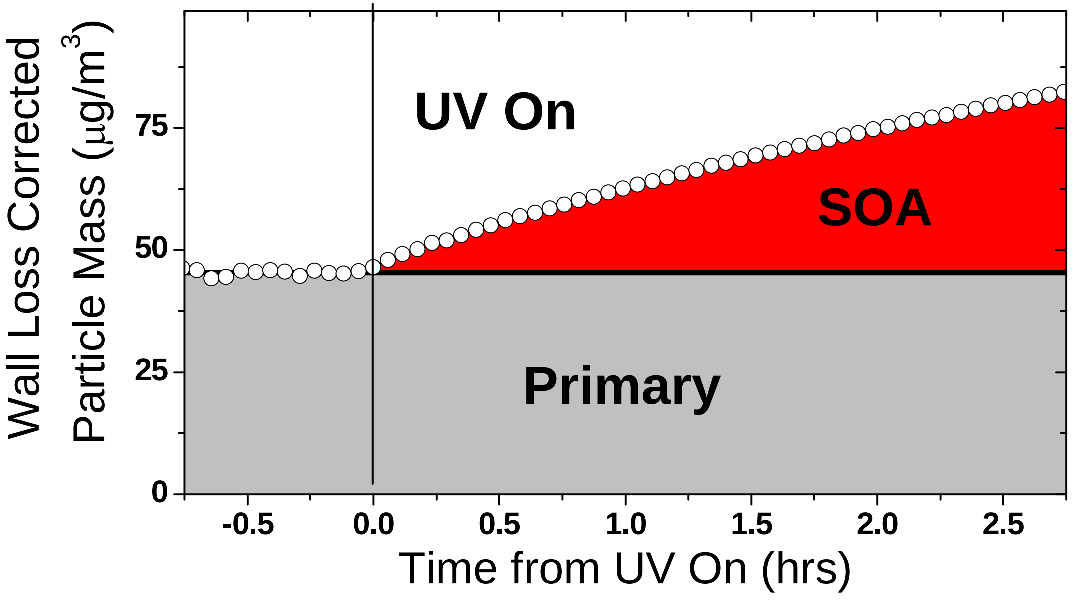
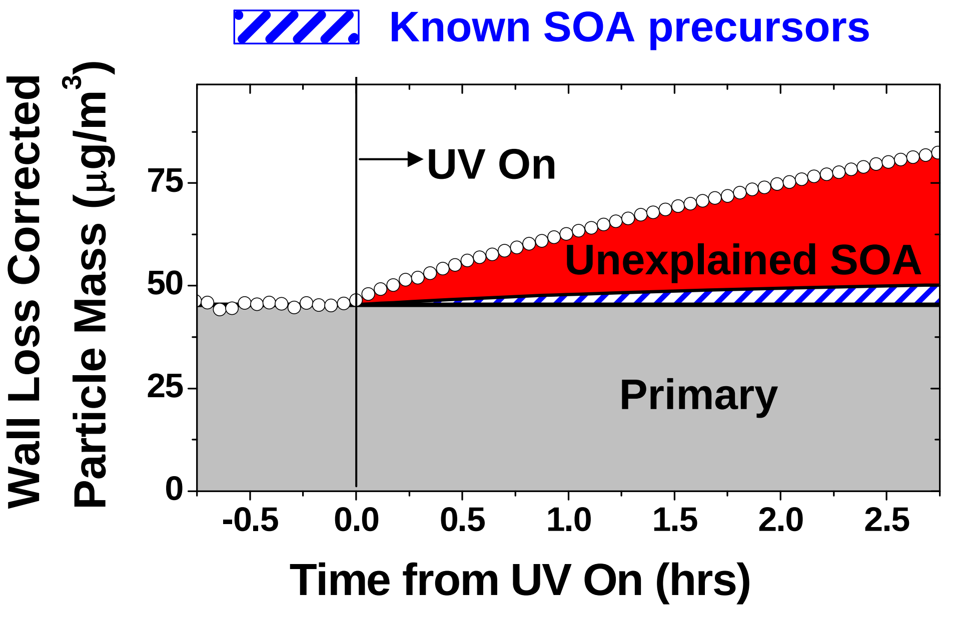


Photo-oxidation creates significant amounts of SOA



Robinson et al. Science 2007.

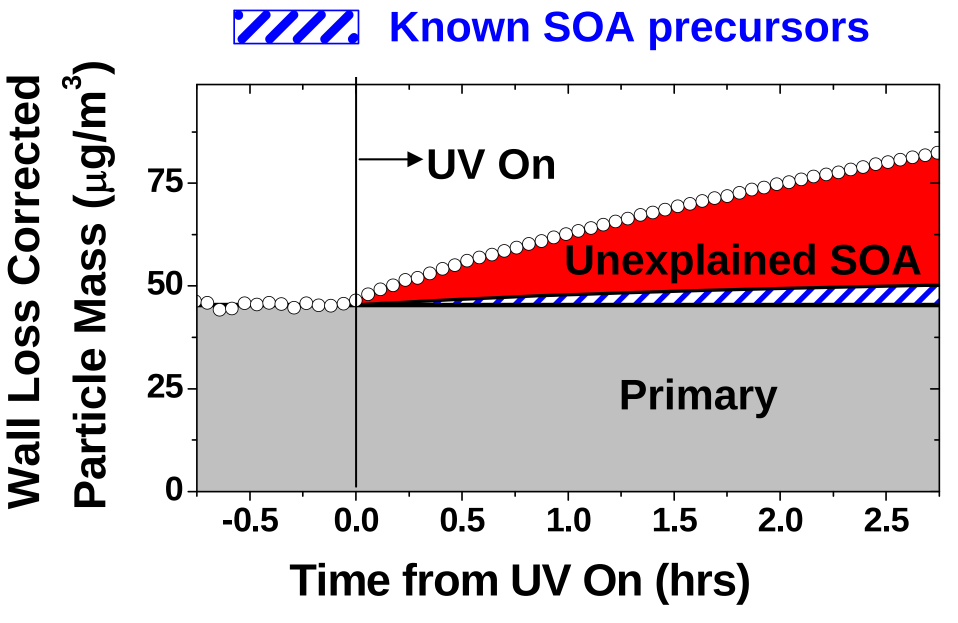
What is contribution of known SOA precursors?

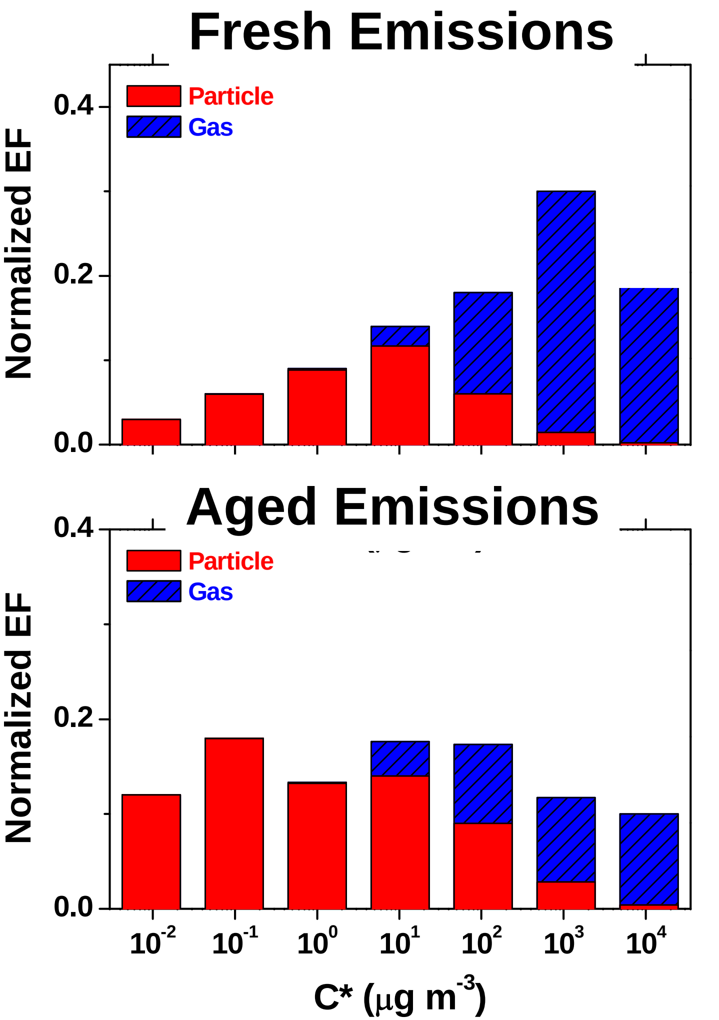


- SOAM II **(Koo et al. 2003)**
- 58 precursors
  - **Measured Aromatics**
  - **Estimates for other species**
- Assume ideal solution
- Wall losses

Robinson et al. Science 2007.

Aging of low volatility vapors source of unexplained SOA

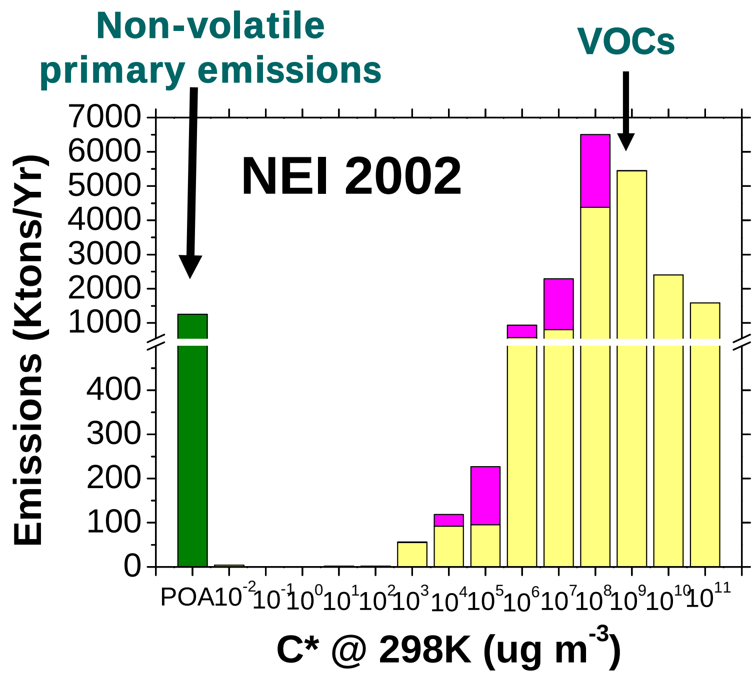


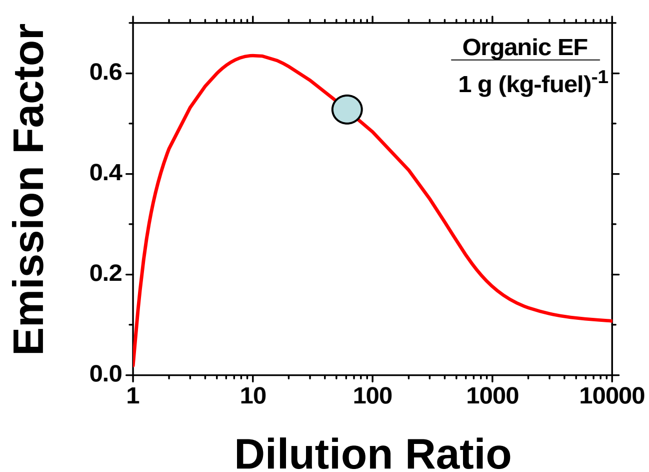


Robinson et al. Science 2007.

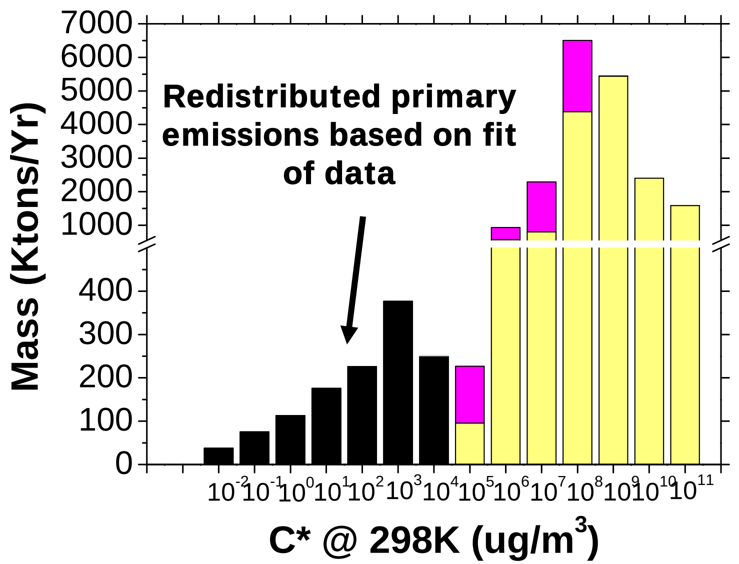
Revised framework for primary emissions

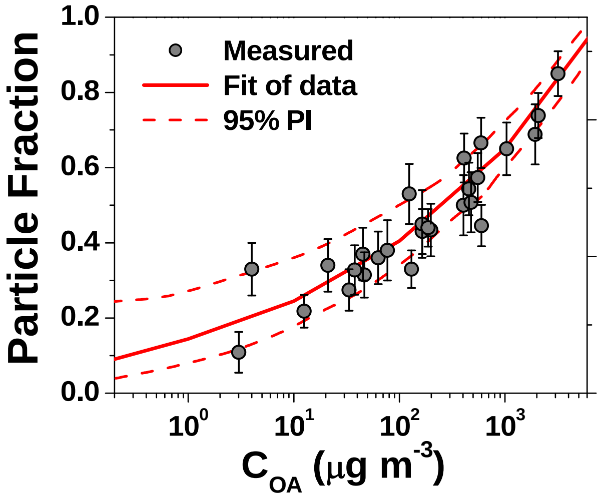
Traditional Approach



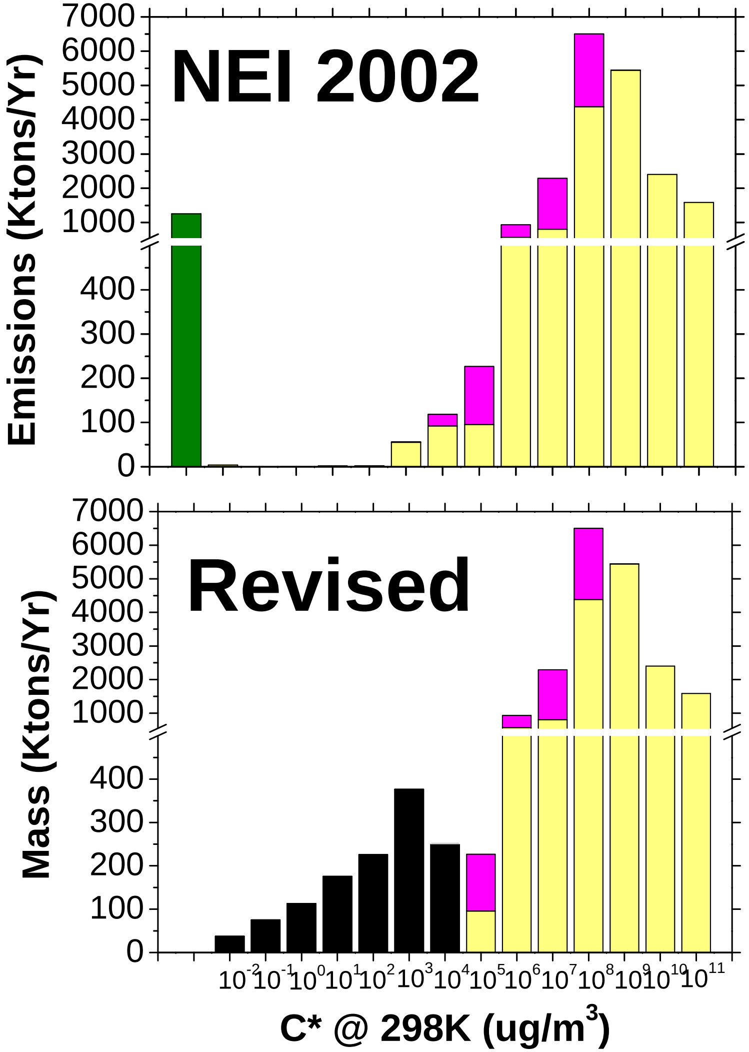


New Framework

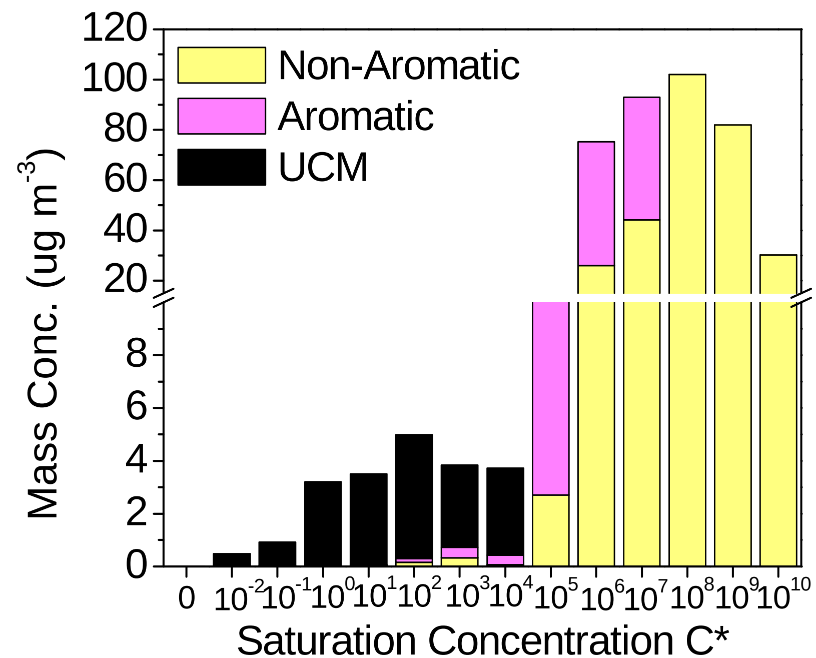




Revised framework consistent with ambient data



Ambient Data from LA

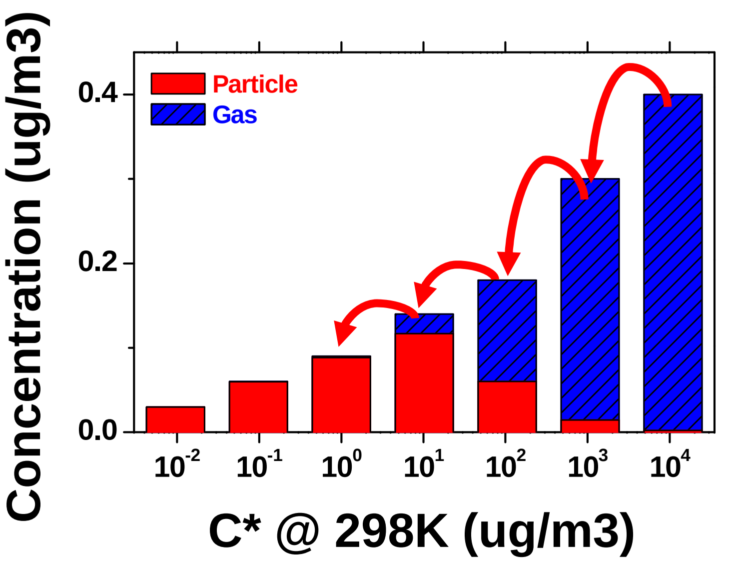


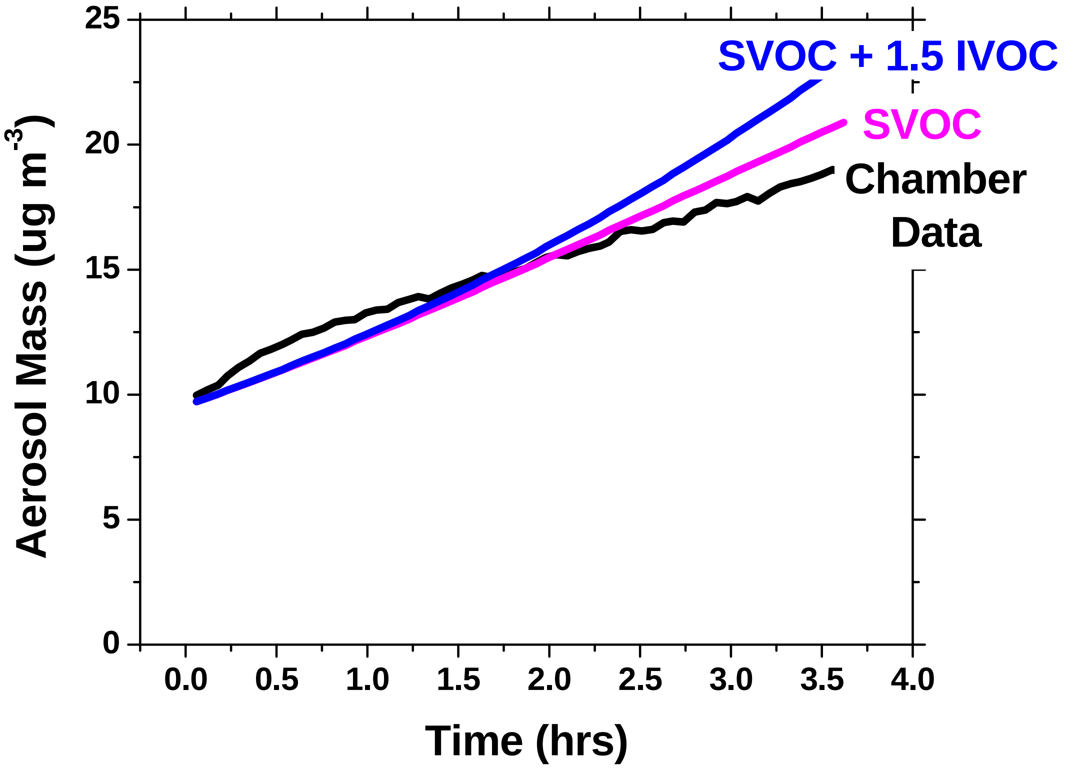
Fraser et al. EST 1997, 1998

Aging Scheme

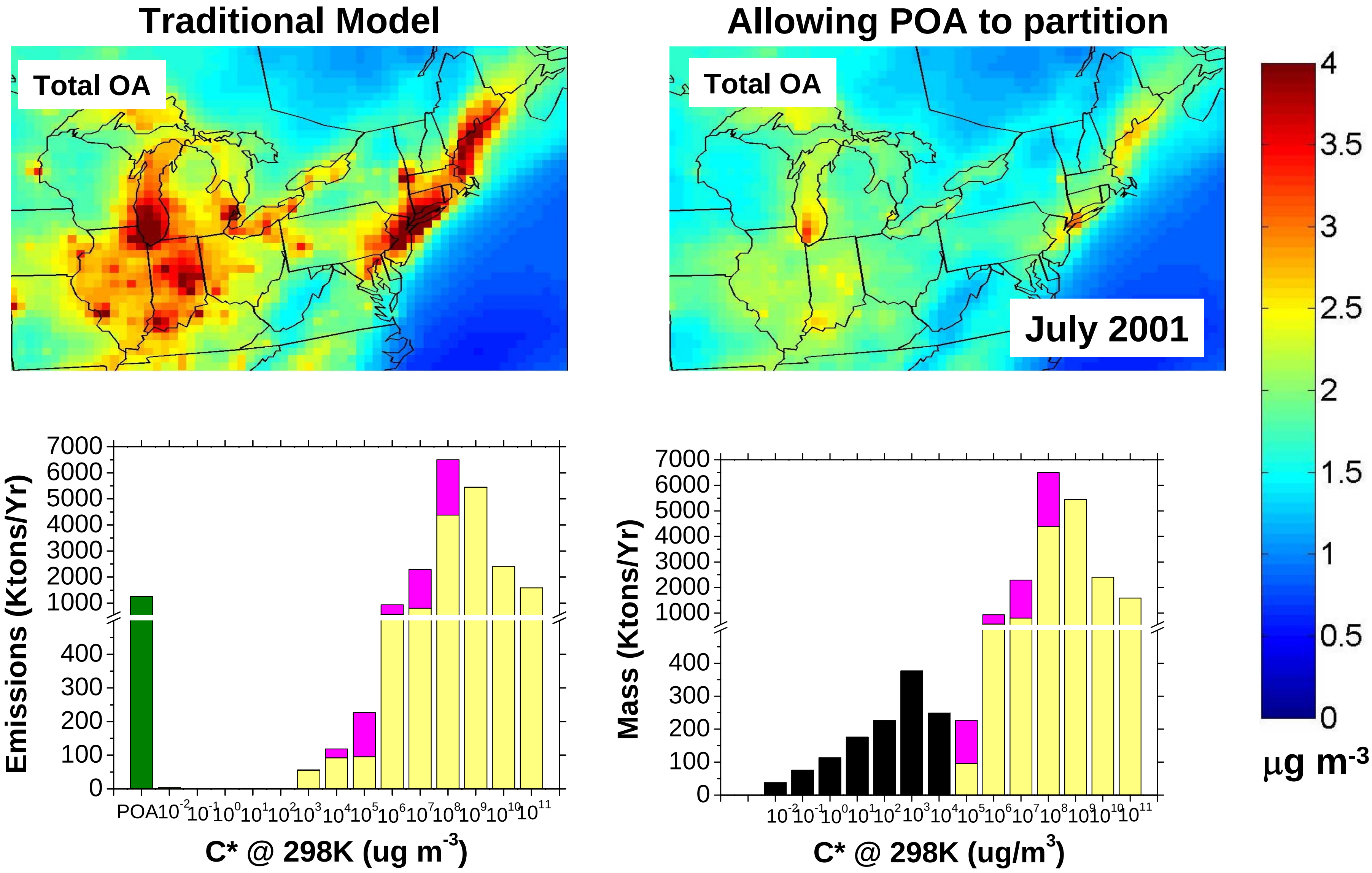
Gas-phase Aging

k_{OH} = 4 x 10^{-11} cm^3 (molec s)$^{-1}$



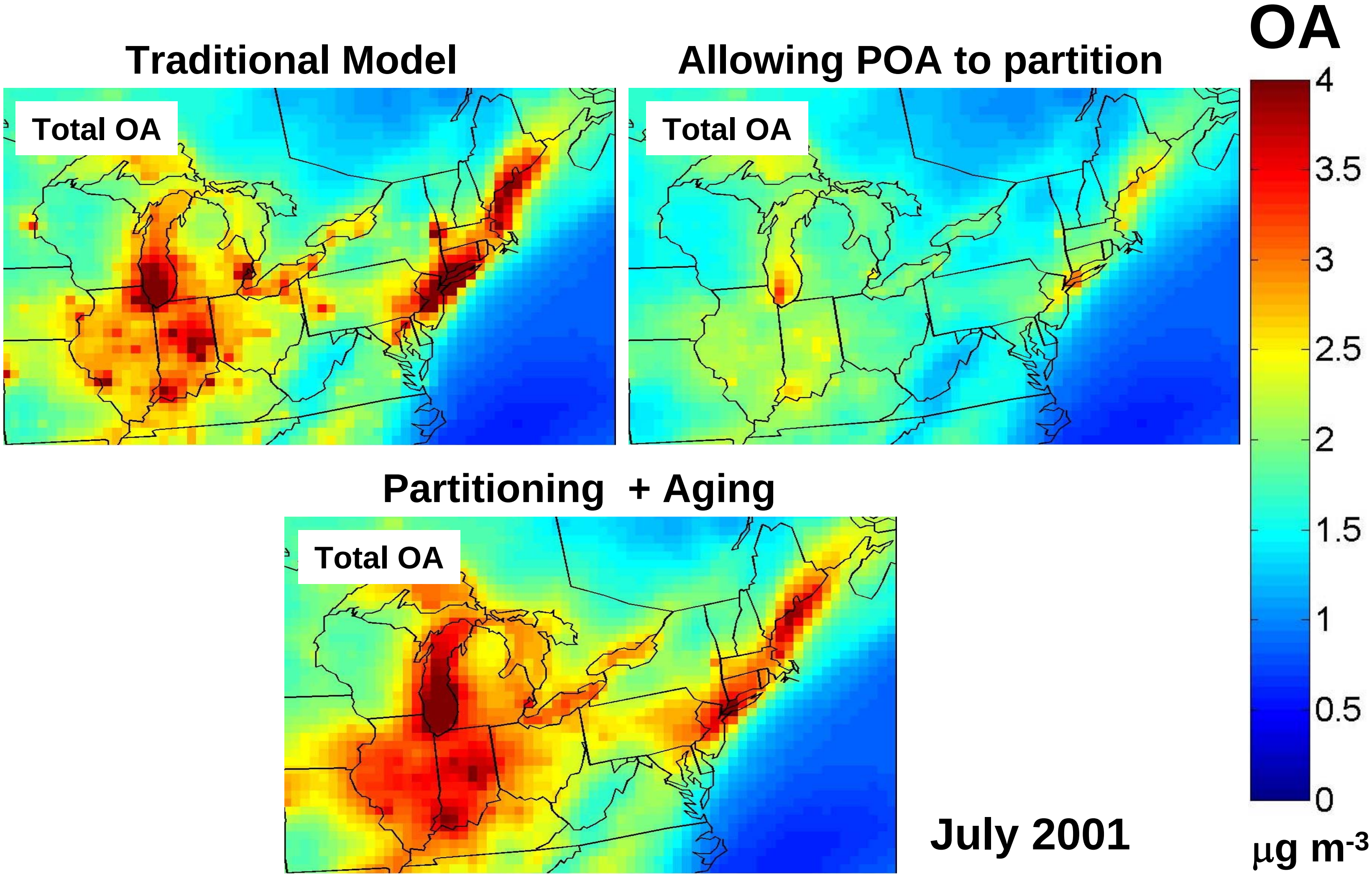


Evaporation dramatically reduces POA



Robinson et al. Science 2007.

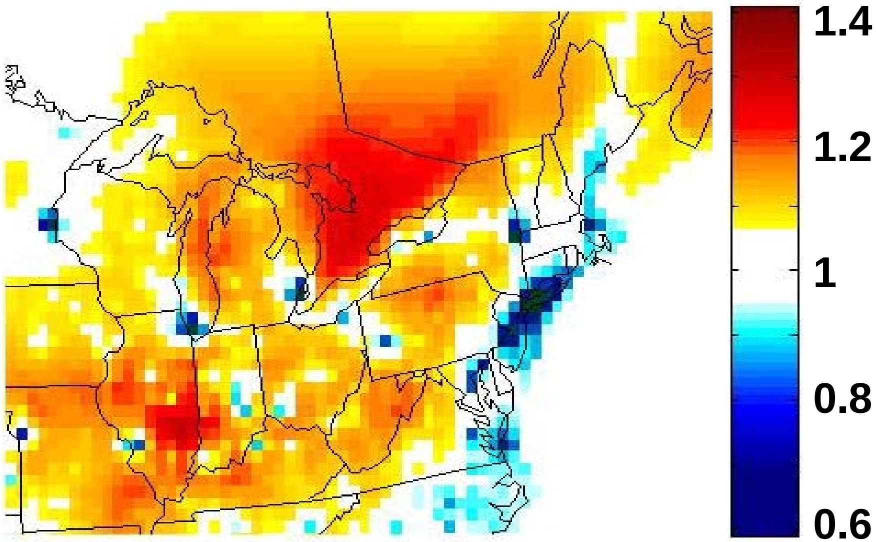
Aging Creates Regional SOA



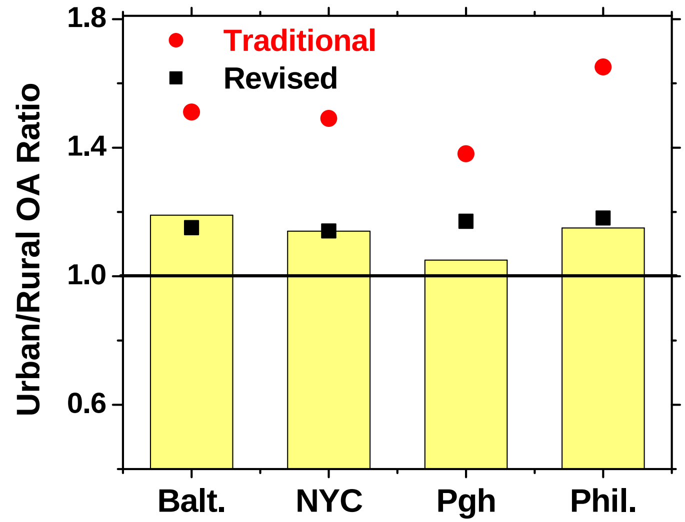
Robinson et al. Science 2007.

Revised model predicts a more regional aerosol

Ratio of Revised-to-Traditional Model Predicted OA levels



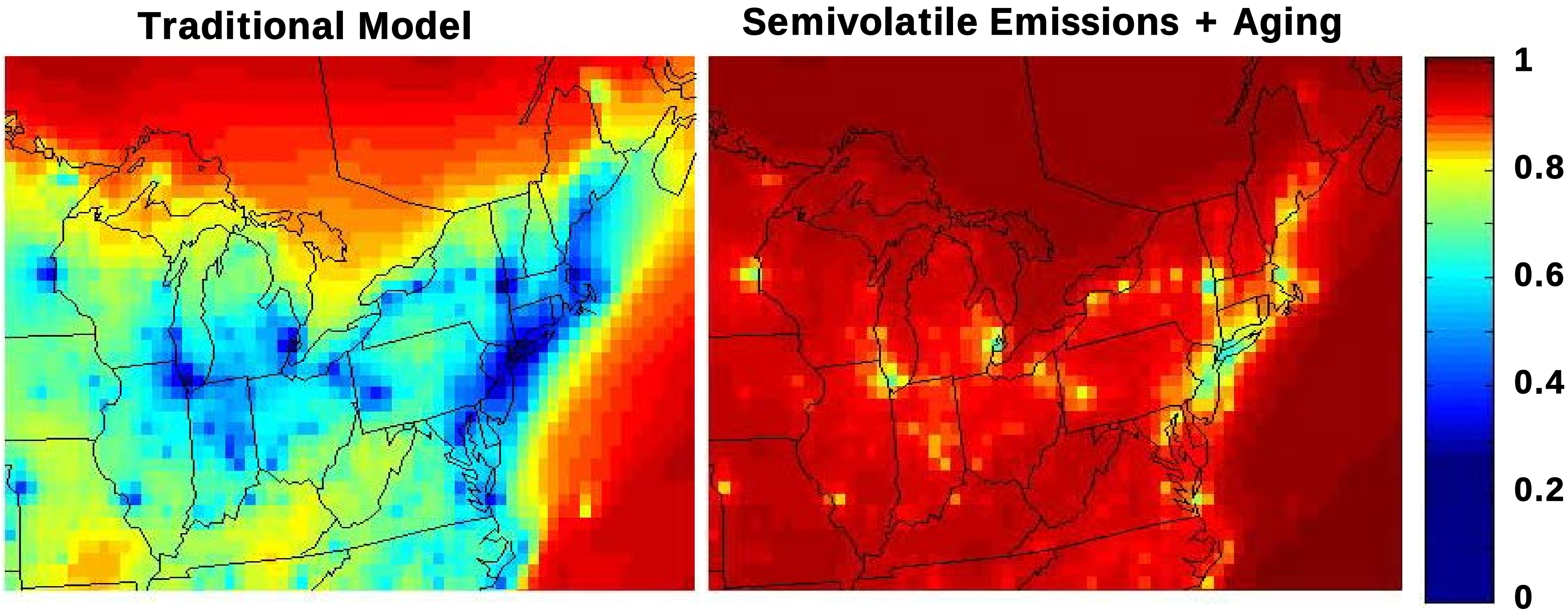
Model-Measurement Comparison



Robinson et al. Science 2007.

Dramatic shift in primary-secondary split

Predicted fractional contribution of SOA to total OA concentration

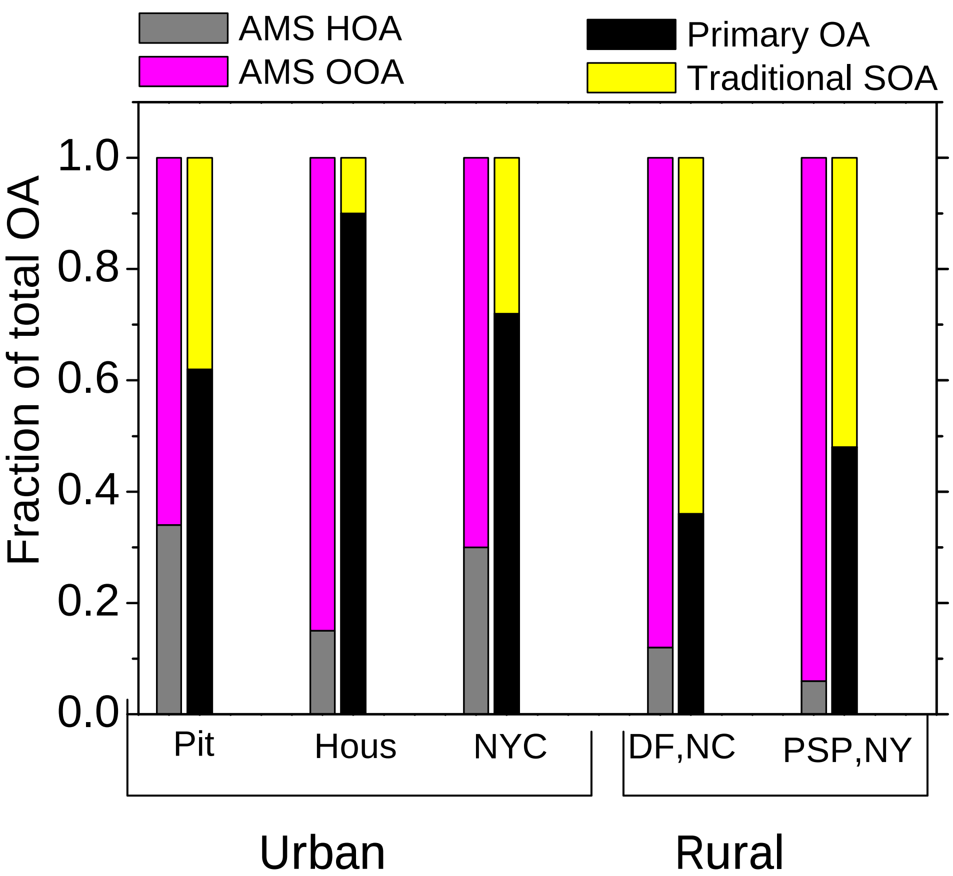


Robinson et al. Science 2007.

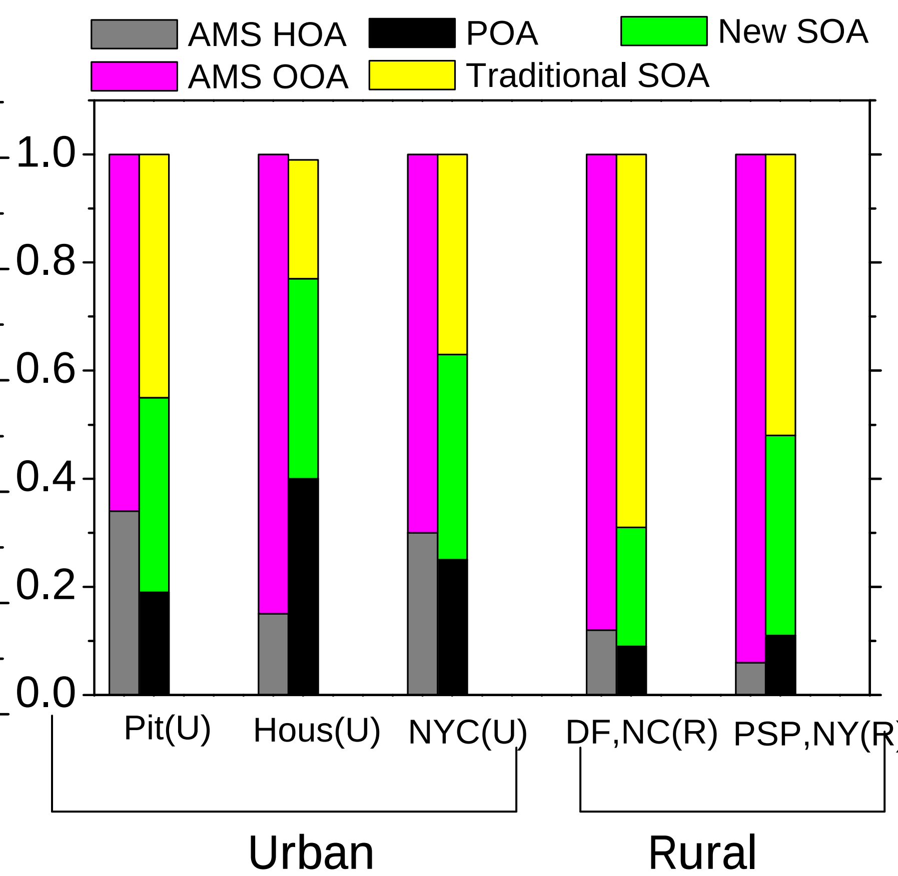
July 2001

Model vs. AMS HOA/OOA Measurements

Non-volatile: Basecase



Revised Model



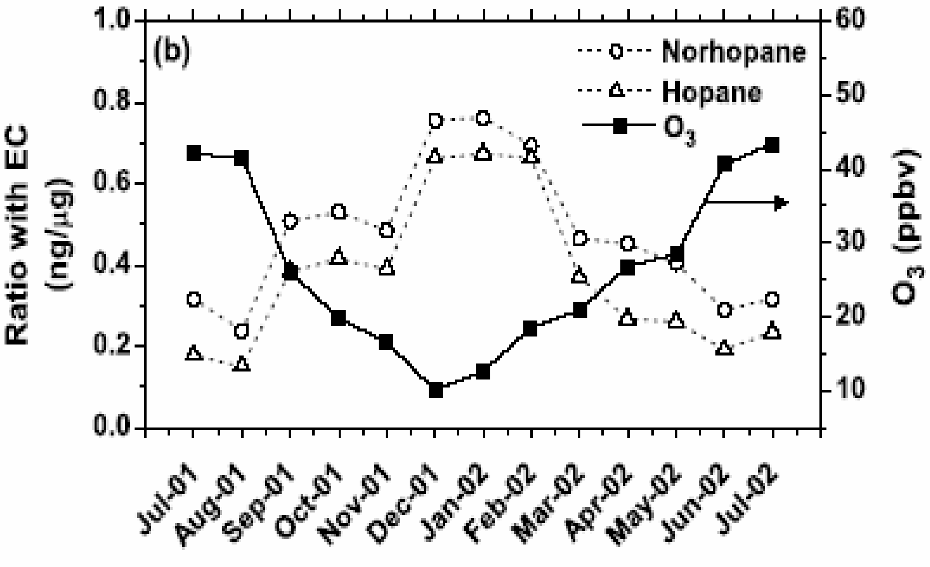
AMS data from Qi Zhang et al. 2007, (GRL, in press)

Conclusions #1

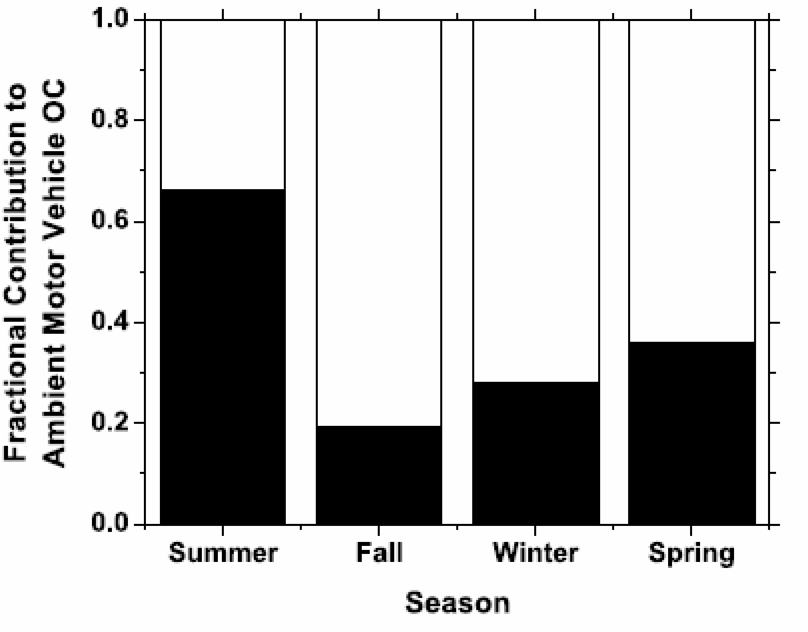
- Primary Emissions are Semivolatile
  - Gas-particle partitioning of POA
  - Photochemical aging of low volatility organic vapors
- Implications for regional OA
  - Reduce POA
  - Increase SOA
  - Developing control strategies?
- Need to update methods used to measure and simulate POA

Is POA non-reactive?

Pittsburgh Ambient Data



CMB Results for Gasoline-Diesel Split



Robinson et al. JGR 2006

Laboratory measurements of aging of Molecular Markers

Particle Input:

- **Meat cooking grease**

- **Motor Oil**

Gas Input:

- **Oxidants and oxidant precursors**
- **Gas phase tracers**

CMU smog chamber

1500+ μg/m^3 aerosol

T=22 ± 2 ^{o}C
RH= 7 ± 3%

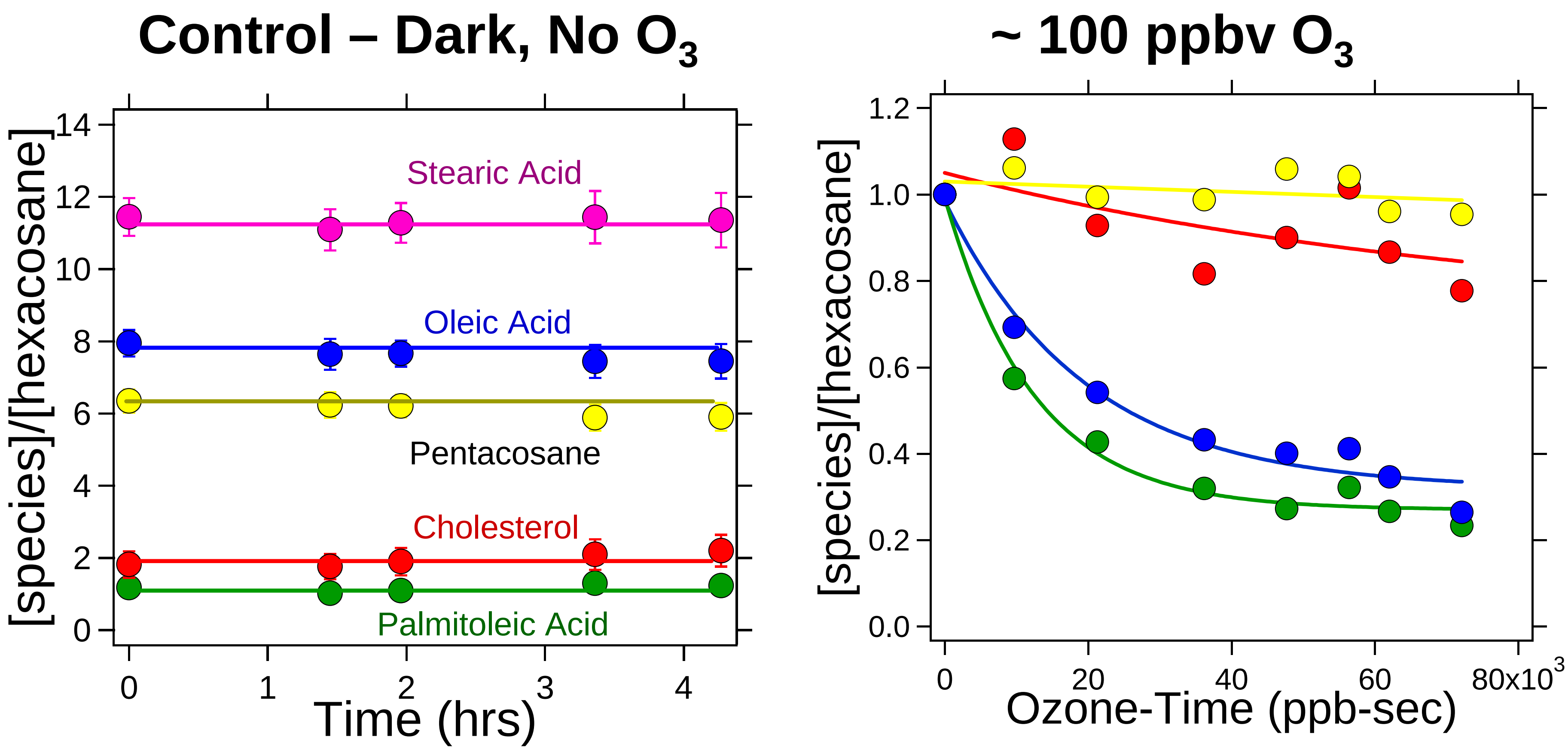
Particle Measurements:

- **Filters & GC/MS**
- **SMPS**
- **AMS**

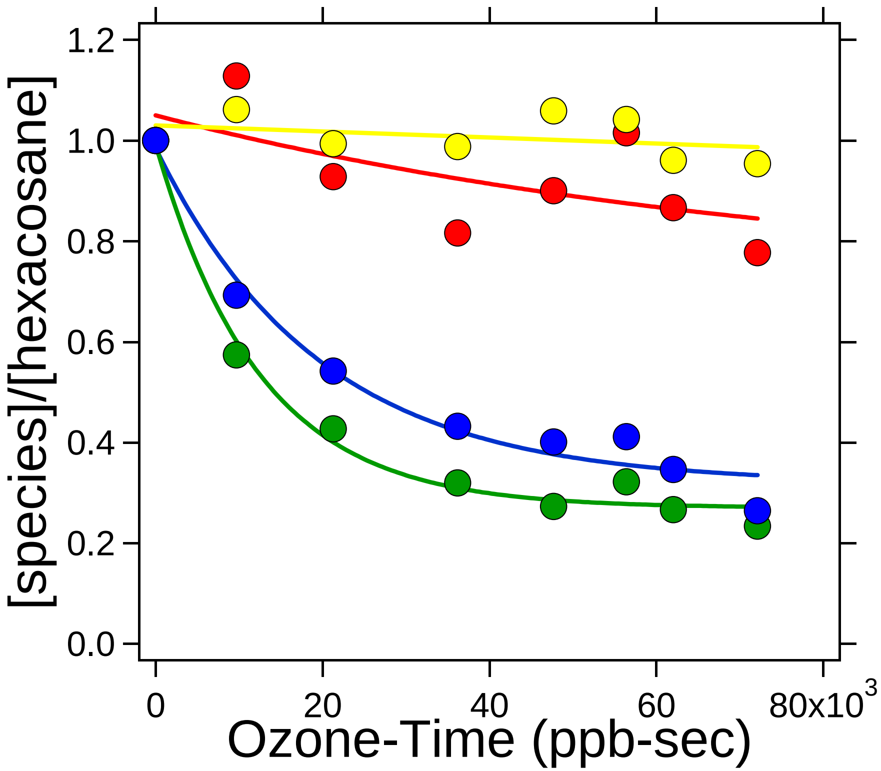
Gas Measurements:

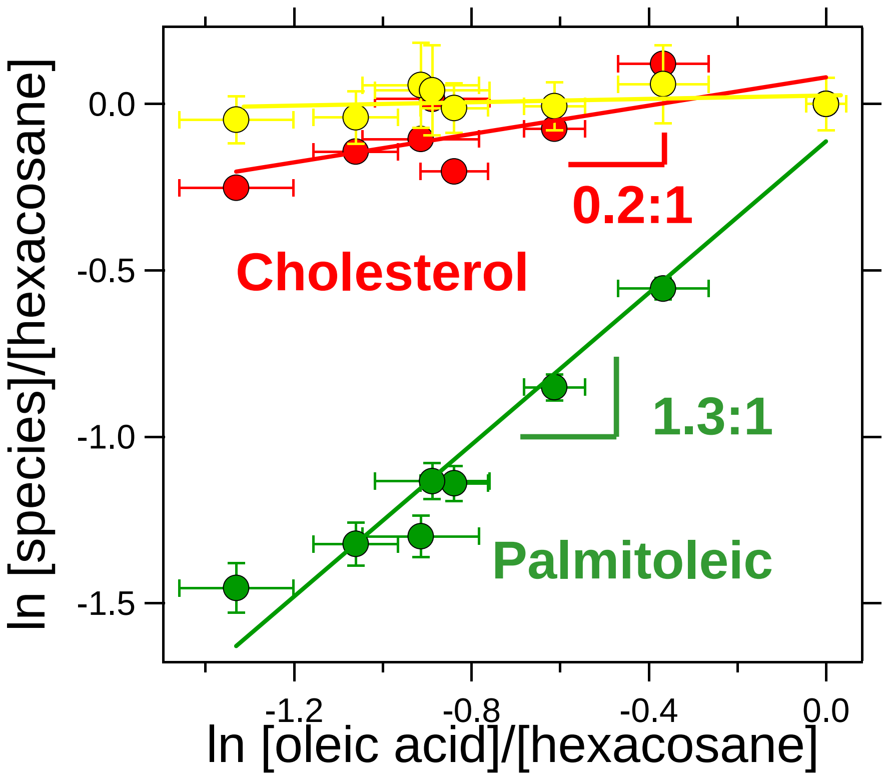
- **Ozone Monitor**
- **GC-FID**
- **PTR-MS**

Rapid Oxidation of Molecular Markers in Hamburger Grease Aerosol



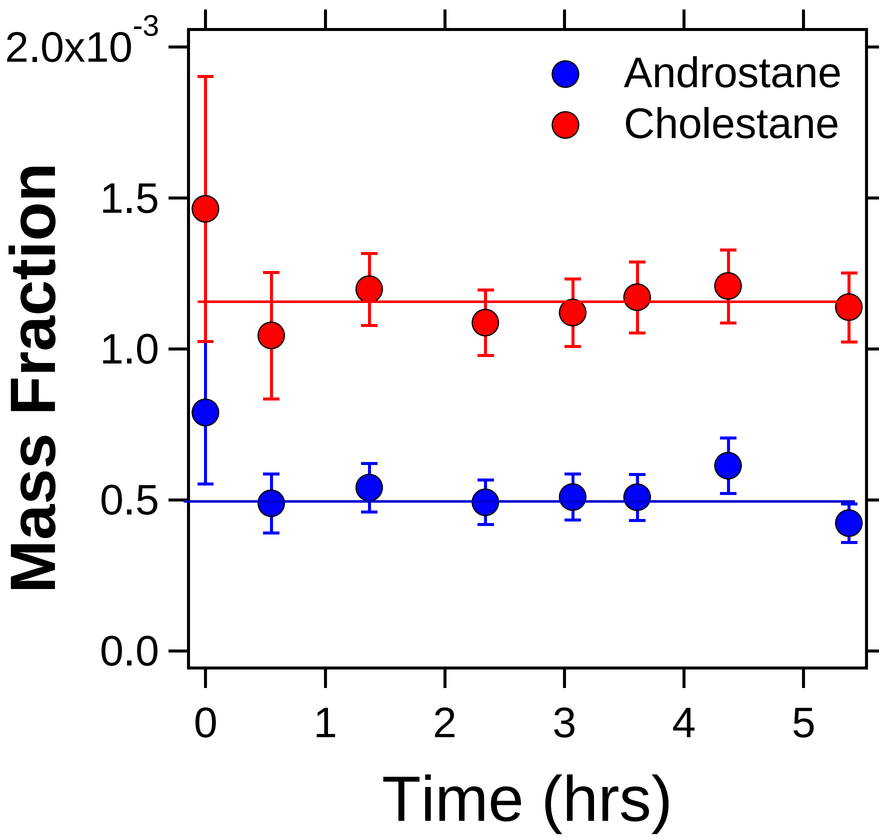
Relative Rate Analysis



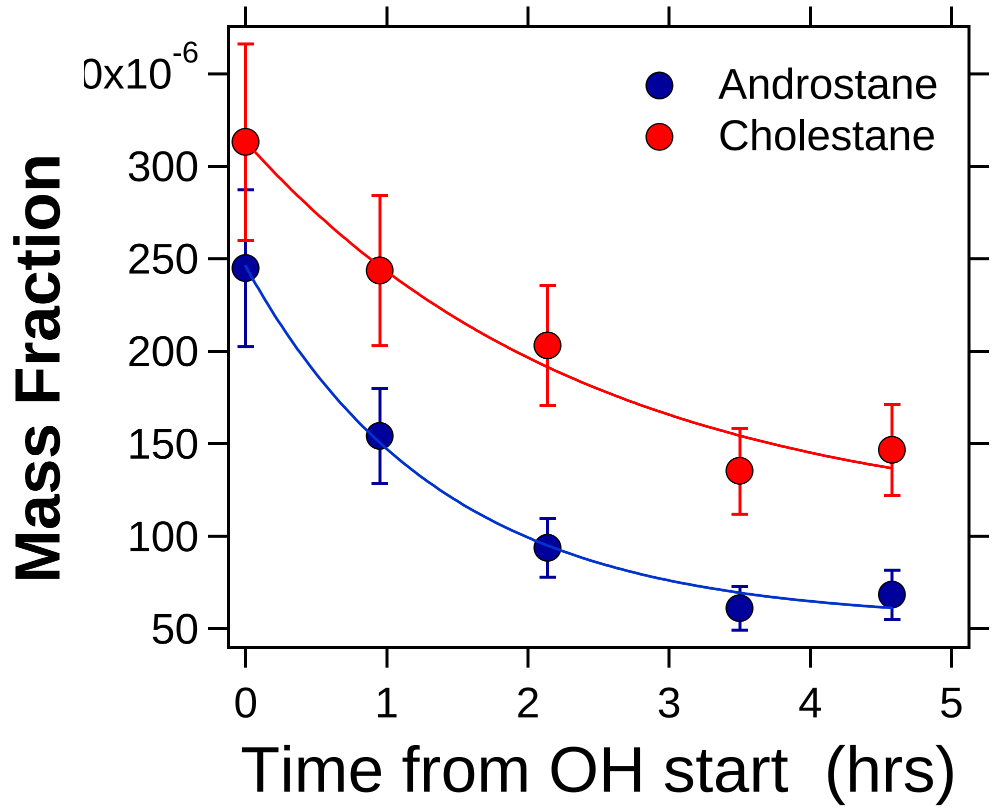


Motor Oil and OH

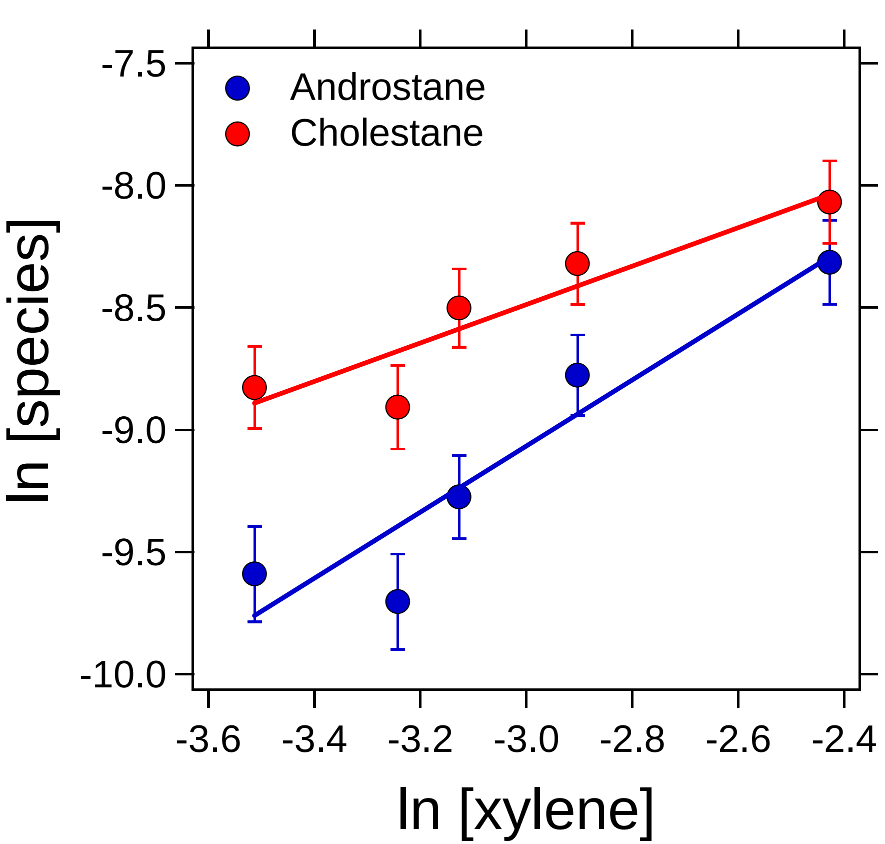
Control – No OH

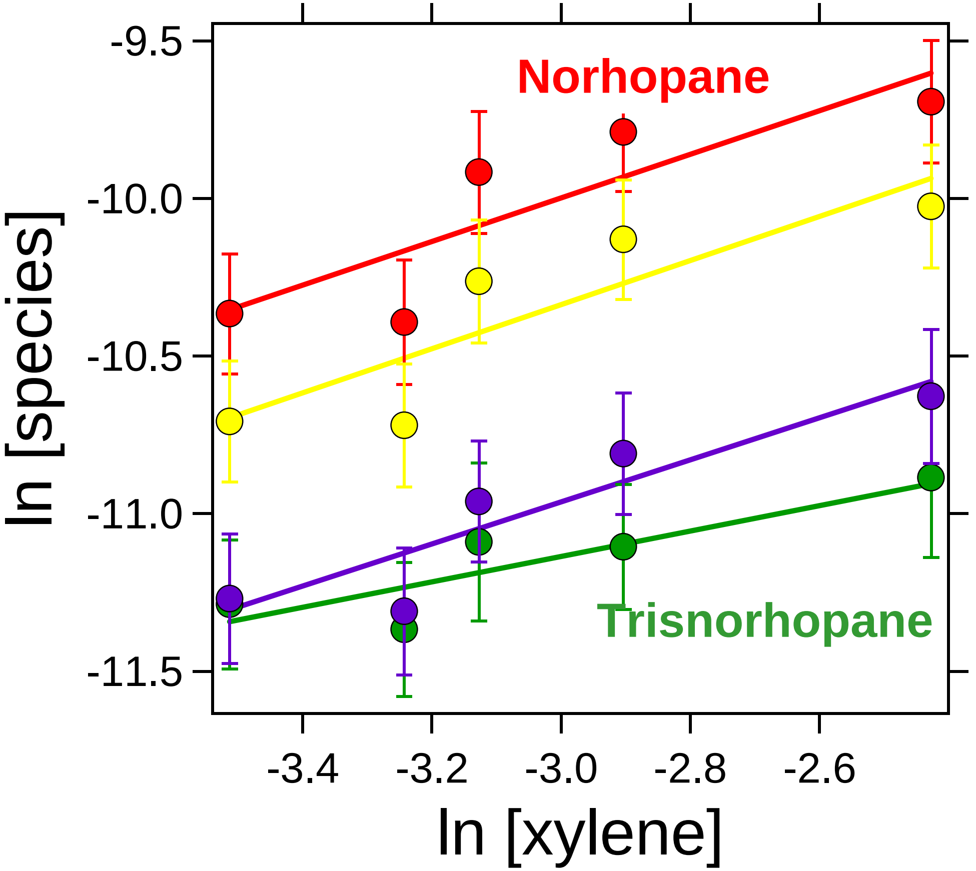


[OH] ~ 3 x 10^6 mol/cm^3



Hopanes and Steranes Oxidize at Approximately Half Rate of Xylene





Conclusions #2

- **Molecular markers aging in realistic systems**
- **Treat mixing and aging as first order processes**

Acknowledgments

- Carnegie Mellon Personnel
  - Faculty – Neil Donahue, Spyros Adams, Peter Adams
  - Postdoctoral Fellow – Kara Huff-Hartz
  - Graduate Students – Emily Weitkamp, Manish Shrivastava, Amy Sage, R. Subramanian, Timothy Lane, Andrew Grieshop, Andrew Lambe, Jeffrey Pierce, Robert Pinder
- LADCO – inventories and met files
- Funding
  - EPA STAR
  - Dreyfus Foundation
  - State of Pennsylvania – PITA
  - Allegheny County Health Department
  - Carnegie Mellon
  - NSF