



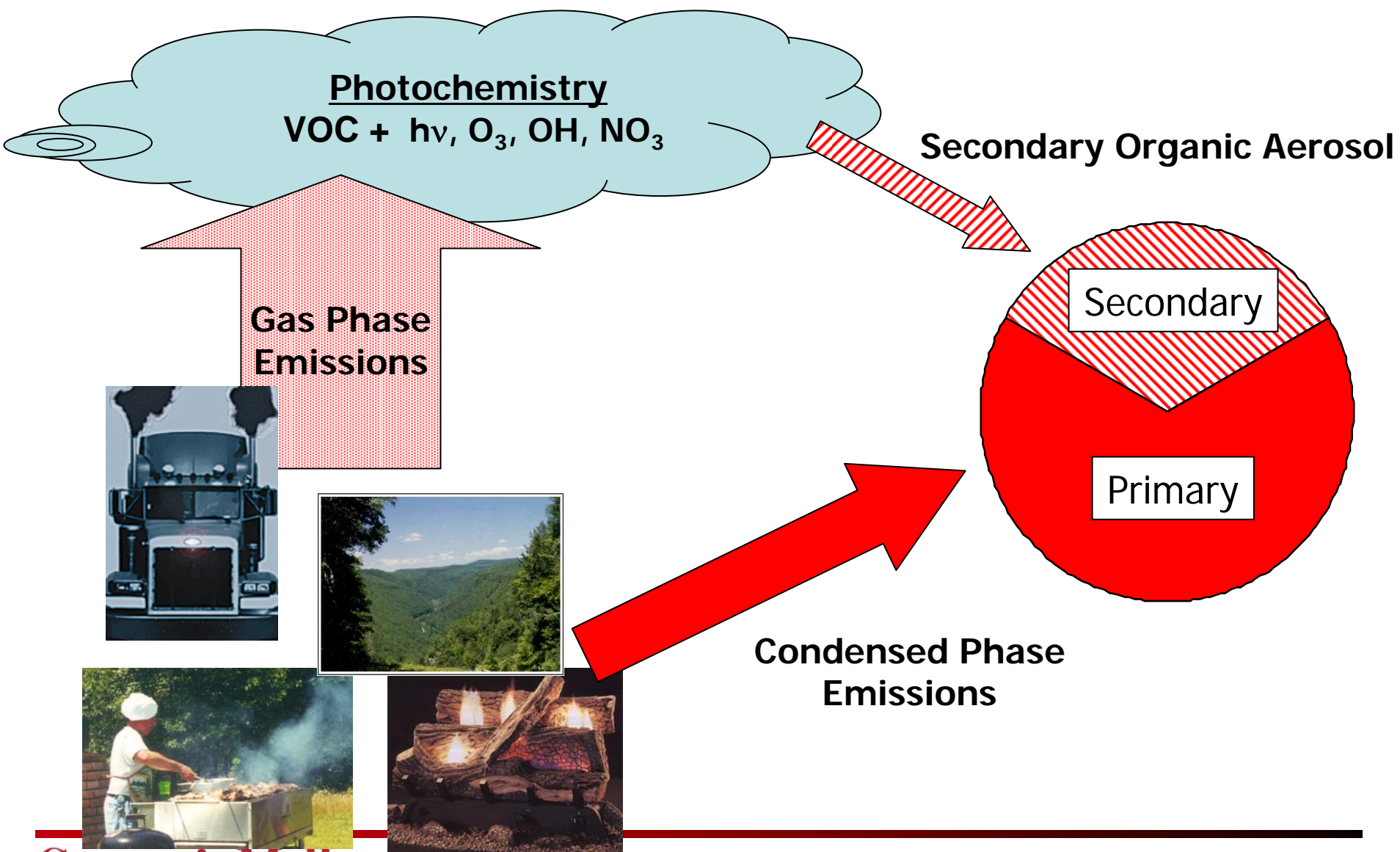
Source-Appportionment of Primary Organic Carbon in the Eastern United States Combining Receptor-Models, Chemical Transport Models, and Laboratory Oxidation Experiments

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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)



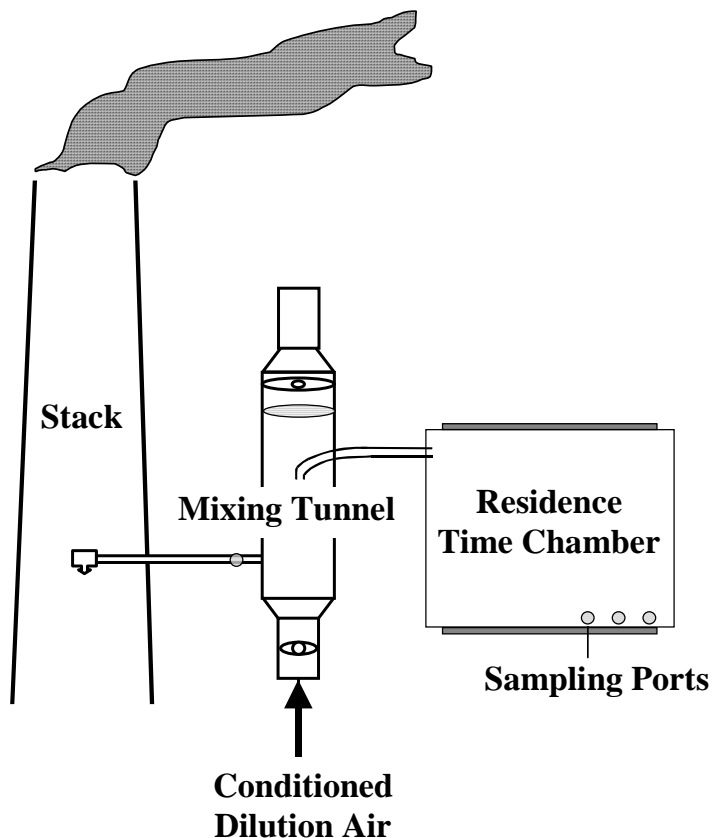
Current conceptual model for organic aerosol

- Primary organic aerosol
 - **Non-volatile**
 - **Non-reactive**

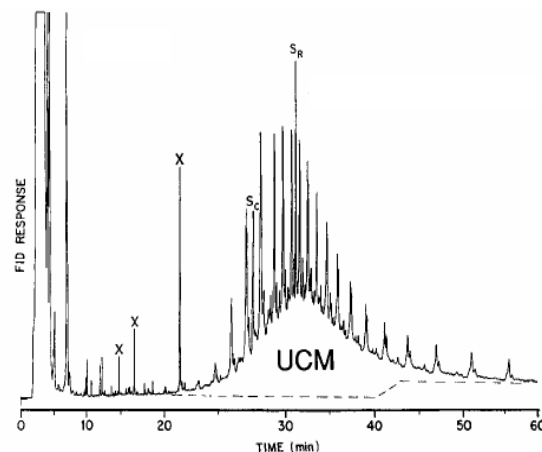
- Secondary organic aerosol
 - **High flux, but very volatile precursors**
 - Light aromatics
 - Monoterpenes
 - **Absorptive partitioning of non-reactive condensable products**

What is primary organic aerosol?

Measure with dilution sampler



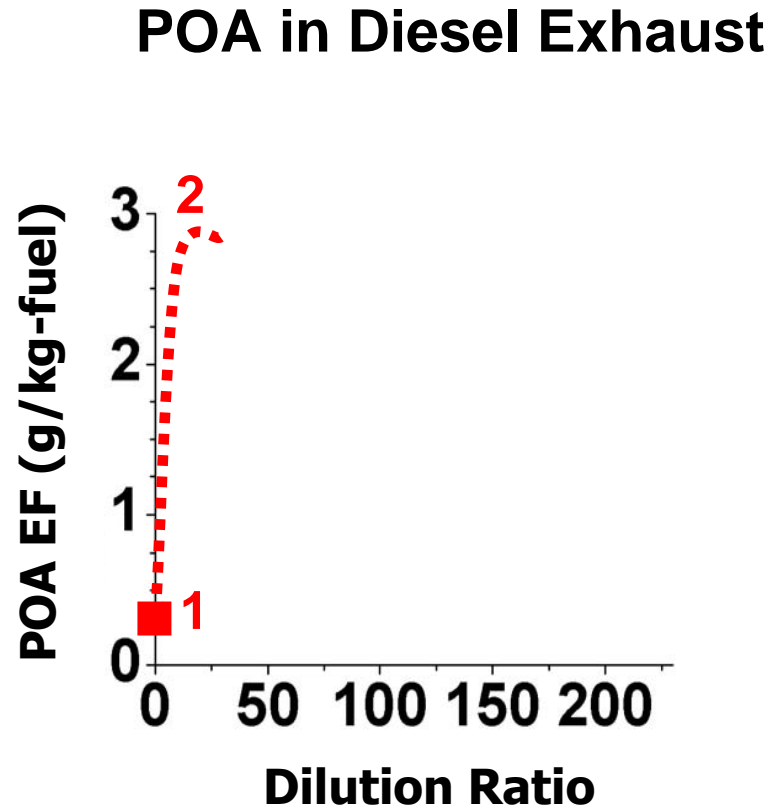
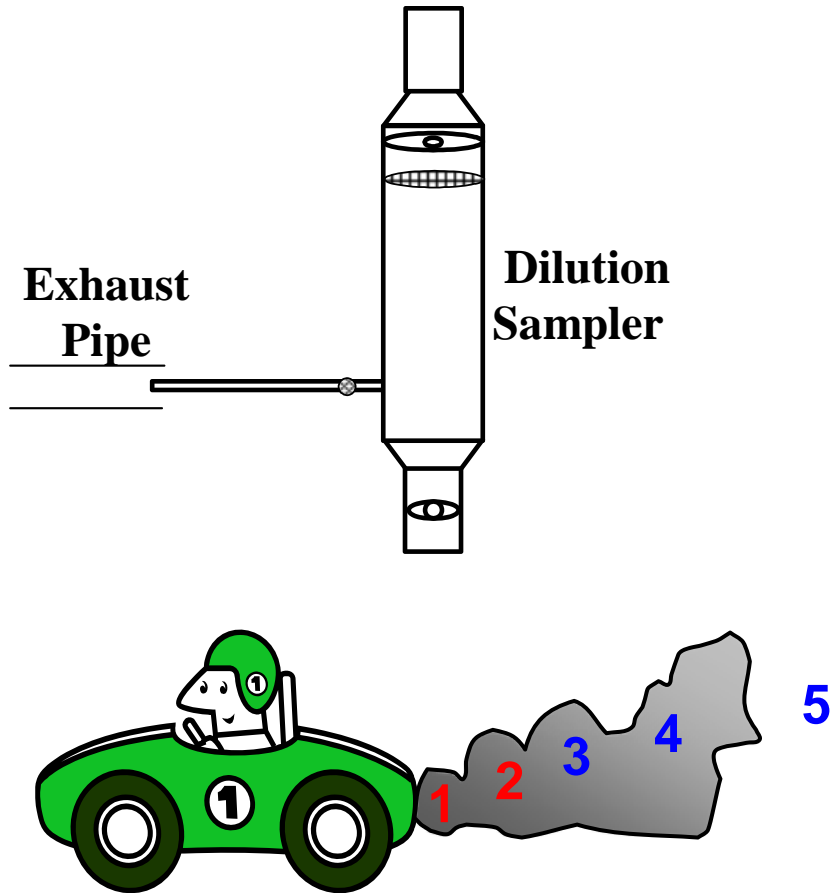
GC/FID of extracted filter sample



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

Hildemann et al. AS&T 1989, EST 1991

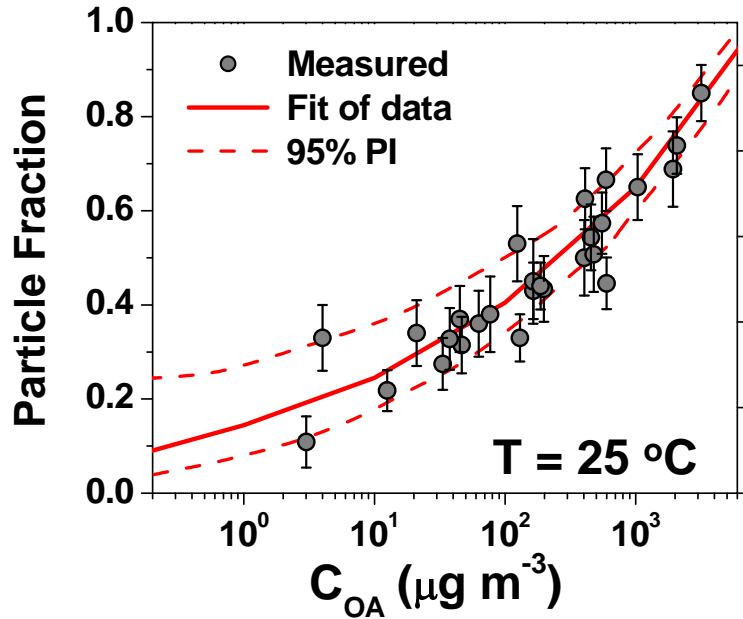
Gas-particle partitioning of primary emissions with dilution



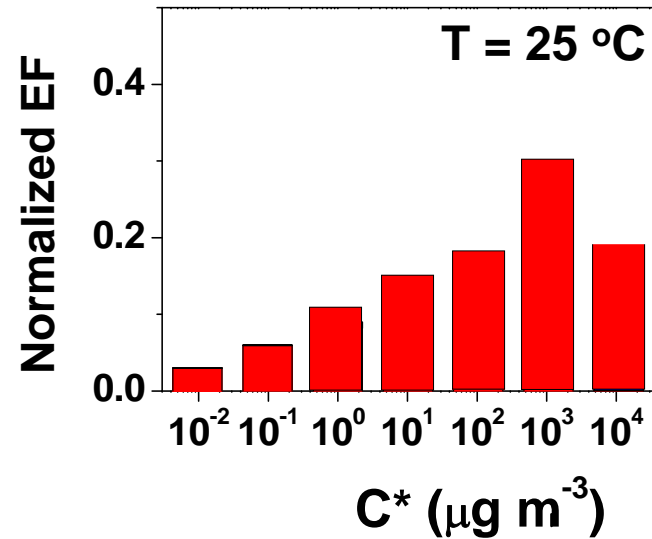
Hildeman et al. AST 1989
Lipsky and Robinson ES&T 2006

Volatility distribution of diesel exhaust

Partitioning Plot



Volatility distribution

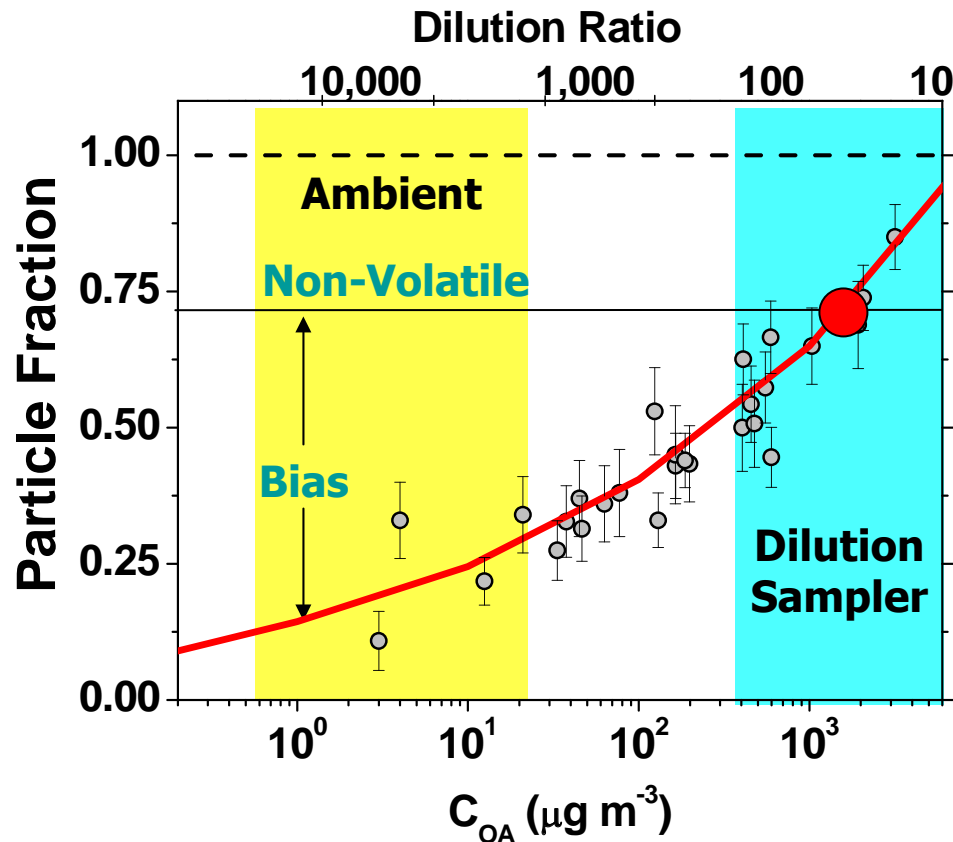


$$X_p = \sum_{i=1}^n f_i \left(1 + \frac{C_i^*}{C_{OA}} \right)^{-1}$$

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

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

Traditional POA emission factors biased high

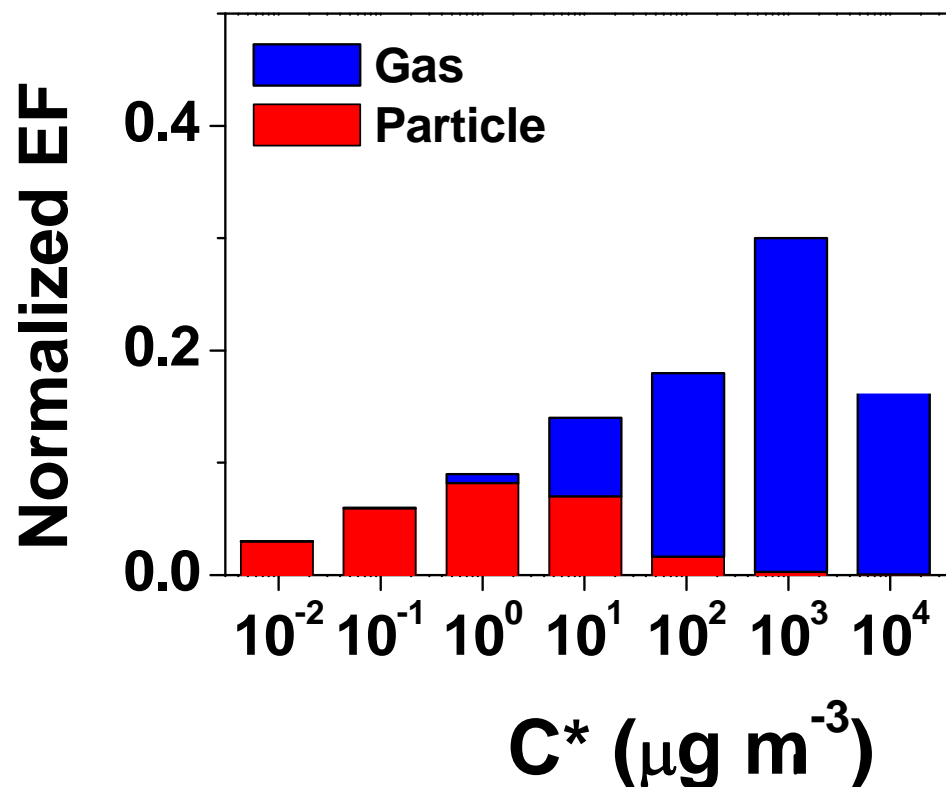


POA emissions for high emitting sources may be biased by a factor of 5!

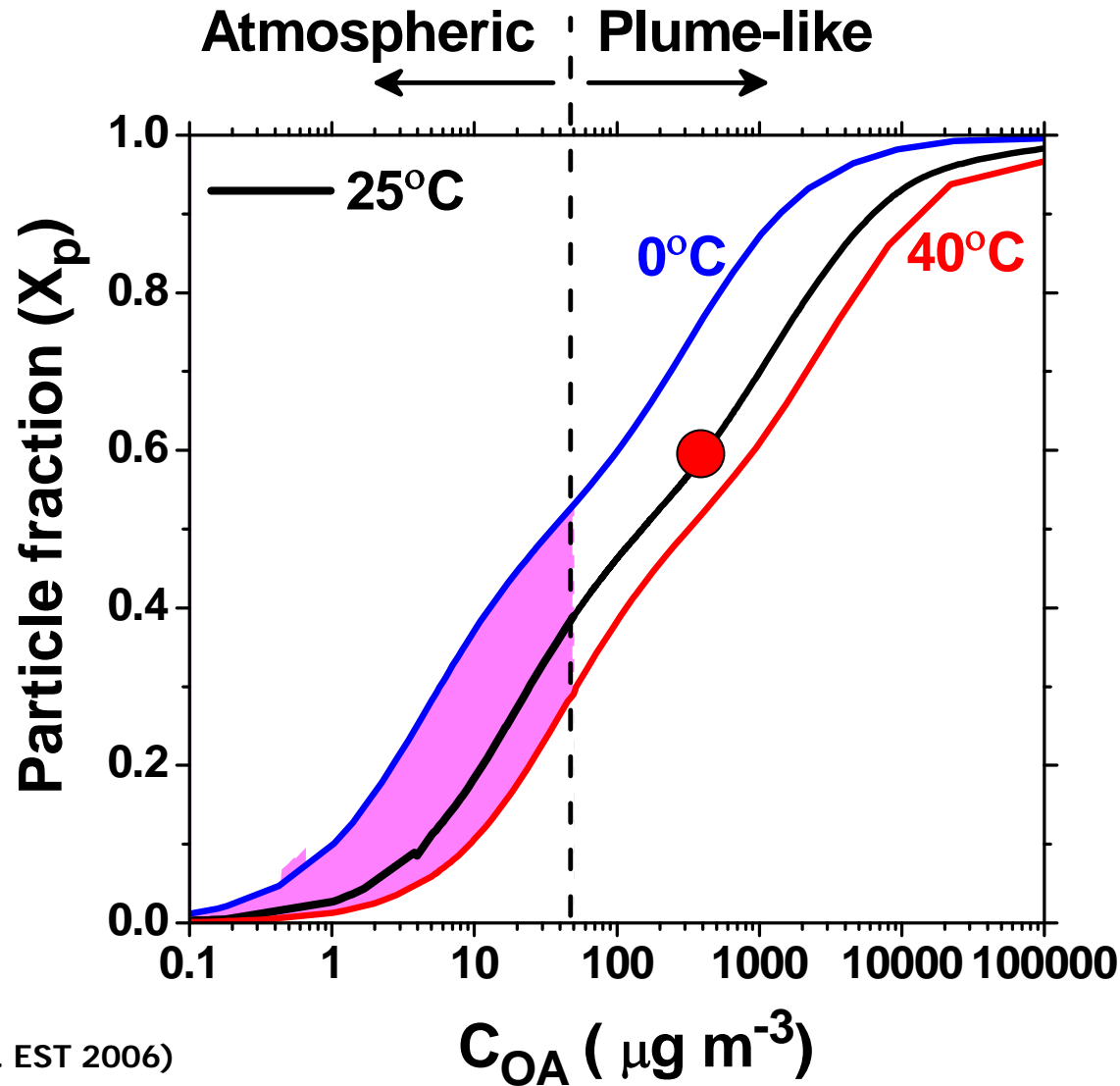
Shrivastava et al. EST 2006.

“Large” Amounts of Low Volatility Organic Vapors

Predicted Gas-Particle Partitioning at
 $T = 298 \text{ K}$, $10 \mu\text{g}/\text{m}^{-3}$ of OA



POA varies with atmospheric conditions



(Shrivastava et al. EST 2006)



Photochemical aging of diesel exhaust

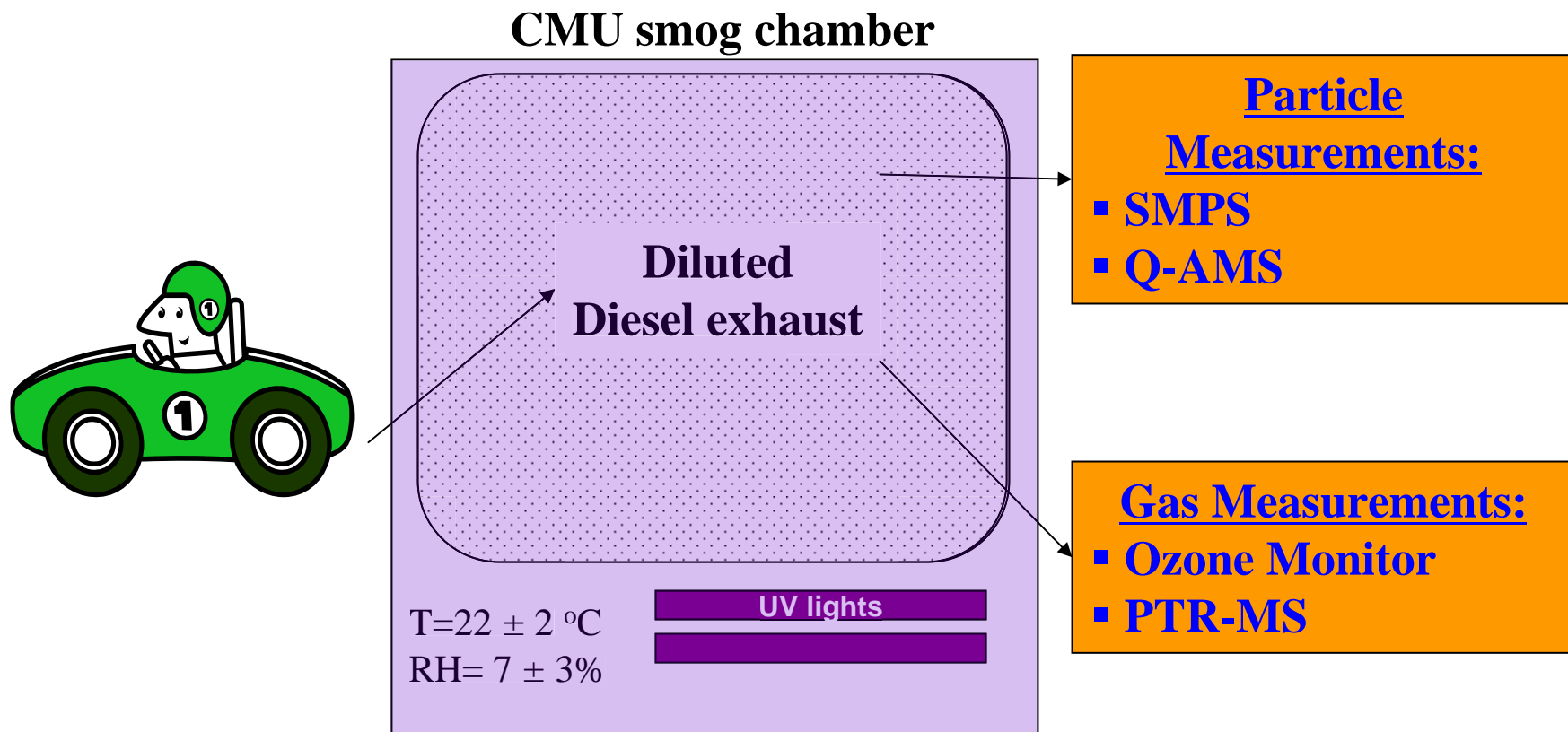
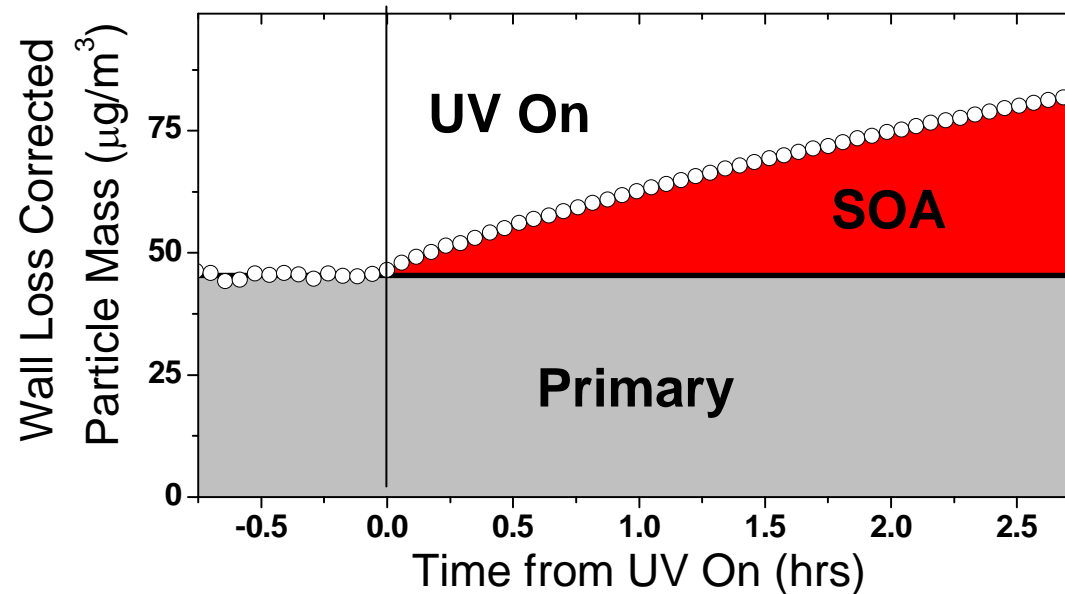


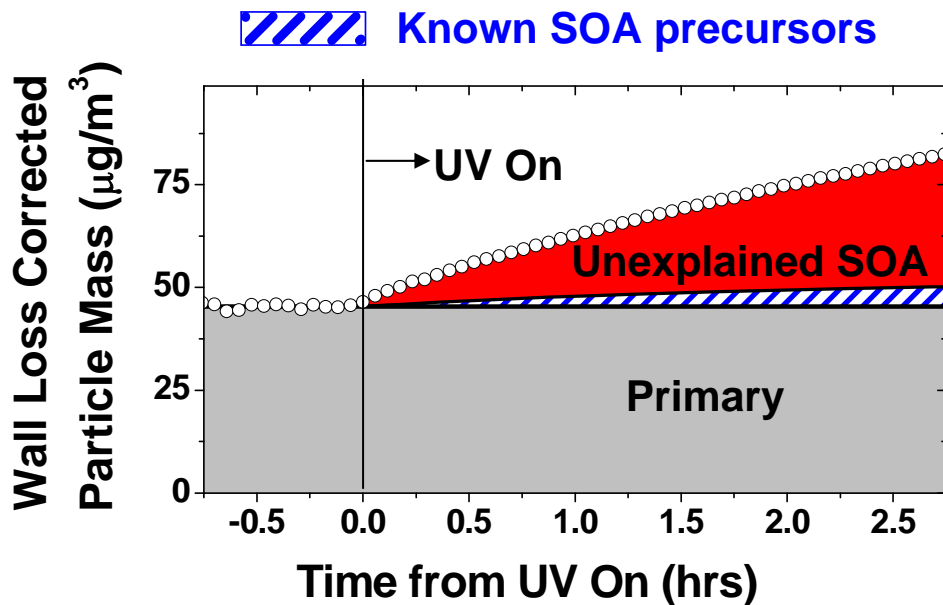


Photo-oxidation creates significant amounts of SOA



Robinson et al. Science 2007.

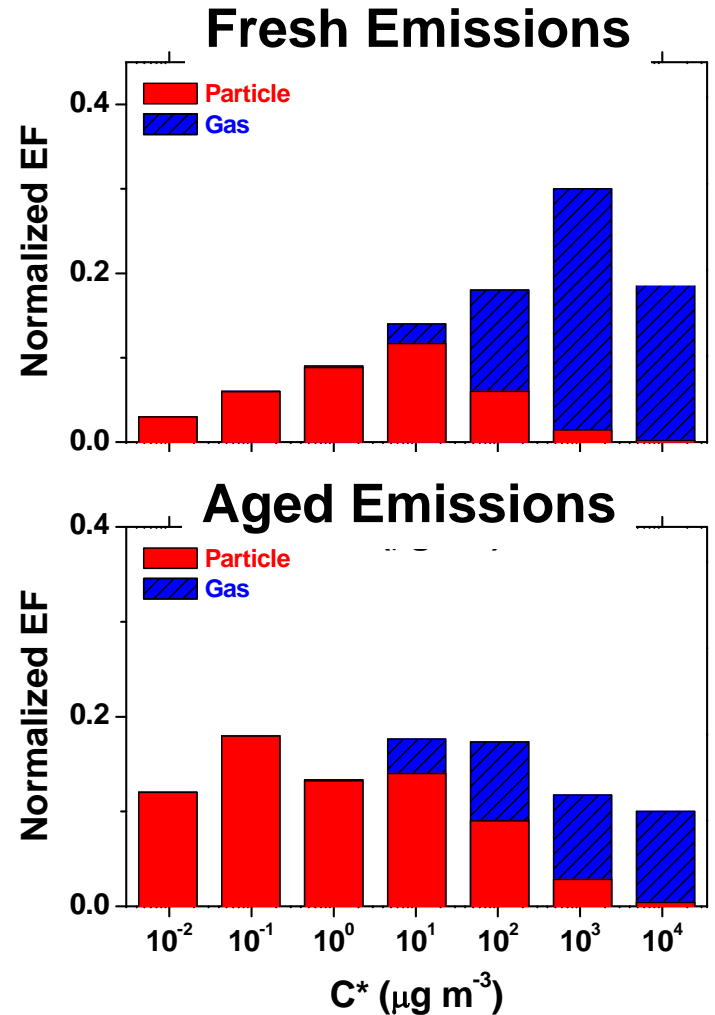
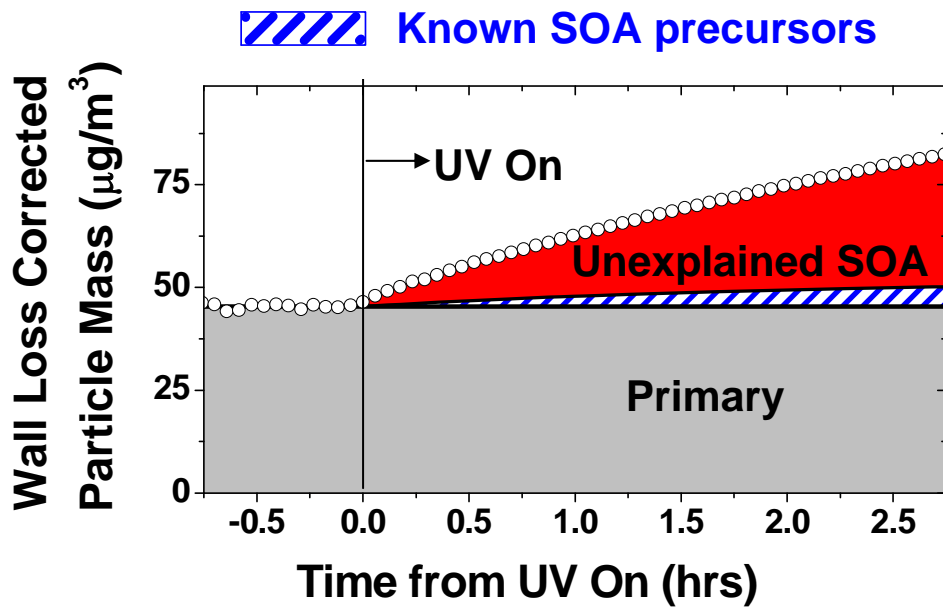
What is contribution of known SOA precursors?



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

Robinson et al. Science 2007.

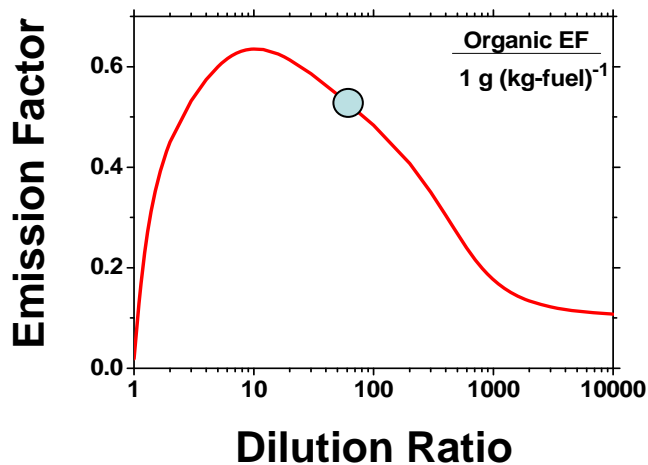
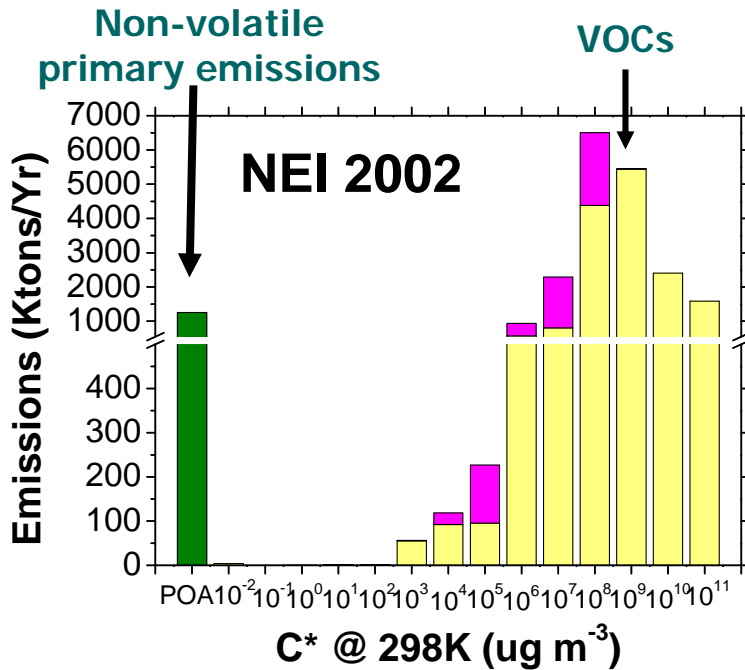
Aging of low volatility vapors source of unexplained SOA



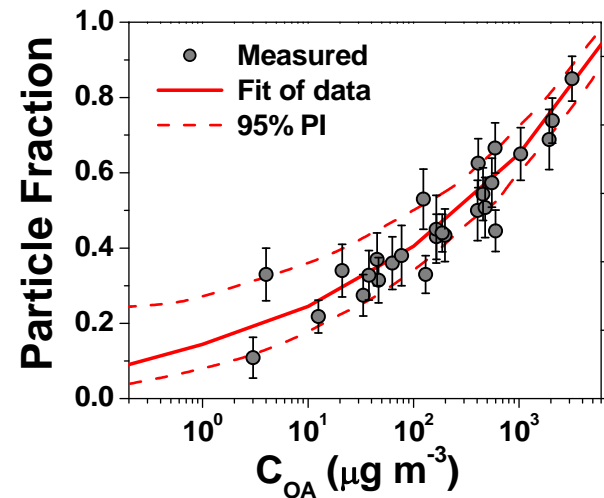
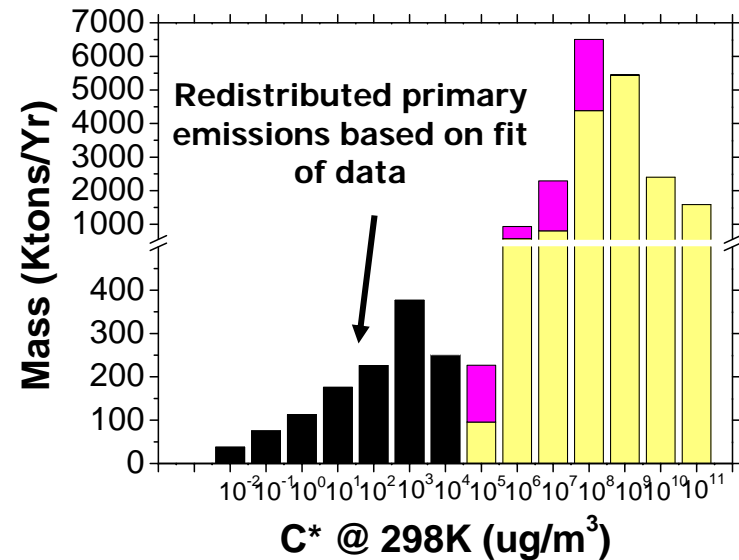
Robinson et al. Science 2007.

Revised framework for primary emissions

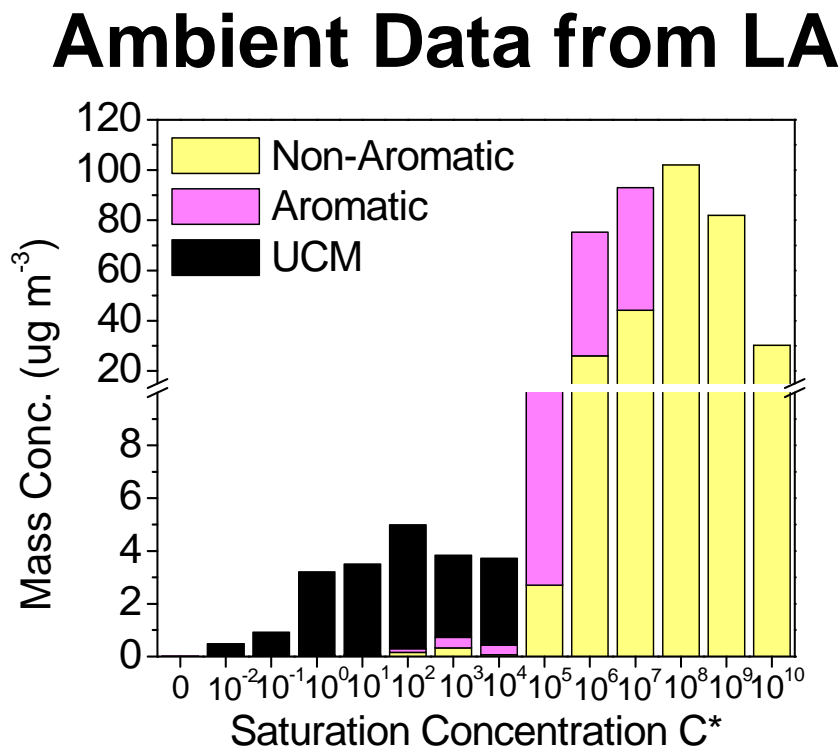
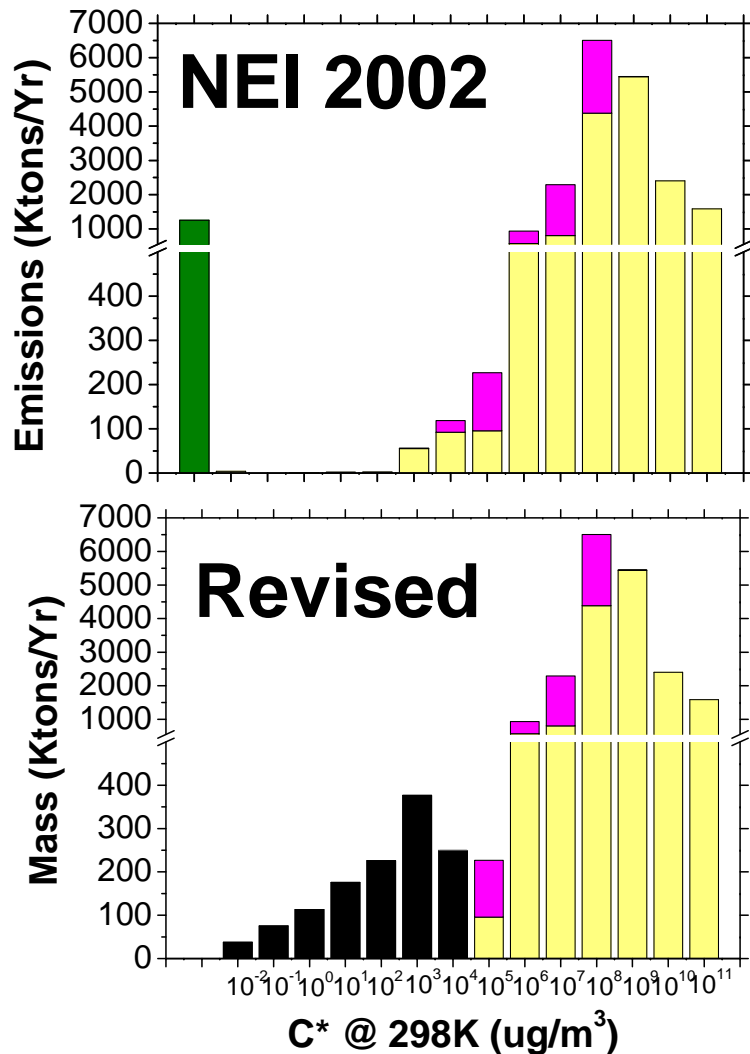
Traditional Approach



New Framework



Revised framework consistent with ambient data

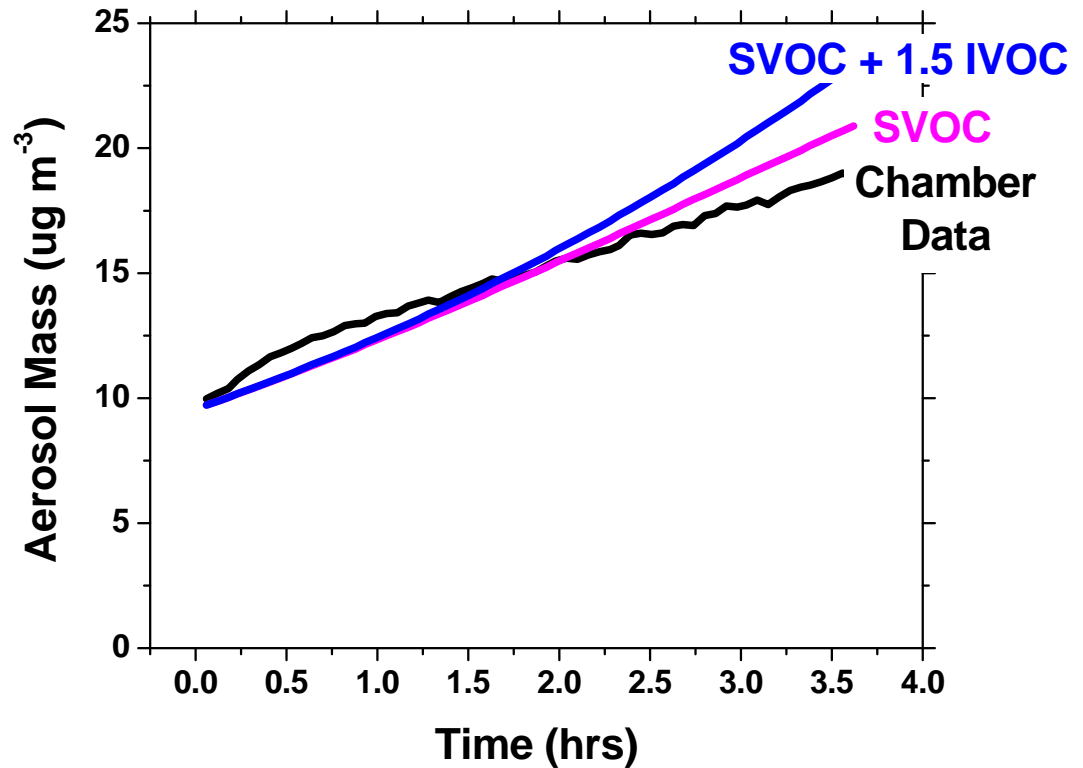
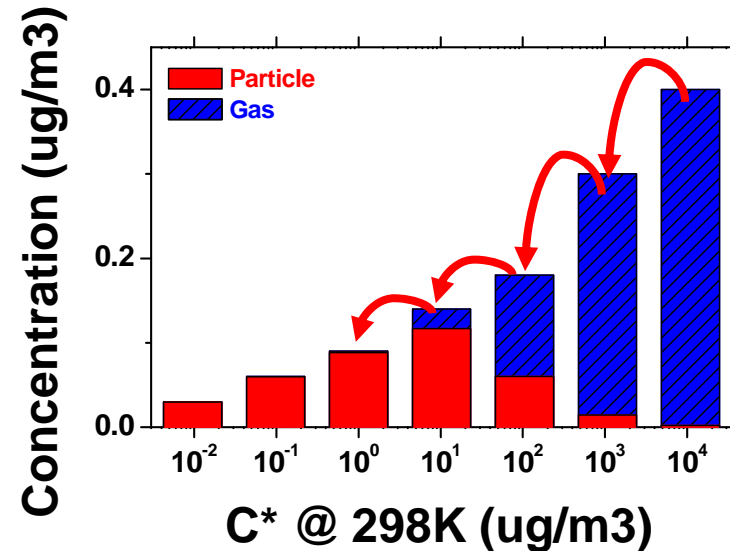


Fraser et al. EST 1997, 1998

Aging Scheme

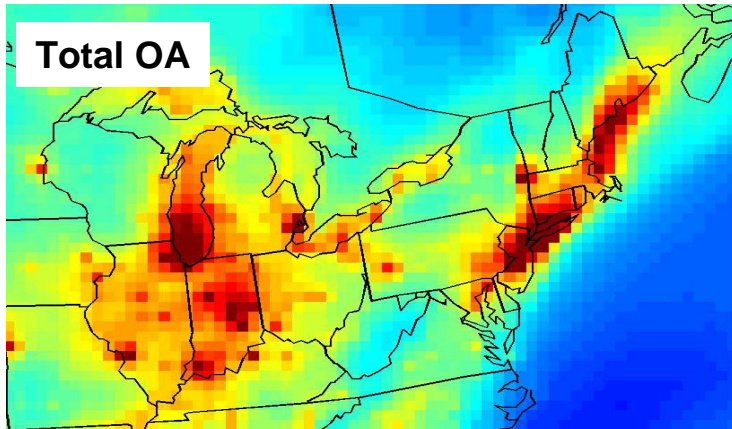
Gas-phase Aging

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

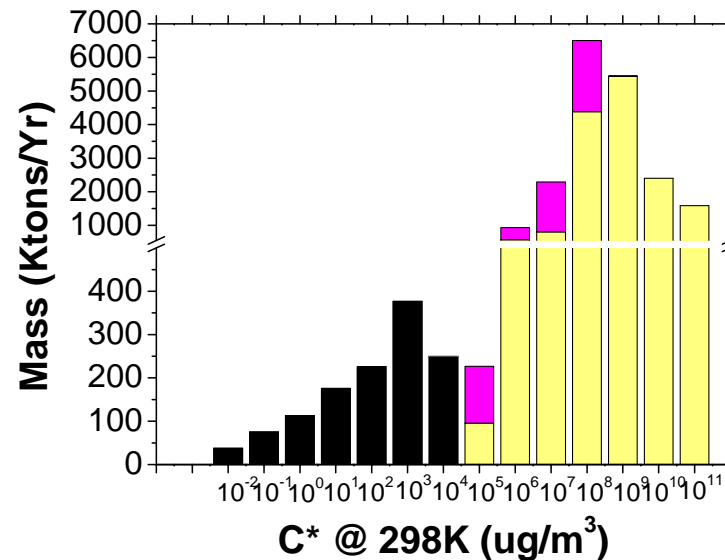
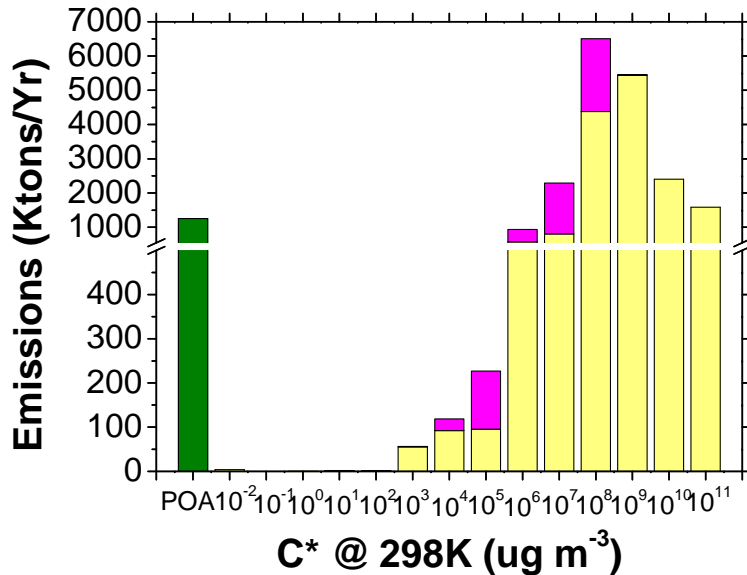
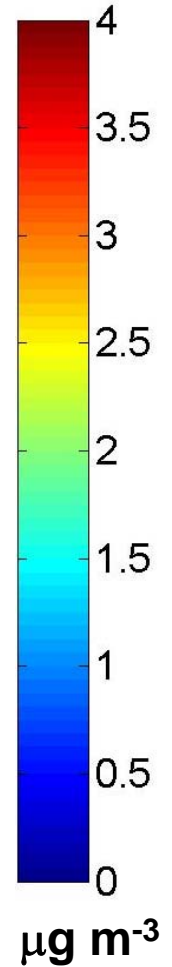
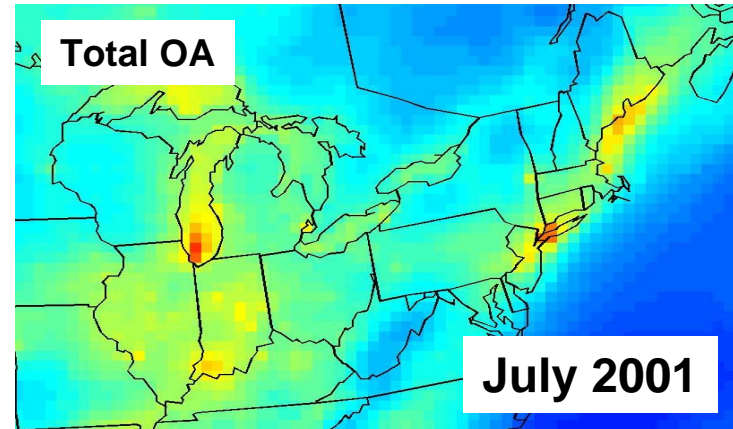


Evaporation dramatically reduces POA

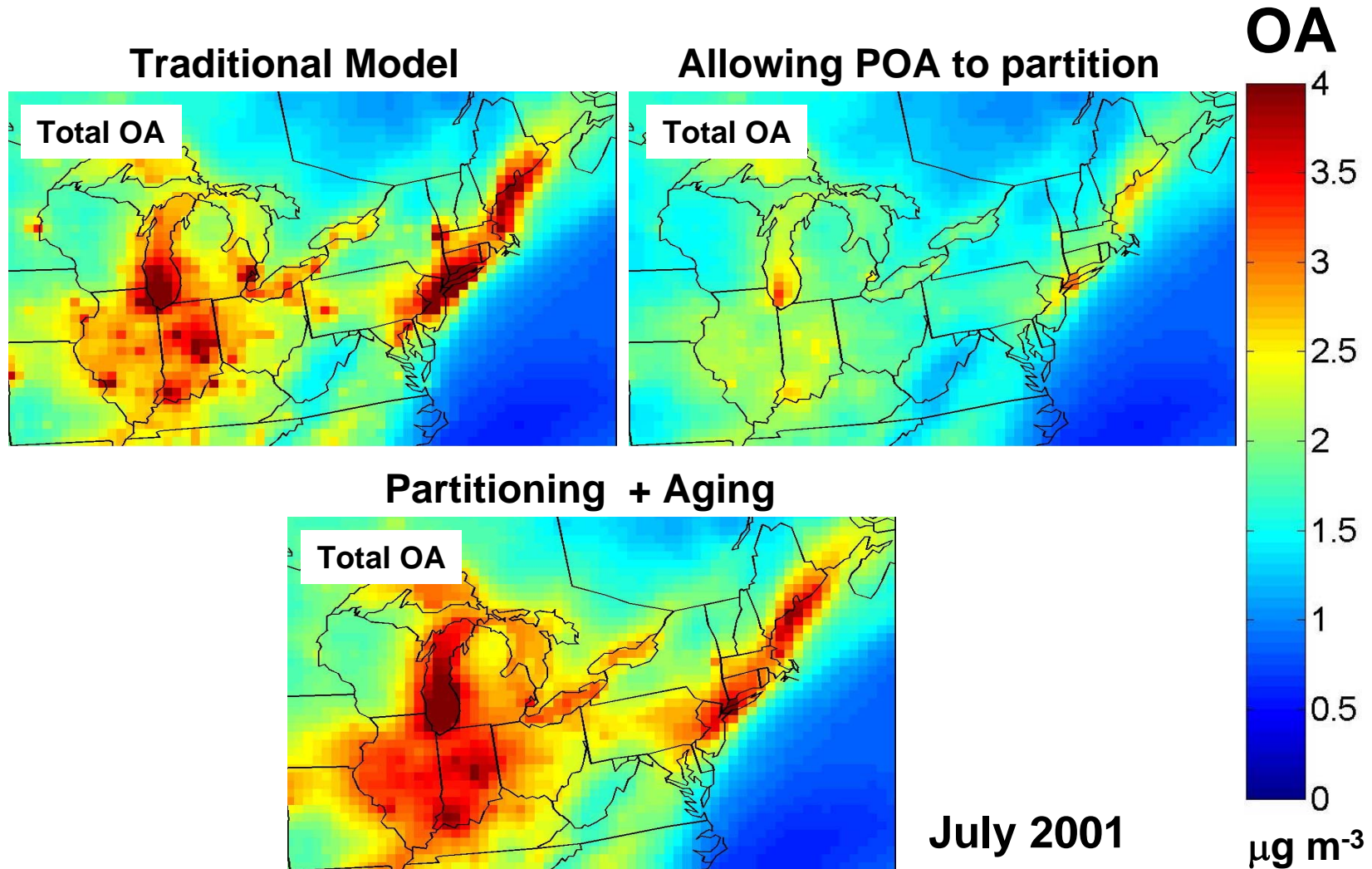
Traditional Model



Allowing POA to partition



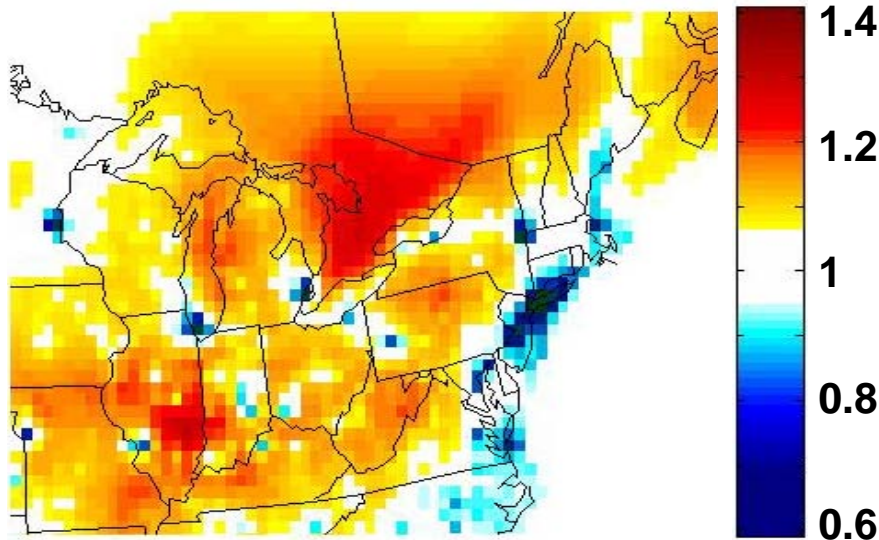
Aging Creates Regional SOA



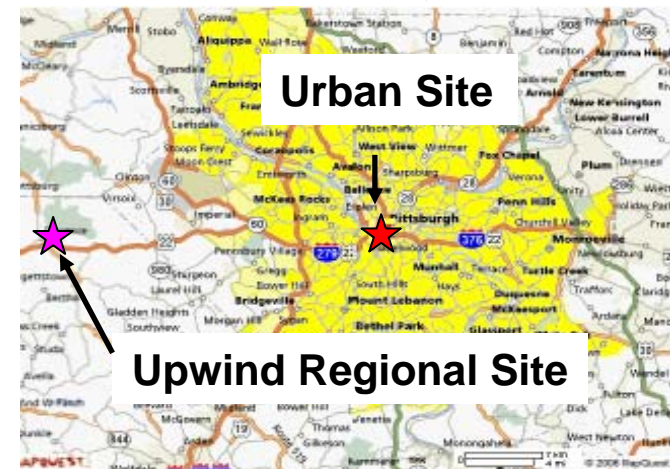
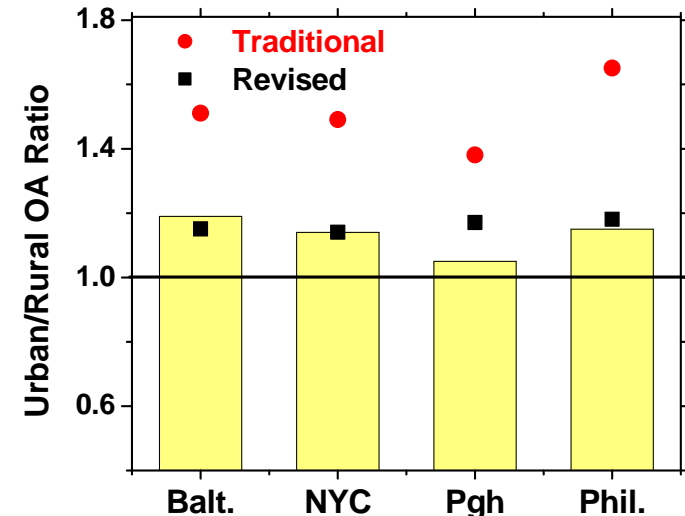
Robinson et al. Science 2007.

Revised model predicts a more regional aerosol

Ratio of Revised-to-Traditional Model Predicted OA levels



Model-Measurement Comparison



Robinson et al. Science 2007.

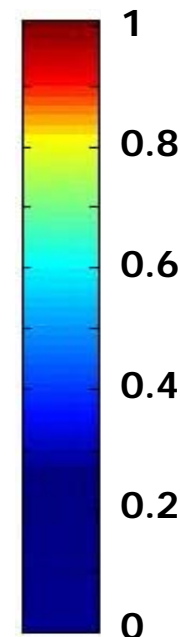
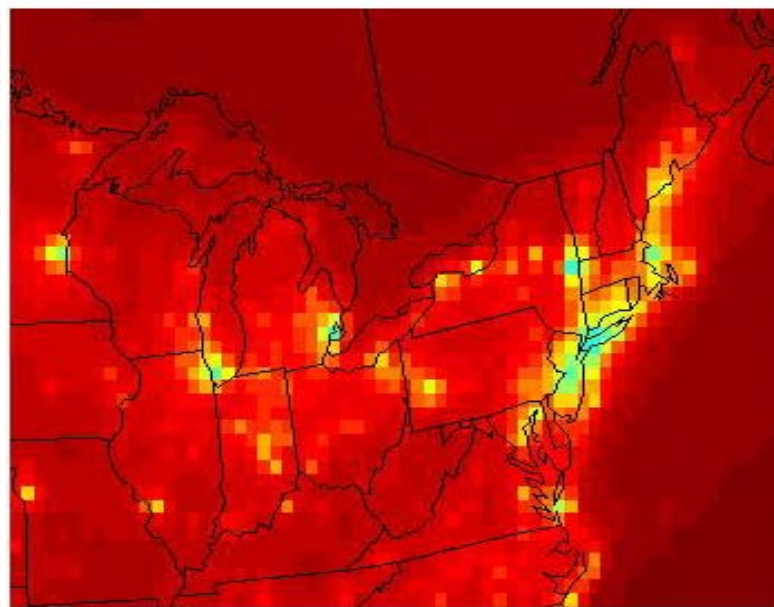
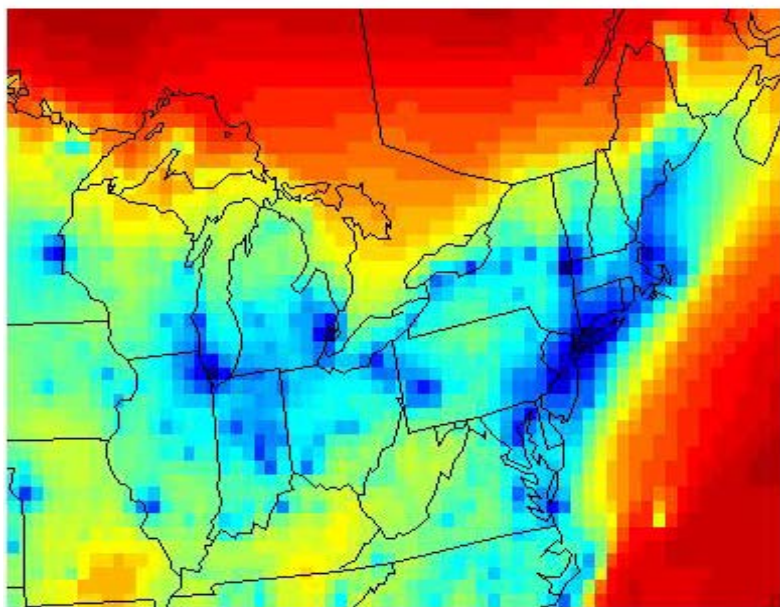


Dramatic shift in primary-secondary split

Predicted fractional contribution of SOA to total OA concentration

Traditional Model

Semivolatile Emissions + Aging



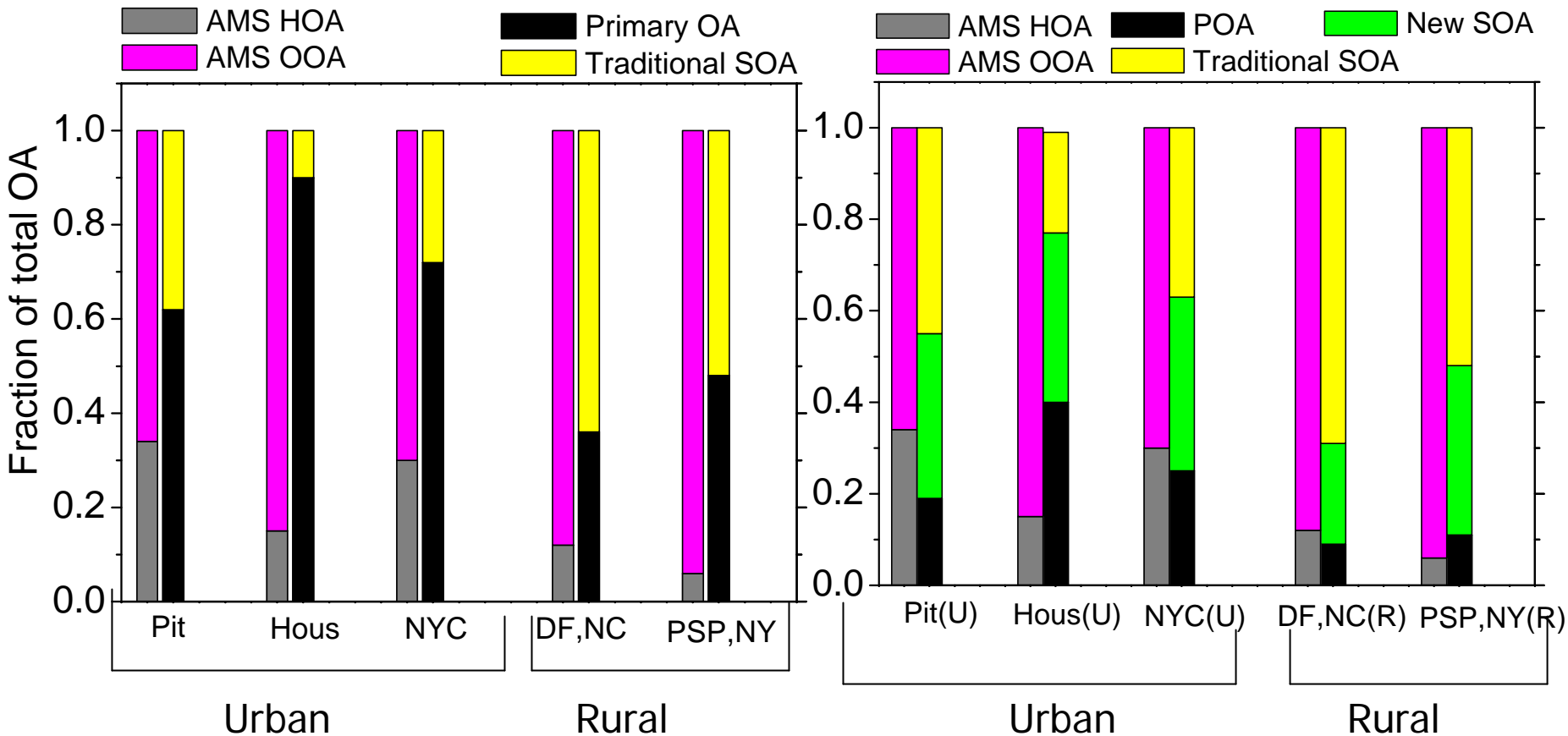
July 2001

Robinson et al. Science 2007.

Model vs. AMS HOA/OOA Measurements

Non-volatile: Basecase

Revised Model



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

Conclusions #1

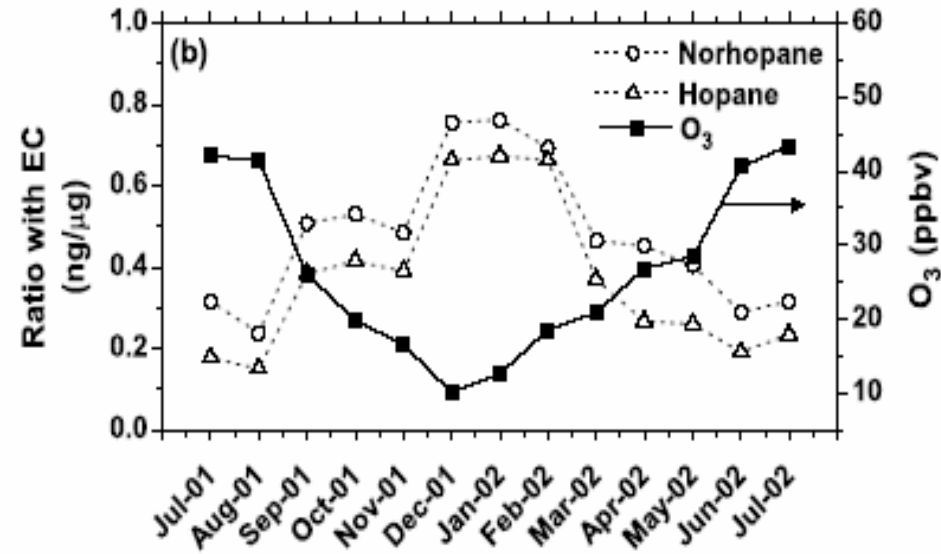
- ❑ **Primary Emissions are Semivolatile**
 - Gas-particle partitioning of POA
 - Photochemical aging of low volatility organic vapors

- ❑ **Implications for regional OA**
 - Reduce POA
 - Increase SOA
 - Developing control strategies?

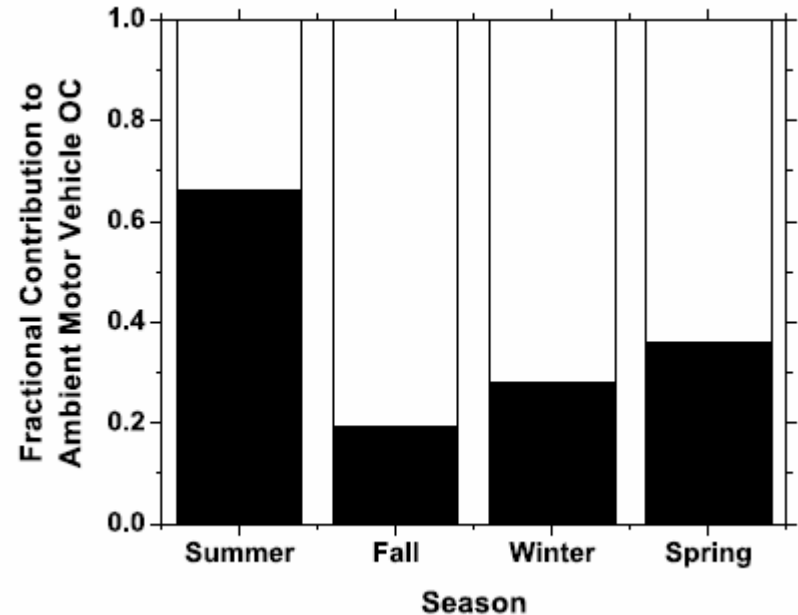
- ❑ **Need to update methods used to measure and simulate POA**

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



CMU smog chamber

1500+ $\mu\text{g}/\text{m}^3$ aerosol

$T=22 \pm 2 \text{ }^\circ\text{C}$
 $\text{RH}= 7 \pm 3\%$

Particle

Measurements:

- Filters & GC/MS
- SMPS
- AMS

Gas Measurements:

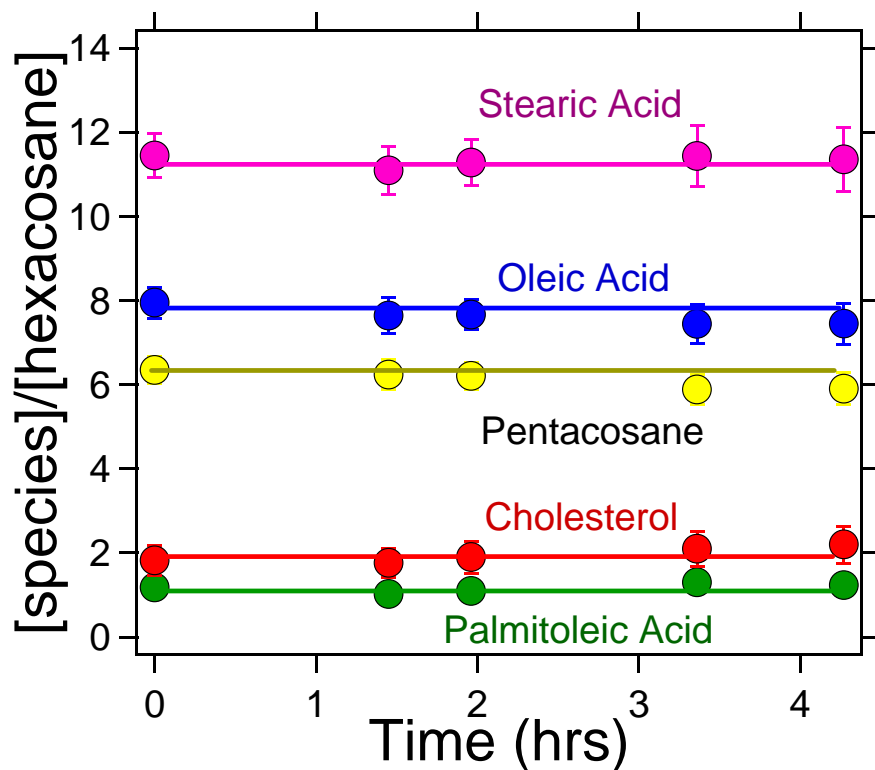
- Ozone Monitor
- GC-FID
- PTR-MS

Gas Input:

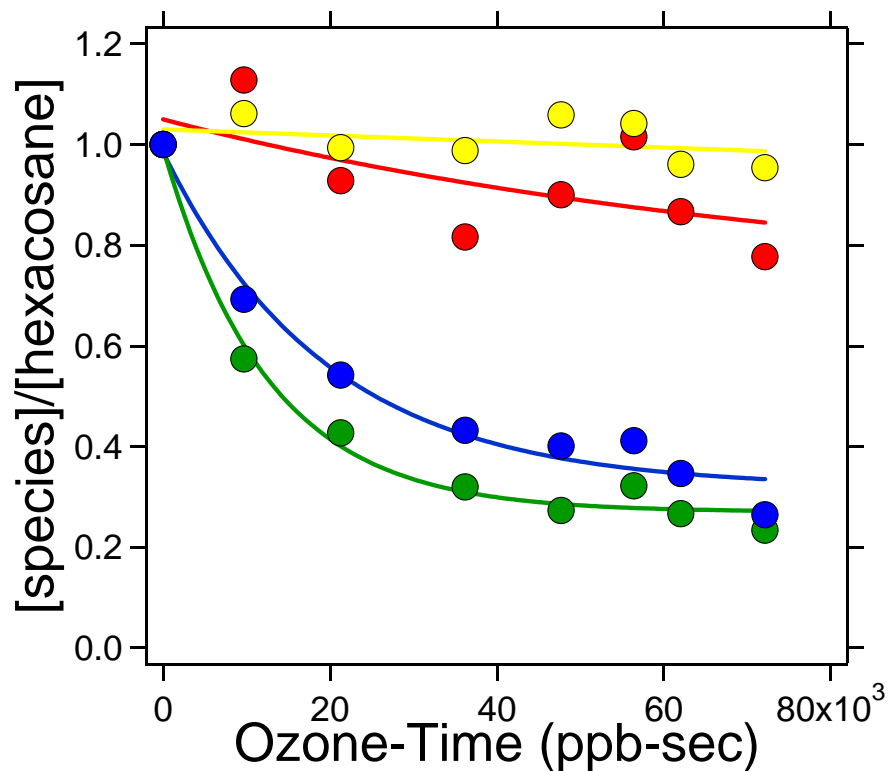
- Oxidants and oxidant precursors
- Gas phase tracers

Rapid Oxidation of Molecular Markers in Hamburger Grease Aerosol

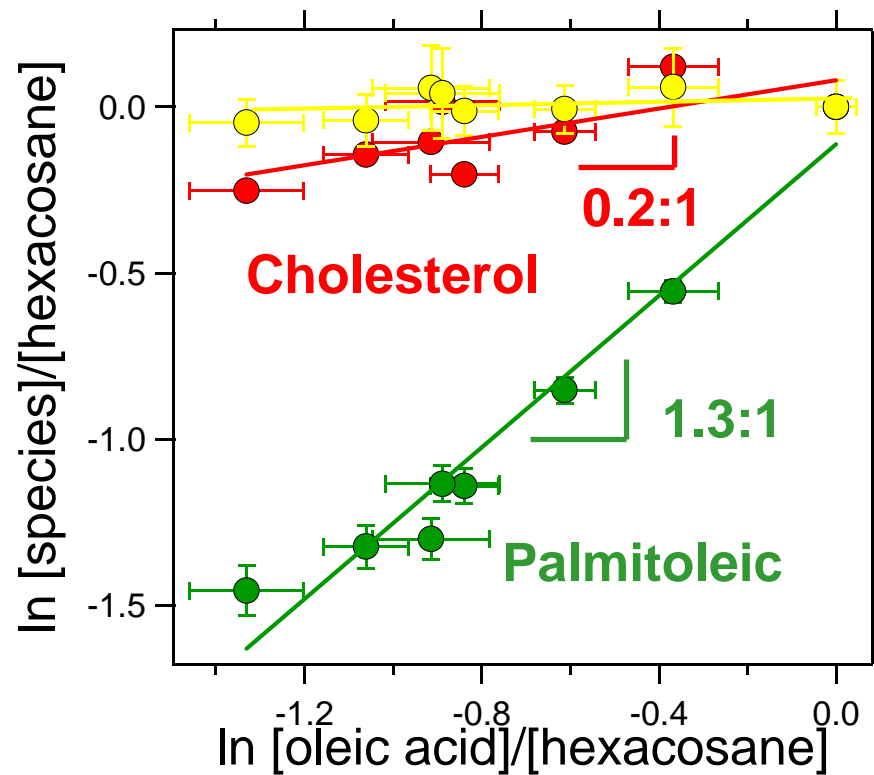
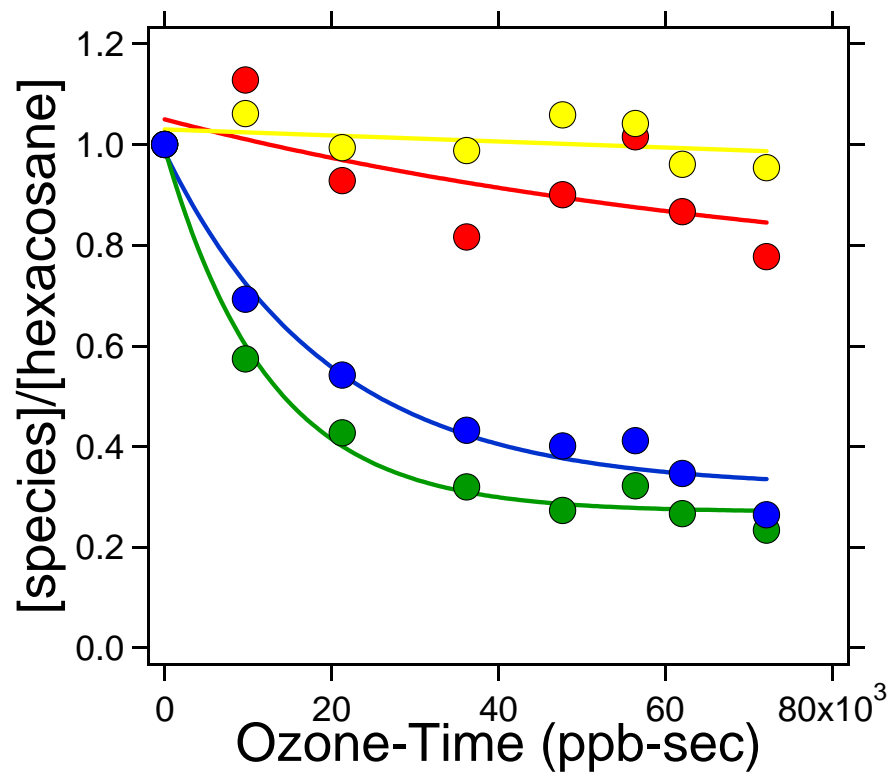
Control – Dark, No O₃



~ 100 ppbv O₃

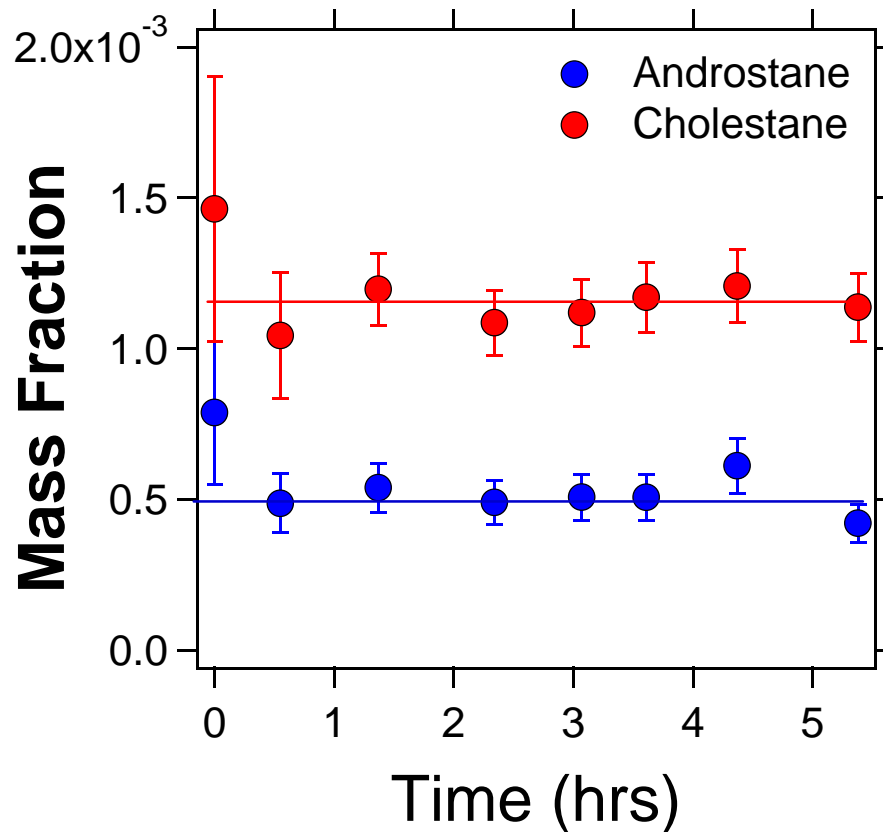


Relative Rate Analysis

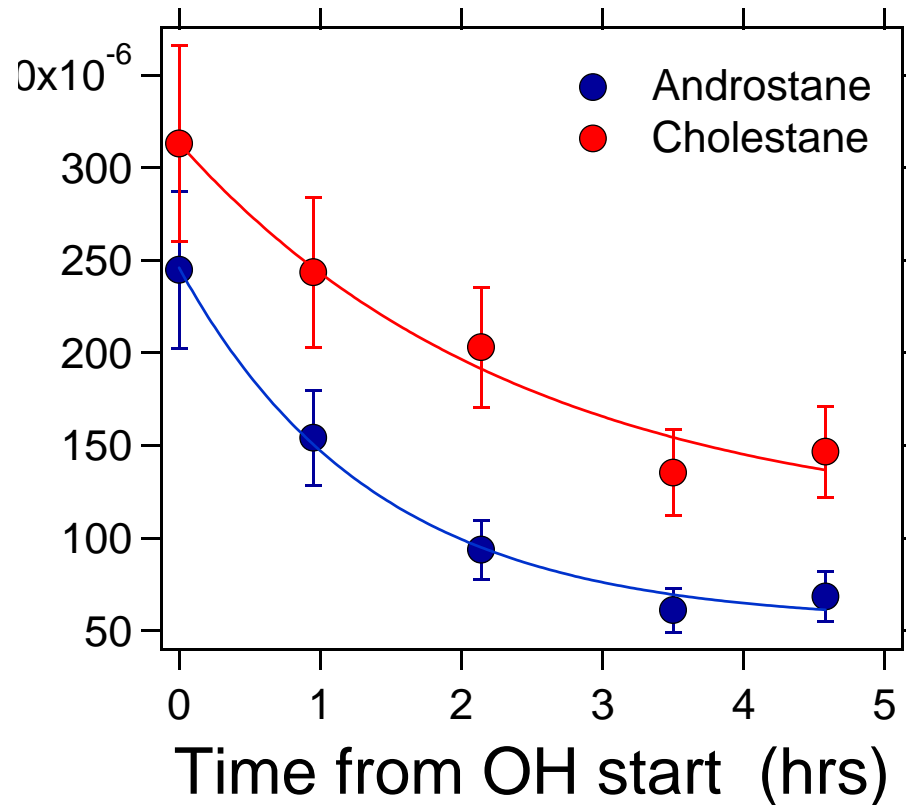


Motor Oil and OH

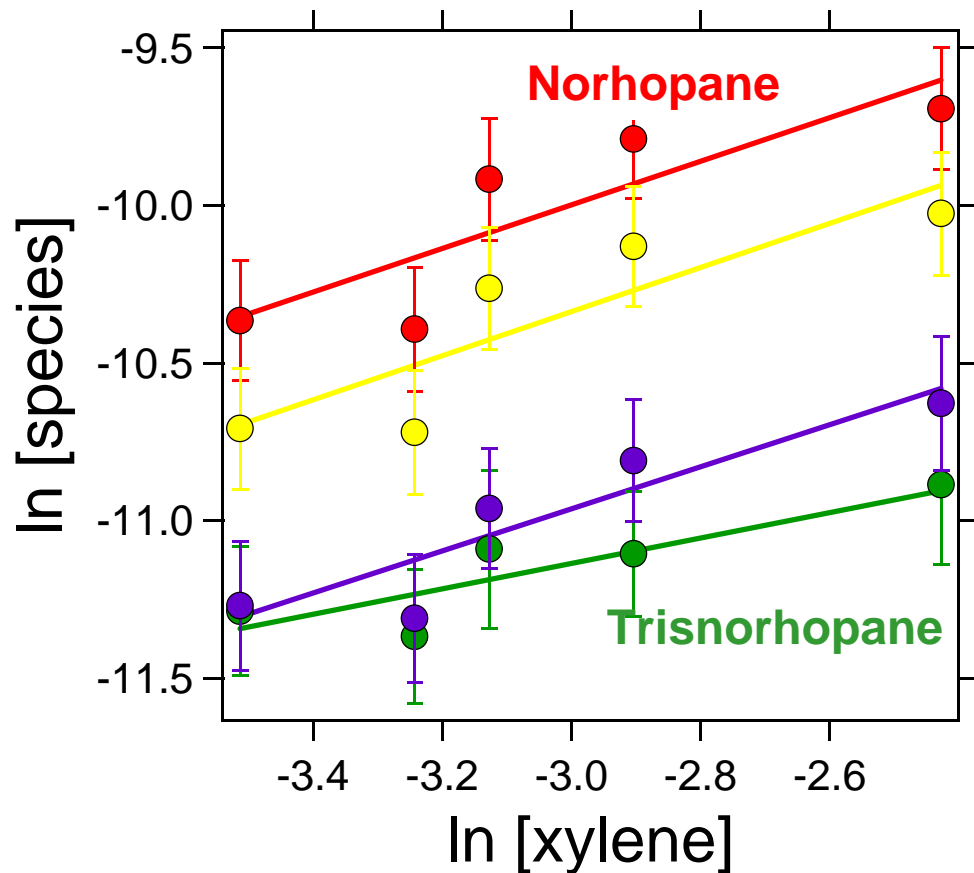
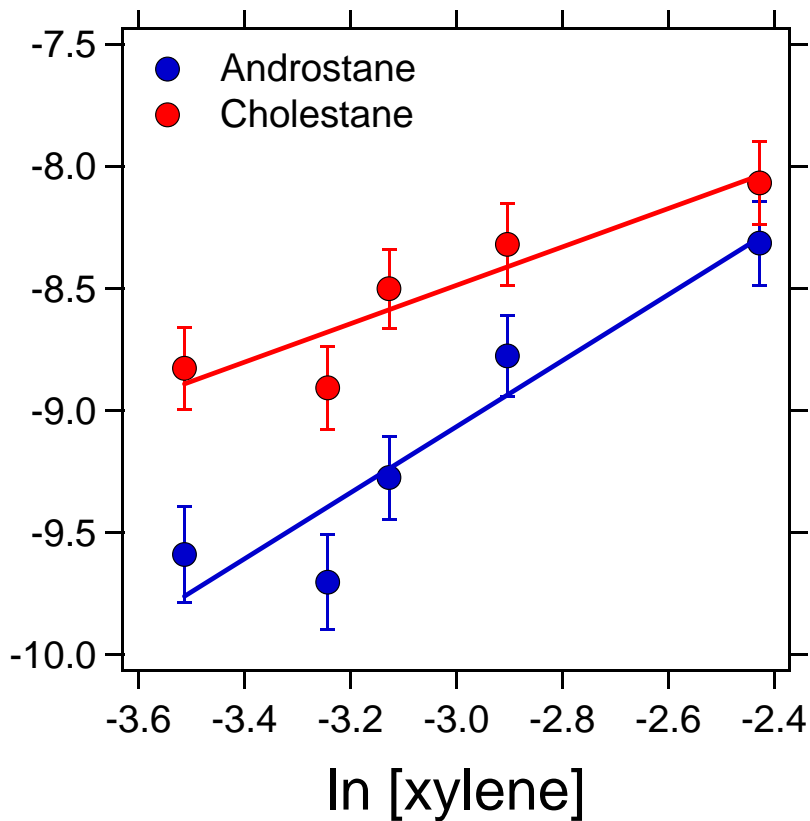
Control – No OH



[OH] $\sim 3 \times 10^6$ mol/cm³



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

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