Sources of Organic Aerosol: Semivolatile Emissions and Photochemical Aging

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A knowledge gap. . .

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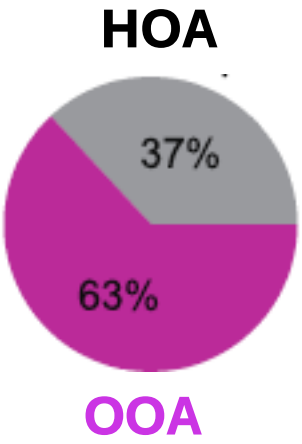
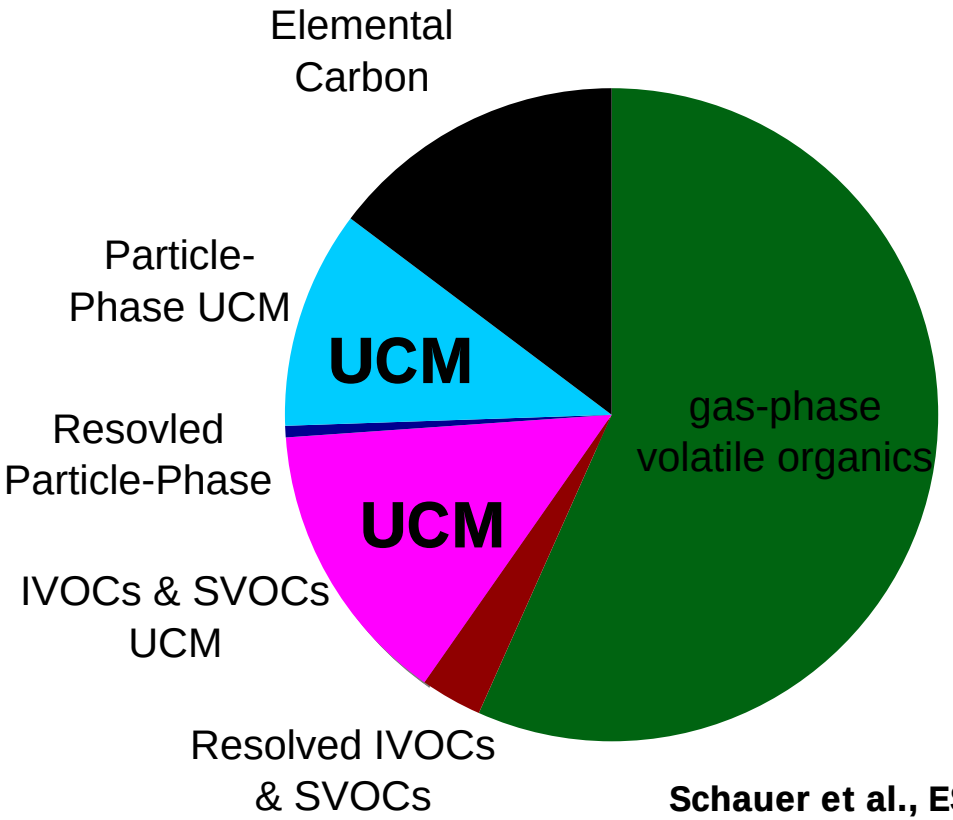


Average urban OA
Zhang et al, GRL, 2007

Complexity of Combustion Emissions

Diesel exhaust



Schauer et al., ES&T 2002

87 % of particle-phase & SVOC/IVOC emissions are UCM

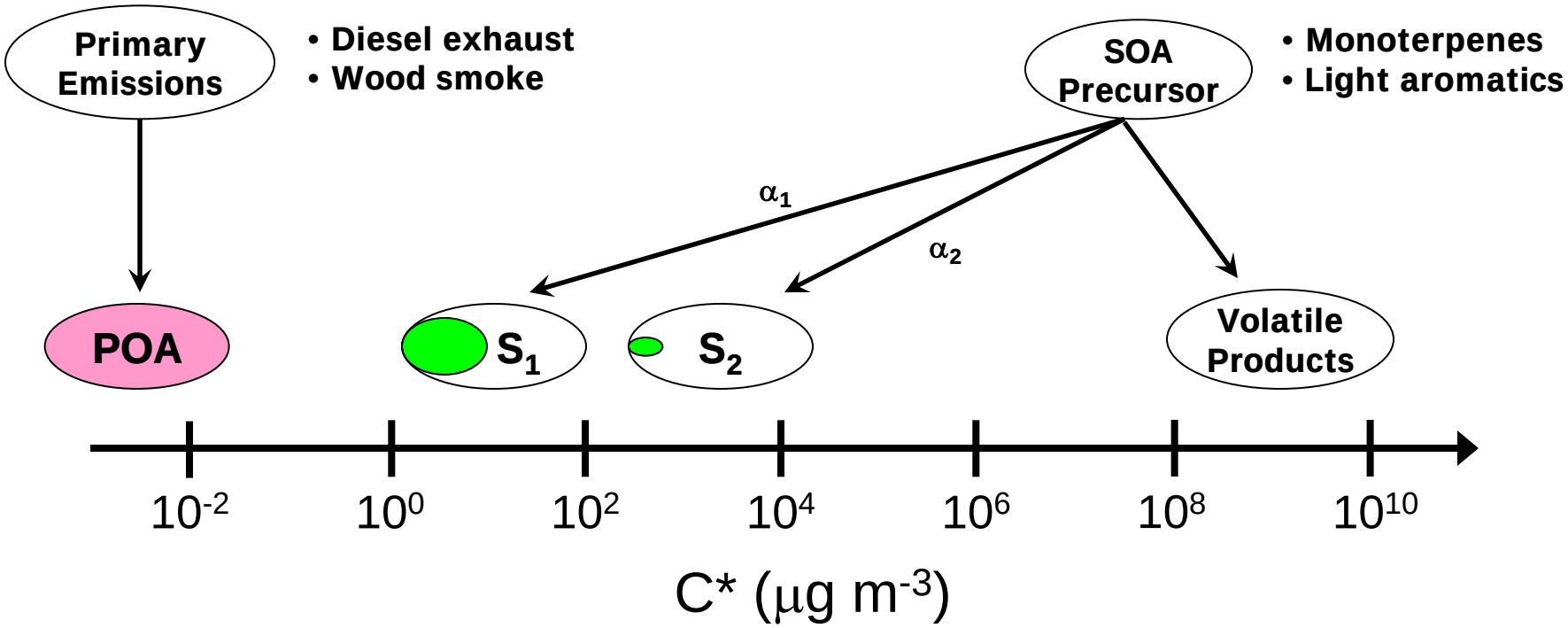
Old conceptual model

Primary Organic Aerosol

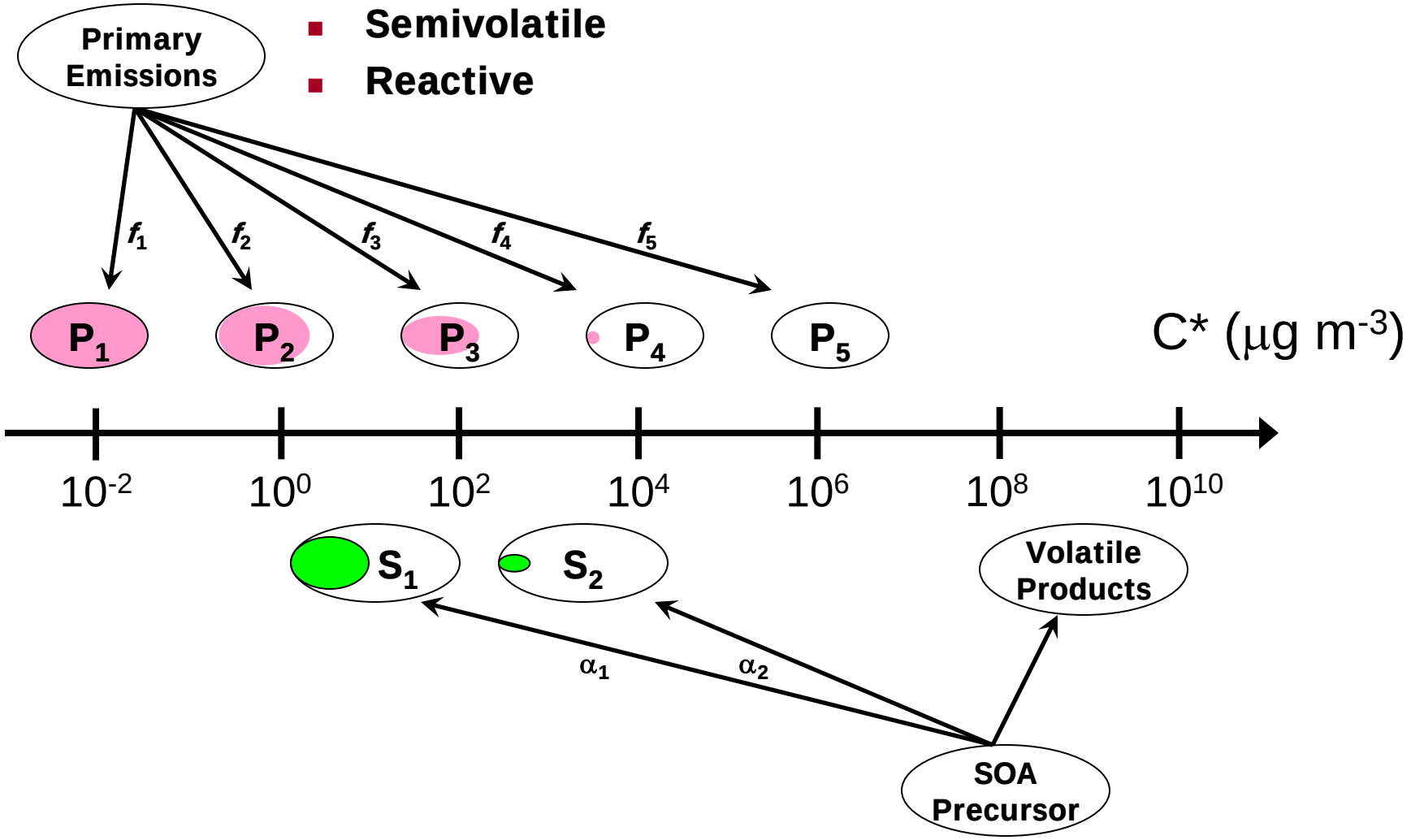
- **Non-volatile**
- **Non-reactive**

Secondary Organic Aerosol

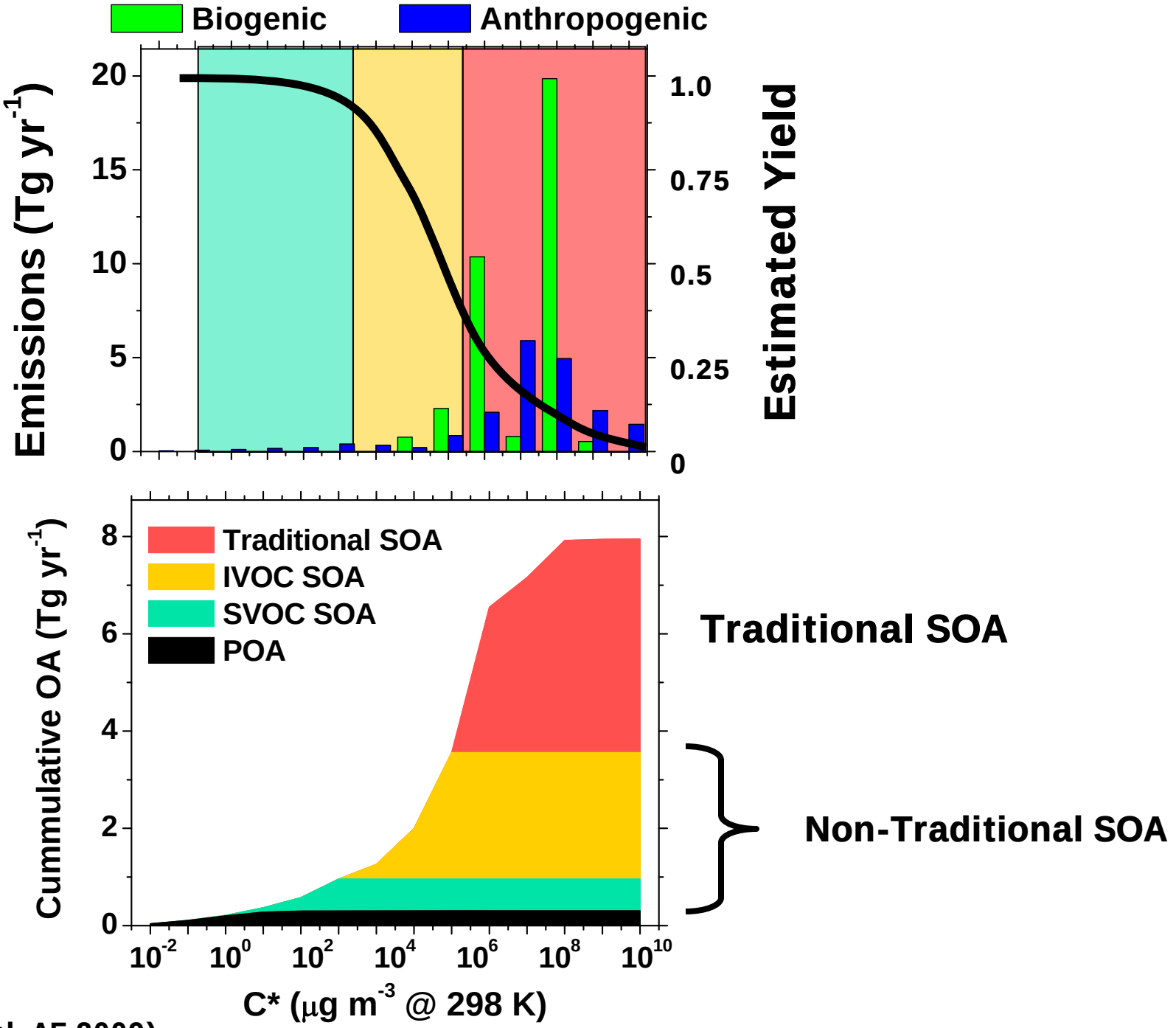
- **Very volatile precursors**
- **Semivolatile products**



Revised conceptual model



(Robinson et al. Science 2007)



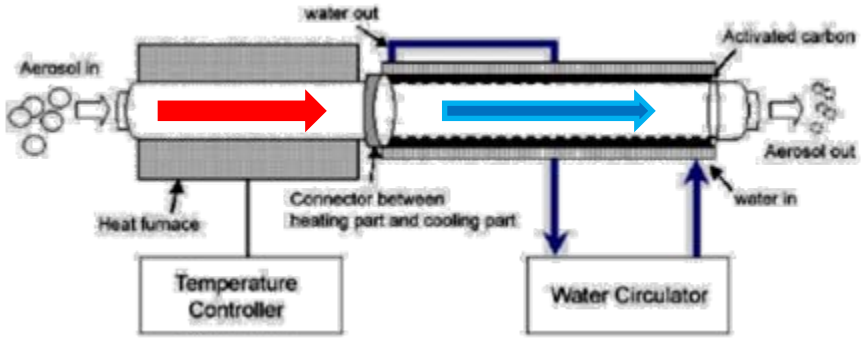
(Donahue et al. AE 2009)

Objectives of Research

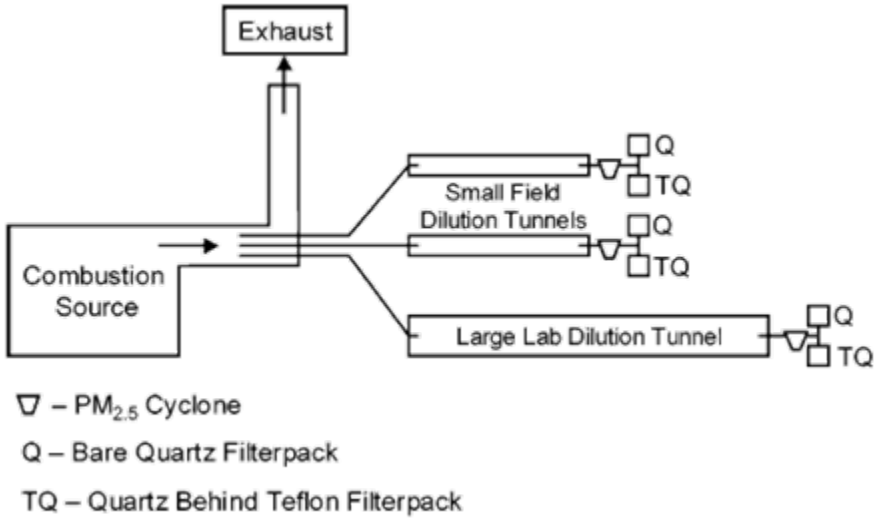
- What is the volatility distribution of fresh emissions?
- What is the effect of aging on primary emissions?
- What are the implications for urban and regional organic aerosol concentrations?

Objective 1. Quantifying volatility distributions

Thermodenuder



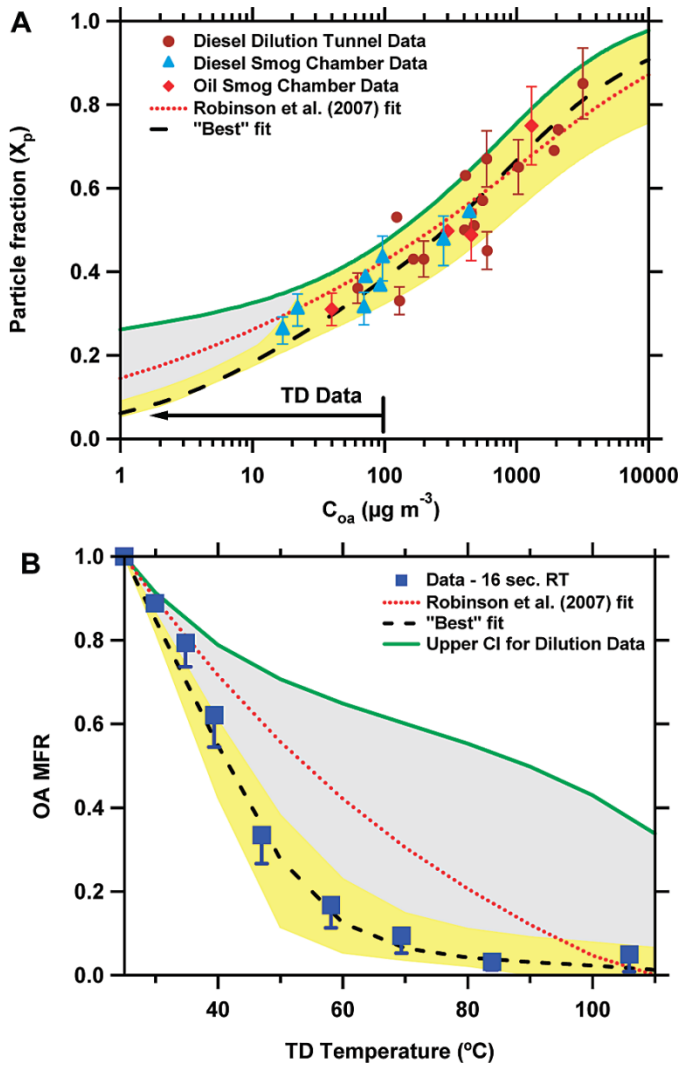
Dilution Sampler

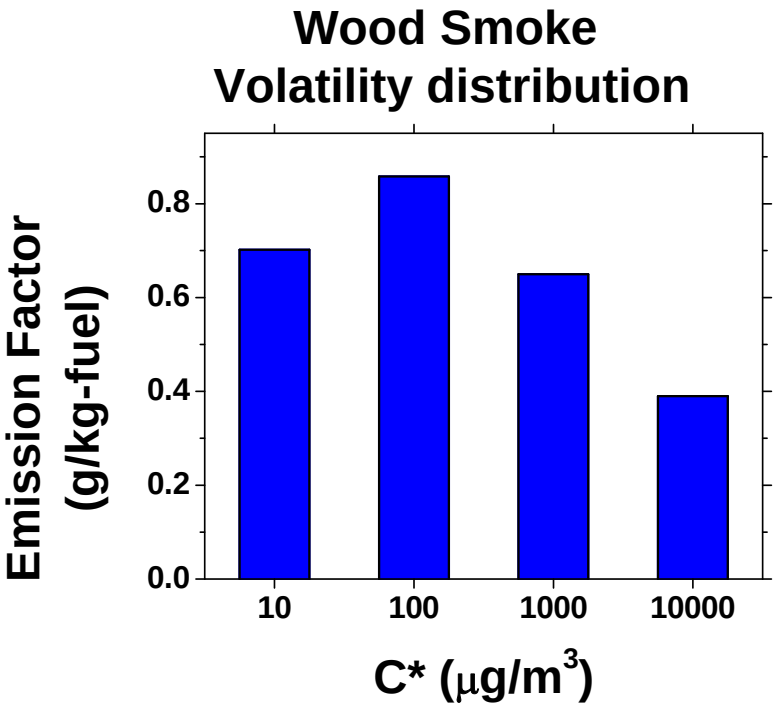


- Change T or C_{OA}
- Measure changes in partitioning
- Fit data to derive volatility distribution

Lipsky et al., ES&T, 2006
An et al., J. Aerosol Sci., 2007

Combining TD and Dilution Data

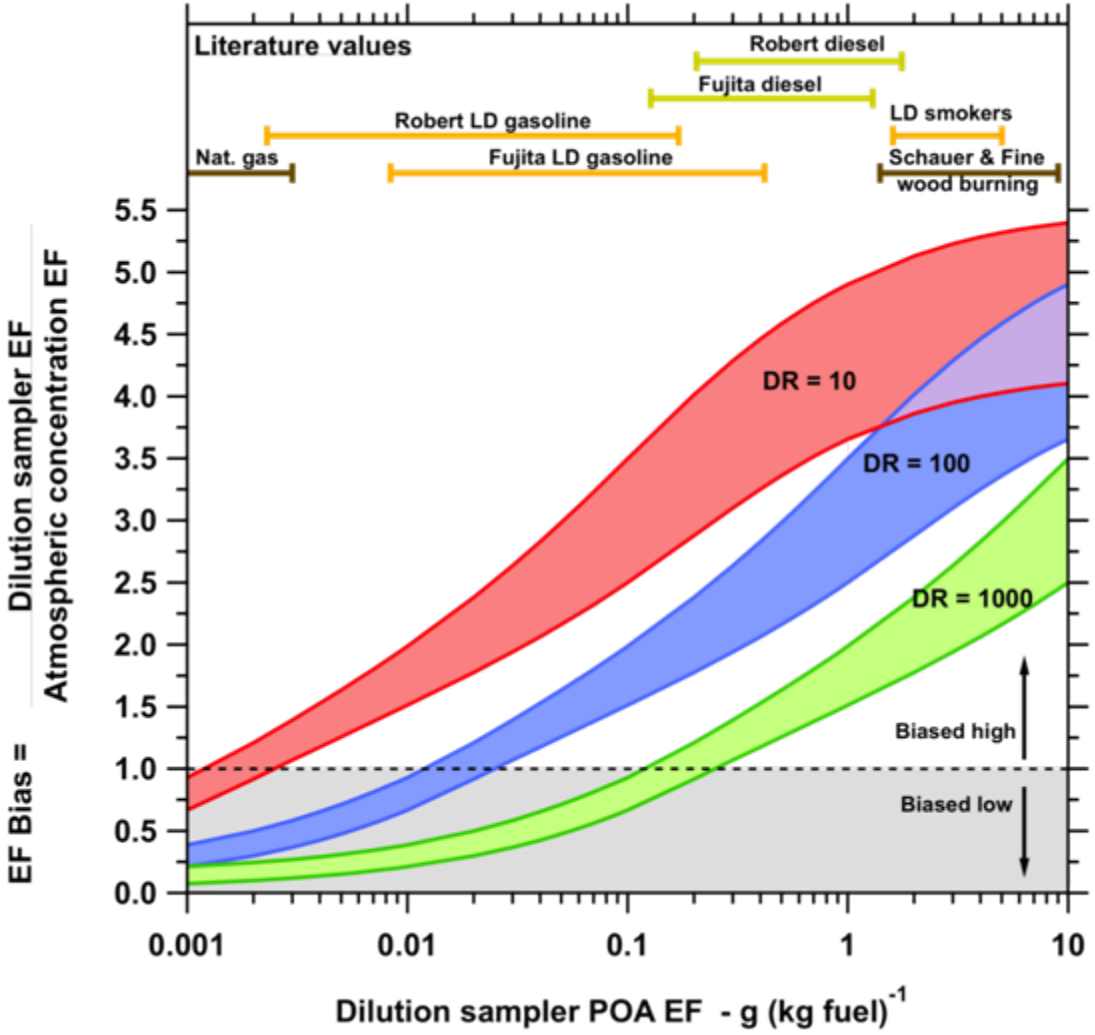




$$X_p = \frac{f_1}{1+\frac{10}{C_{OA}}} + \frac{f_2}{1+\frac{100}{C_{OA}}} + \cdots + \frac{f_4}{1+\frac{1000}{C_{OA}}}$$

Grieshop et al. EST 2010

Partitioning and POA Emission Factors

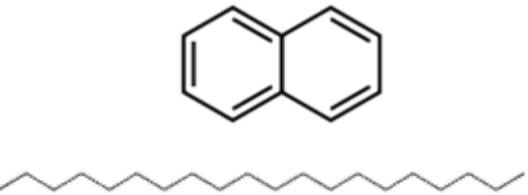


Robinson et al. JAWMA 2010

Objective 2. Effects of aging

Experiments with increasingly complex mixtures

Single components



- ***n*-alkanes**
- **branched alkanes**
- **aromatics**
- **simple mixtures**

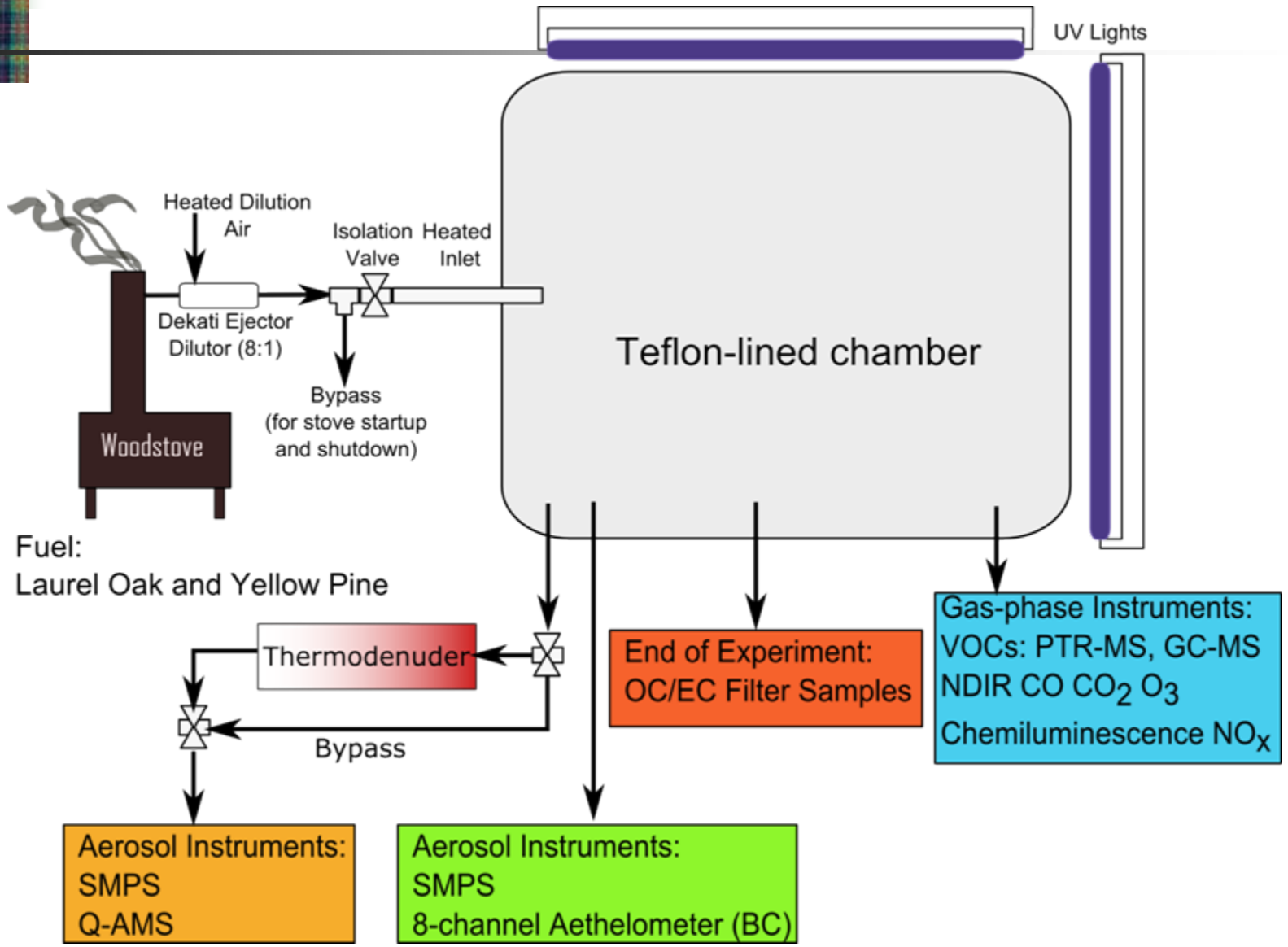
Emission Surrogates

- **motor oil (new & used)**
- **diesel fuel**
- **mixtures of fuel & oil**

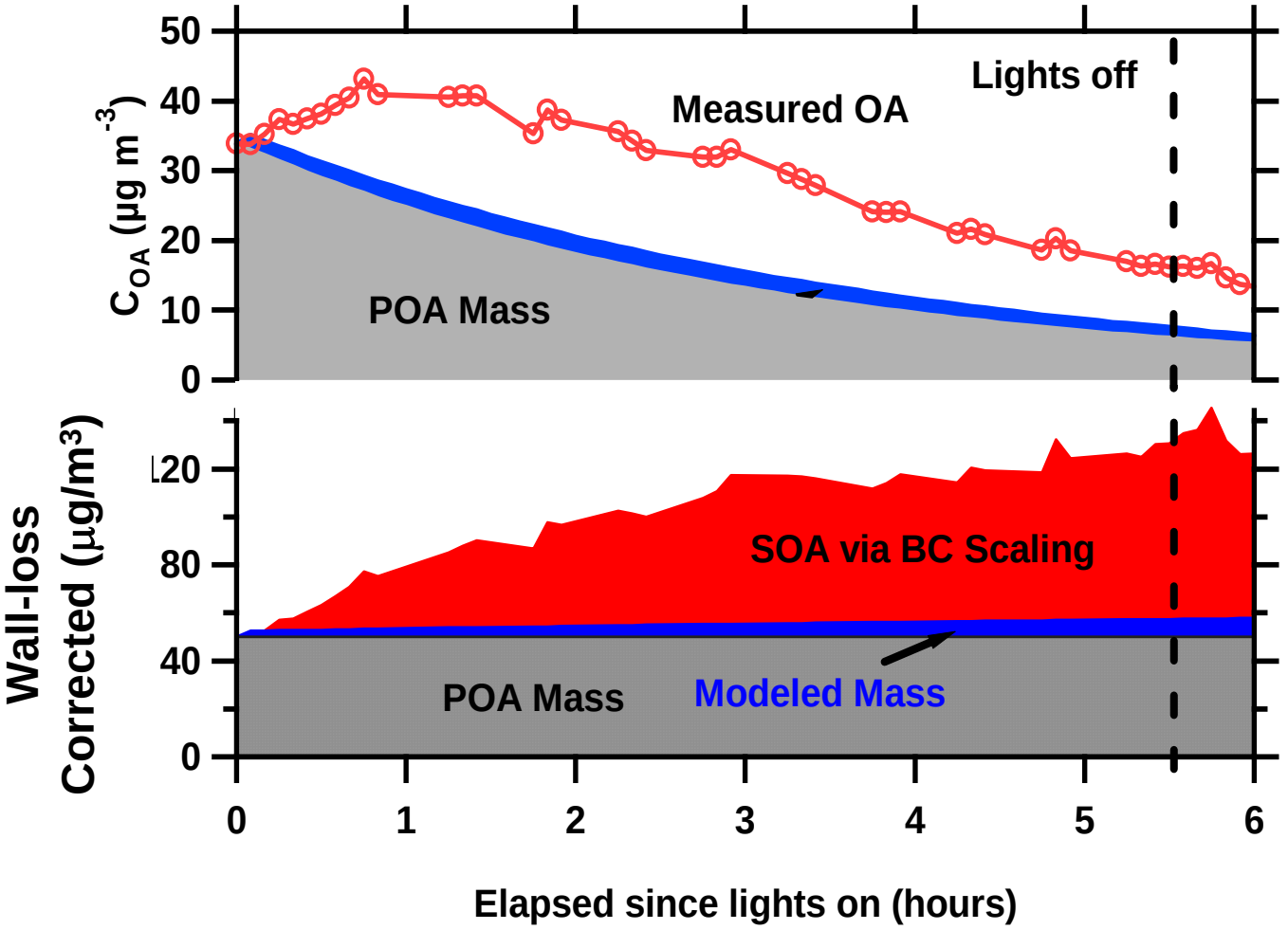
Diluted exhaust

- **diesel exhaust**
- **wood smoke**
- **aircraft exhaust**

Aging of Wood Smoke Experimental Setup

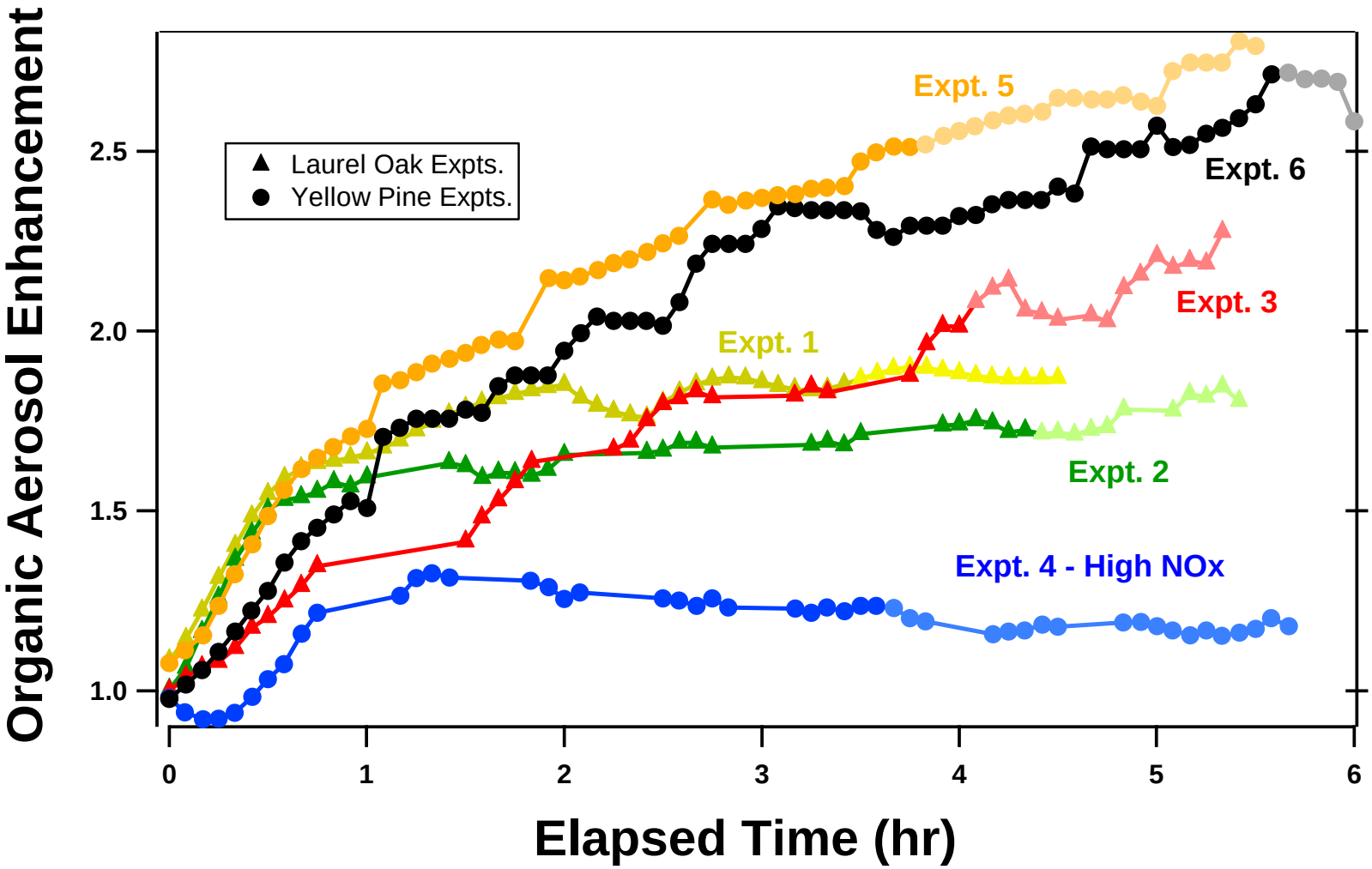


Wood smoke Aging Rapidly Creates Lots of "SOA"



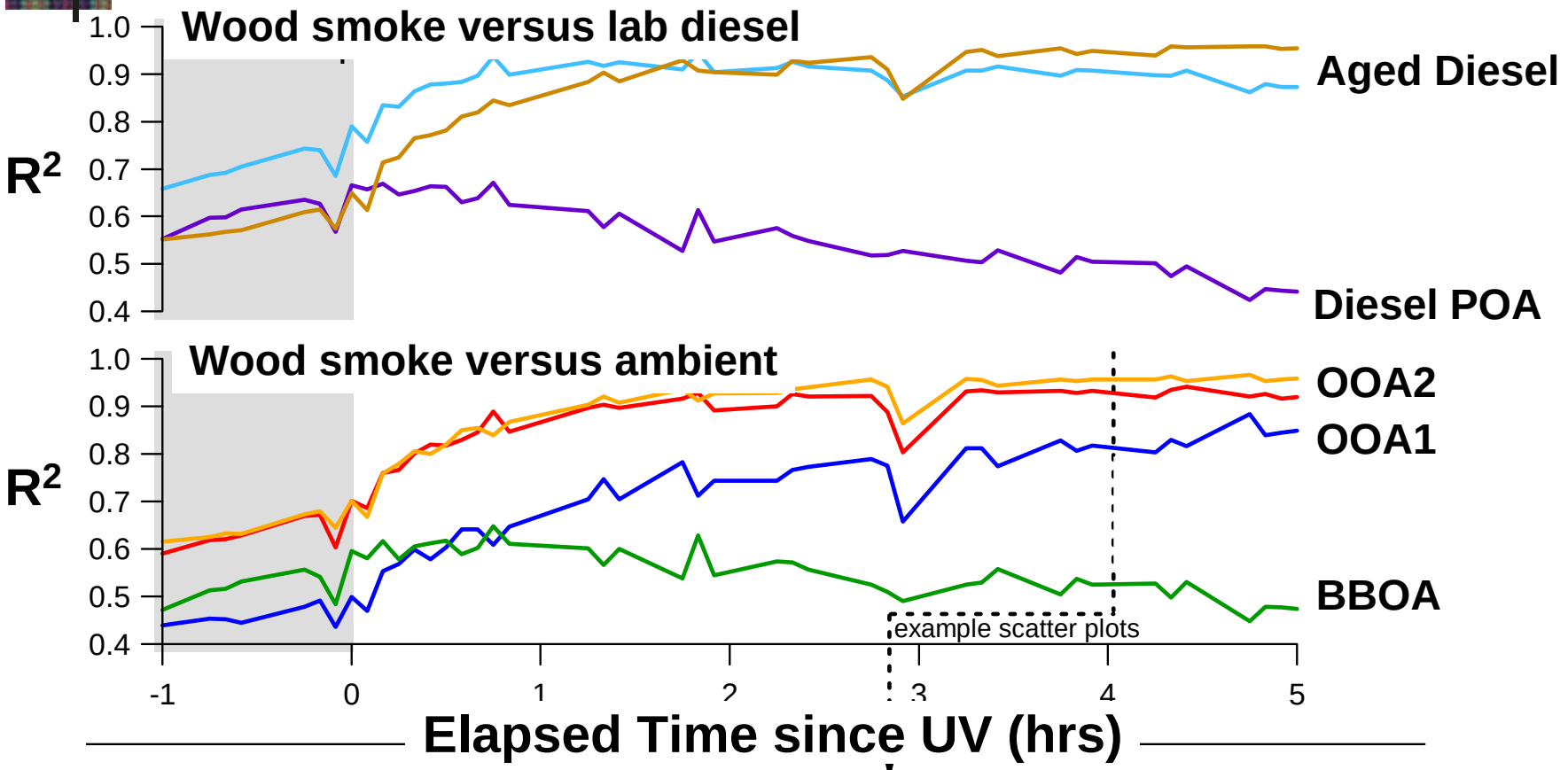
(Grieshop et al. ACP 2009)

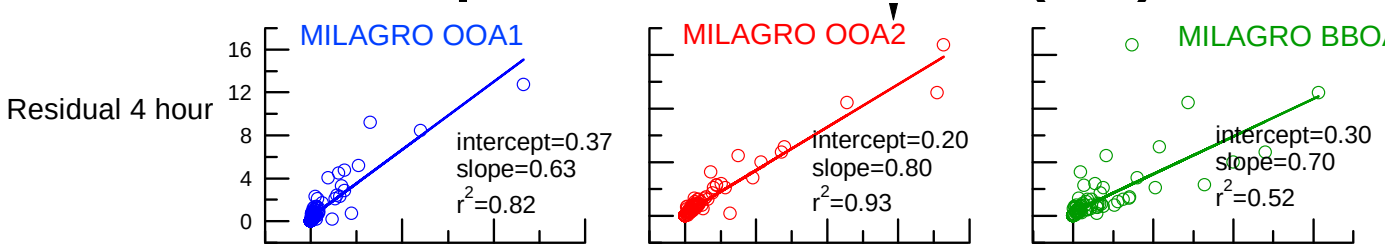
Data from multiple wood smoke aging experiments



(Grieshop et al. ACP 2009)

Similarity of Aged Organic MS

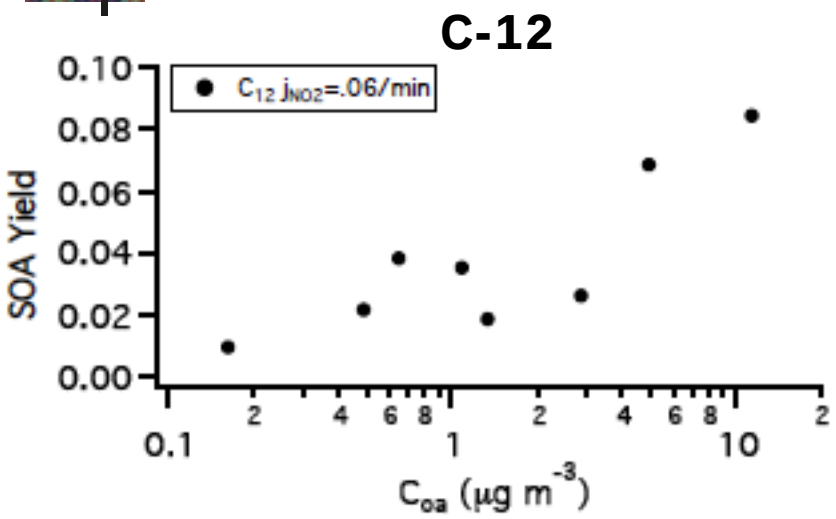


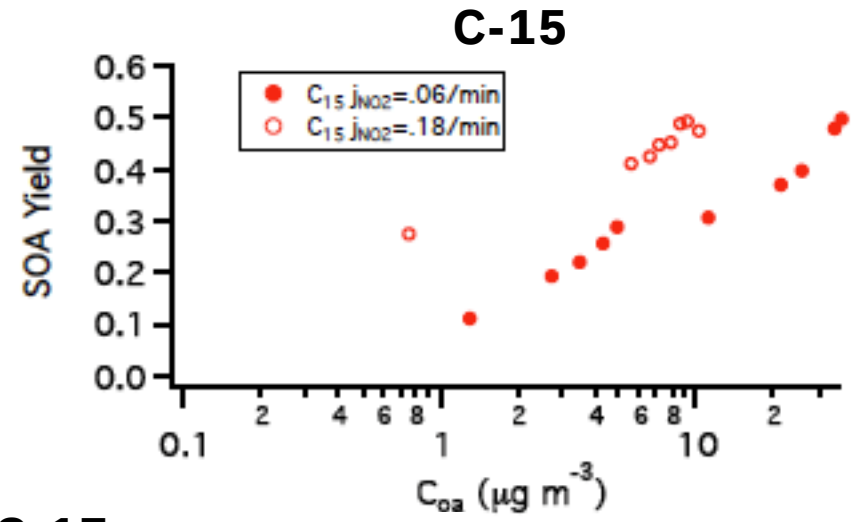


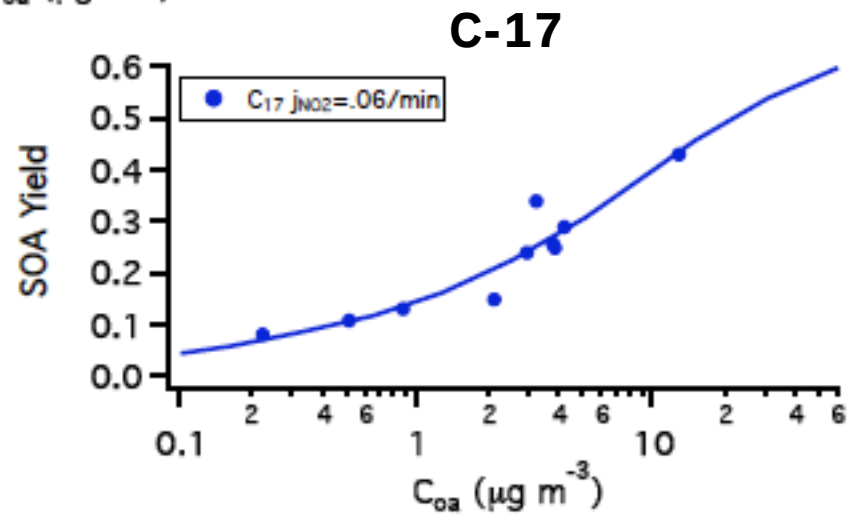
(Grieshop et al. ACP 2009)

Ambient Factors courtesy of J. Jimenez CU Boulder

n-alkane high NOx SOA yields

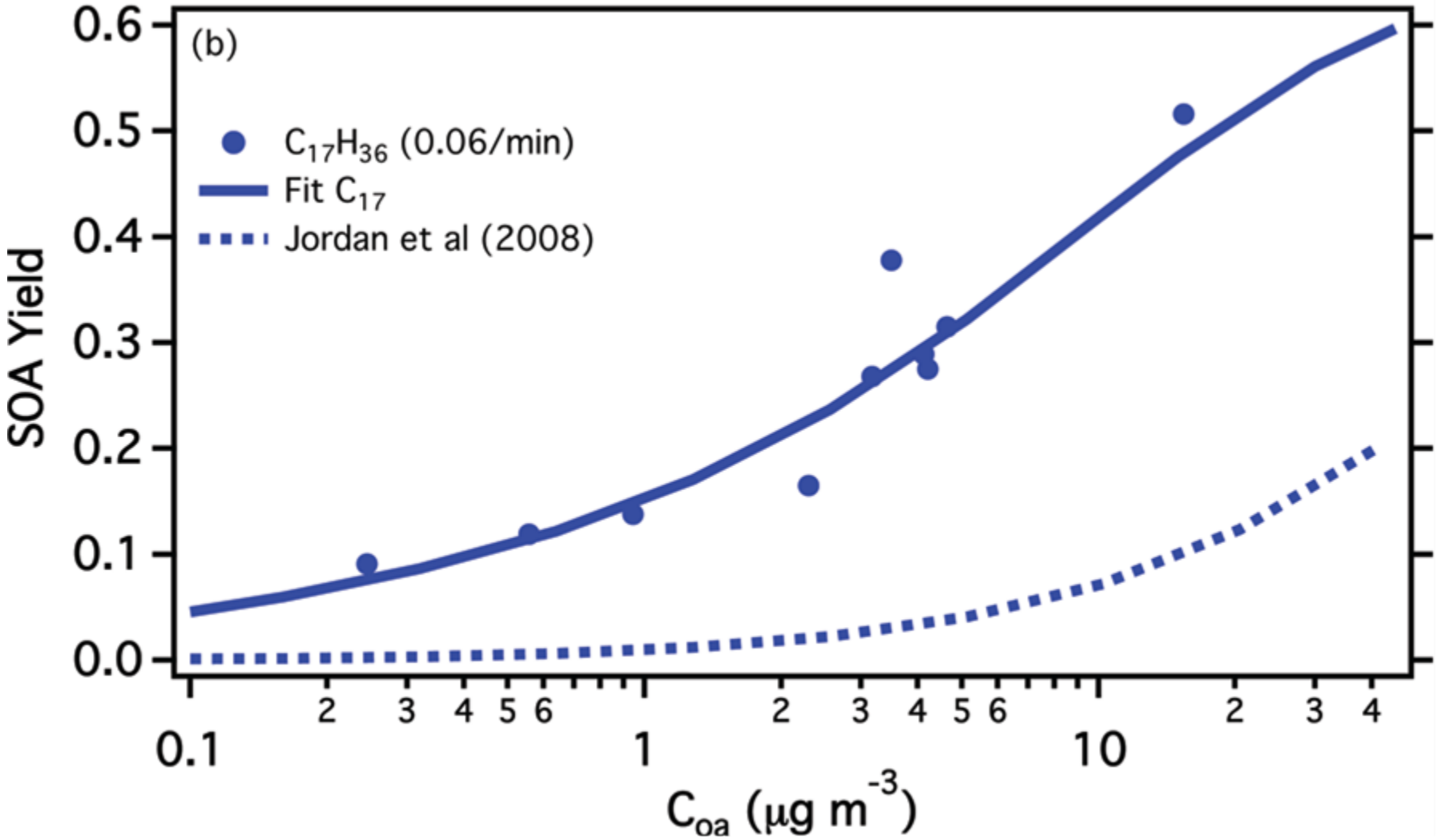




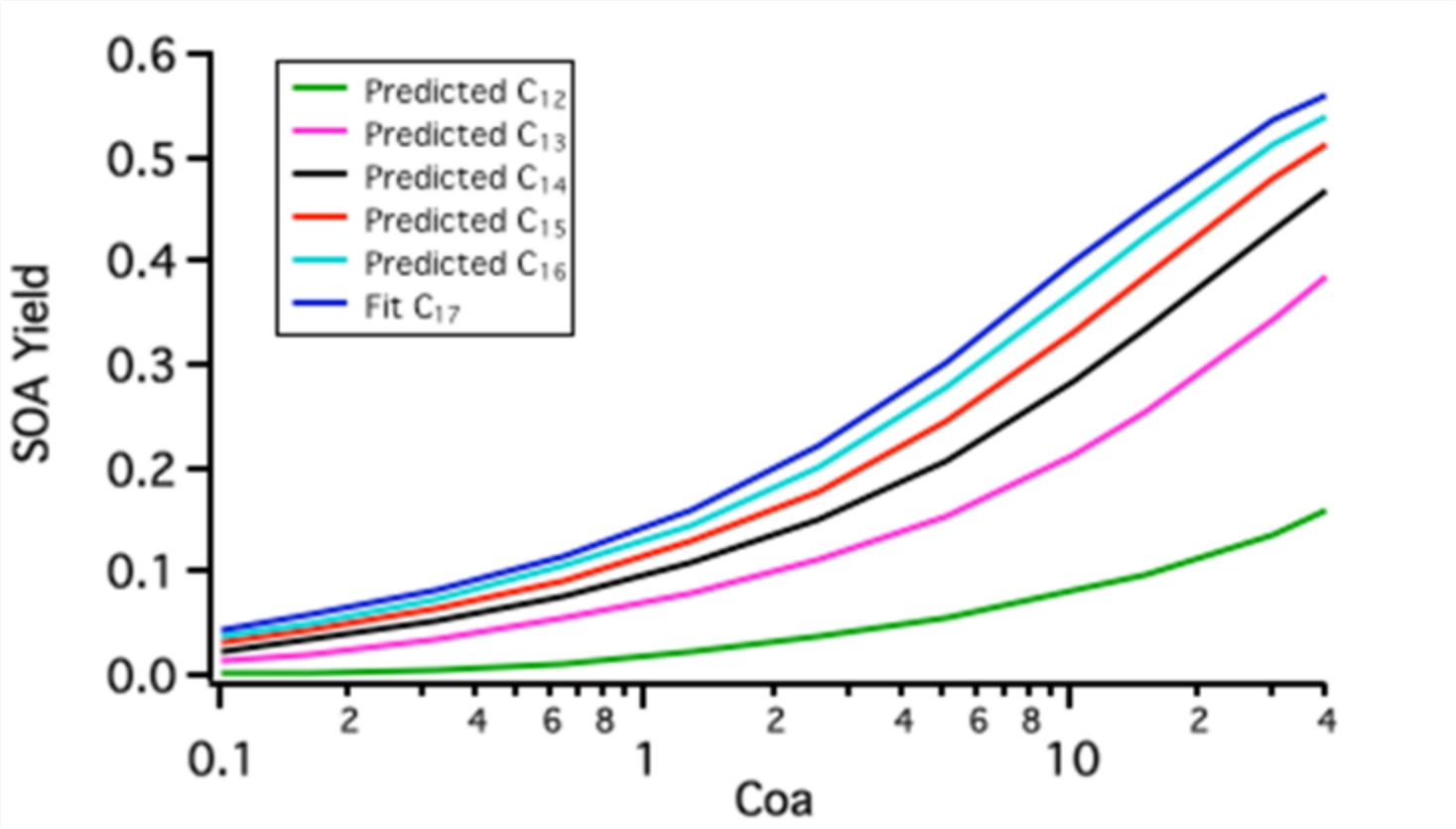


(Presto et al. EST 2010)

Yields are “high”

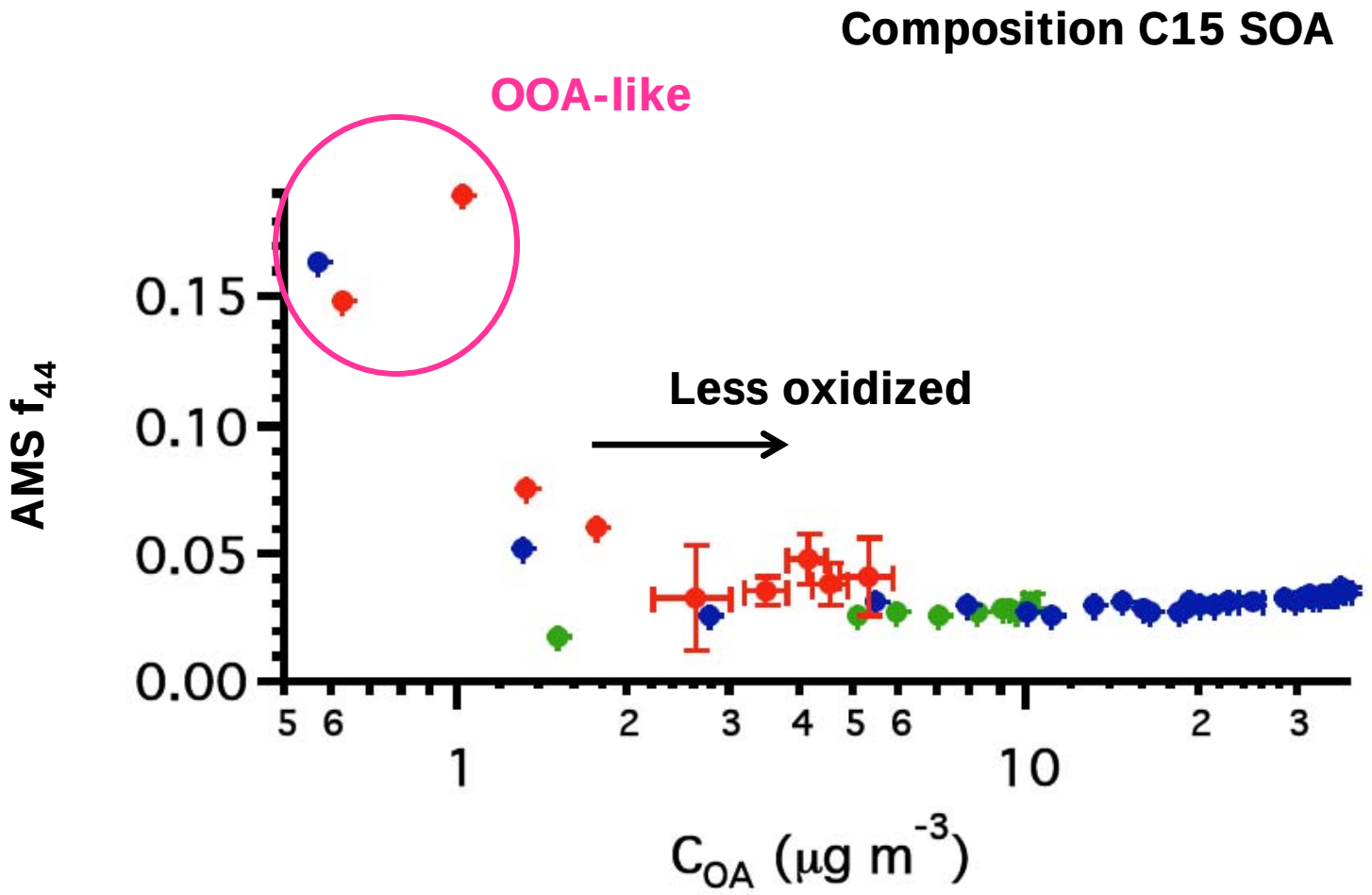


Parameterizing yields based on C*



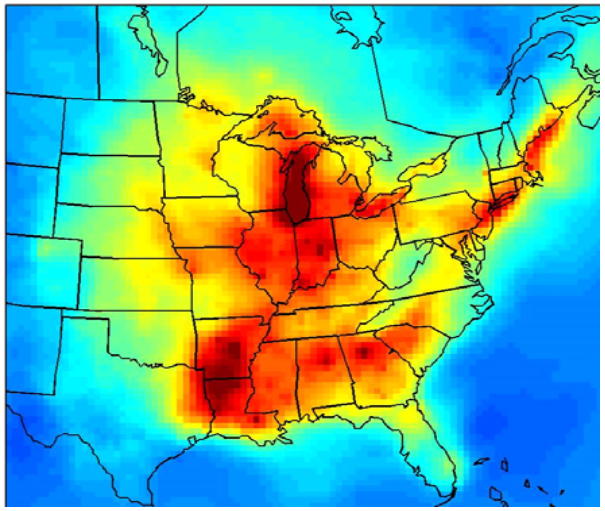
(Presto et al. EST 2010)

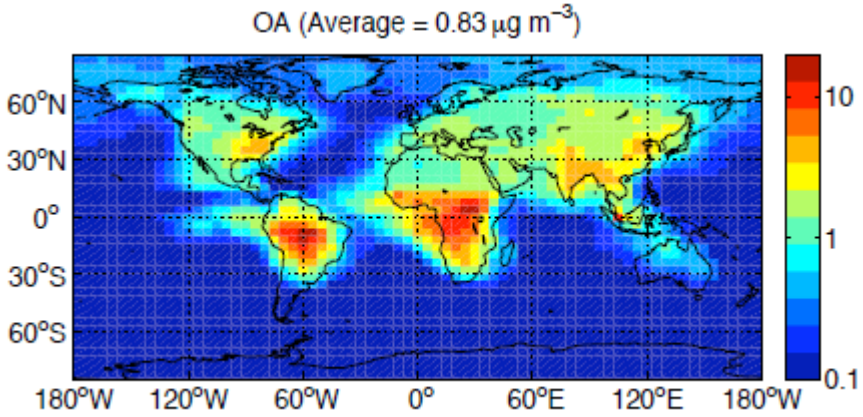
SOA from IVOCs can be highly oxygenated



(Presto et al. EST 2009 & 2010)

Objective 3. Regional and global modeling to quantify organic aerosol



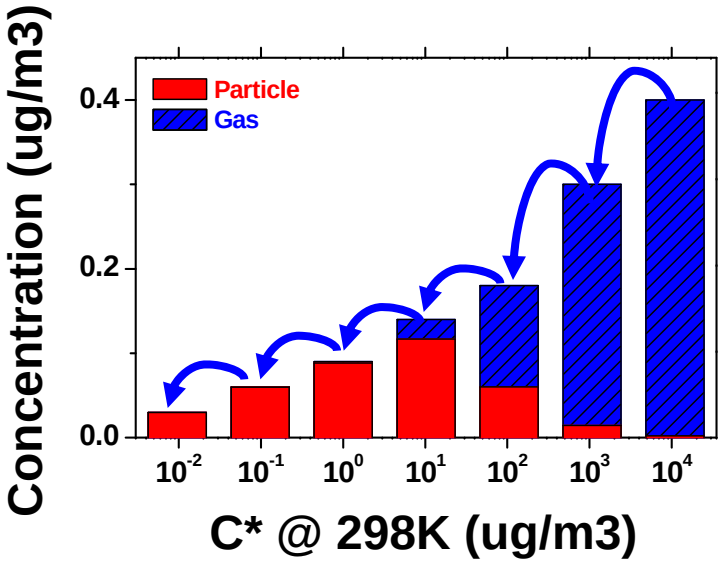


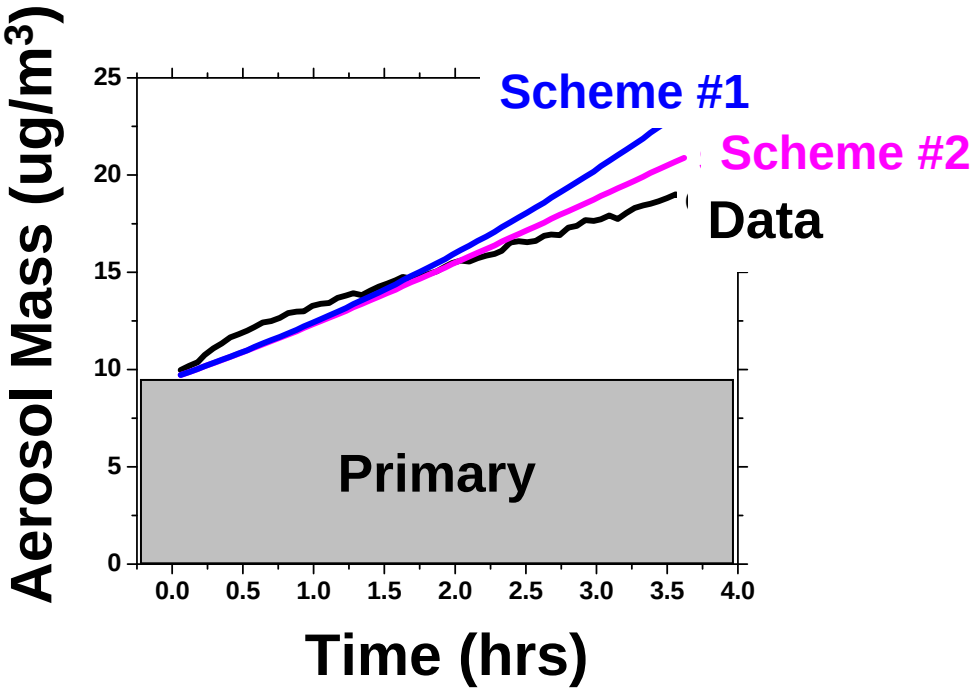
- Modifications
  - Update inventory
  - Added species
  - Aging
- Critical inputs
  - Volatility distribution
  - Aging mechanism
  - IVOC emissions
  - Activity coefficients

Aging mechanism

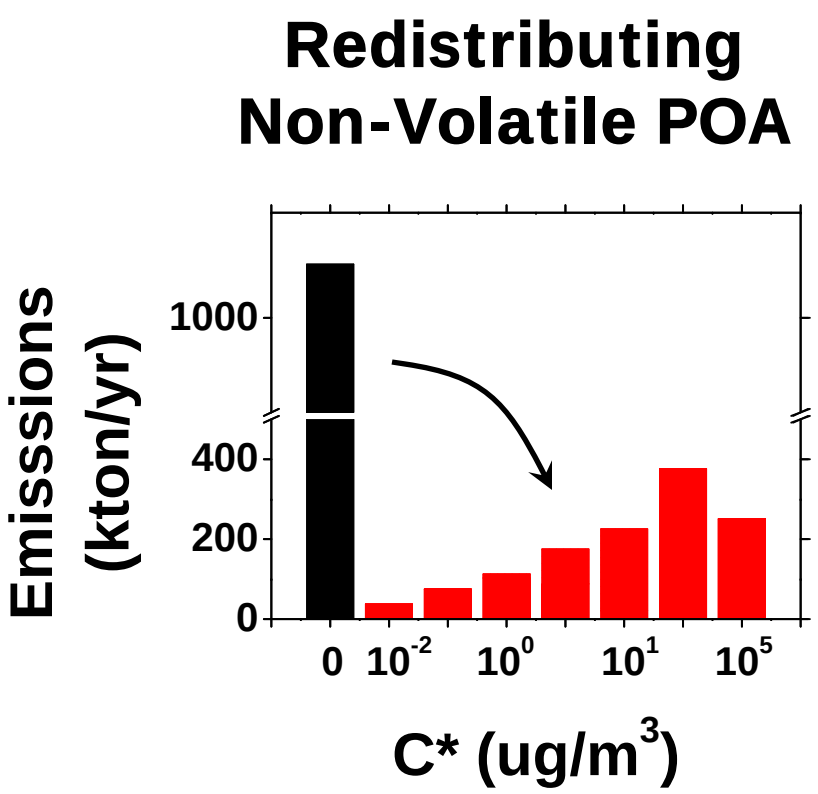
Aging Scheme

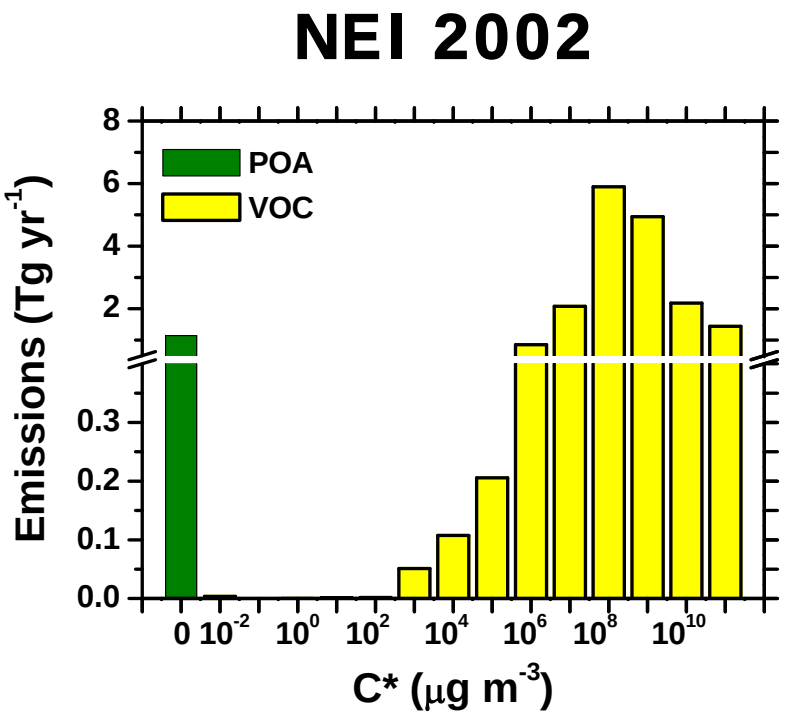
- **Gas-phase Reactions w / OH**
- **k_{OH} = 4 x 10^{-11} cm^3 (molec s)$^{-1}$**

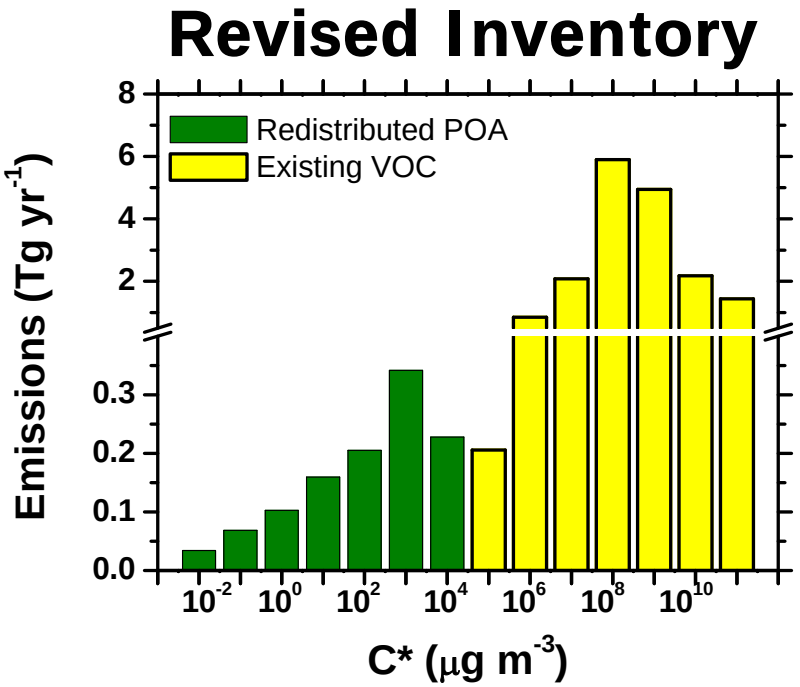




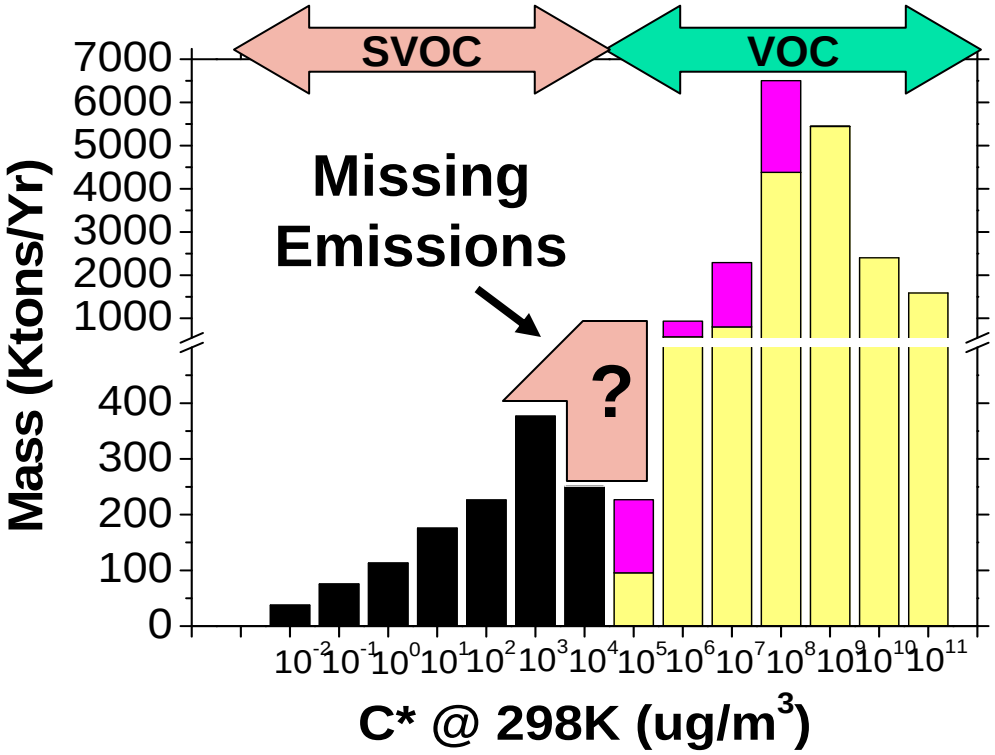
Updating Emission Inventories

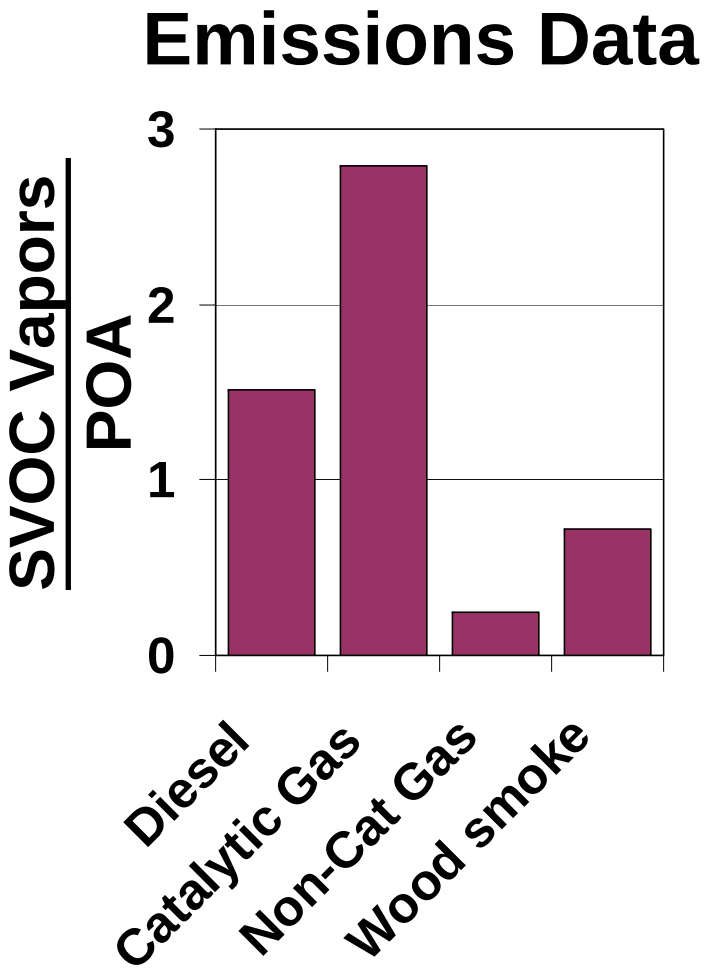






Are there missing emissions?





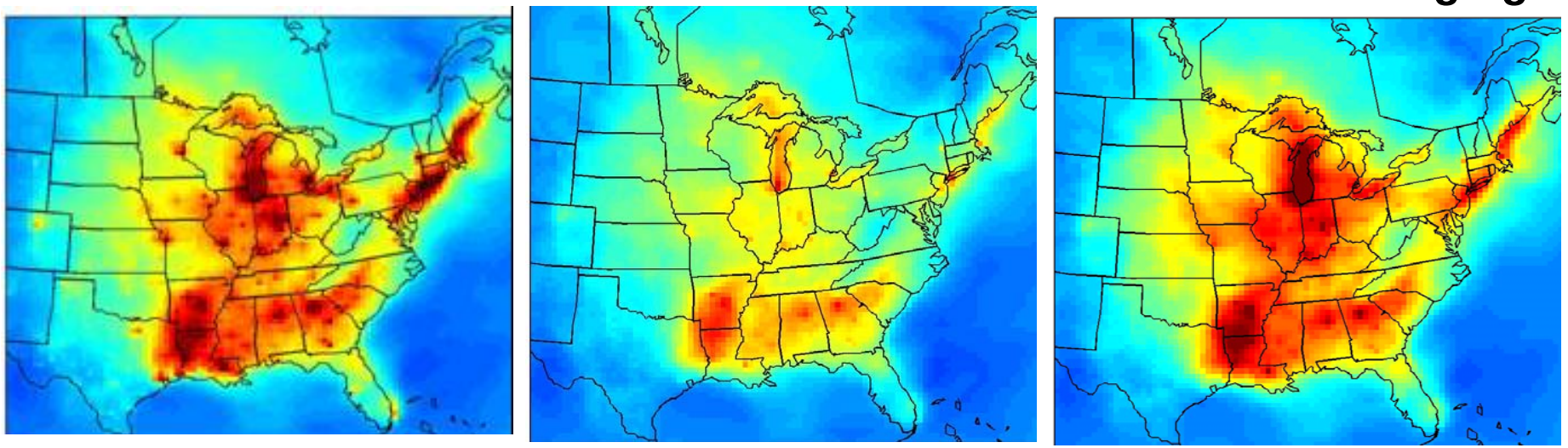
(Schauer et al. EST 99, 00, 02)

Summertime OA Predictions

Traditional Non-volatile POA

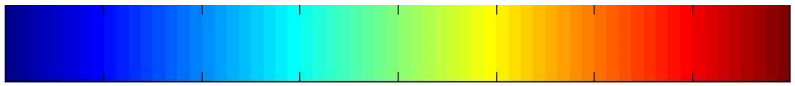
Semivolatile POA

Revised Semivolatile + Aging



July 2001

OA
μg m^{-3}



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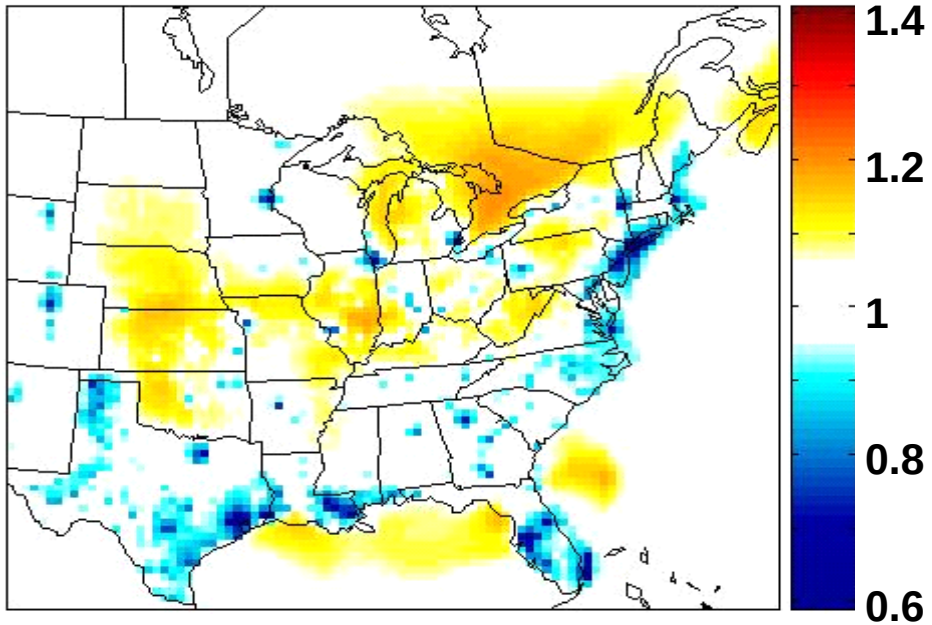
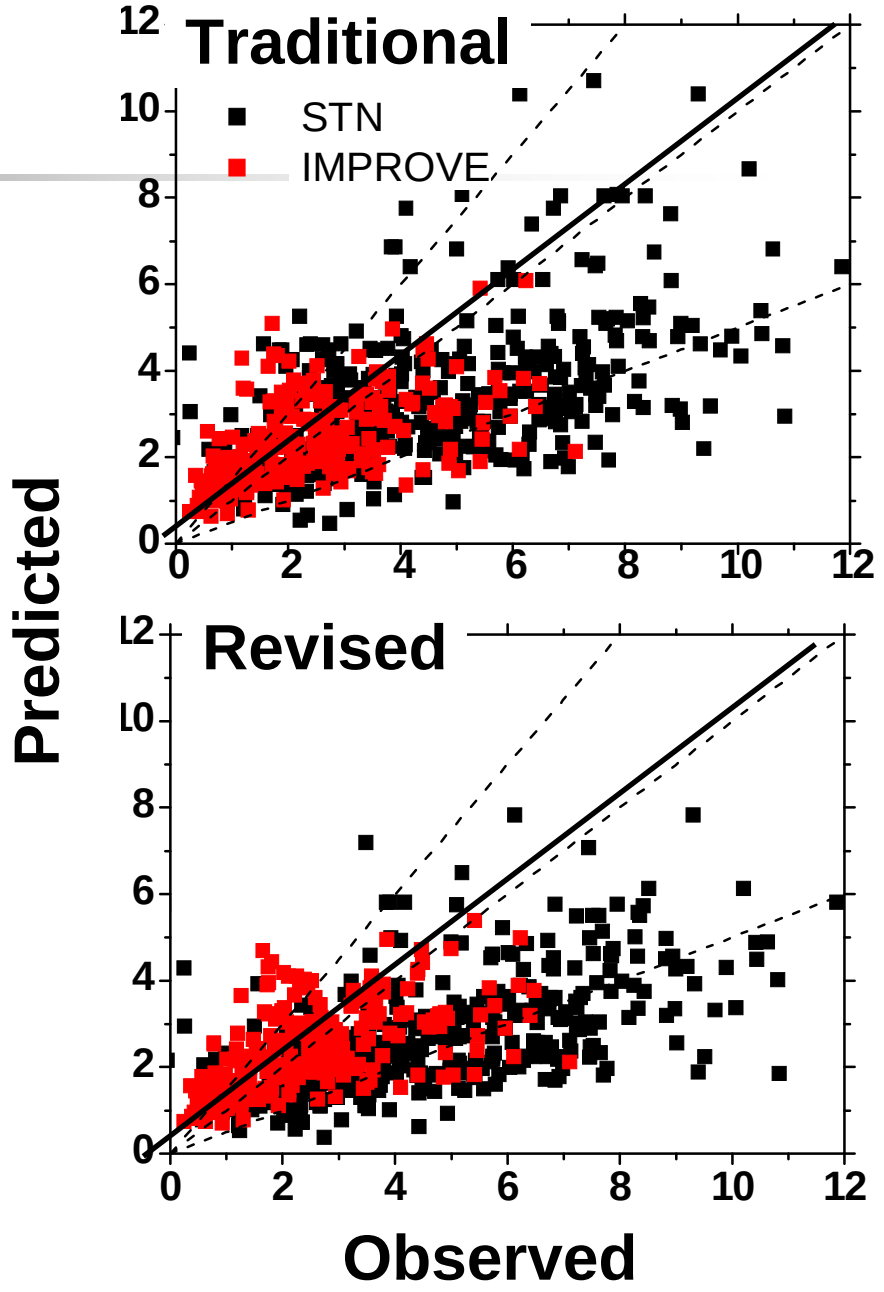
Shrivastava et al. JGR 2008

Carnegie Mellon

July 2001 OA

Ratio of Revised-to-Traditional Predicted OA levels





Shrivastava et al. JGR 2008

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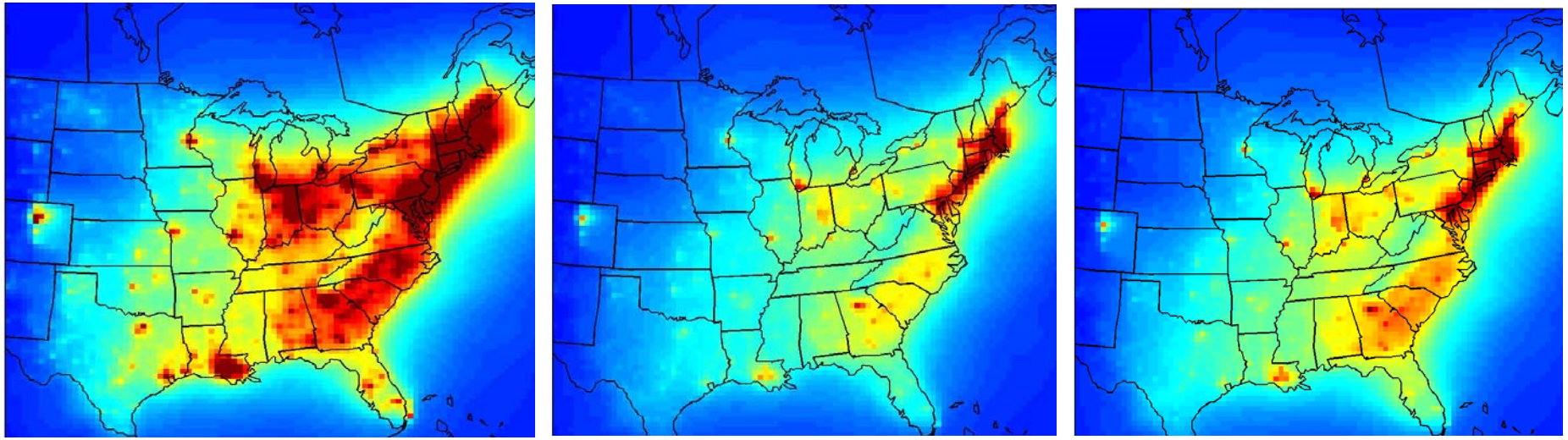
Wintertime OA Predictions

Traditional Non-volatile POA

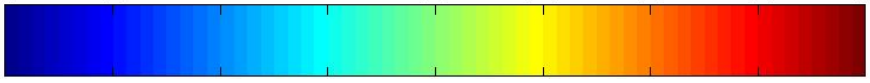
Semivolatile POA

Revised Semivolatile + Aging



January 2002

OA
μg m^{-3}



Shrivastava et al. JGR 2008

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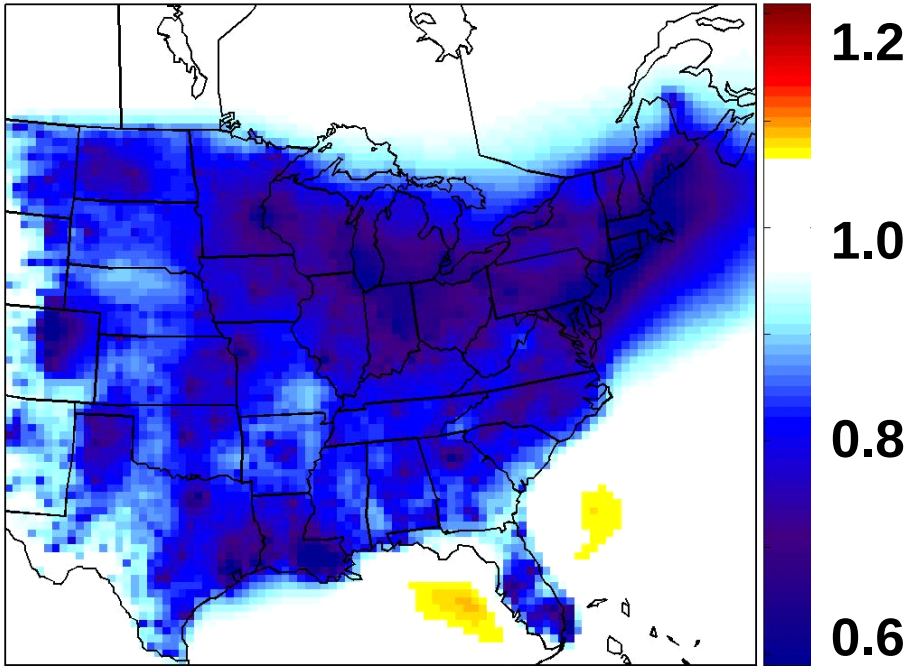
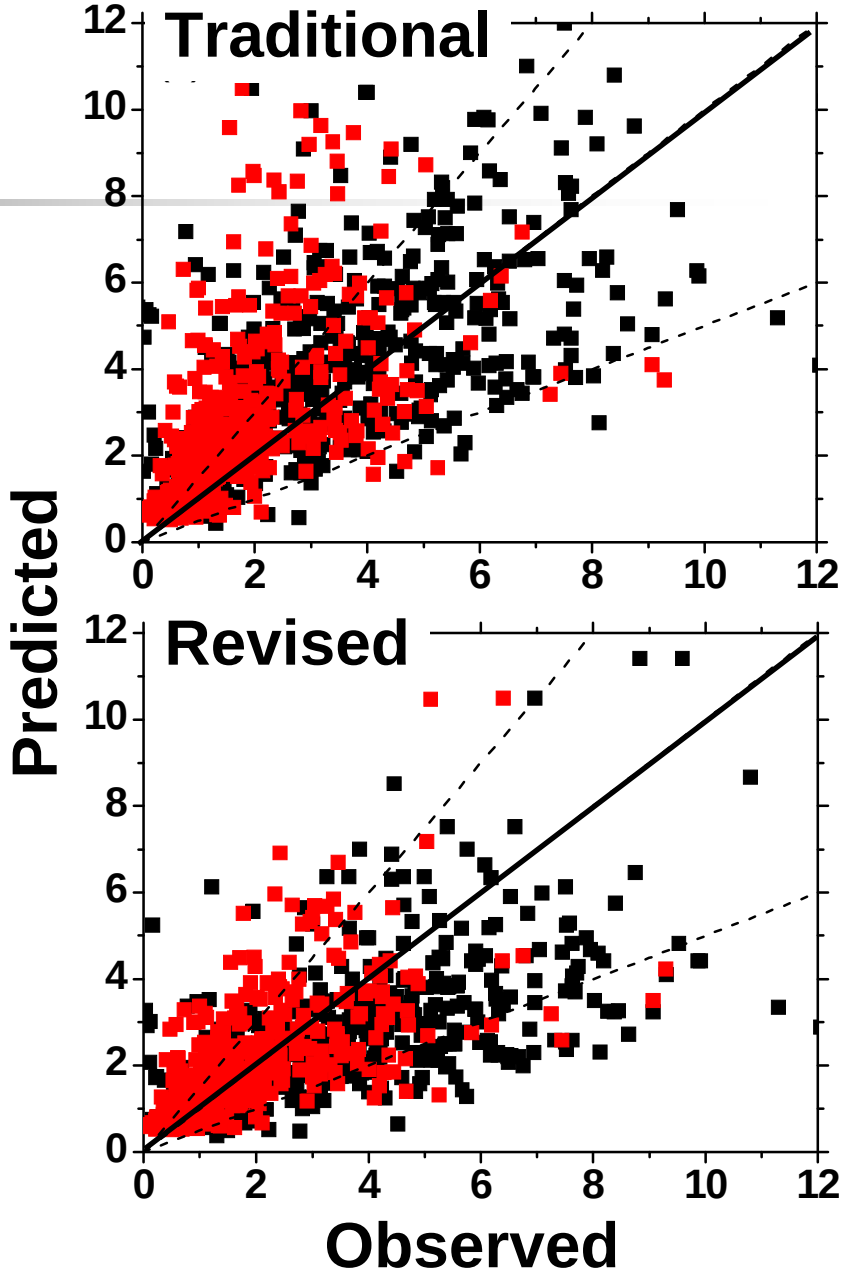
January 2002

Ratio of Revised-to-Traditional Predicted OA levels





Shrivastava et al. JGR 2008

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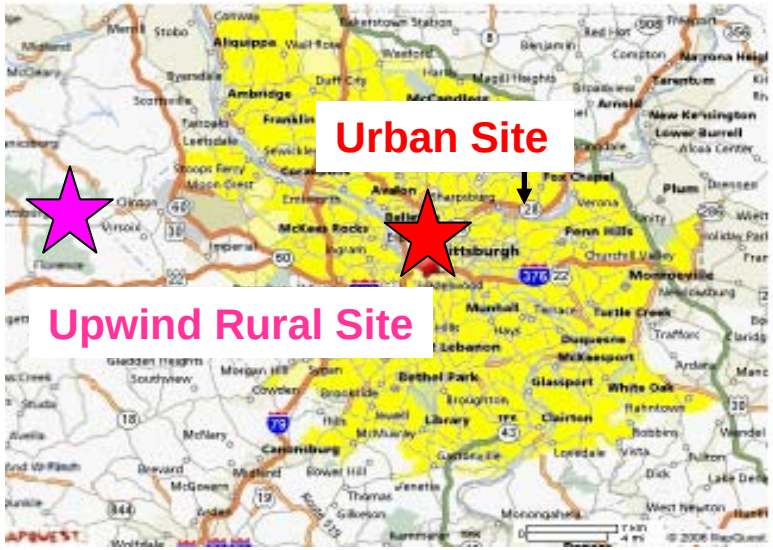
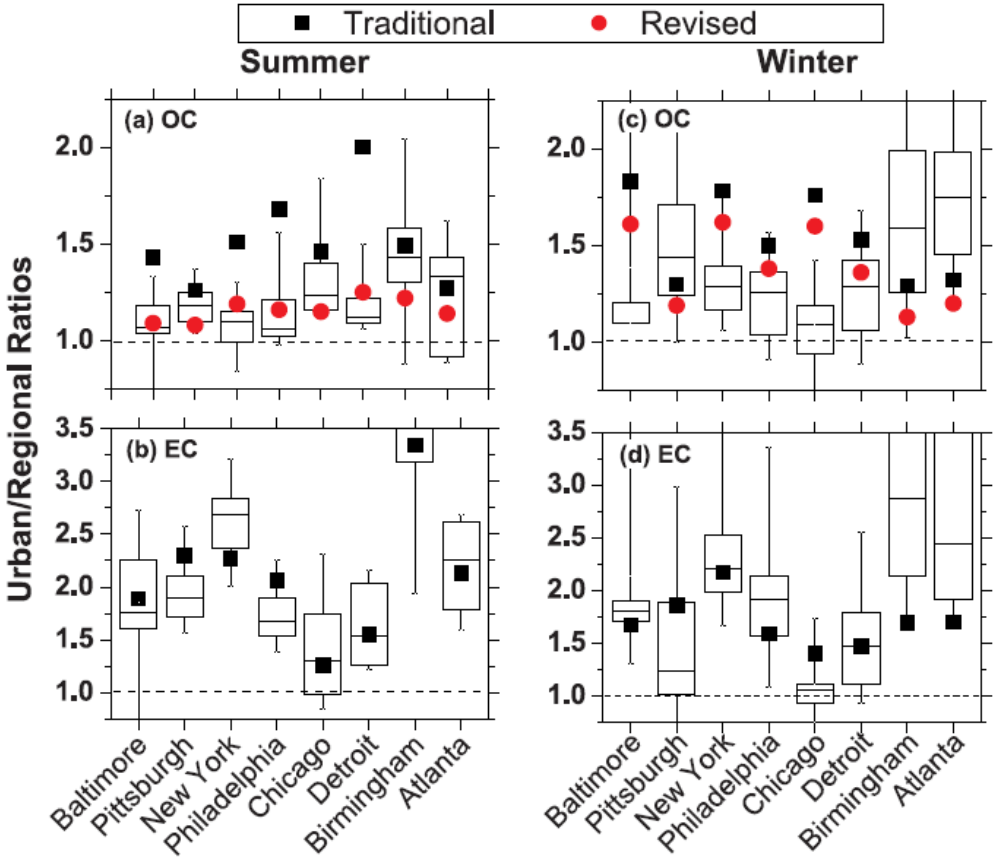
Revised model predicts a more regional aerosol





Shrivastava et al. JGR 2008

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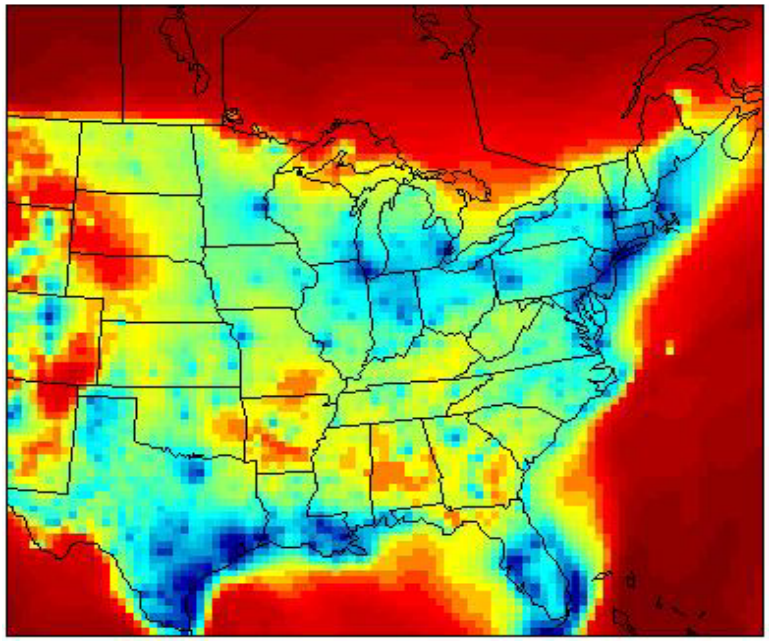
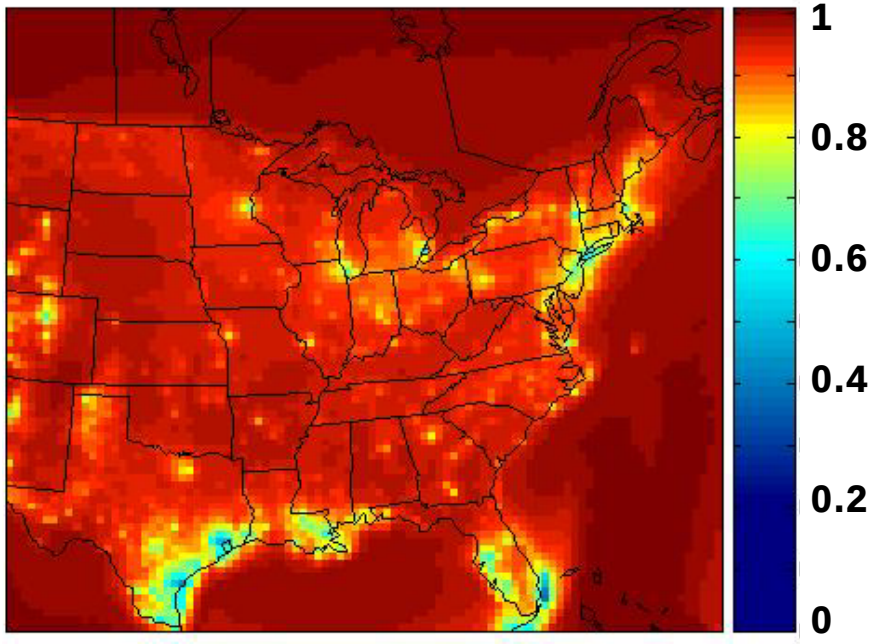
Oxygenated Organics Dominate in Summer

Traditional Model
Non-Volatile POA



Traditional SOA
Total OA

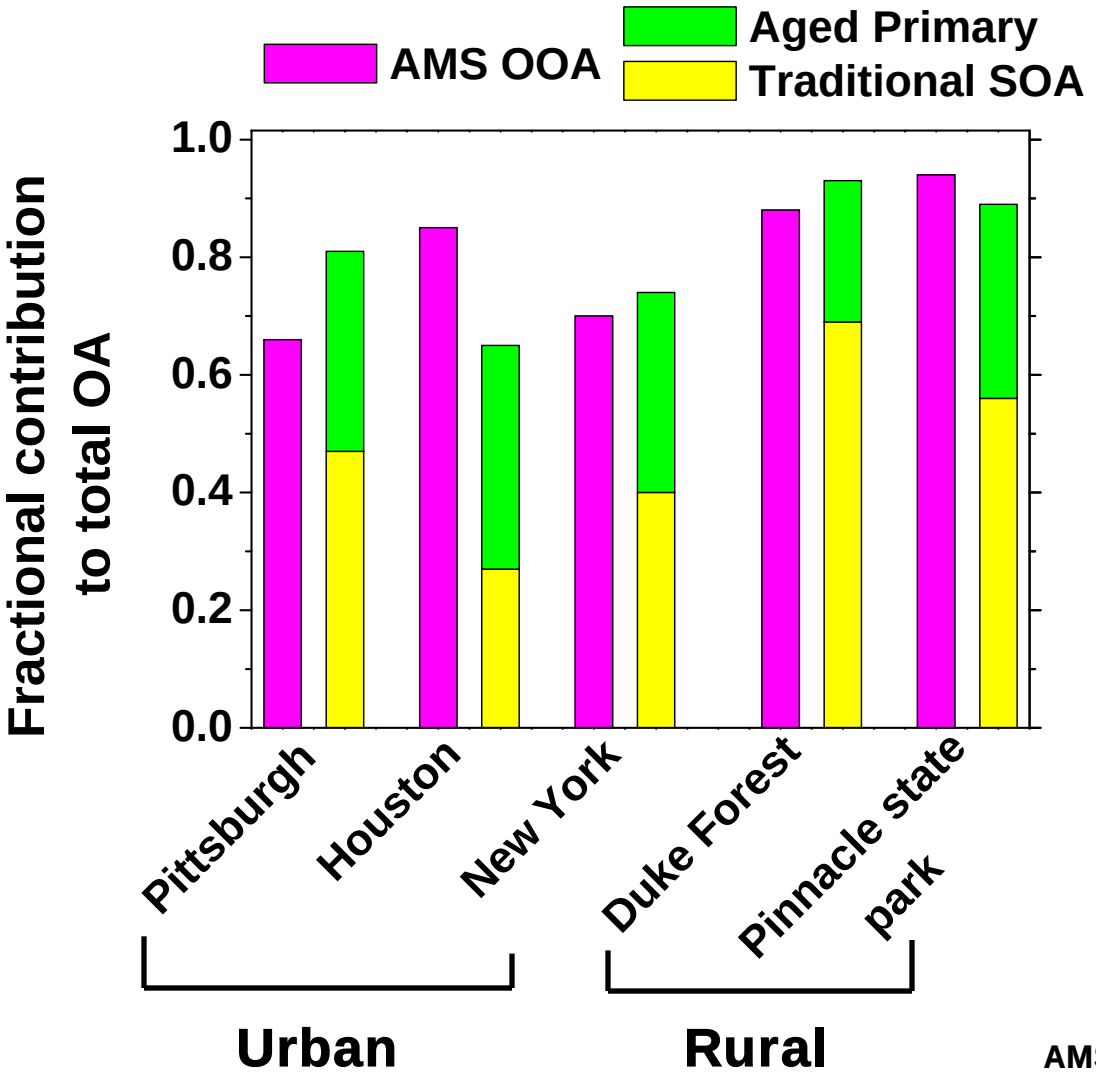
Revised model
Semivolatile + Aging



Traditional SOA + Aged Primary
Total OA

July 2001

Revised Model and AMS OOA



AMS data Zhang et al. GRL 2007

Conclusions

- Primary emissions are semivolatile
- Aging of emissions create substantial SOA
- Accounting for aging and partitioning improves predictions of CTMs
- Important implications for developing control strategies

Journal Papers

- A.L. Robinson, A.P. Grieshop, N.M. Donahue, S.W. Hunt “Updating our conceptual model for fine particle mass emissions from combustion systems,” Journal of the Air and Waste Management Association, in press.
- A.A. Presto, M.A. Miracolo, N.M. Donahue, A.L. Robinson “Secondary Organic Aerosol Formation from High-NO_x Photo-Oxidation of Low-Volatility Precursors: n-Alkanes” Environmental Science & Technology, 44 (6), 2029–2034, 2010.
- M.A. Miracolo, A.A. Presto, A.T. Lambe, C.J. Hennigan, N.M. Donahue, J.H. Kroll, D.R. Worsnop, A.L. Robinson “Photo-Oxidation of Low-Volatility Organics found in Motor Vehicle Emissions: Production and Chemical Evolution of Organic Aerosol Mass,” Environmental Science & Technology, 44(6), 2029–2034, 2010.
- J.L. Jimenez, M.R. Canagaratna, N.M. Donahue, A.S.H. Prevot, Q. Zhang, J.H. Kroll, P.F. DeCarlo, J.D. Allan, H. Coe, N.L. Ng, A.C. Aiken, K.D. Docherty, I.M. Ulbrich, A.P. Grieshop, A.L. Robinson, J. Duplissy, J. D. Smith, K.R. Wilson, V.A. Lanz, C. Hueglin, Y.L. Sun, A. Laaksonen, T. Raatikainen, J. Rautiainen, P. Vaattovaara, M. Ehn, M. Kulmala, J.M. Tomlinson, D.R. Collins, M.J. Cubison, E.J. Dunlea, J.A. Huffman, T.B. Onasch, M.R. Alfarra, P.I. Williams, K. Bower, Y. Kondo, J. Schneider, F. Drewnick, S. Borrmann, S. Weimer, K. Demerjian, D. Salcedo, L. Cottrell, R. Griffin, A. Takami, T. Miyoshi, S. Hatakeyama, A. Shimono, J.Y Sun, Y.M. Zhang, K. Dzepina, J.R. Kimmel, D. Sueper, J.T. Jayne, S.C. Herndon, A.M. Trimborn, L.R. Williams, E.C. Wood, C.E. Kolb, U. Baltensperger, and D.R. Worsnop, “Evolution of Organic Aerosols in the Atmosphere,” Science, 326, 1525-1529, 2009.

Journal Papers

- A. Asa-Awuku, M. A. Miracolo, J. H. Kroll, A. L. Robinson, N. M. Donahue "Mixing and phase partitioning of primary and secondary organic aerosols," Geophysical Research Letters, 36, L15827, doi:10.1029/2009GL039301, 2009.
- A.P. Grieshop, M.A. Miracolo, N.M. Donahue, and A.L. Robinson, "Constraining the Volatility Distribution and Gas-Particle Partitioning of Combustion Aerosols Using Isothermal Dilution and Thermodenuder Measurements," Environmental Science & Technology, 43(13), 4750-4756.
- A.A. Presto, M.A. Miracolo, J.H. Kroll, D.R. Worsnop, A.L. Robinson, and N.M. Donahue, "Intermediate-Volatility Organic Compounds: A Potential Source of Ambient Oxidized Organic Aerosol," Environmental Science & Technology, 43(13), 4744–4749.
- A.P. Grieshop, N.M. Donahue, and A.L. Robinson, "Laboratory Investigation of Photochemical Oxidation of Organic Aerosol from Wood Fires 2: Analysis of Aerosol Mass Spectrometer Data," Atmospheric Chemistry and Physics, 9, 2227-2240, 2009.
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