Atmospheric Processing of Organic Particulate Matter: Formation, Properties, Long-Range Transport, and Removal

Neil M. Donahue, Spyros N. Pandis, Allen L. Robinson
Peter J. Adams, Cliff I. Davidson

Carnegie Mellon University
Center for Atmospheric Particle Studies

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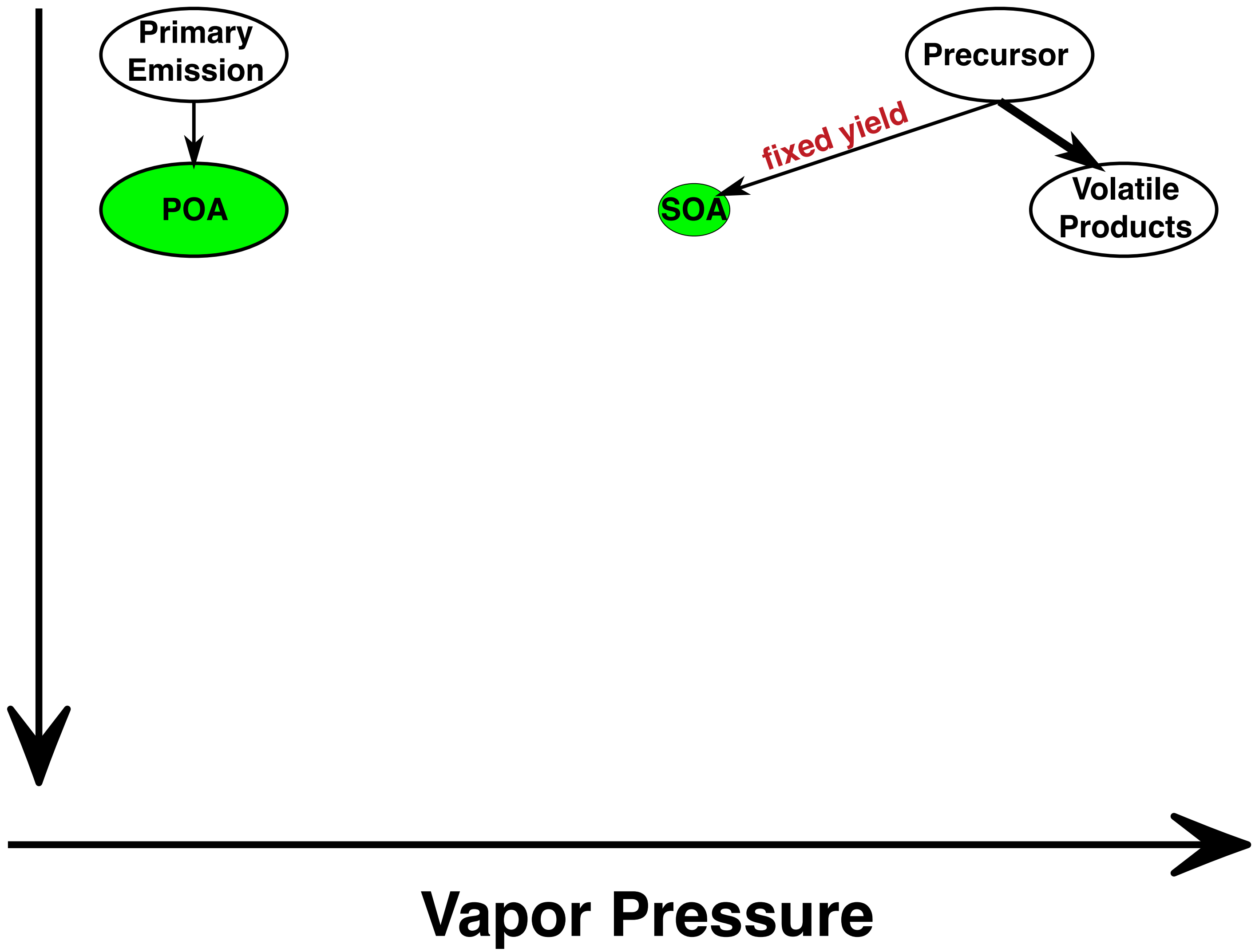
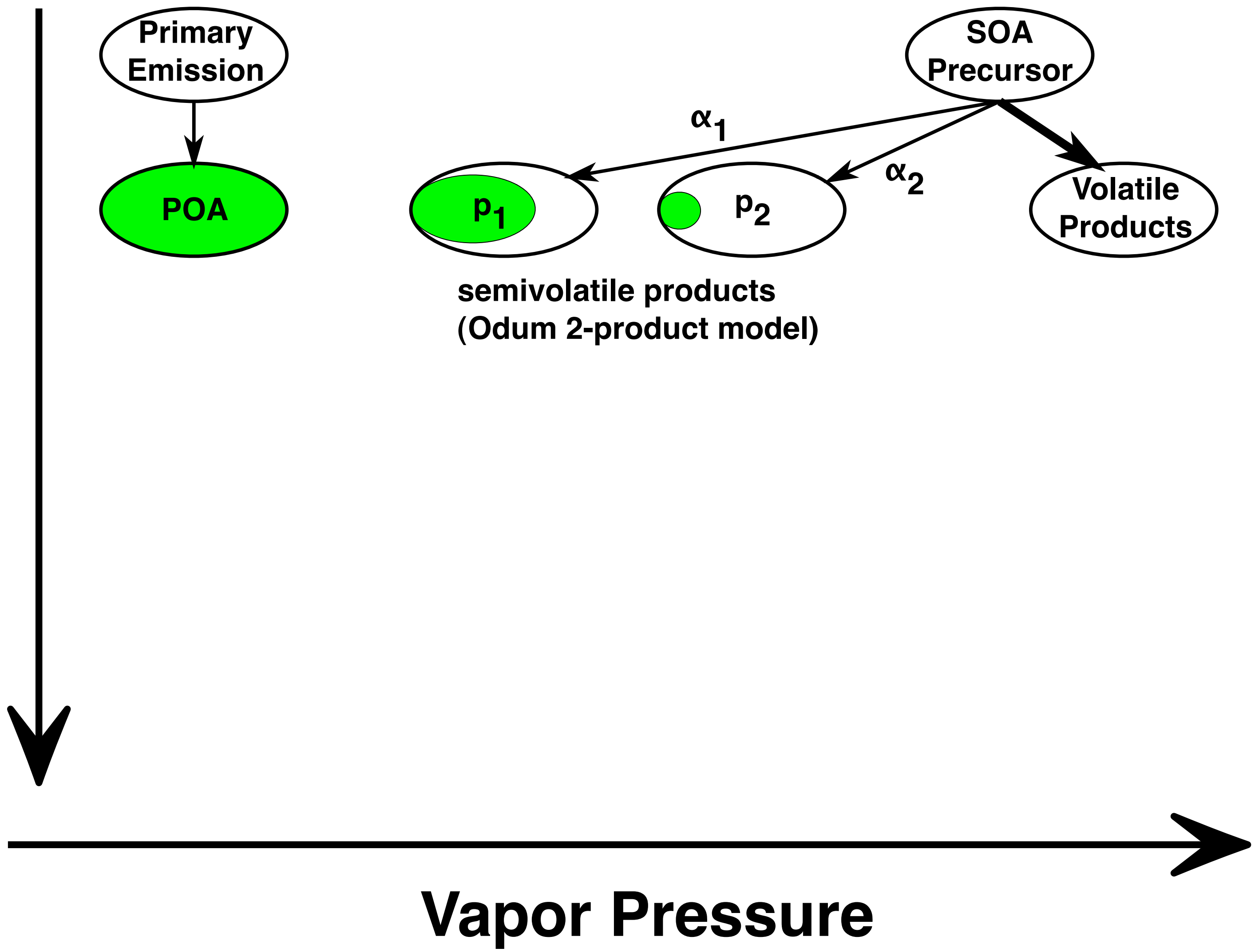
The Center for Atmospheric Particle Studies

Organic Aerosol



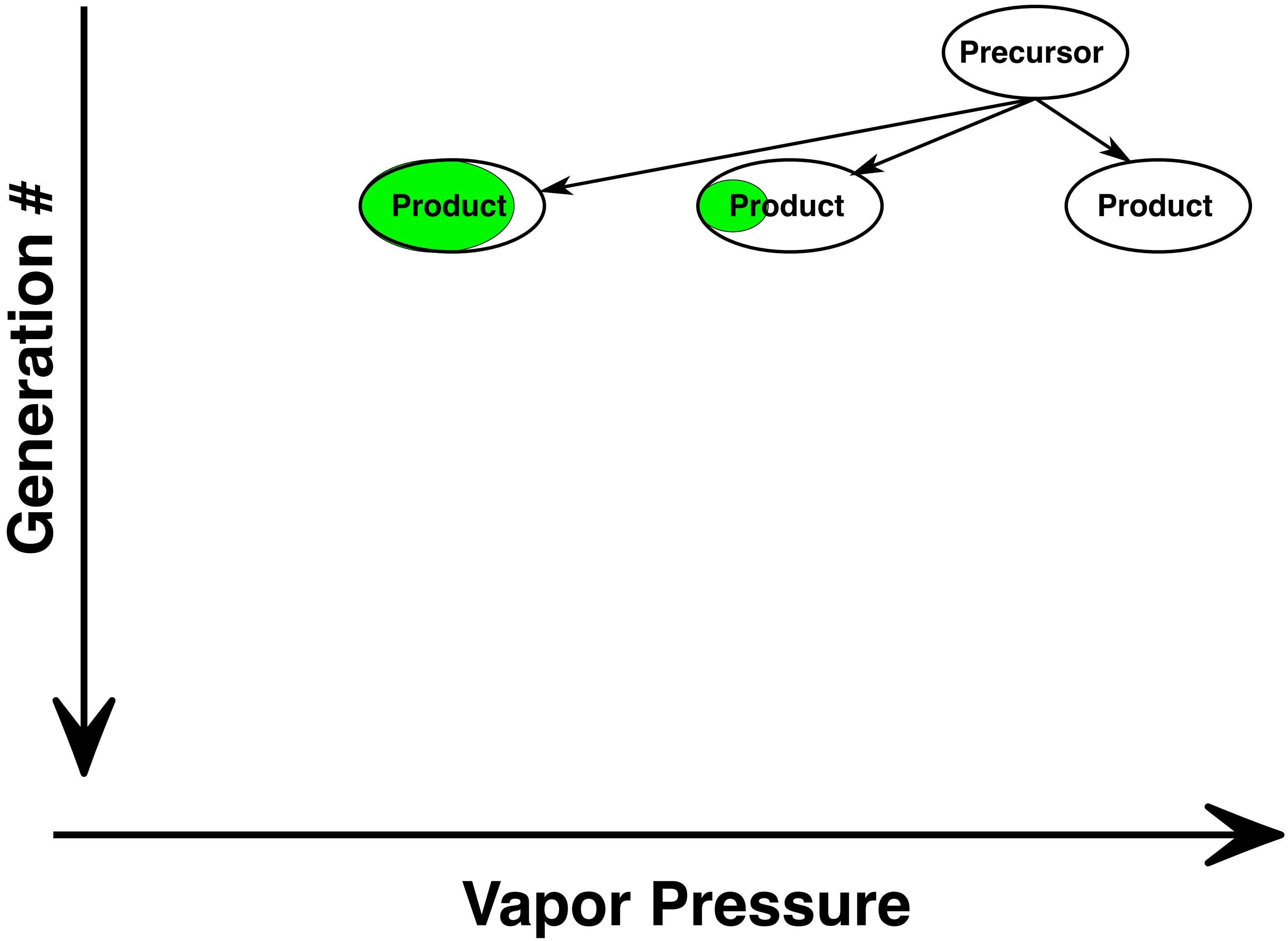
Not quite state of the art, common in models...

Organic Aerosol

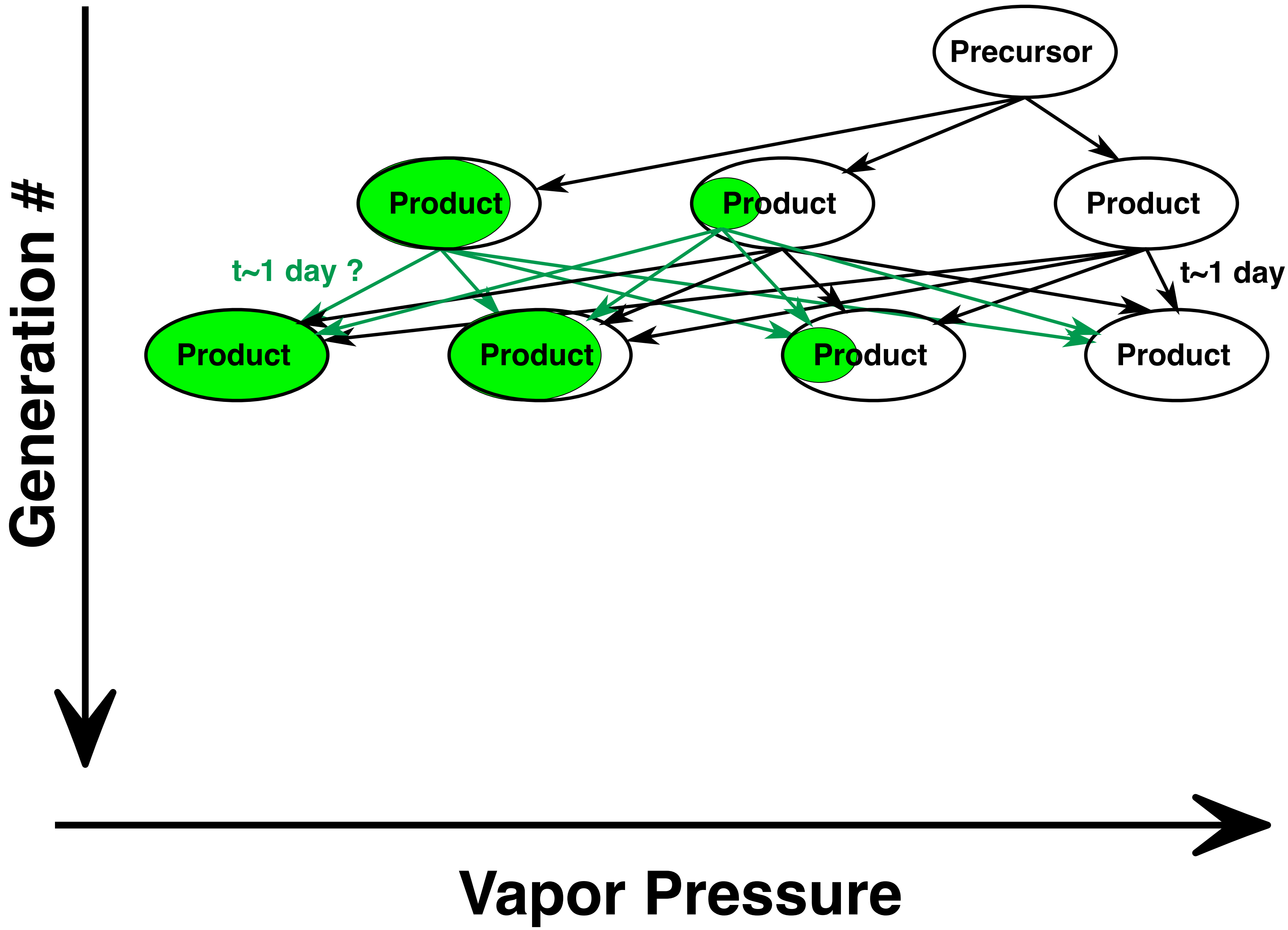


State of the art, in some models...

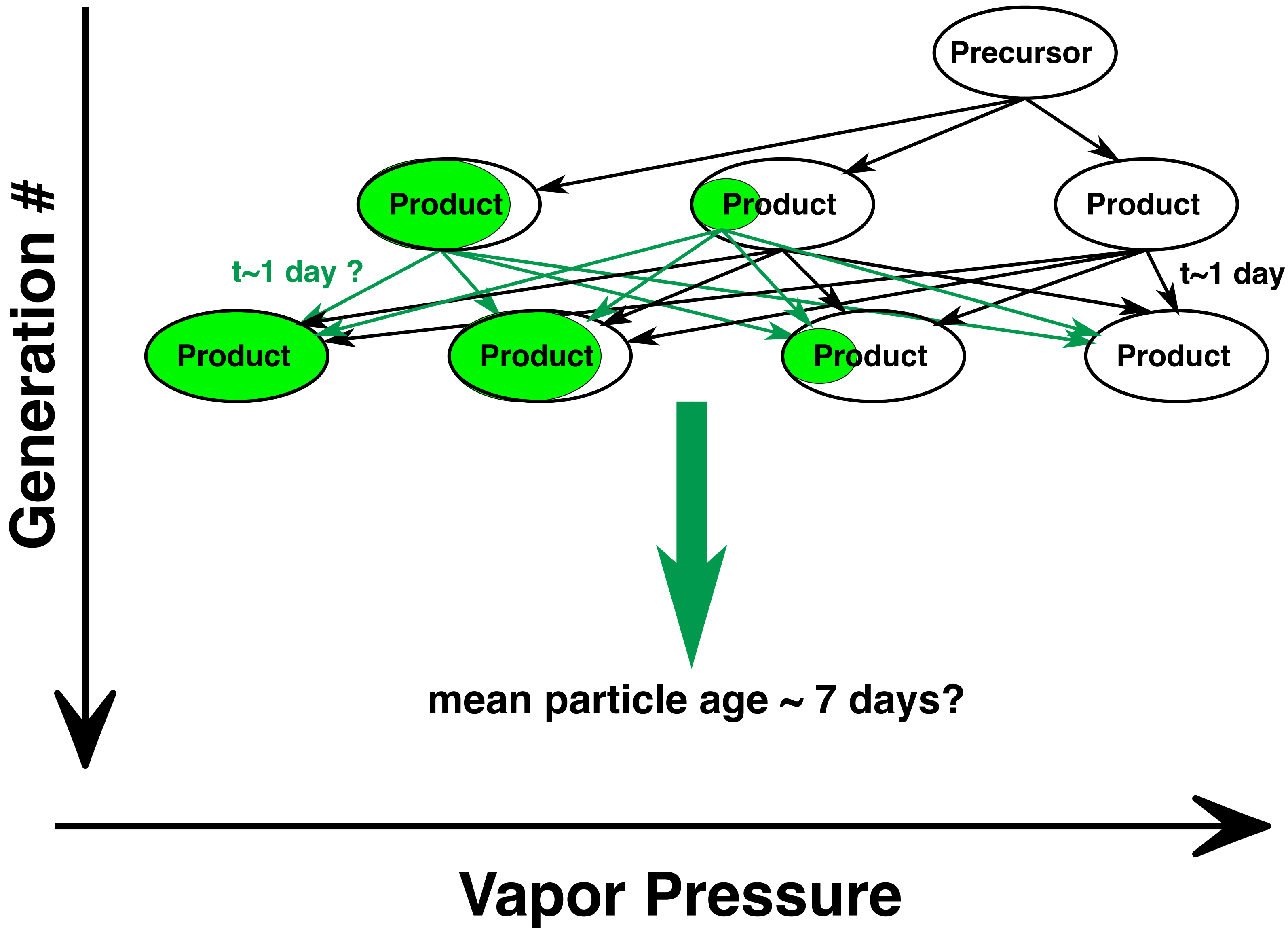
Organic Emissions Processing



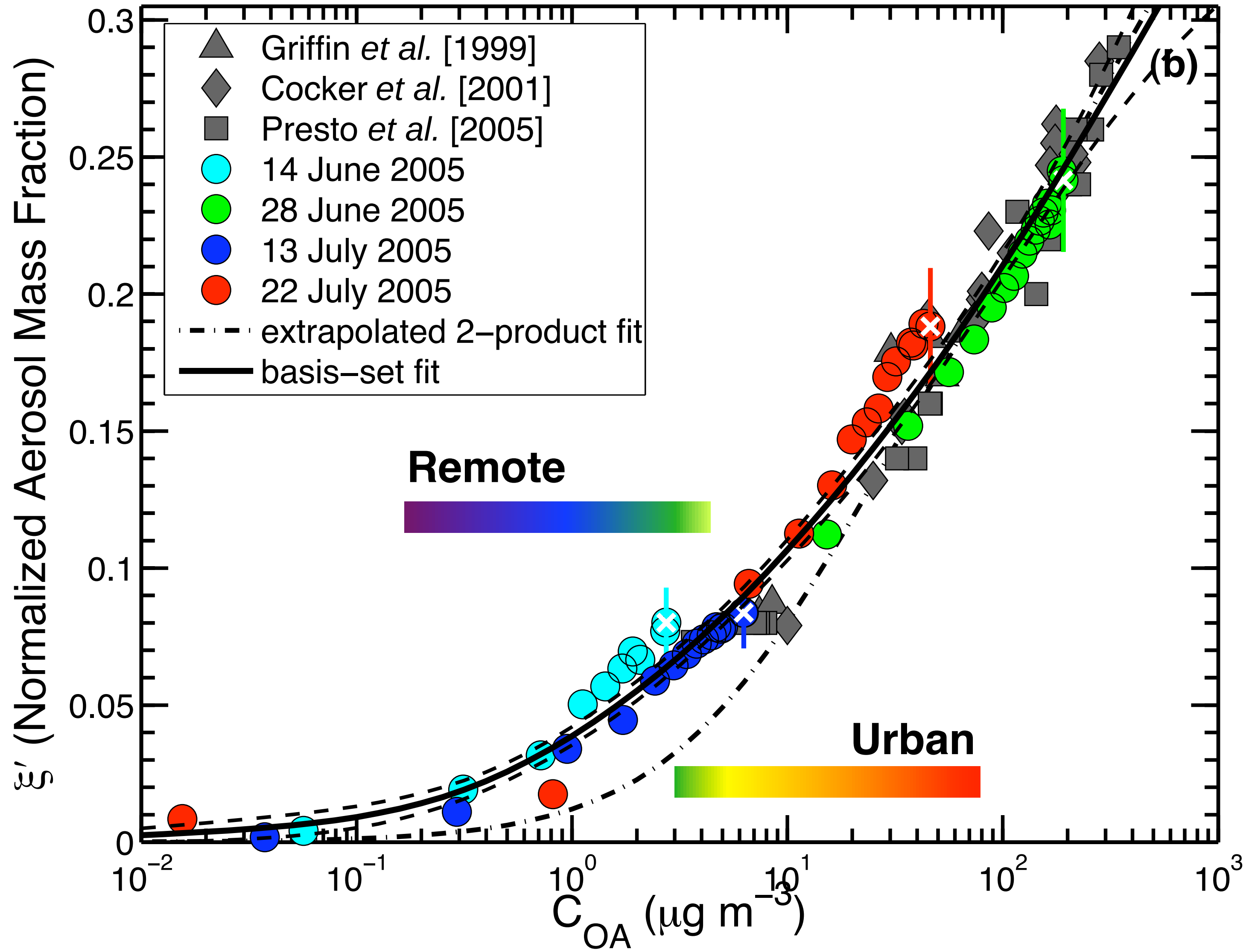
Continued Processing



How Far Does it Go??



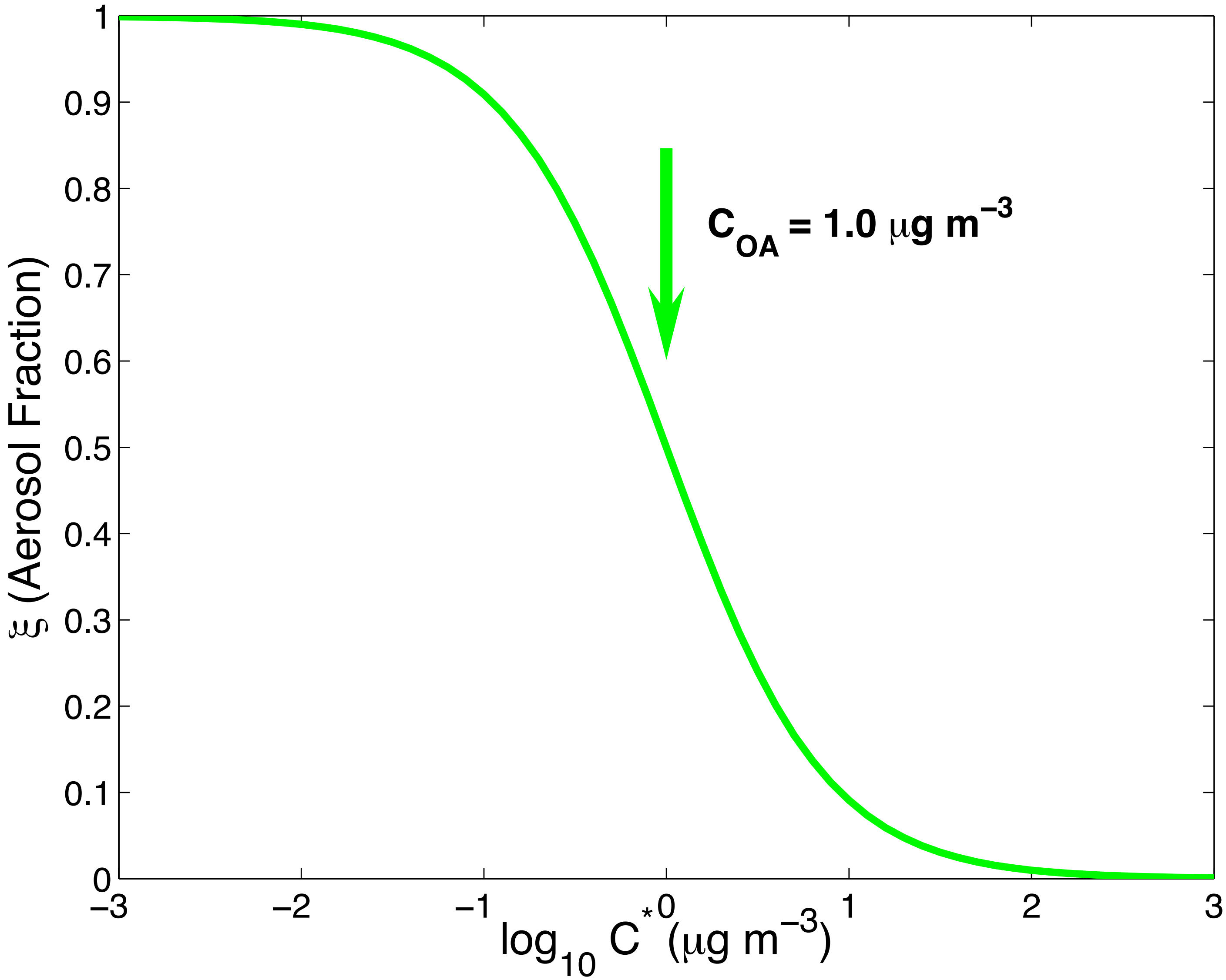
α-pinene + Ozone



$\sim$ 2x SOA under remote atmospheric conditions vs. extrapolation.

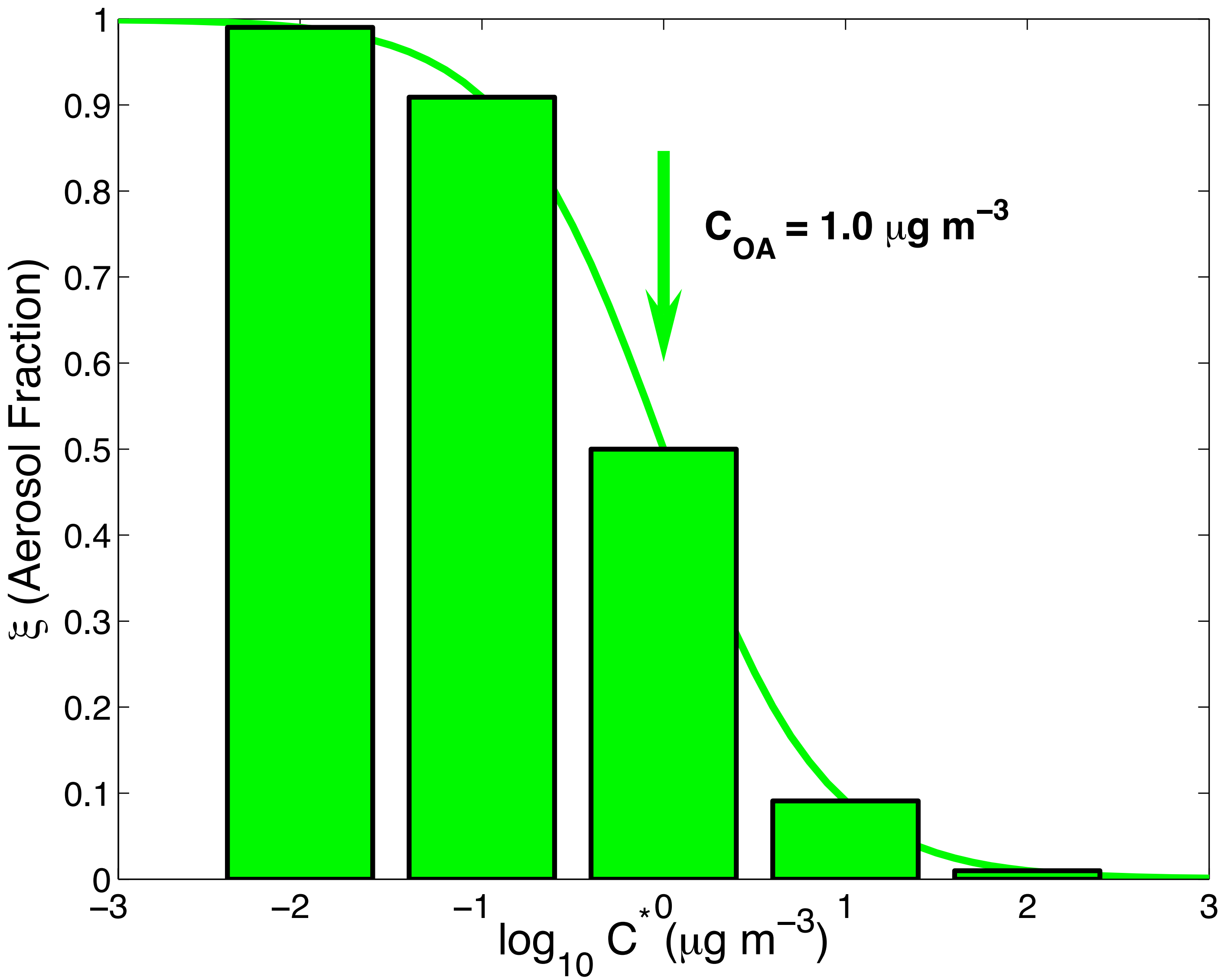
[Presto and Donahue, *ES&T*, 2006]

Partitioning at Specified C_{OA} in Solution



$$\xi_i = \frac{1}{1 + \frac{C_i^*}{C_{OA}}}$$

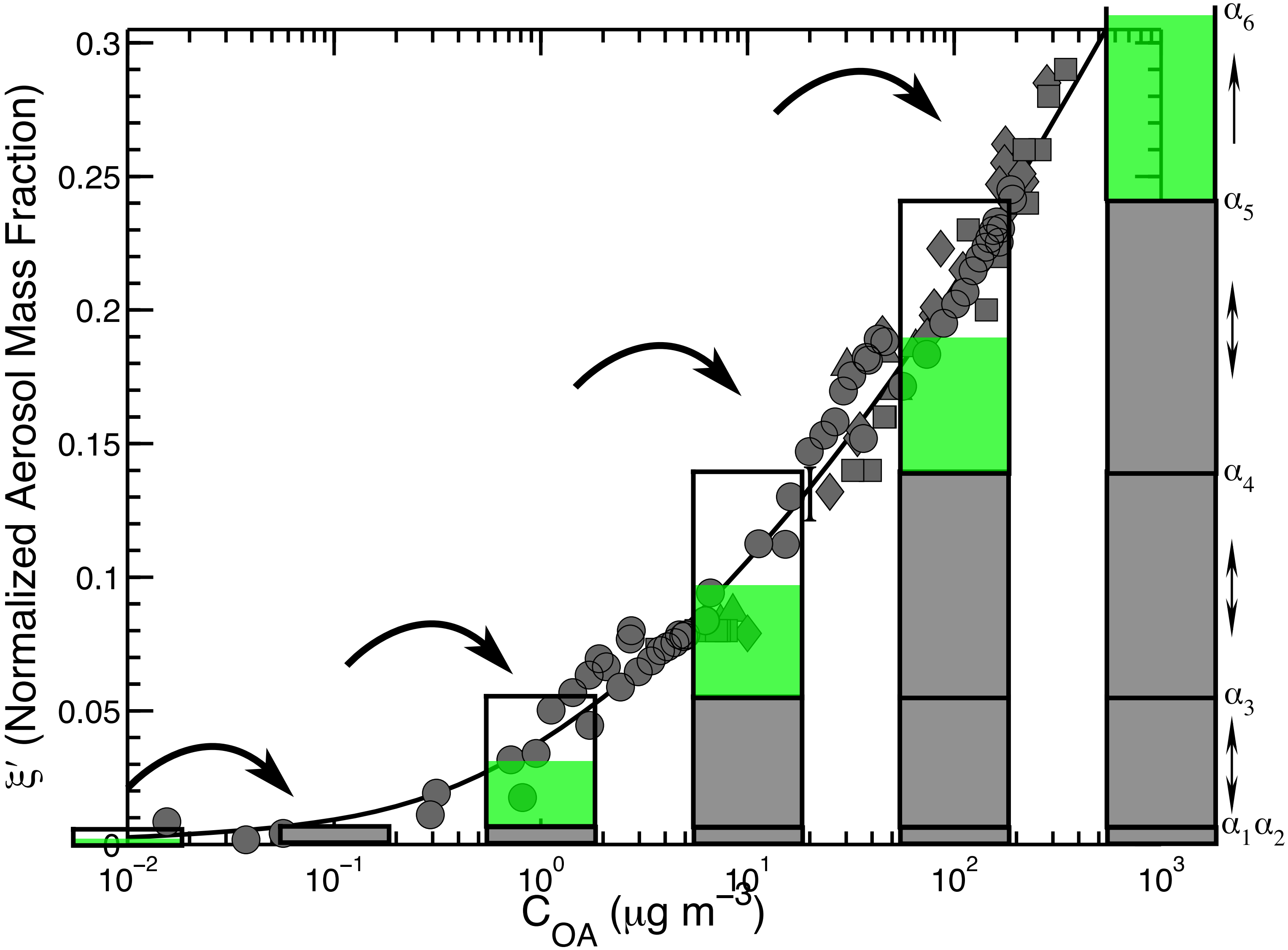
The Volatility Basis Set



$$C_i^* = \left\{0.01, 0.1, 1, 10, 100, 1000, 10^4, 10^5, 10^6\right\}\ \mu g\, m^{-3}$$

[Donahue *et al.*, *ES&T*, 2006]

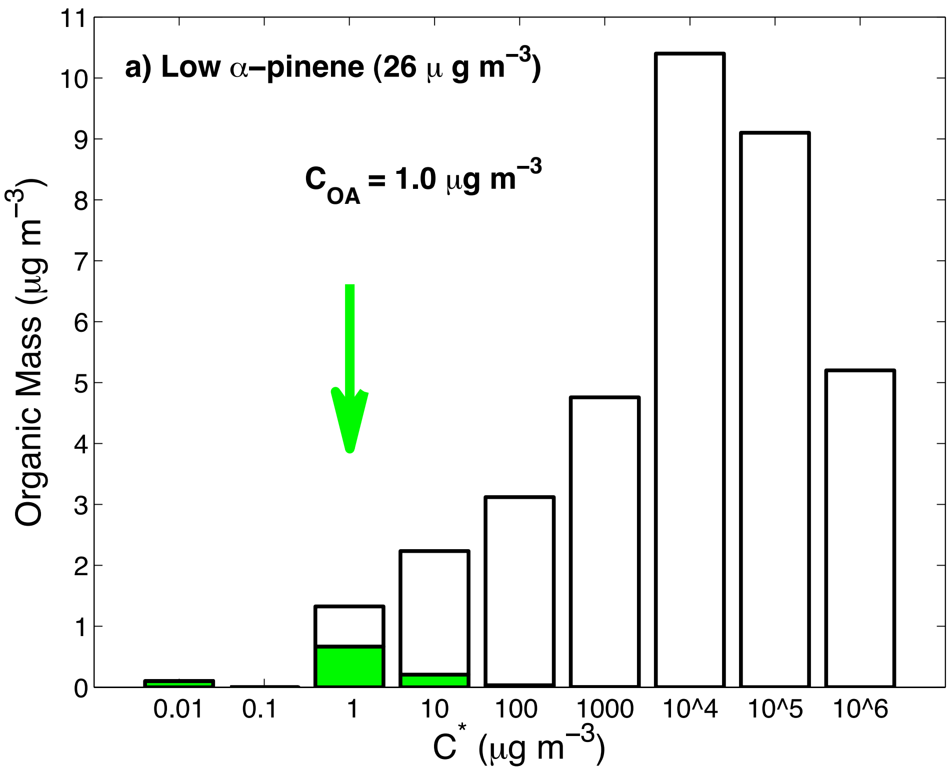
α-pinene and the Basis Set

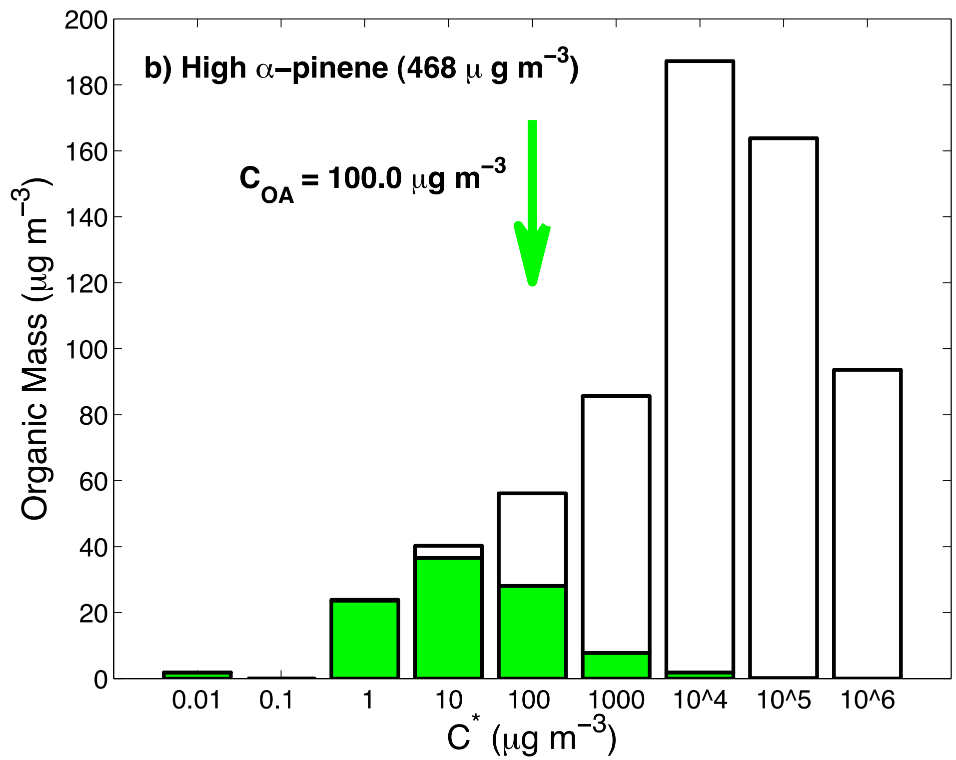


(mass yields α')

$$\alpha'_i = \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, ...\}$$

α-Pinene + Ozone Partitioning

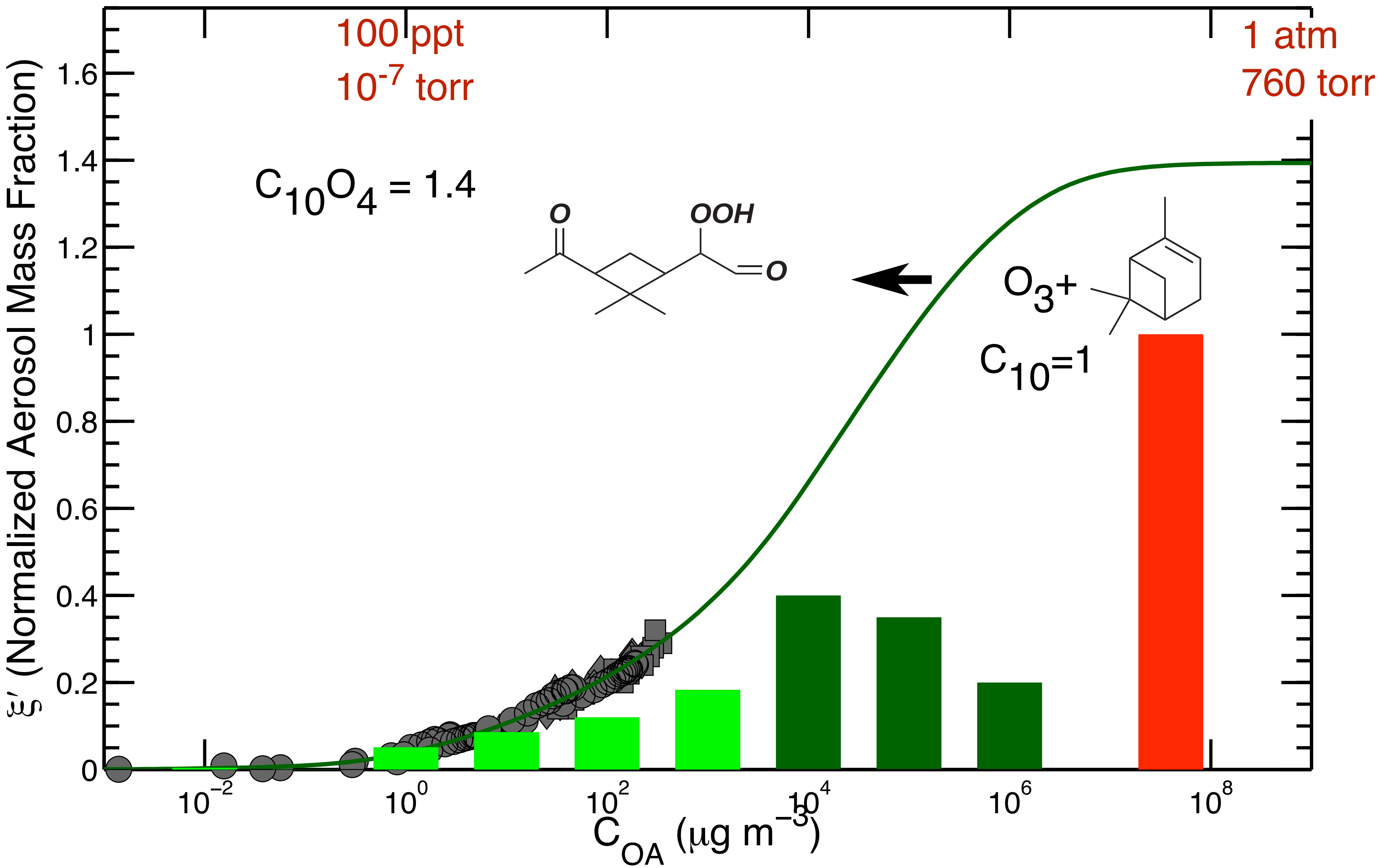




Partitioning changes with mass loading: x18 total loading = x100 C_{OA}.
Most of the OA compounds at $100\,\mu g\, m^{-3}$ are not in the particles at 1.

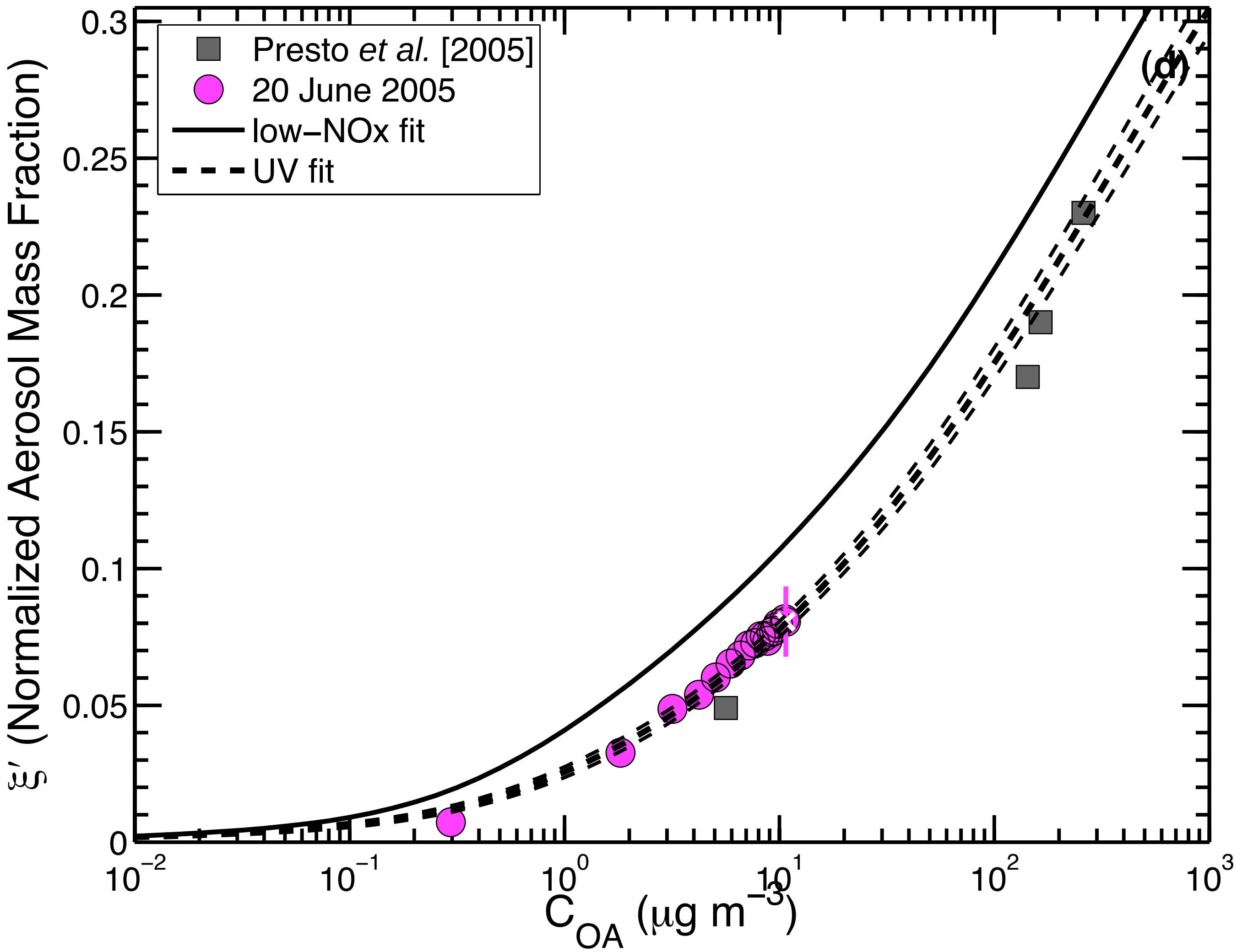
[Donahue *et al.* in prep]

α-Pinene + Ozone Mass Balance



Mass balance for 'nominal product' demands $\xi_{\text{max}} = \sum_i \alpha_i \simeq 1.4$.

α-pinene + Ozone: UV (no NO_x)



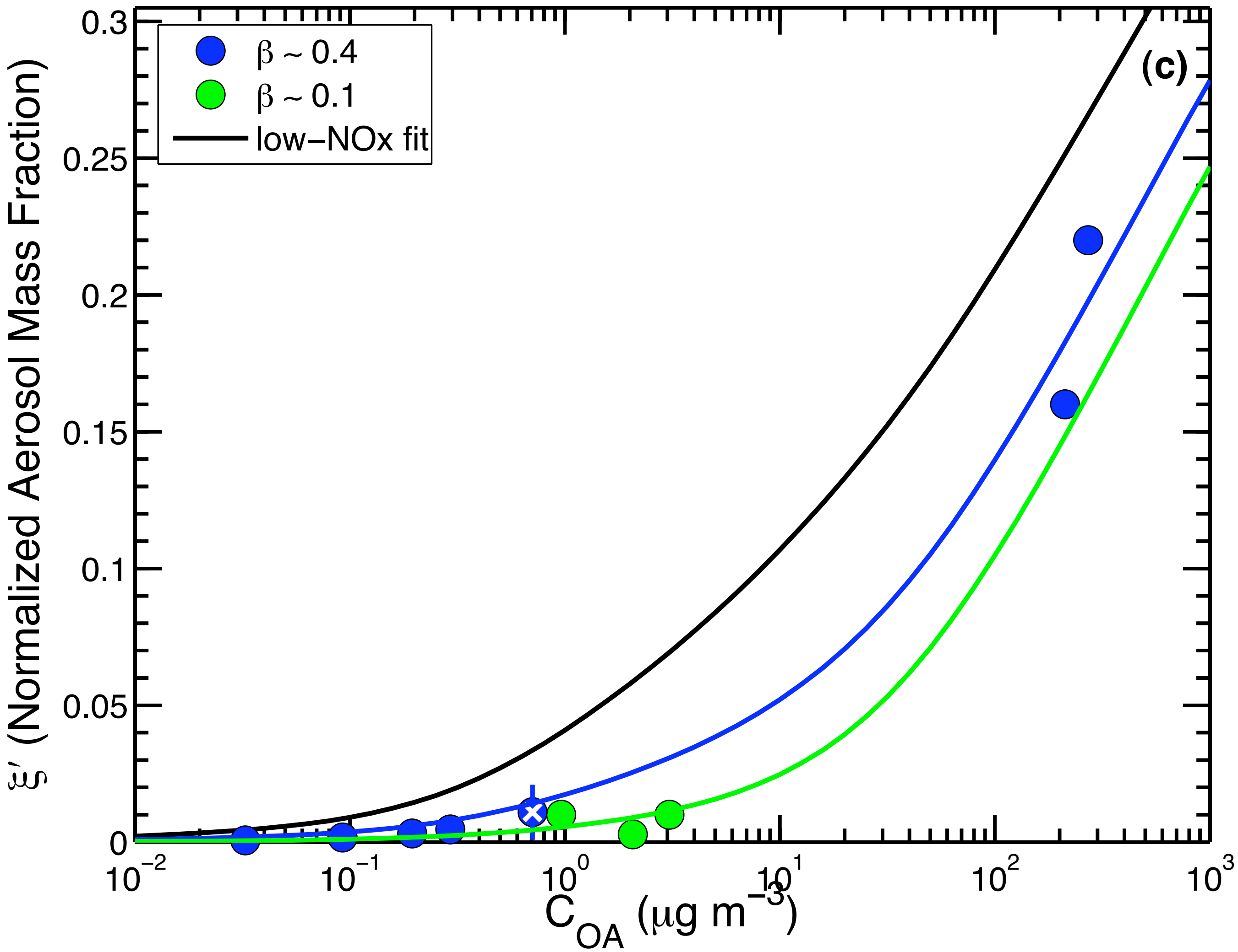
$$\alpha'_{\text{i}} = \{.004, \quad 0, \quad \mathbf{.05}, \quad .09, \quad .12, \quad .18, ...\}$$

$\downarrow$ UV

$$\alpha'_{\text{i}}(\text{UV}) = \{.004, \quad 0, \quad \mathbf{.02}, \quad .08, \quad .12, \quad .18, ...\}$$

[Presto *et al.*, *ES&T*, 2005a]

α-pinene + Ozone: VOC:NO$_x$



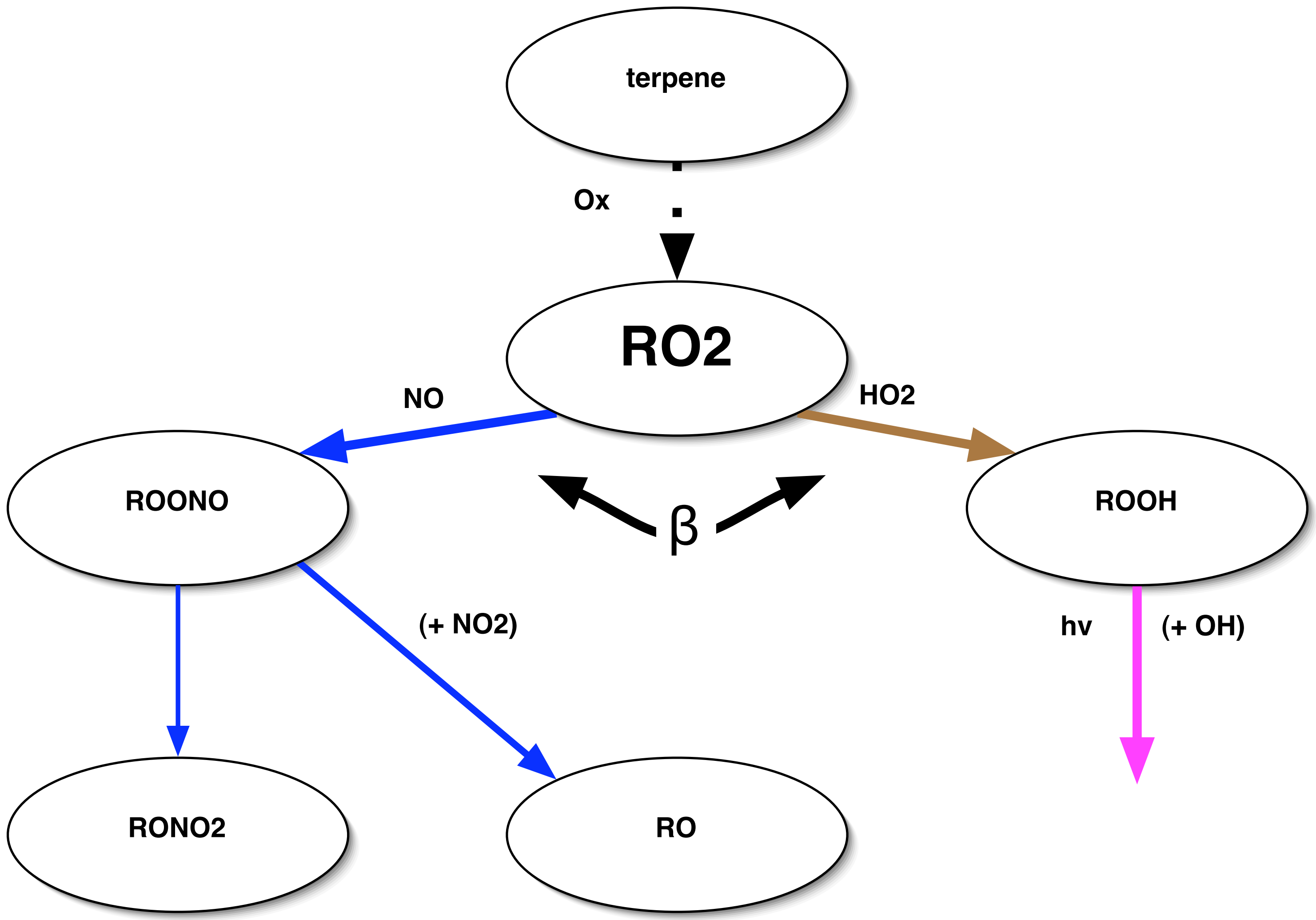
$$\alpha_i'(\mathrm{HO_2}) = \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, \ldots\}$$

$$\downarrow \mathrm{NO_x} \quad \beta = (\mathrm{VOC:NO_x})_0/10, (\mathrm{VOC:NO_x})_0 < 10$$

$$\alpha_i'(\mathrm{NO_x}) = \{0, \quad 0, \quad 0, \quad 0, \quad .15, \quad .2, \ldots\}$$

[Presto *et al.*, *ES&T*, 2005b]

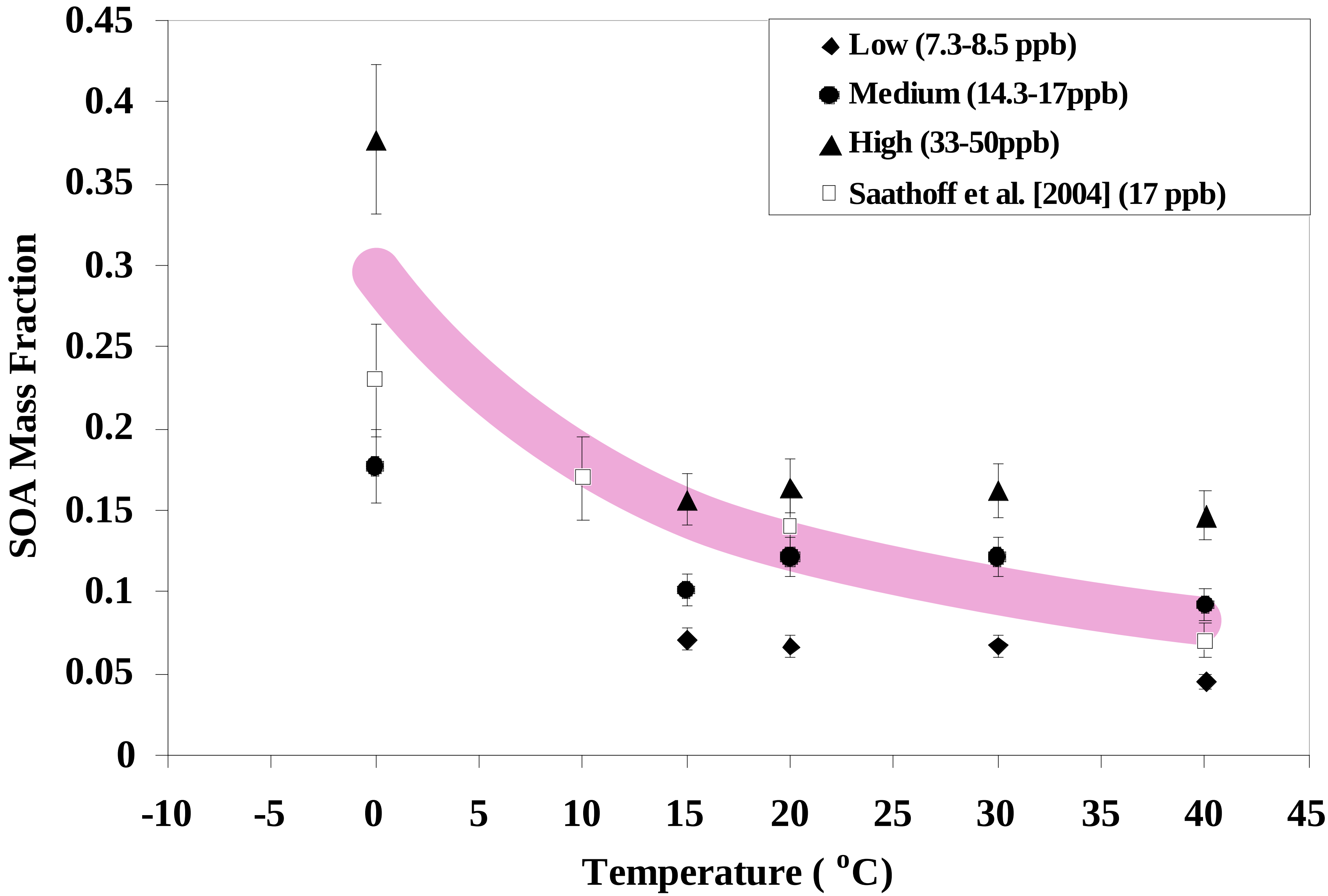
RO_2 Fate



Bottom line – tie SOA module into gas-phase RO_2 chemistry:

$$\{\alpha\} = \beta\,\{\alpha\}^{\mathrm{low-NO_x}} + (1-\beta)\,\{\alpha\}^{\mathrm{high-NO_x}}$$

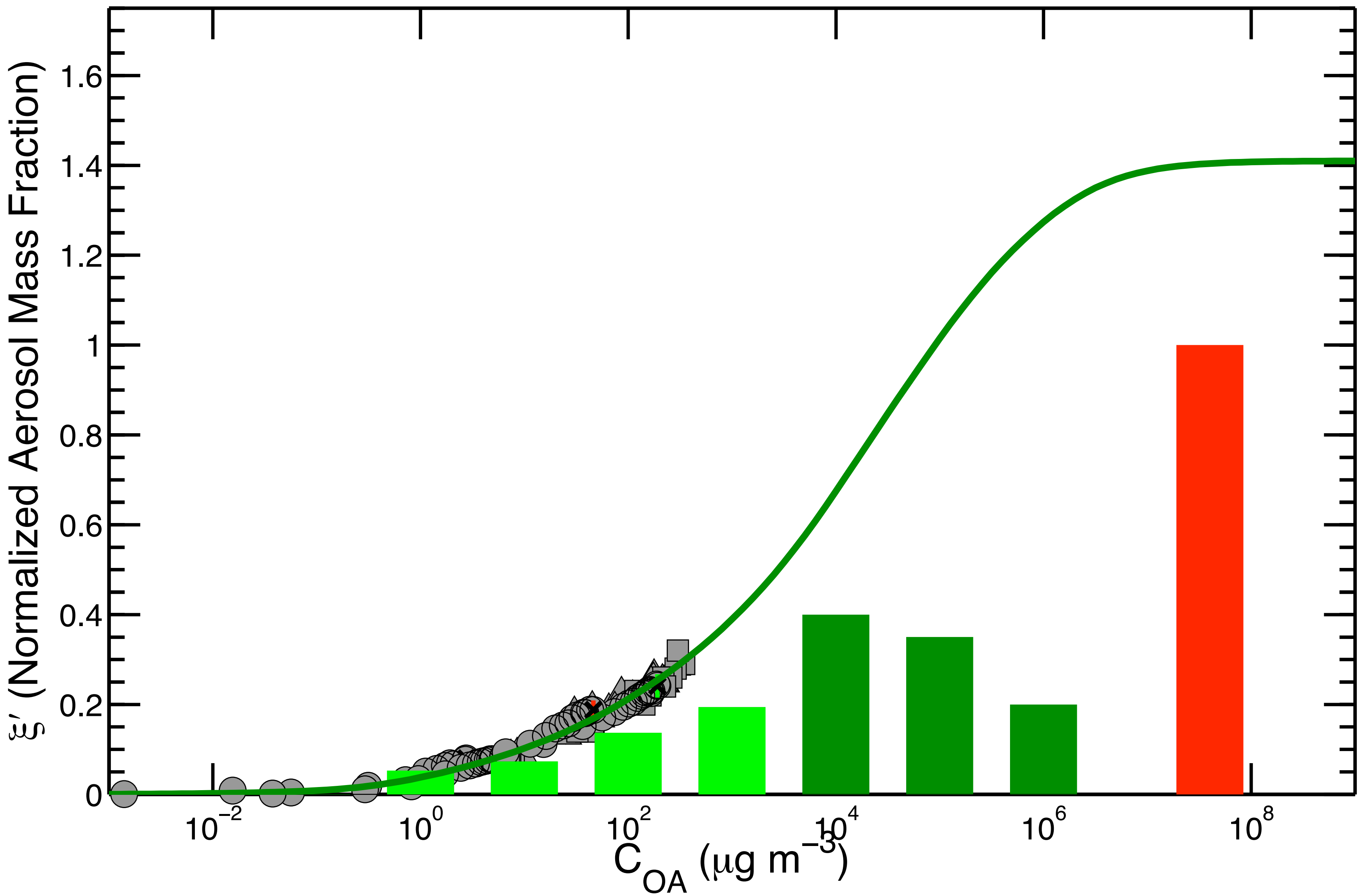
α-Pinene + Ozone T Dependence



Upturn in SOA between 15 and 0°C.

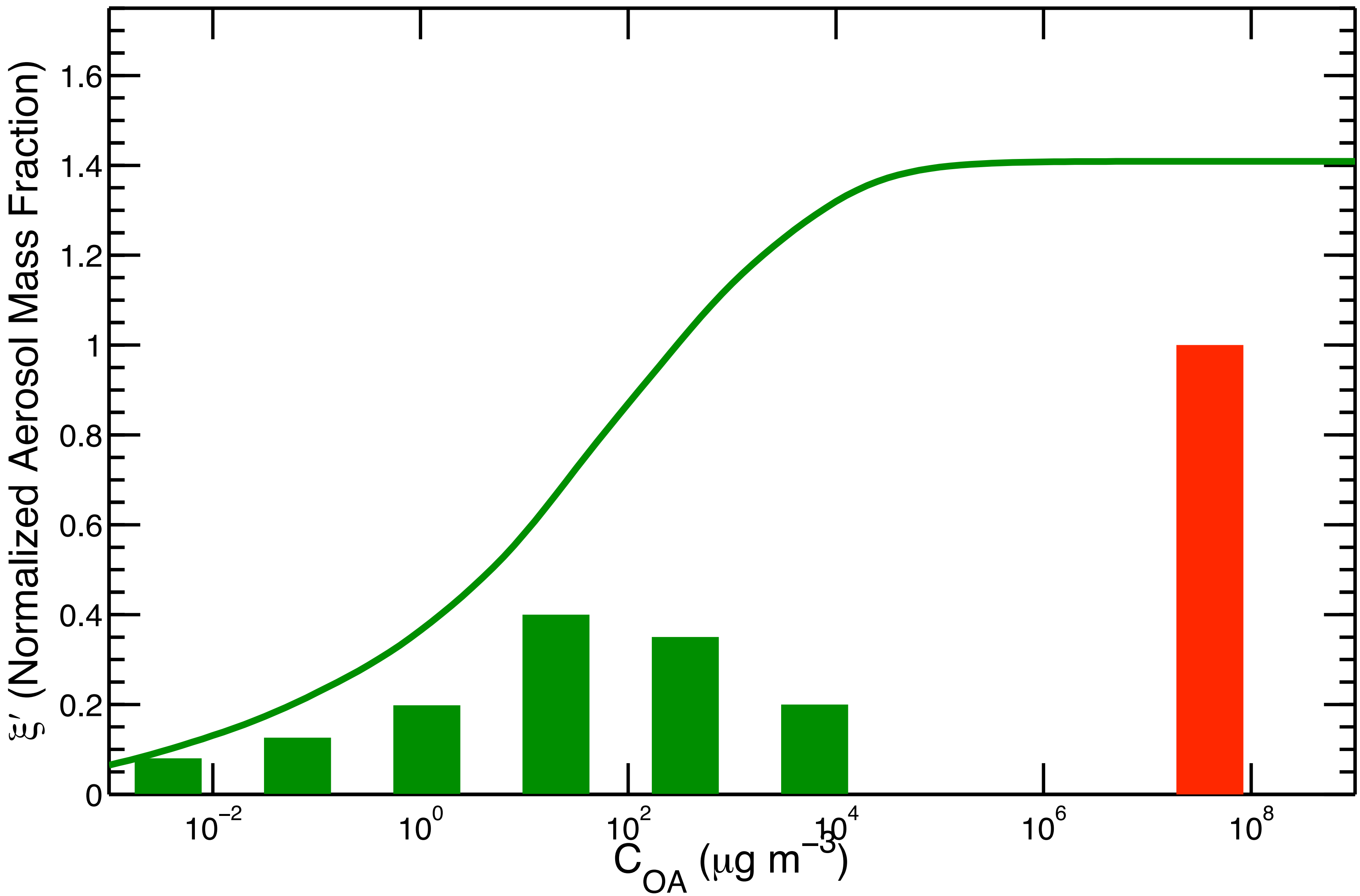
[Pathak *et al.*, *JGR*, 2007], [Stanier *et al.*, *ACPD*, 2007]

α-Pinene + Ozone Total Mass 300 K



Dark green yields are guesses – total is constrained.

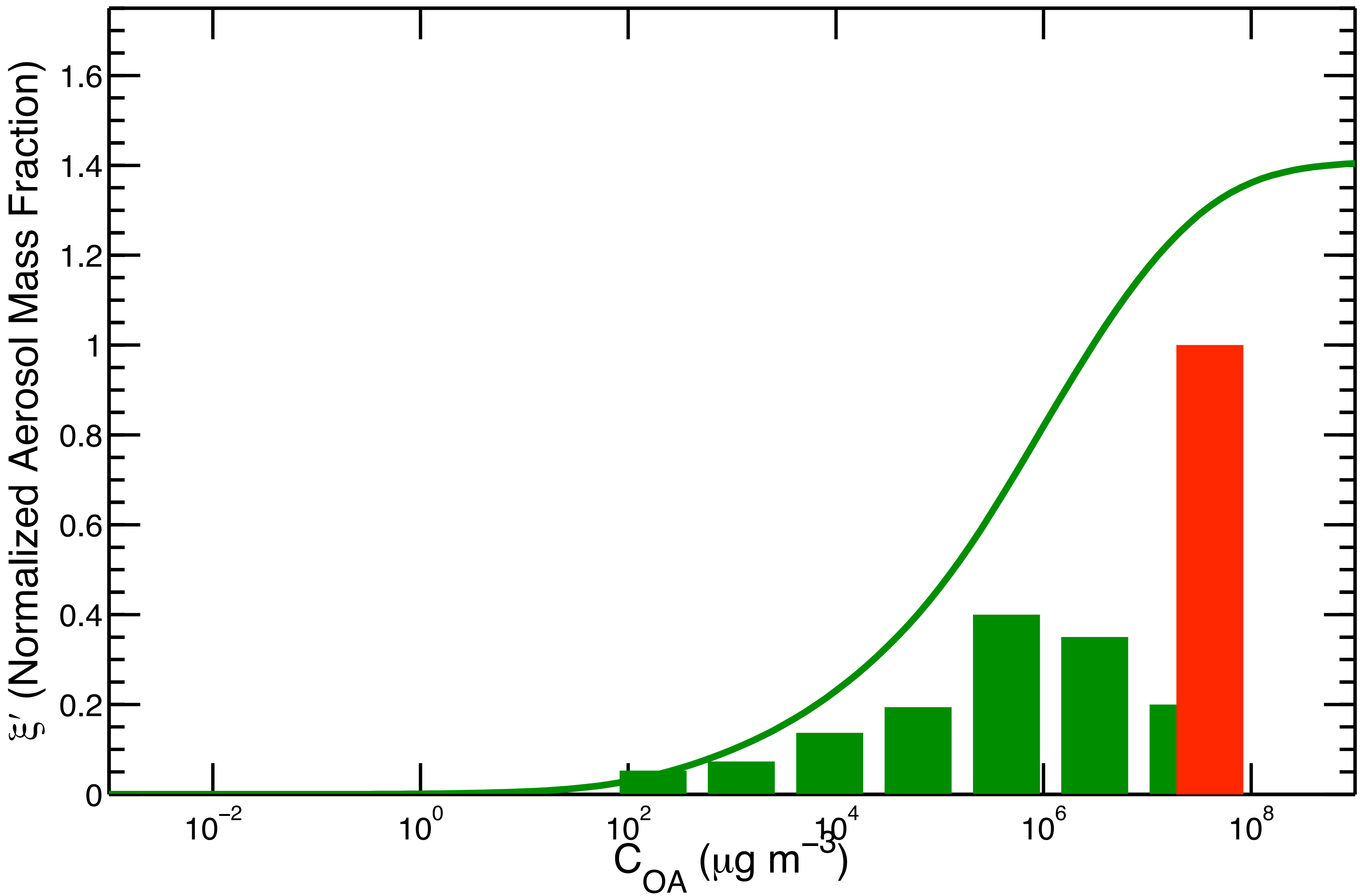
α-Pinene + Ozone Total Mass 243 K



Products shift left by 2.5 orders of magnitude.

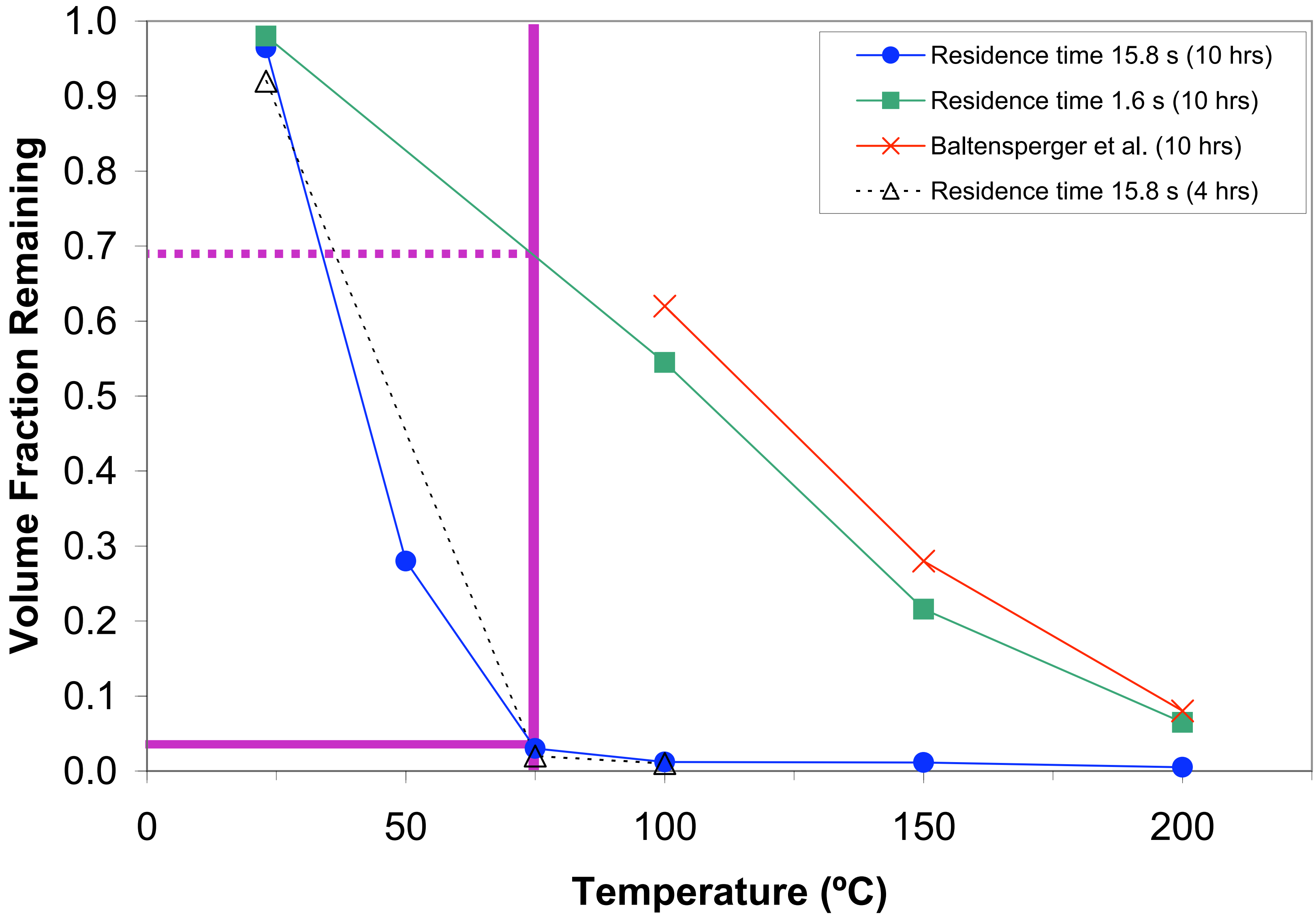
(Note – [Saathoff *et al.* IAC 2006] saw $\sim$1 AMF at 100-200 μg m^{-3} and 243 K.)

α-Pinene + Ozone Total Mass 350 K



Products shift right by 2.5 orders of magnitude.

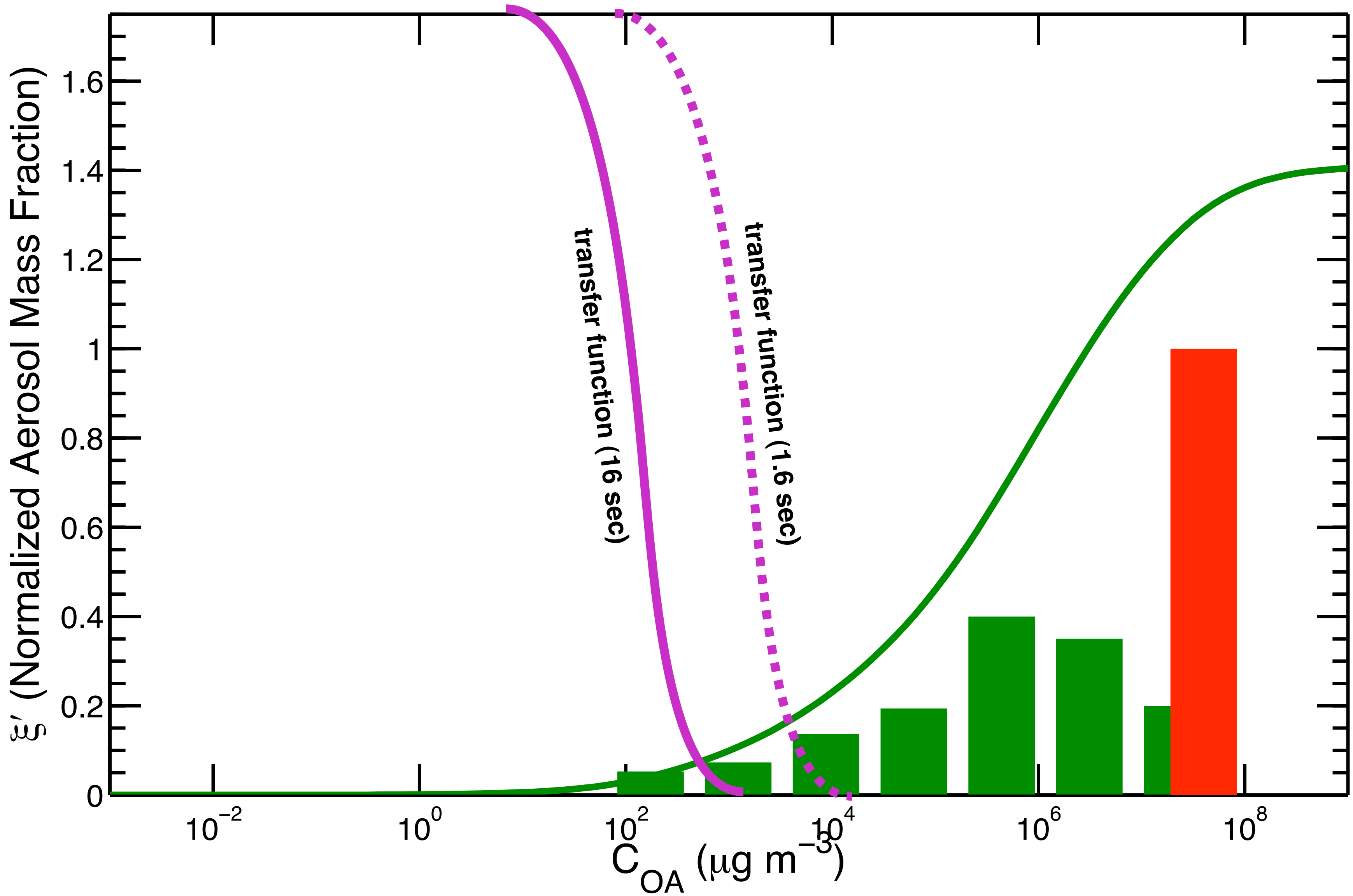
α-Pinene + Ozone Thermodenuder



Given time, *all* SOA evaporates at 70C.

[An *et al., AS&T*, 2007]

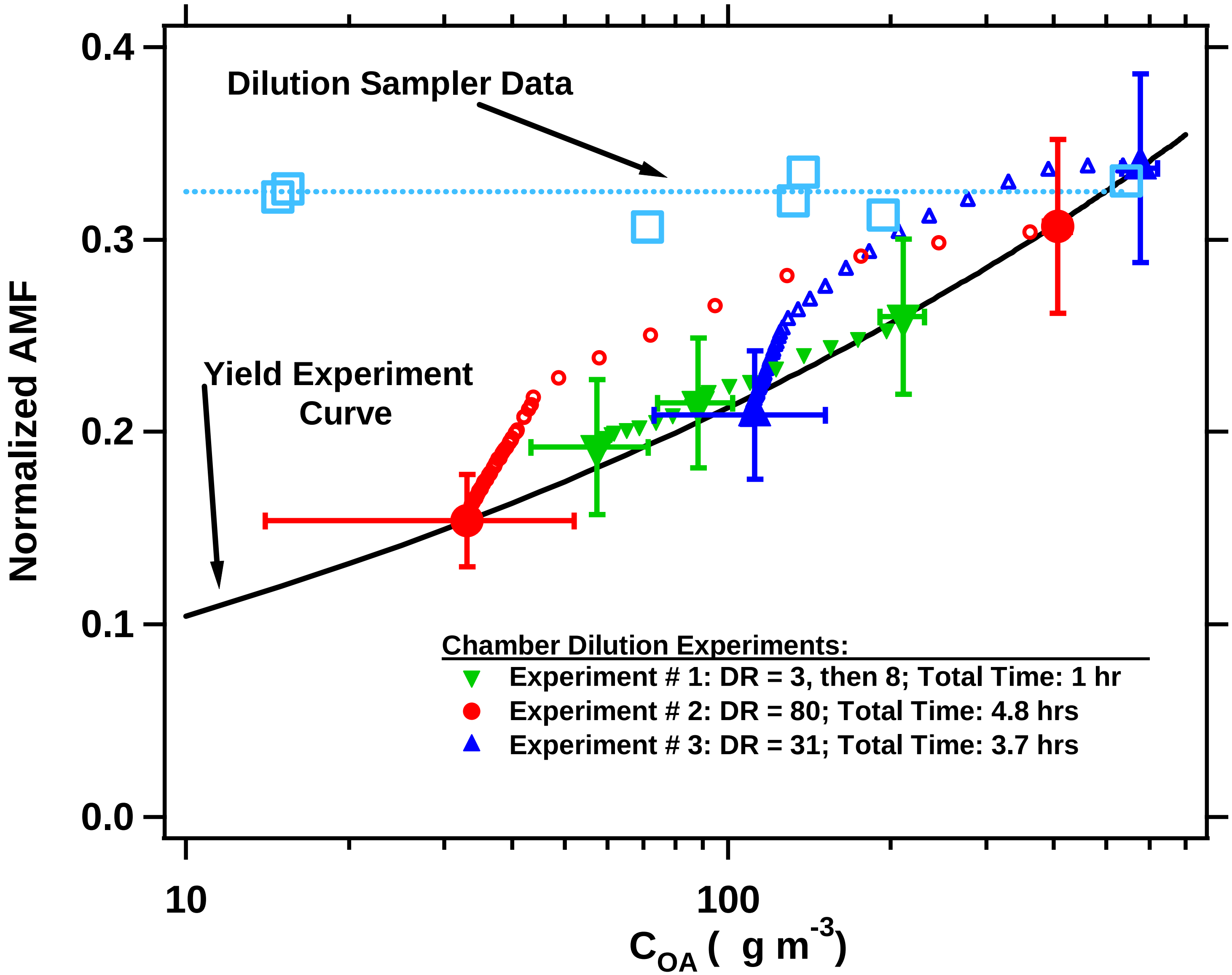
α-Pinene + Ozone Thermodenuder



Denuding is a function of evaporation timescales.

[Pierce *et al.*, *in prep*, 2007]

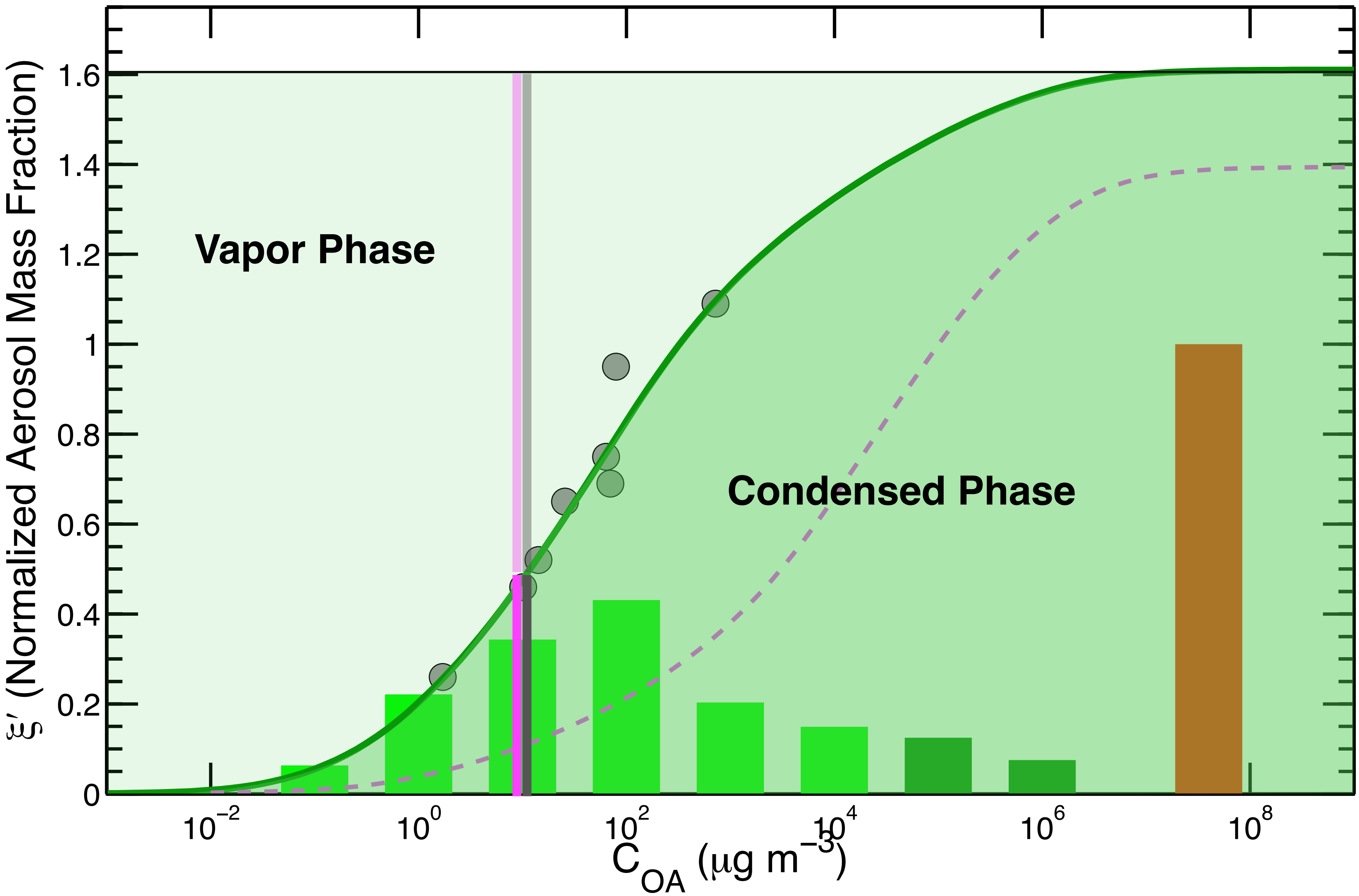
α-pinene + O_3 Dilution



Generate high SOA and then flush 90% of chamber air.

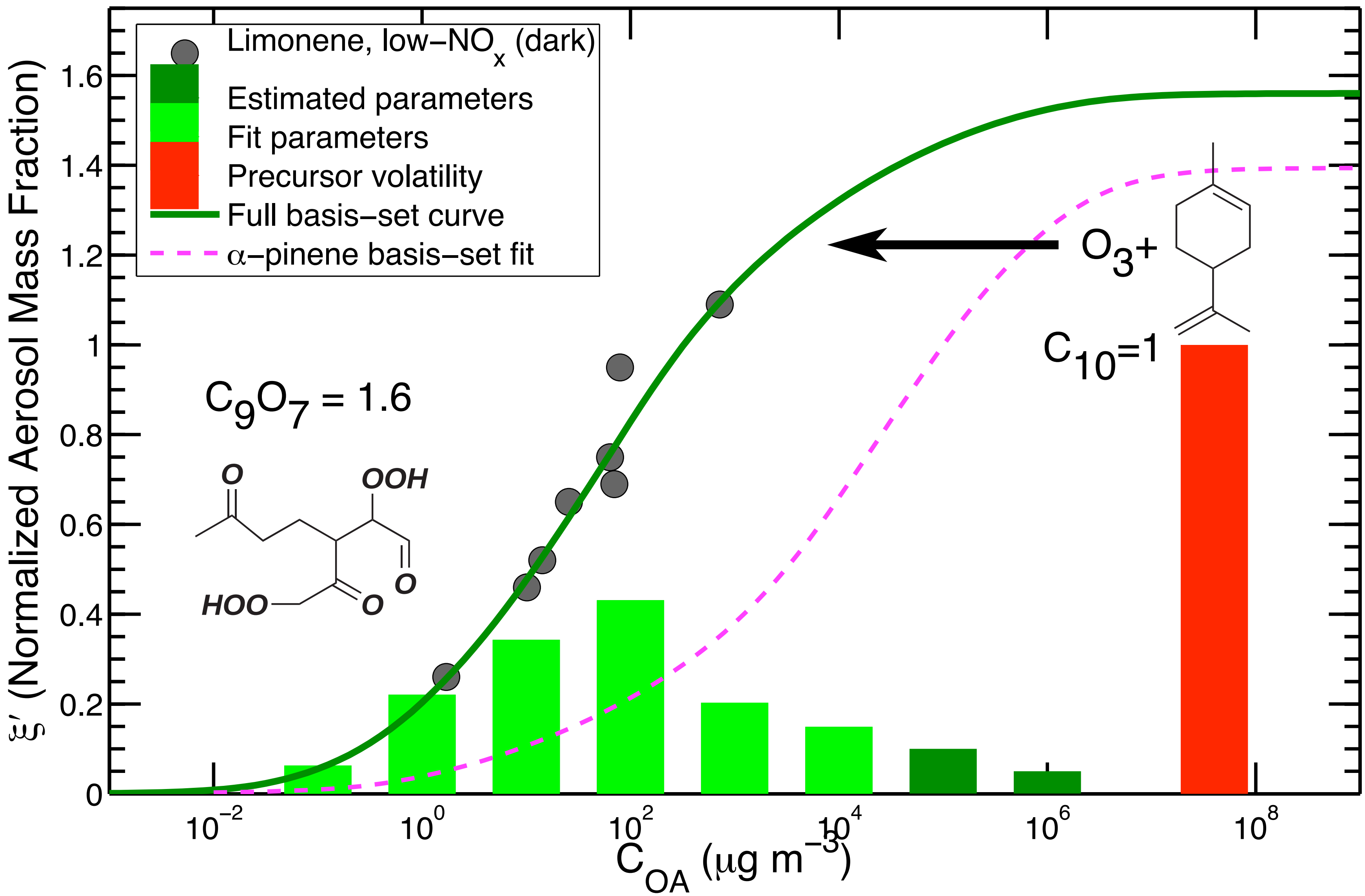
Particles shrink *slowly* to expected size. [Grieshop *et al., GRL* 2007]

Implications: Vapors



The mass not seen in the particles is in the gas phase, very low vapor pressure.

Limonene + Ozone Mass Balance

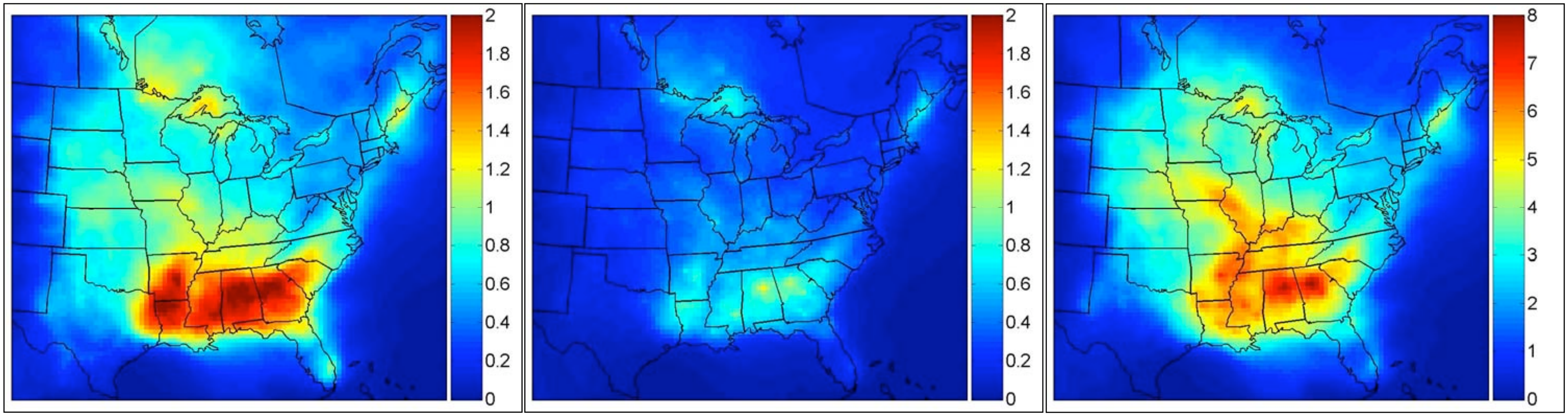


D-limonene + O_3 makes more SOA than α-pinene (2nd generation of oxidation).

[J. Zhang *et al.*, *JPC*, 2006]

Implementing Basis Set in PMCAMx

July 2001 Biogenic SOA



Old ∼constant yield | New Basis set yields | Multi-generation aging

New basis set parameters cause most SOA to evaporate at ambient C_{OA}.
Adding aging (gas-phase OH oxidation) can generate *lots* of SOA.
Aging parameters are not yet known (these are a reasonable guess).

[Lane *et al.* in prep]

Conclusions Picture