Oxidation Chemistry and Evolving Volatility of Organic Aerosol

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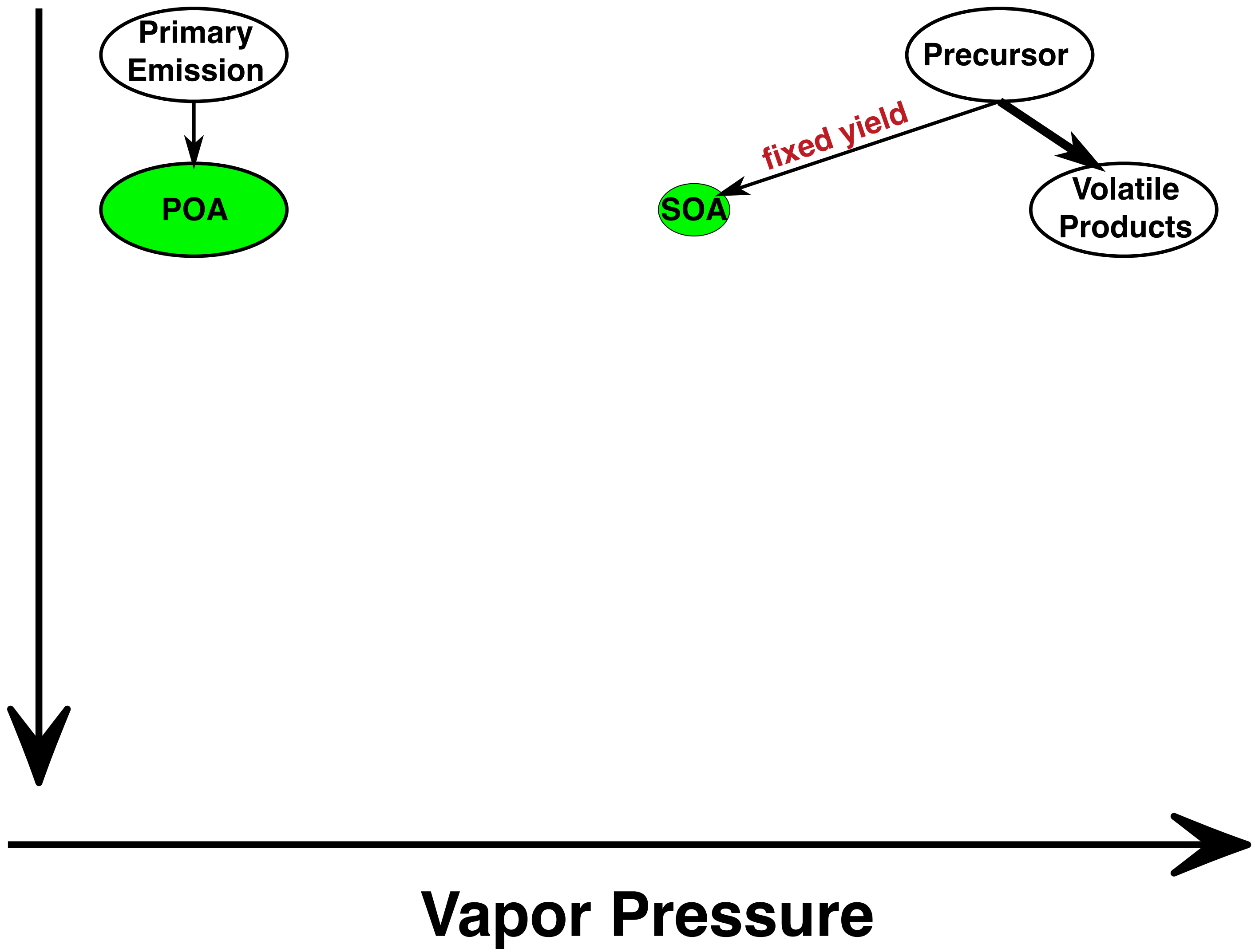
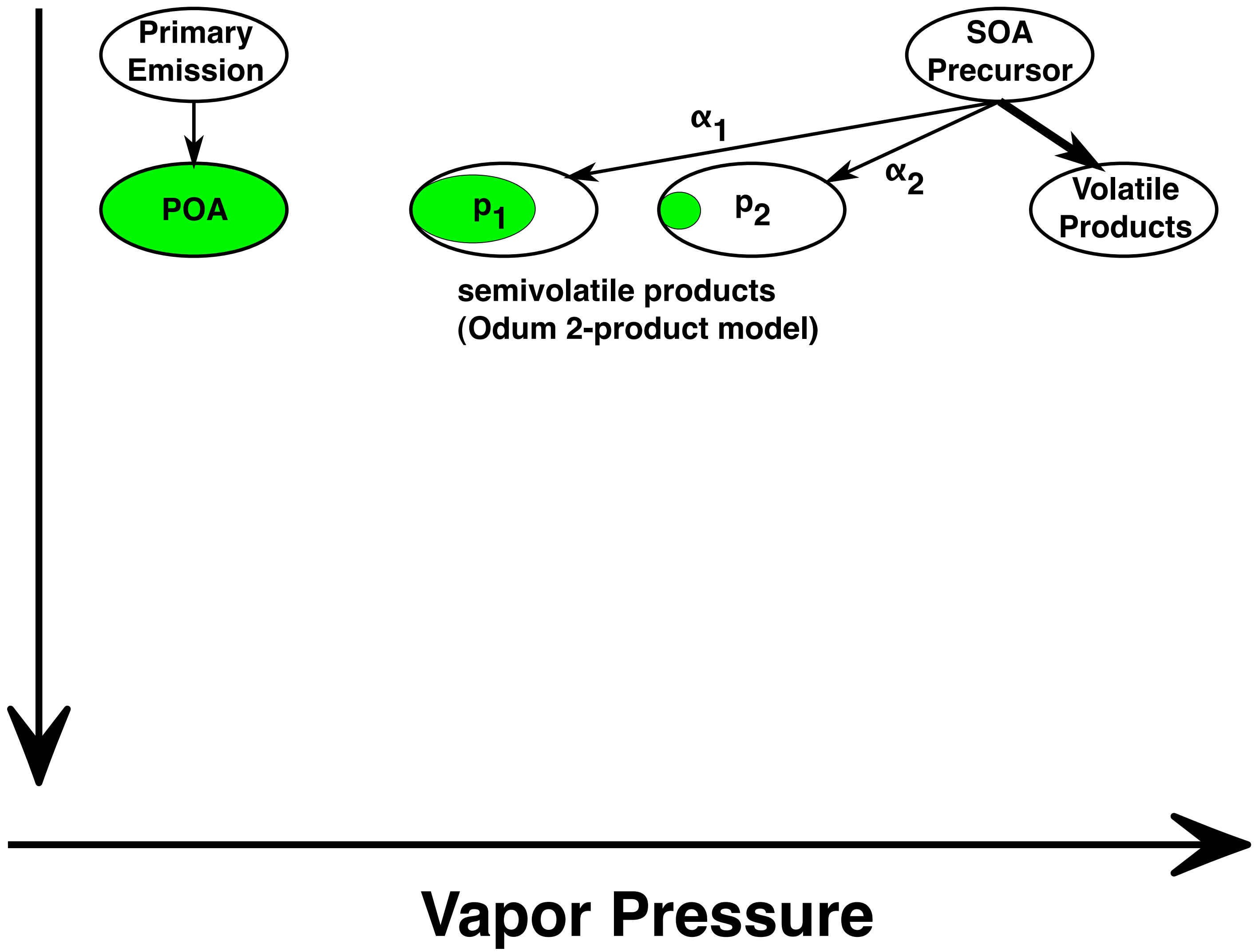
The Center for Atmospheric Particle Studies

Organic Aerosol



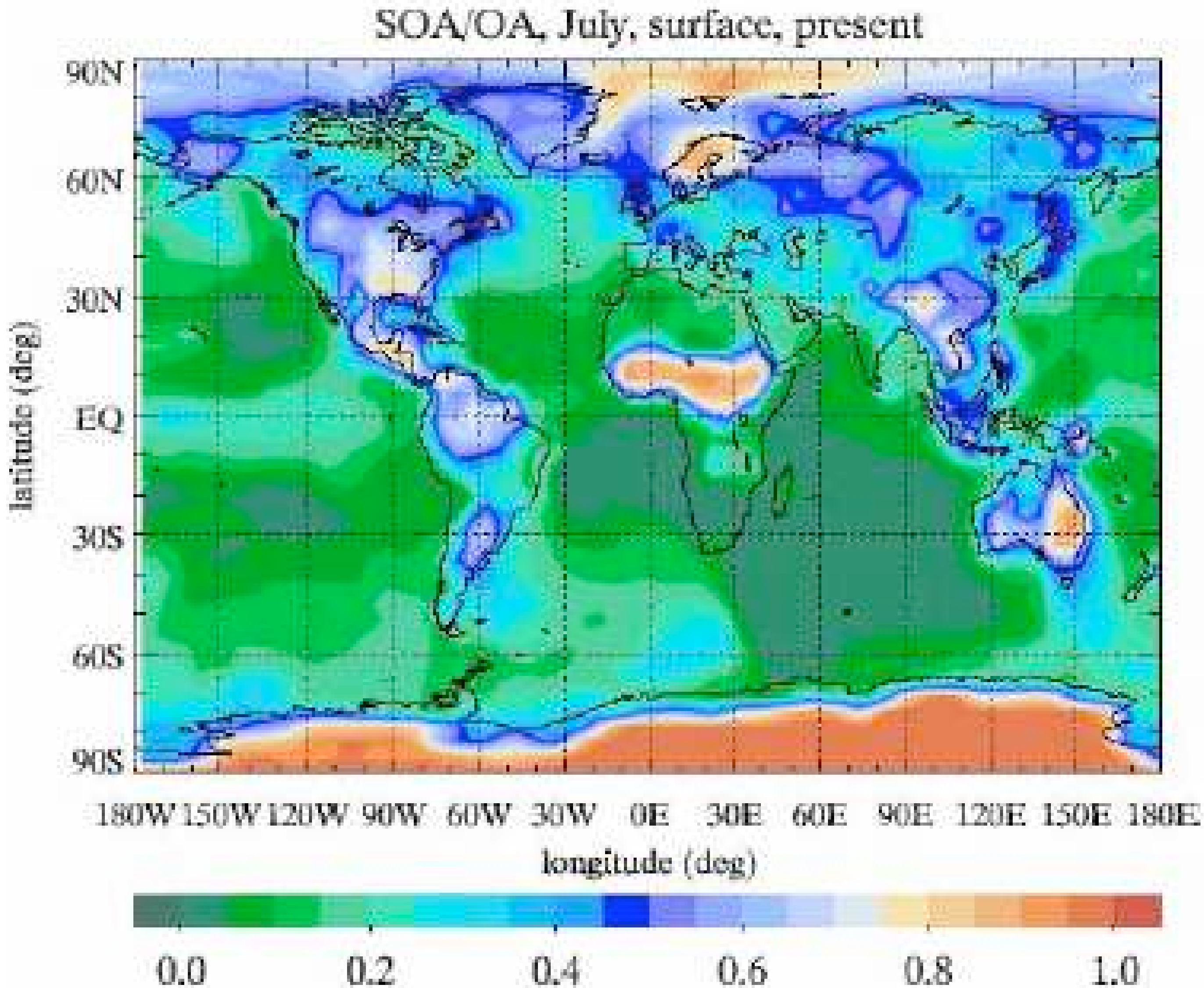
Not quite state of the art, common in models...

Organic Aerosol



State of the art, in some models...

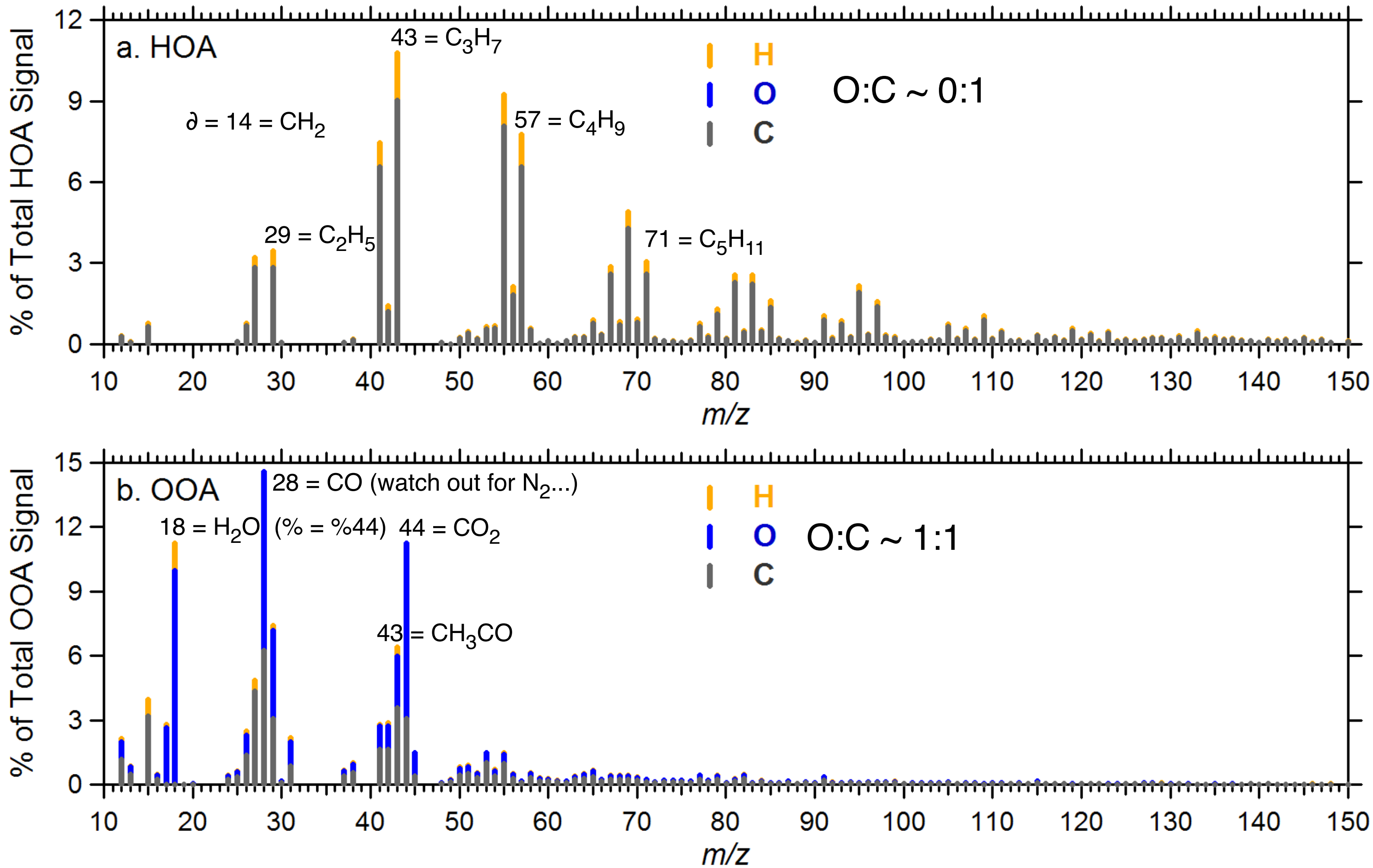
Secondary - Primary Split in Models



Most of the world mostly POA

[Kanakidou *et al. ACP* 2005]

Aerosol Mass Spectrometer Data

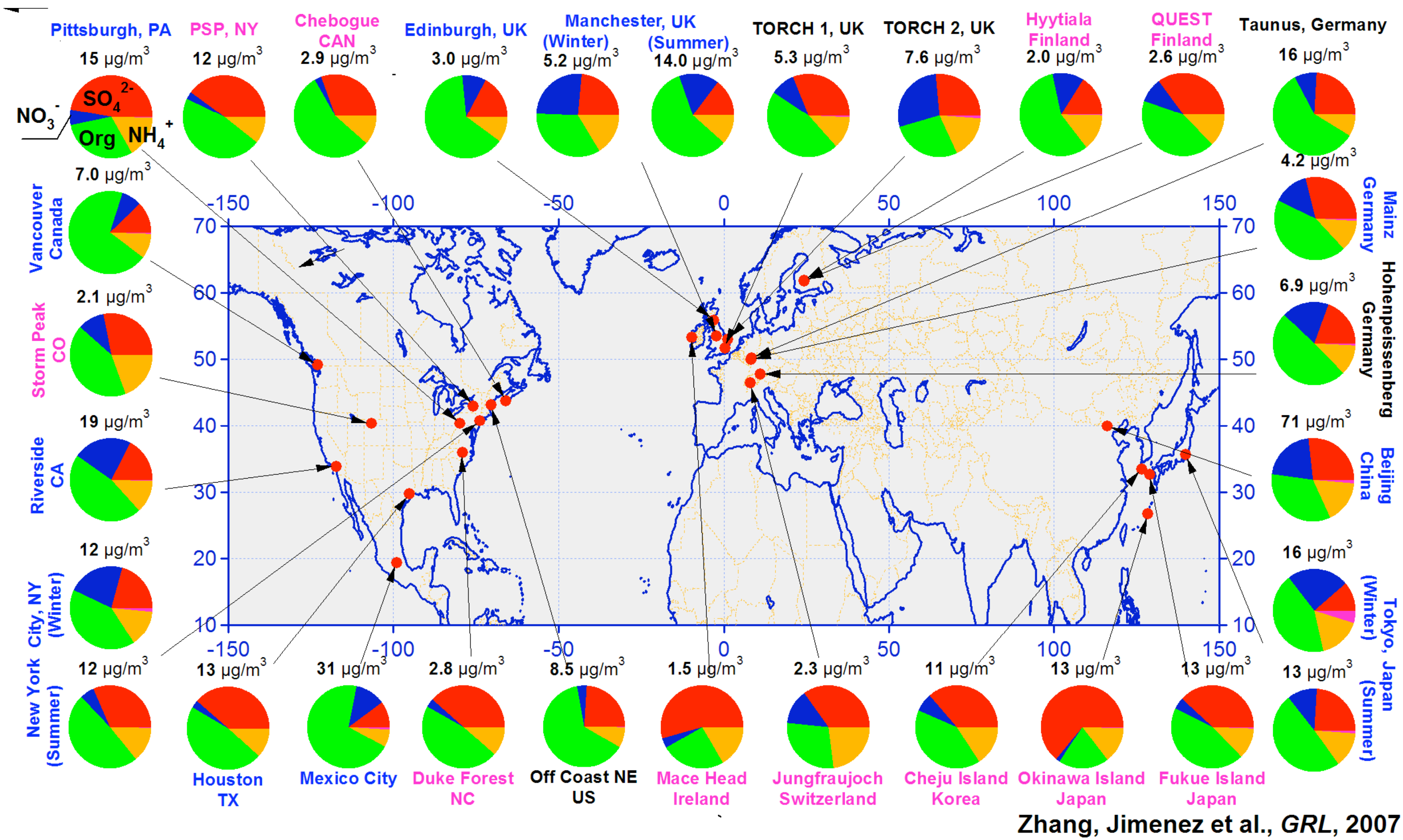


Ambient organic aerosol *in AMS* resolve into 2 factors (these from Pittsburgh).

HOA looks like diesel and has little oxygen.

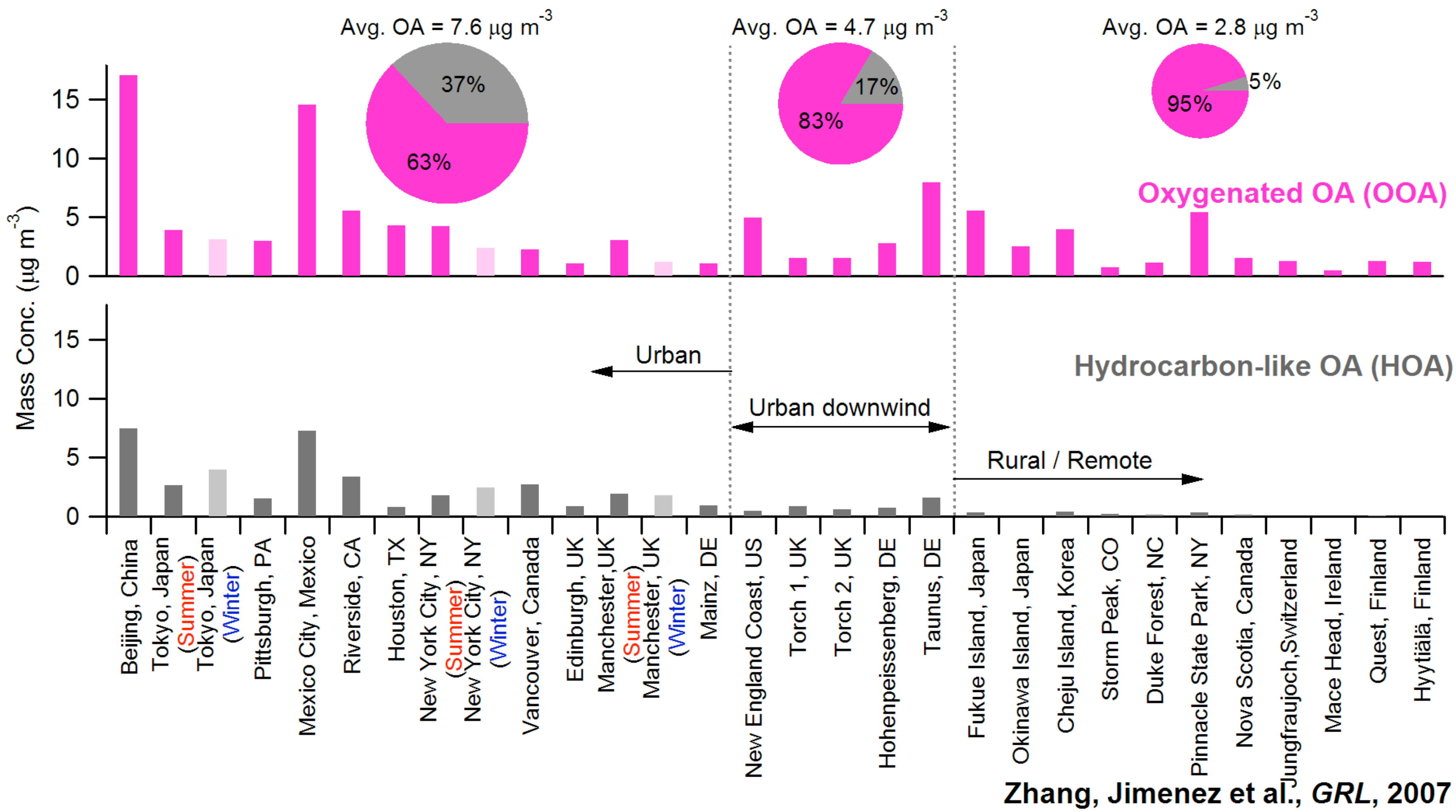
OOA looks highly oxidized. [Qi Zhang *et al. ACP* 2005]

AMS Global Observations



Most of the world 33 - 67% OA [Qi Zhang *et al. GRL* 2007]

AMS OOA

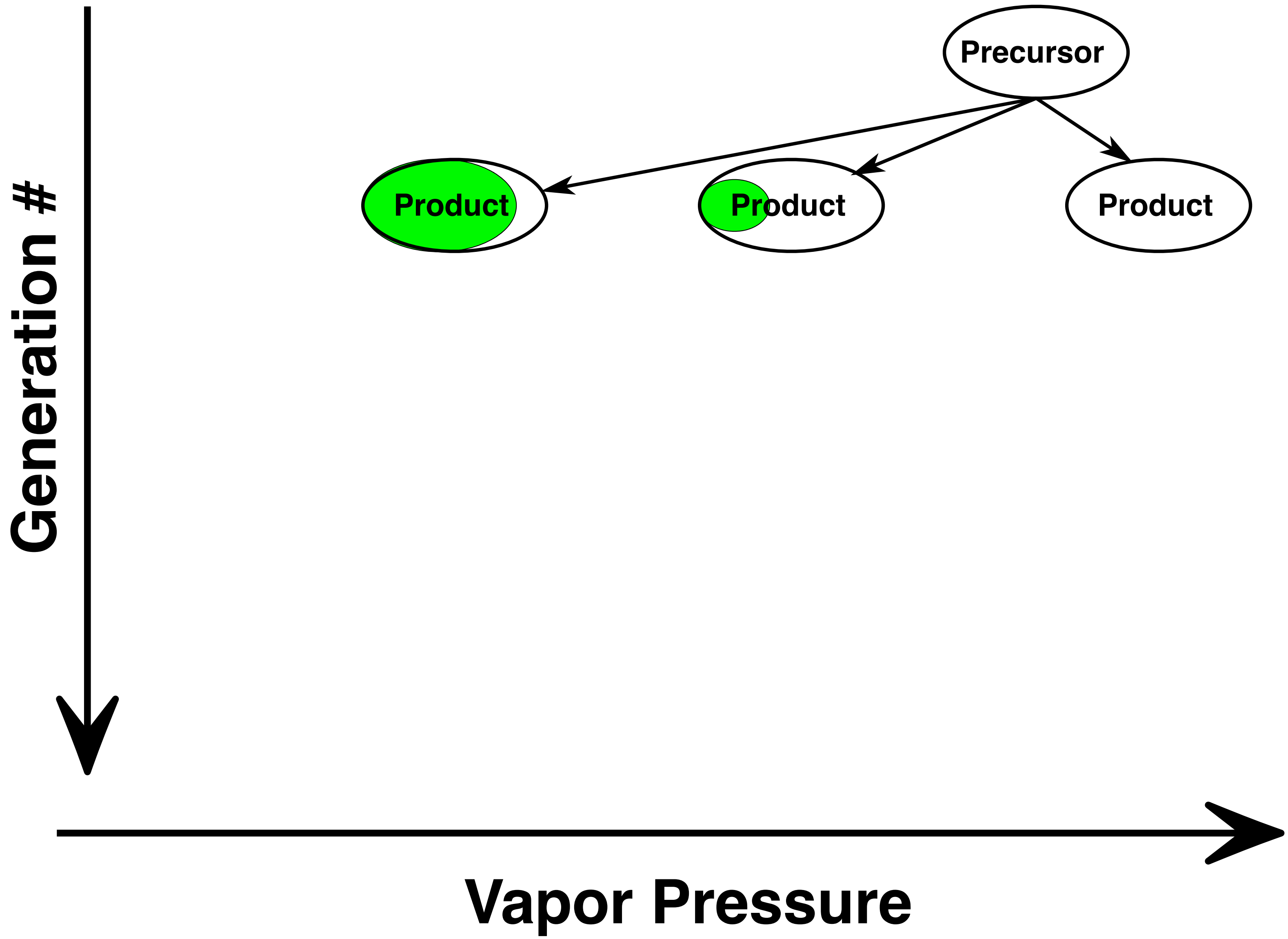


Cities mixed, more than 50% OA

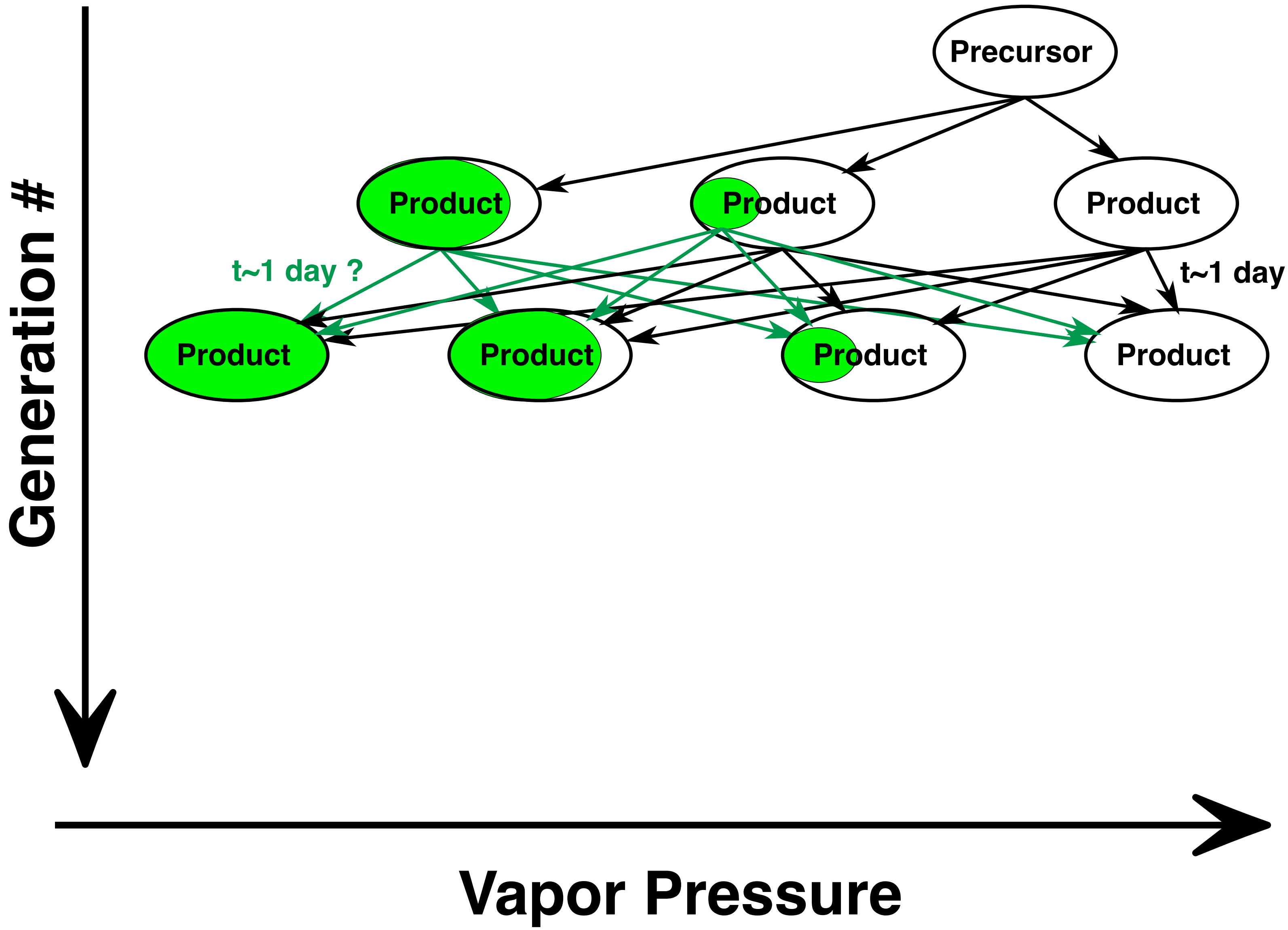
Remote sites almost all OOA [Qi Zhang *et al. GRL* 2007]

OK, so what *is* OOA?? ... HOA is convincingly POA, so ...

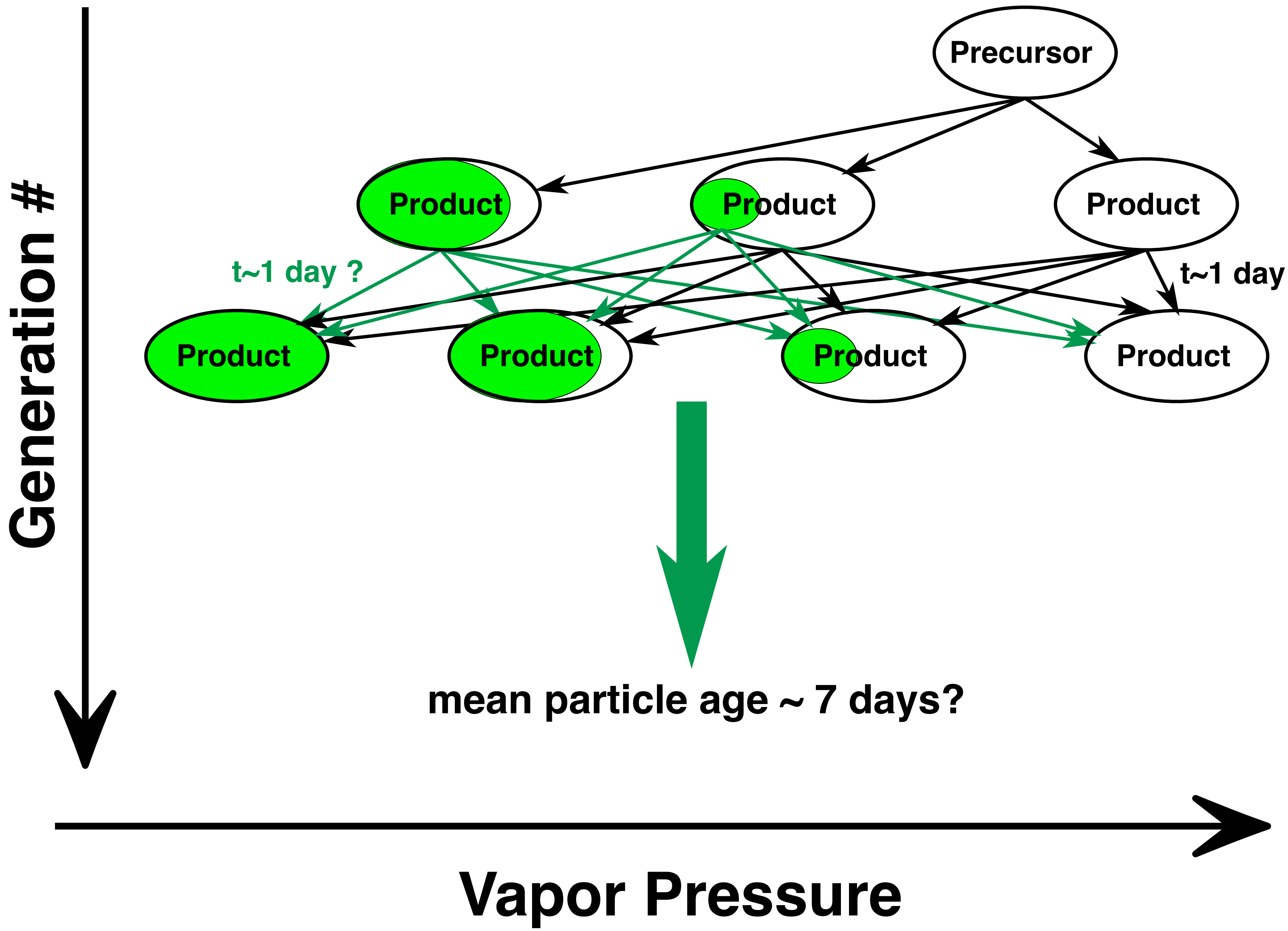
Organic Emissions Processing



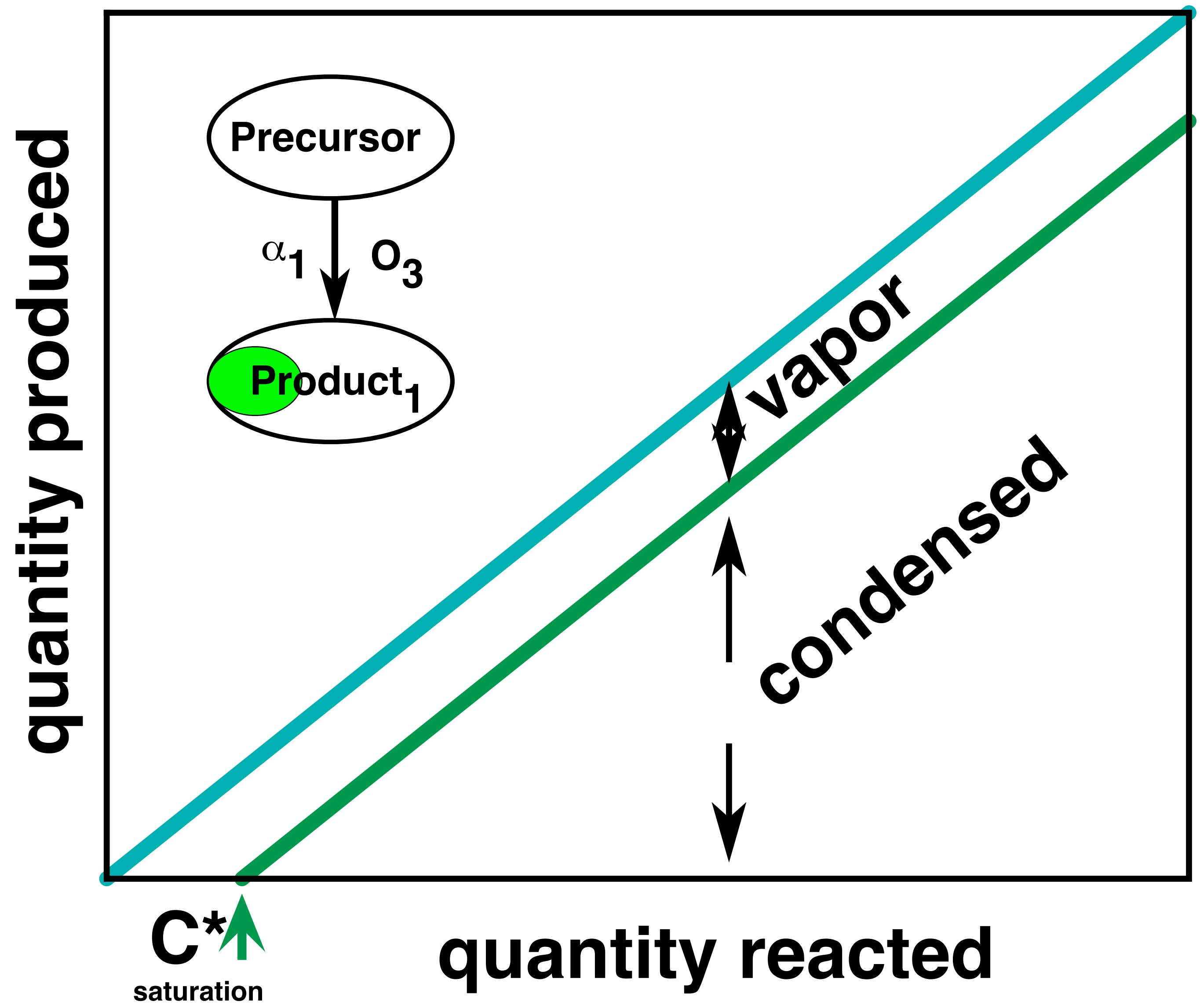
Continued Processing



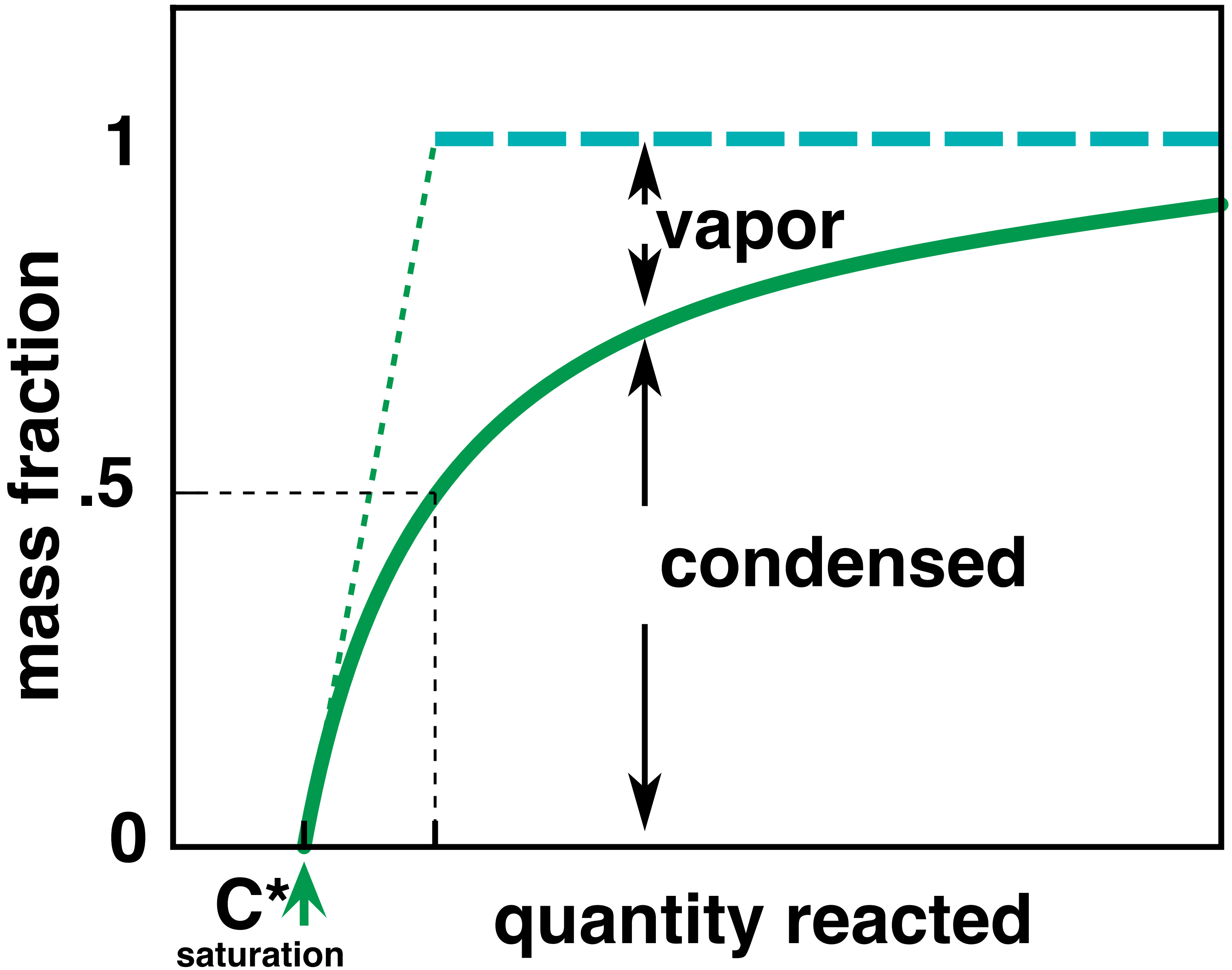
How Far Does it Go??



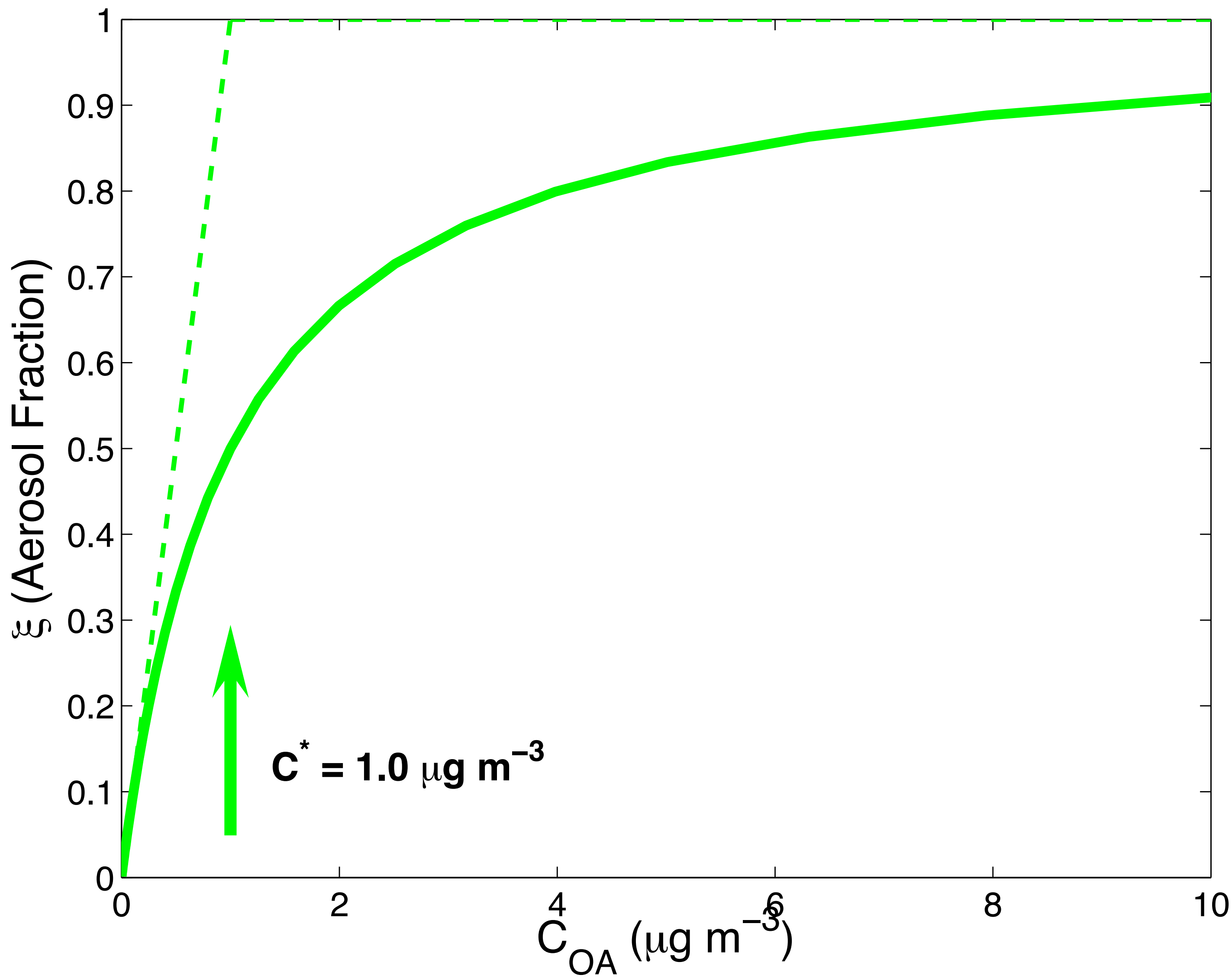
Production of a Semi-Volatile Compound



Semi-Volatile Mass Fraction

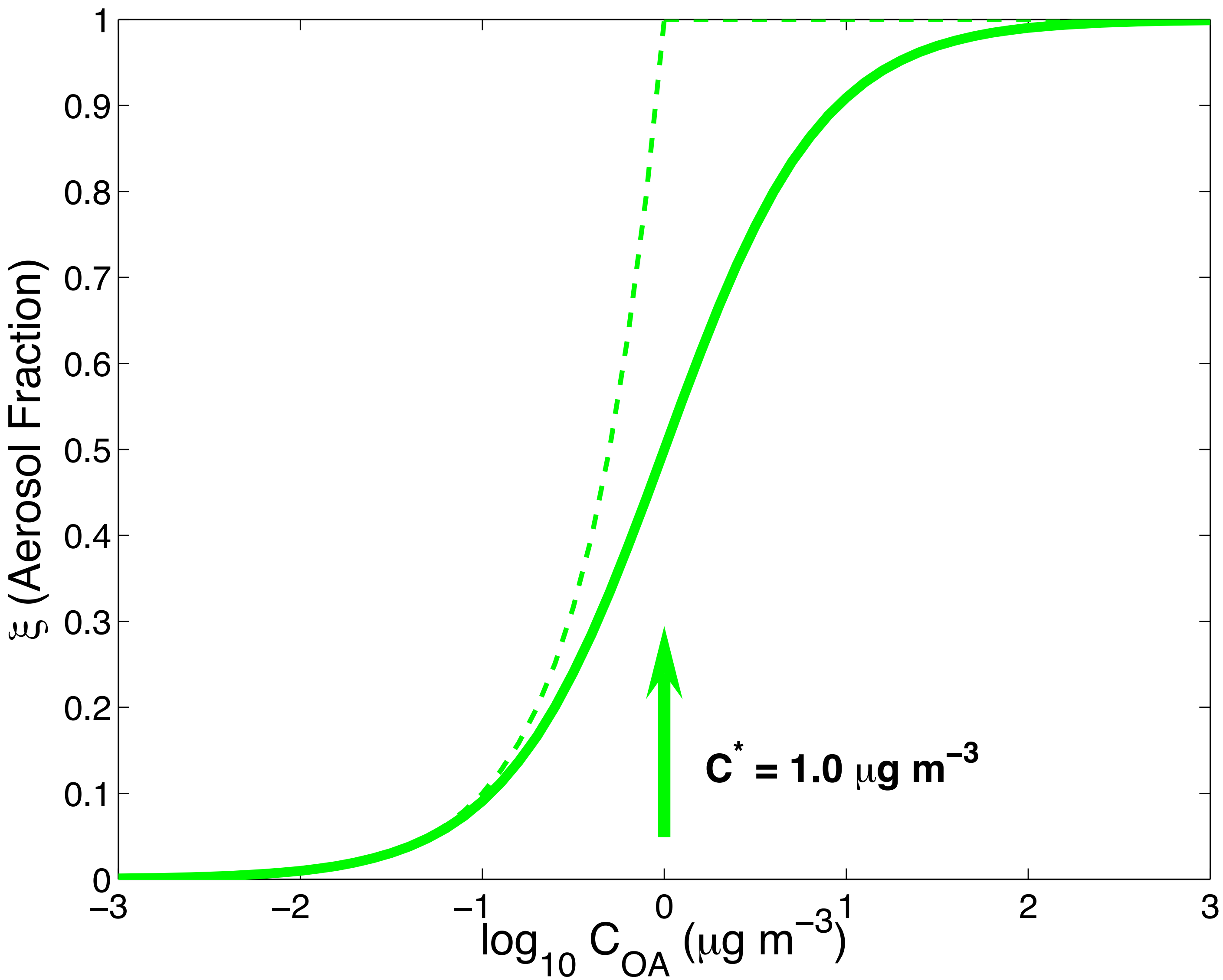


Partitioning of Single Component



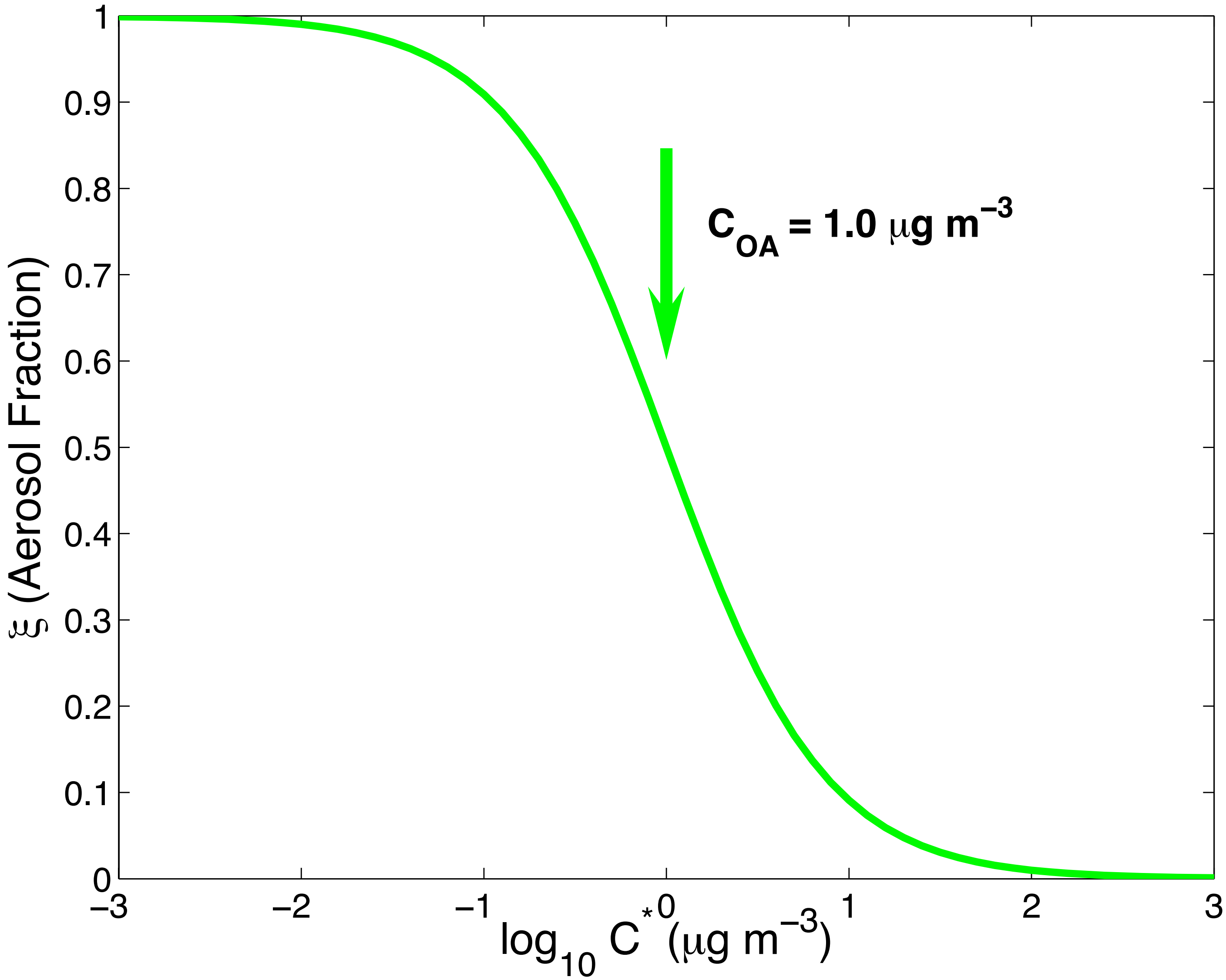
$$\xi_{\mathbf{i}} = \frac{1}{1 + \frac{\mathbf{C}_{\mathbf{i}}^{*}}{\mathbf{C}_{\mathbf{OA}}}}$$

Partitioning of Single Component (log X Axis)



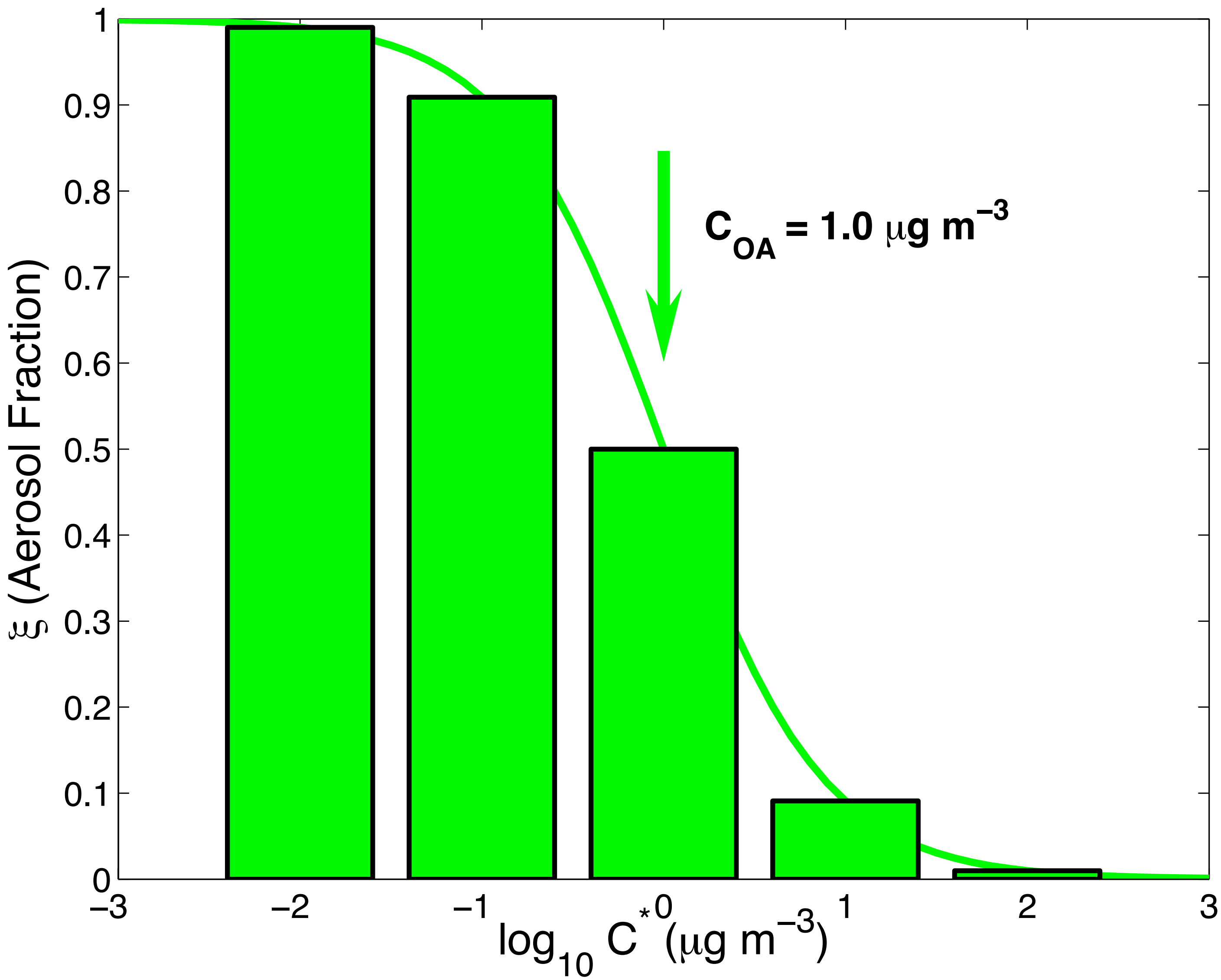
$$\xi_{\mathbf{i}} = \frac{1}{1 + \frac{\mathbf{C}^*_{\mathbf{i}}}{\mathbf{C_{OA}}}}$$

Partitioning at Specified C_{OA} in Solution



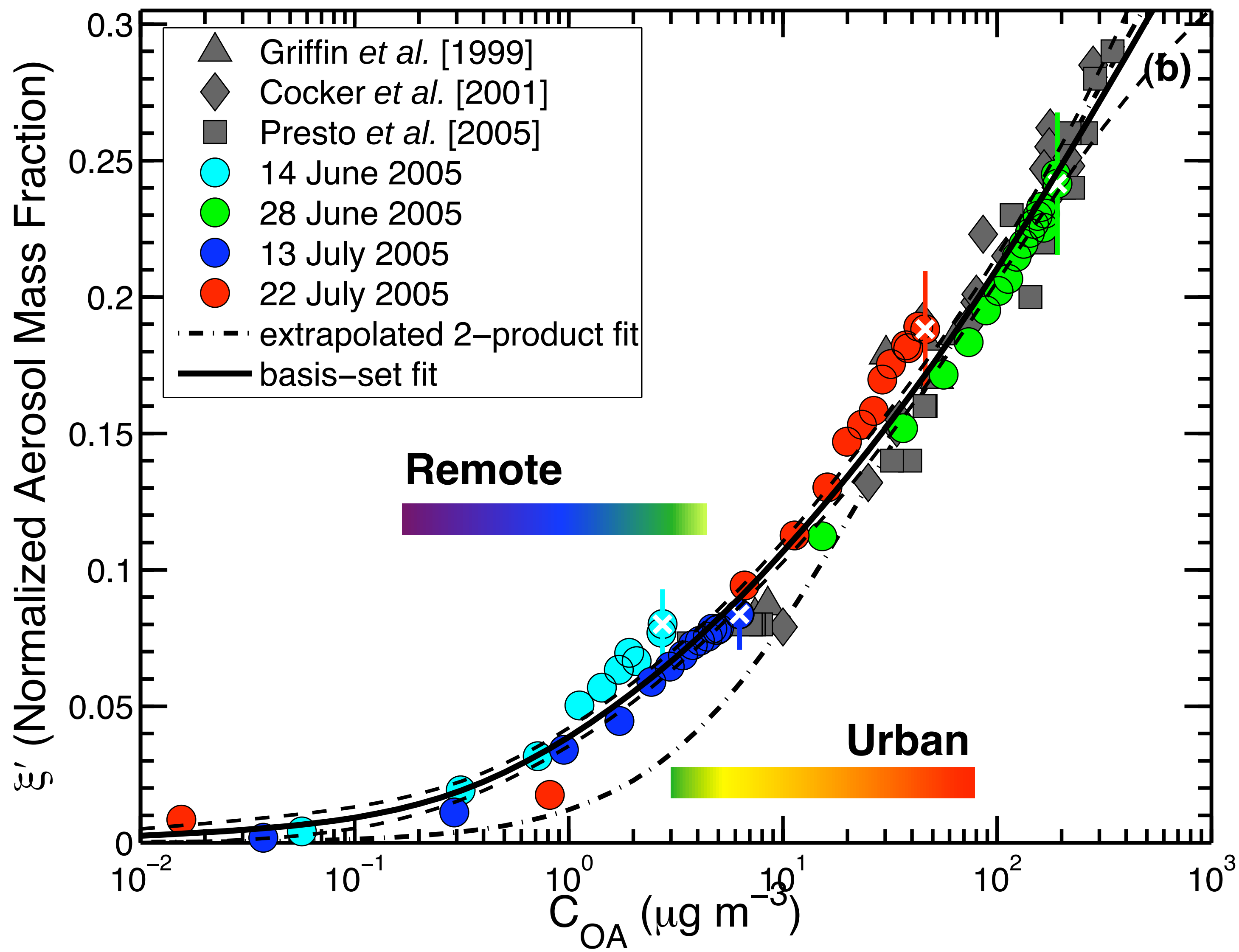
$$\xi_{\mathbf{i}} = \frac{1}{1 + \frac{\mathbf{C_i^*}}{\mathbf{C_{OA}}}}$$

The Volatility Basis Set



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

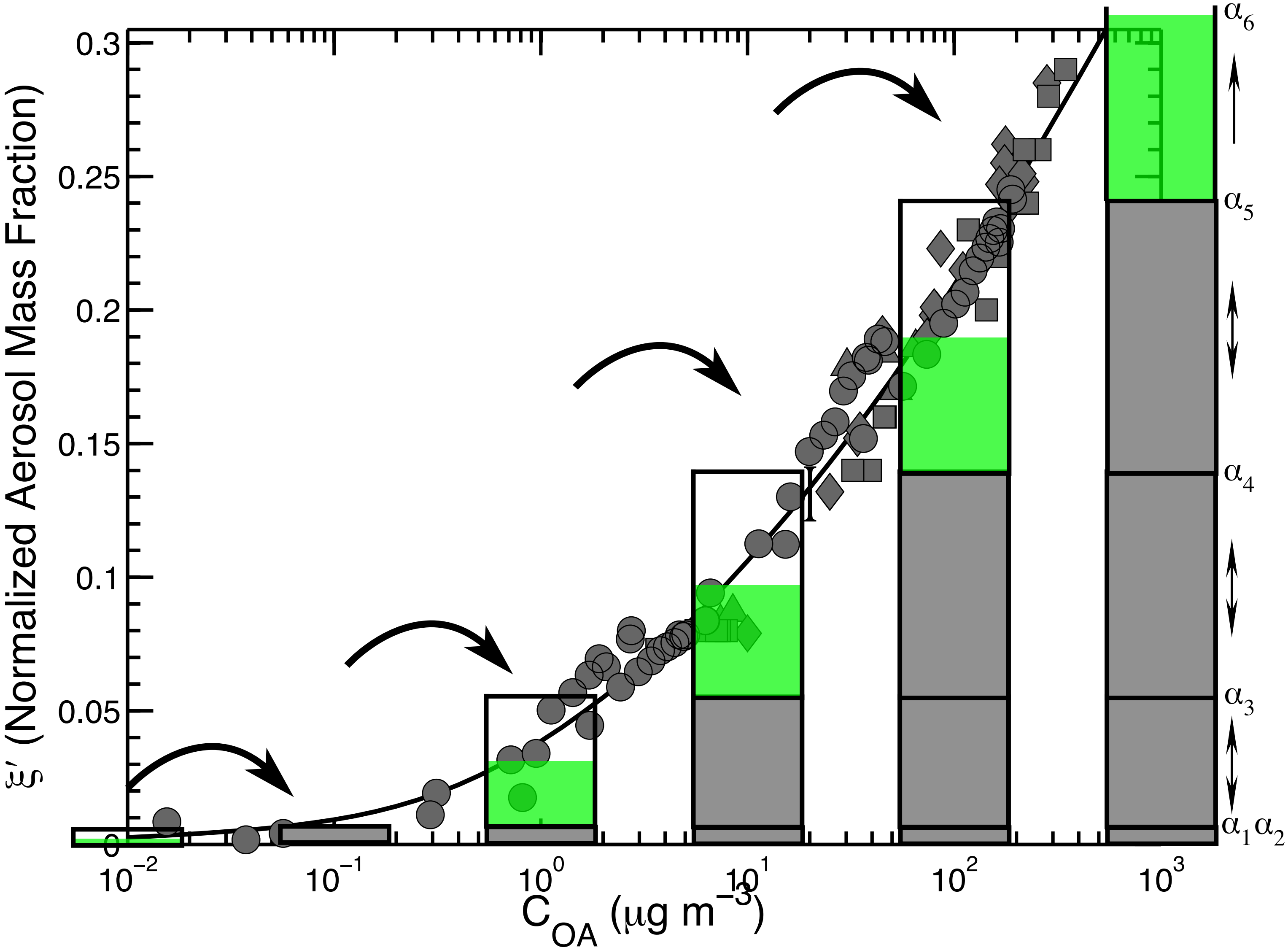
α-pinene + Ozone



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

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

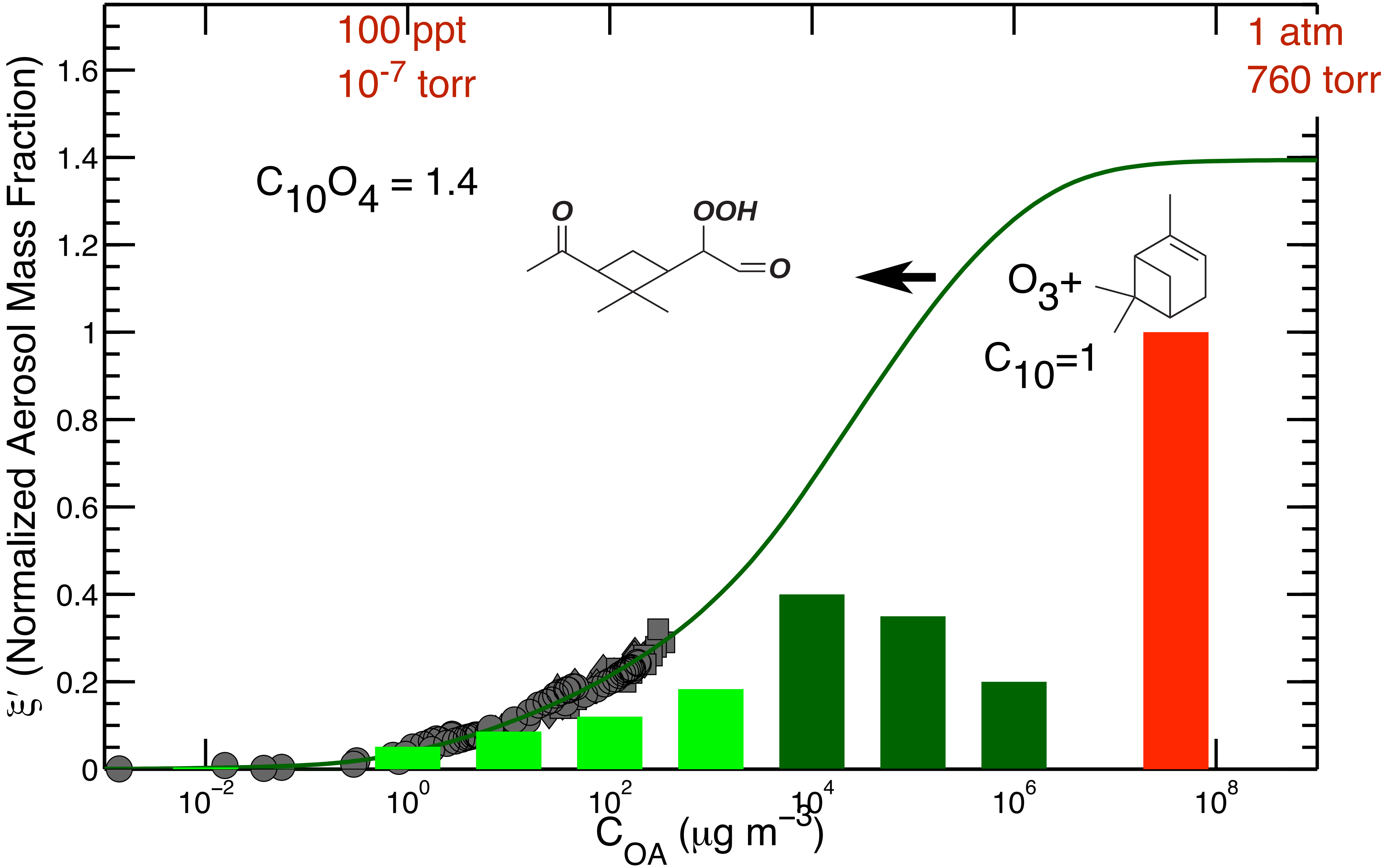
α-pinene and the Basis Set



(mass yields α')

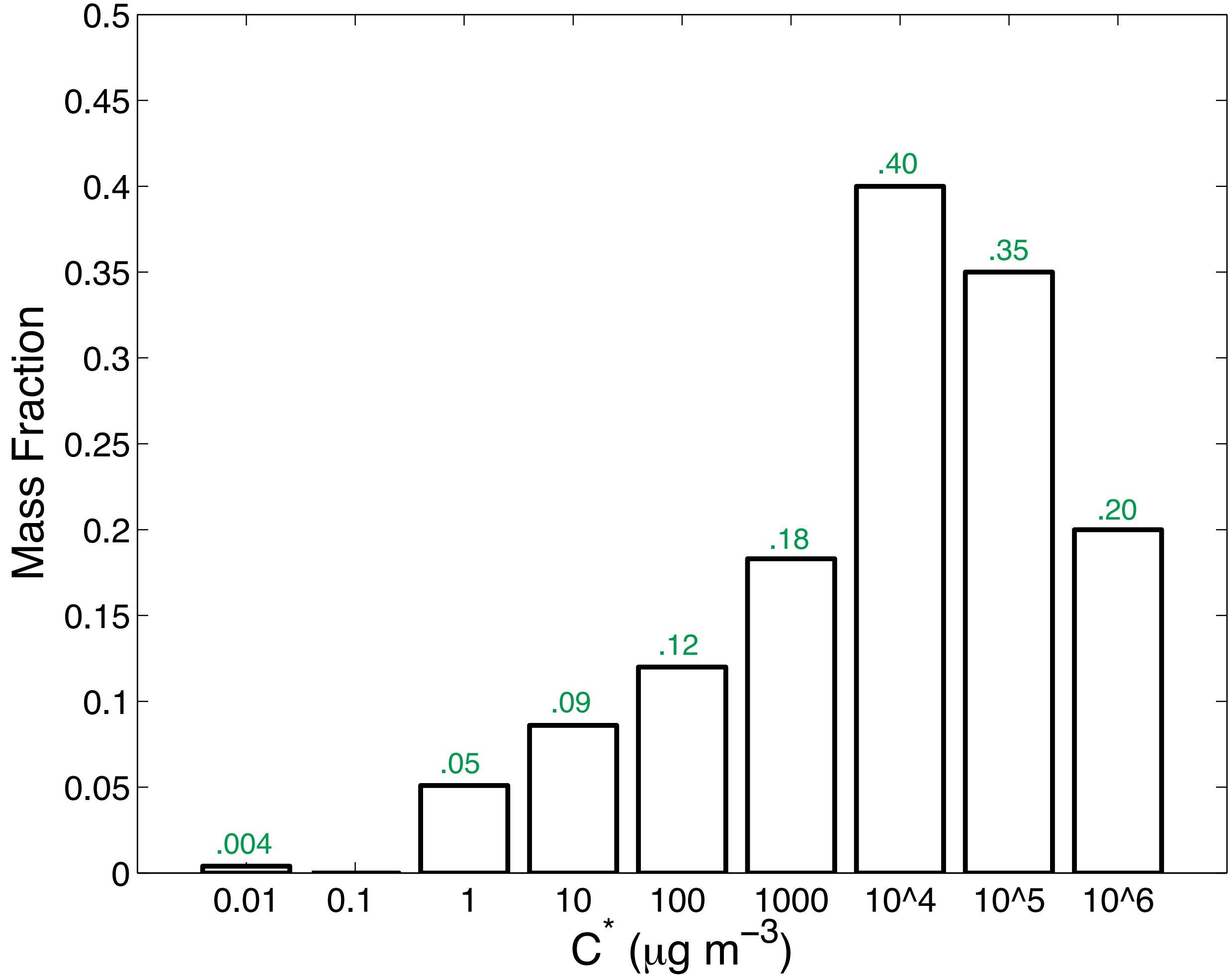
$$\alpha'_{\mathrm{i}} = \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, ...\}$$

α-Pinene + Ozone Mass Balance



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

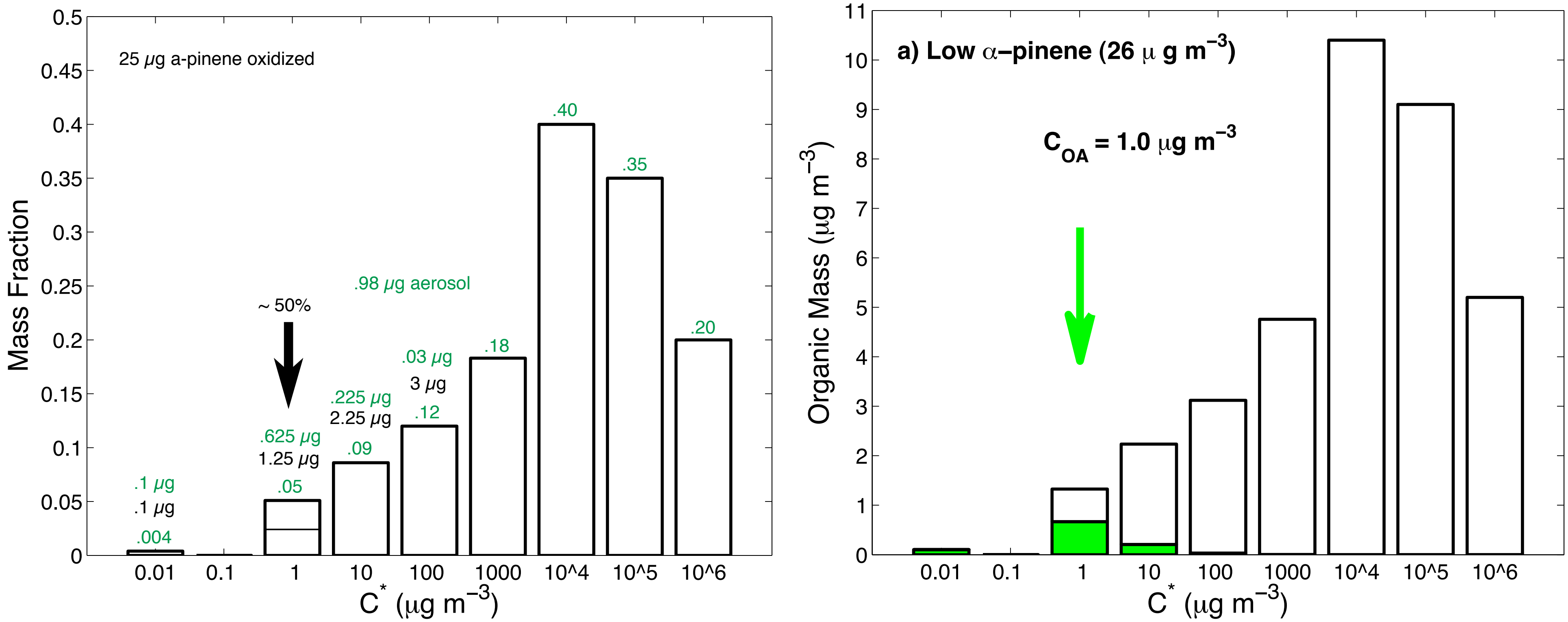
α-Pinene + Ozone Product Distribution



Products distributed over volatility space (a transformation vector)
Note very small yield of ‘nucleator’, consistent with [Burkholder *et al.* 2006]
Multiply yields by mass of α-pinene consumed to get product masses.

[Donahue *et al.* in prep]

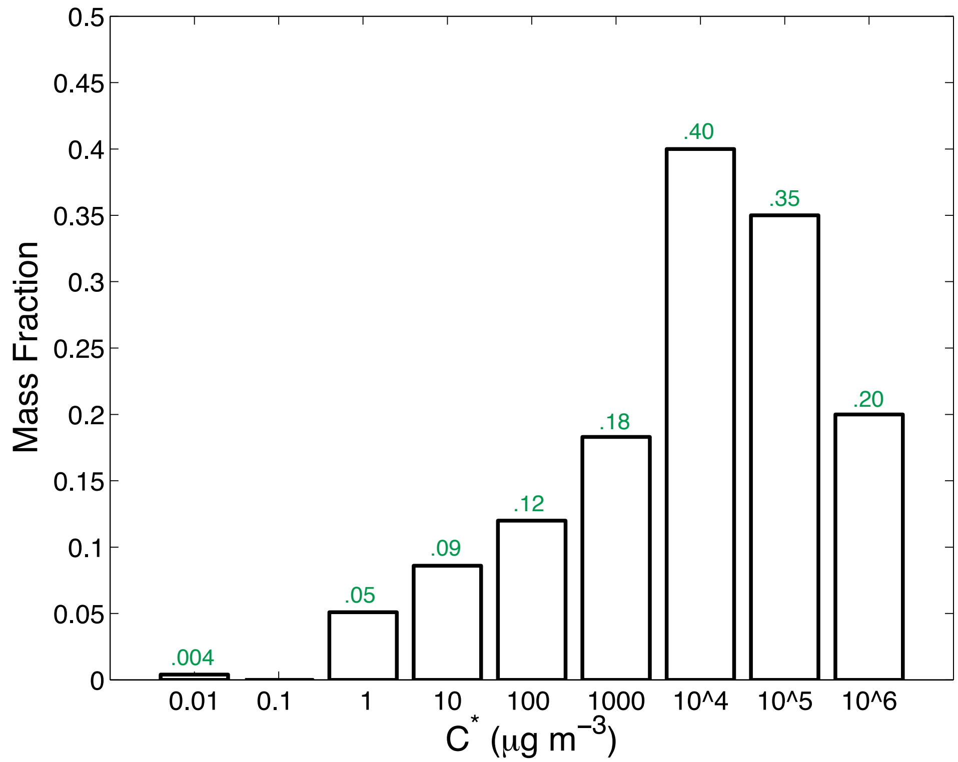
Basis-set 101: Basis Basics



Oxidize some amt. of precursor, say 25 $\mu\mathrm{g\,m^{-3}}$, and distribute products.
Start adding from left and see which bin is roughly saturated.
Partition that bin 50:50, others accordingly. Add salt to taste. Adjust accordingly.

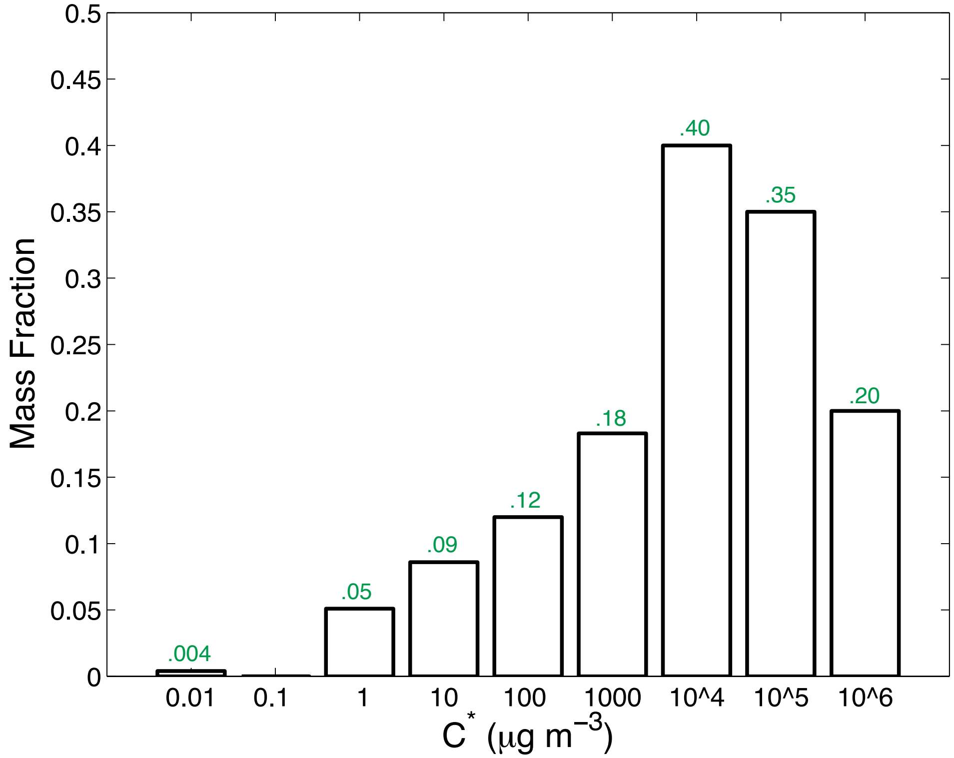
[Donahue *et al.* in prep]

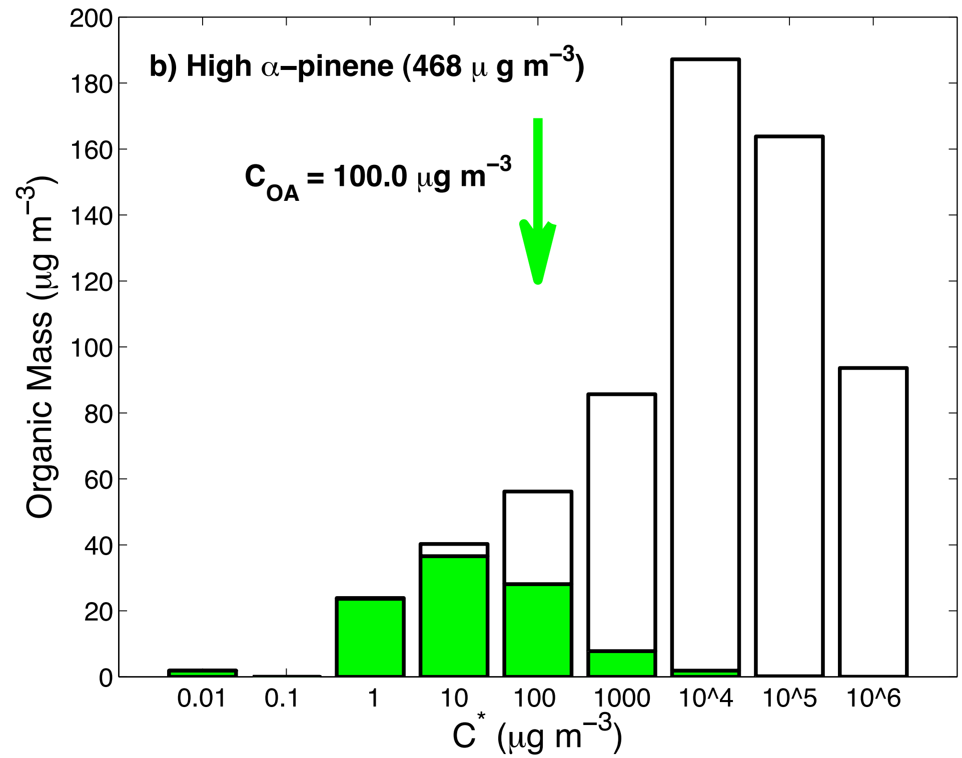
Basis-set 101: Pop Quiz!!



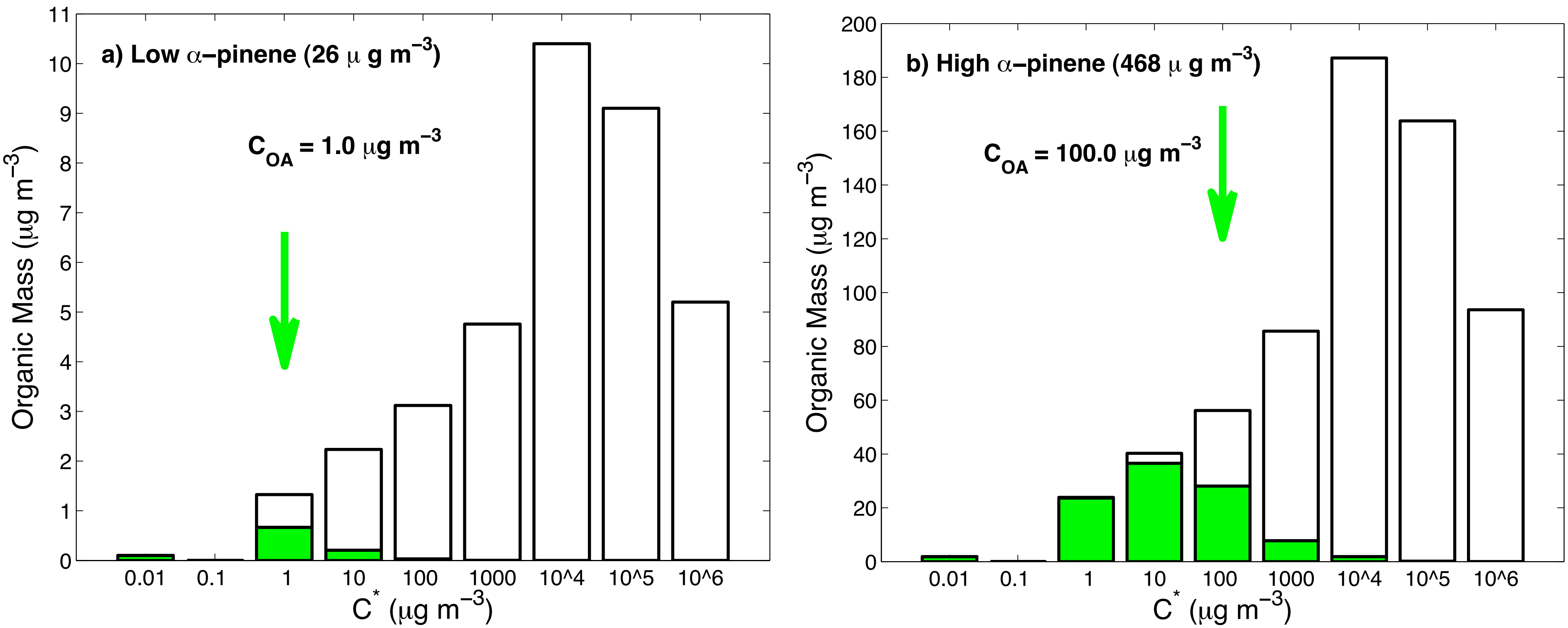
Oxidize $500\,\mu\mathrm{g\,m}^{-3}$, of α-pinene and calculate partitioning.

Basis-set 101: Answer





α-Pinene + Ozone Partitioning

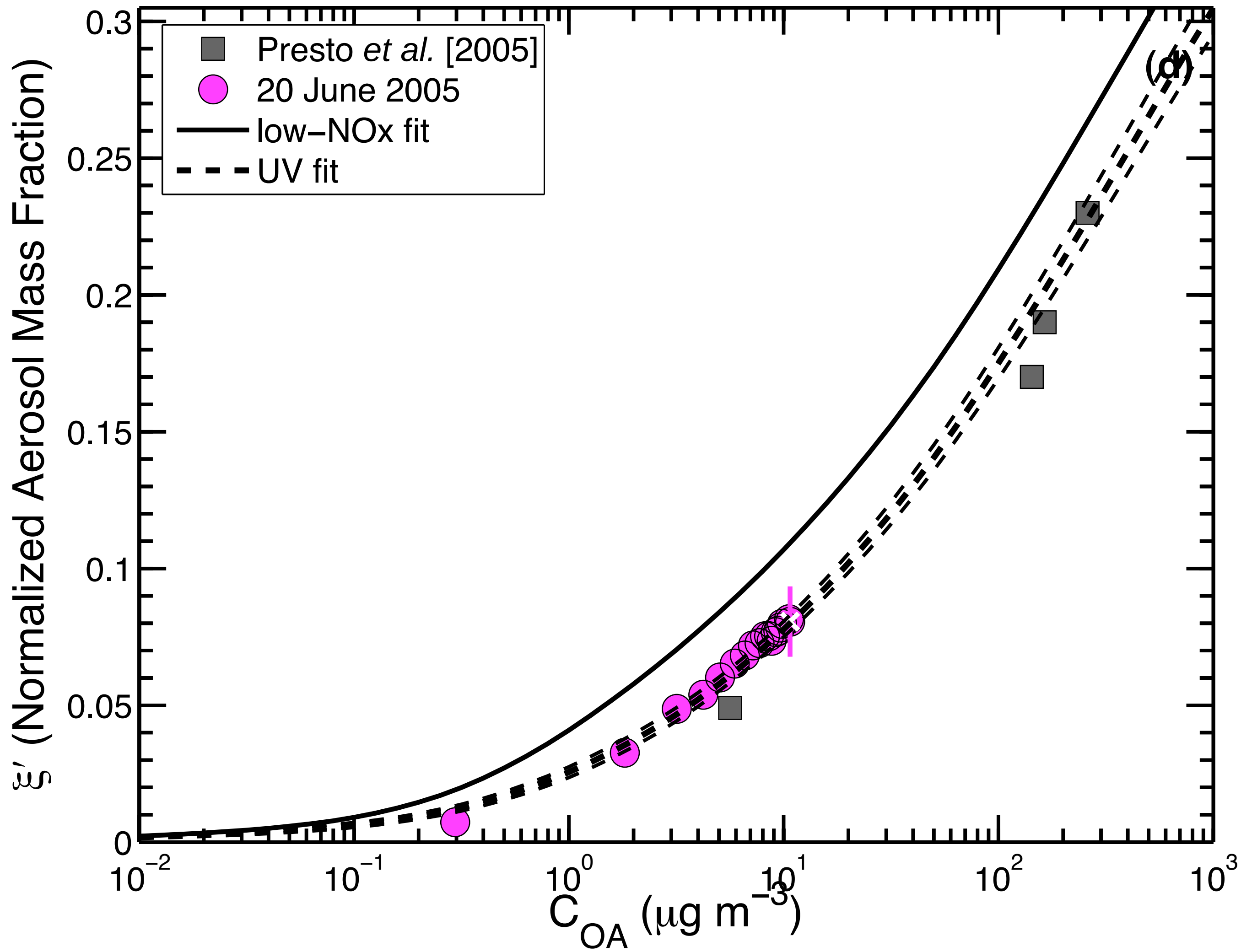


Partitioning changes with mass loading: x18 total loading = x100 C_{OA}.

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: UV (no NO_x)



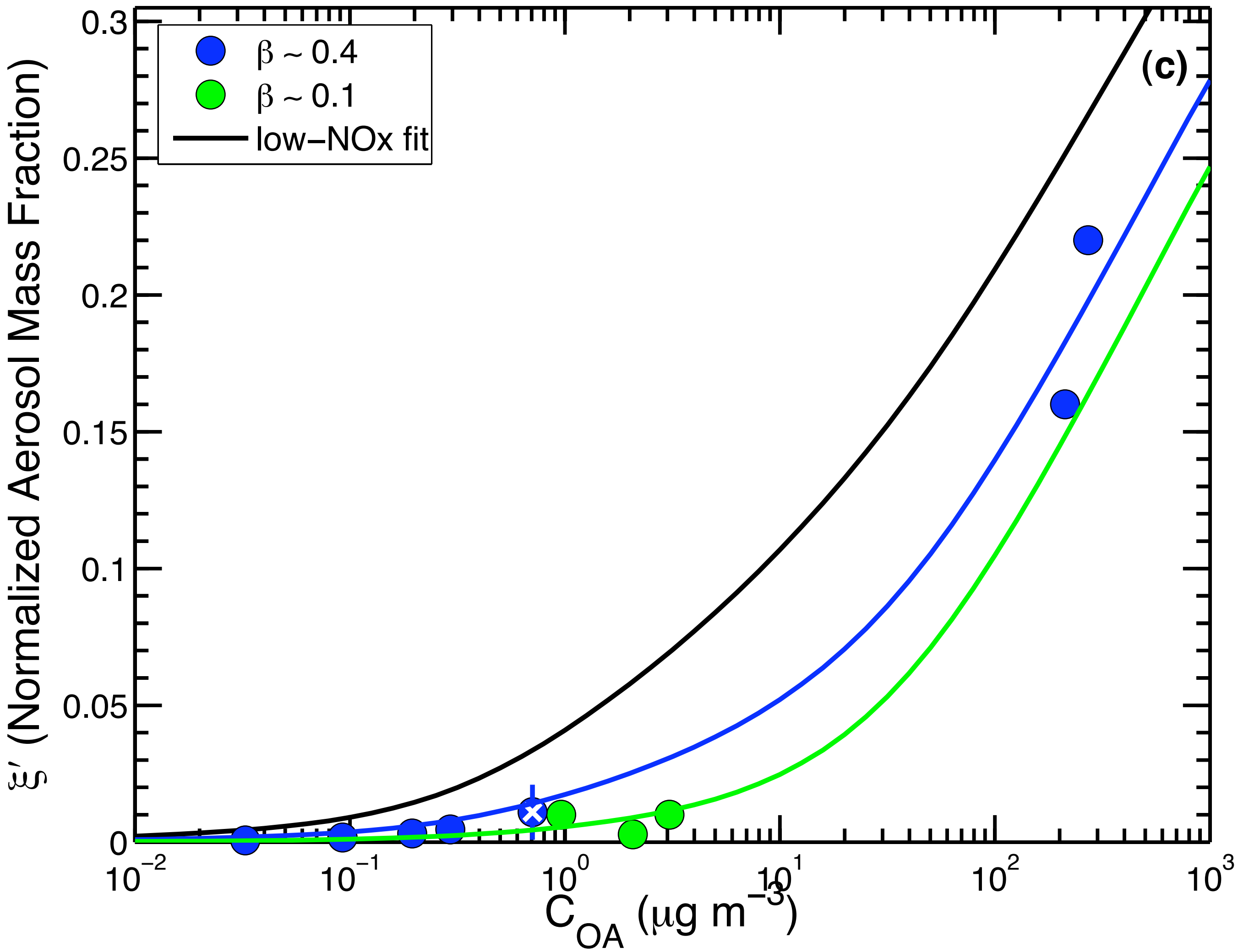
$$\alpha'_{\mathrm{i}} = \{.004, \quad 0, \quad \mathbf{.05}, \quad .09, \quad .12, \quad .18, ...\}$$

$\downarrow$ UV

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

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

α-pinene + Ozone: VOC:NO$_x$



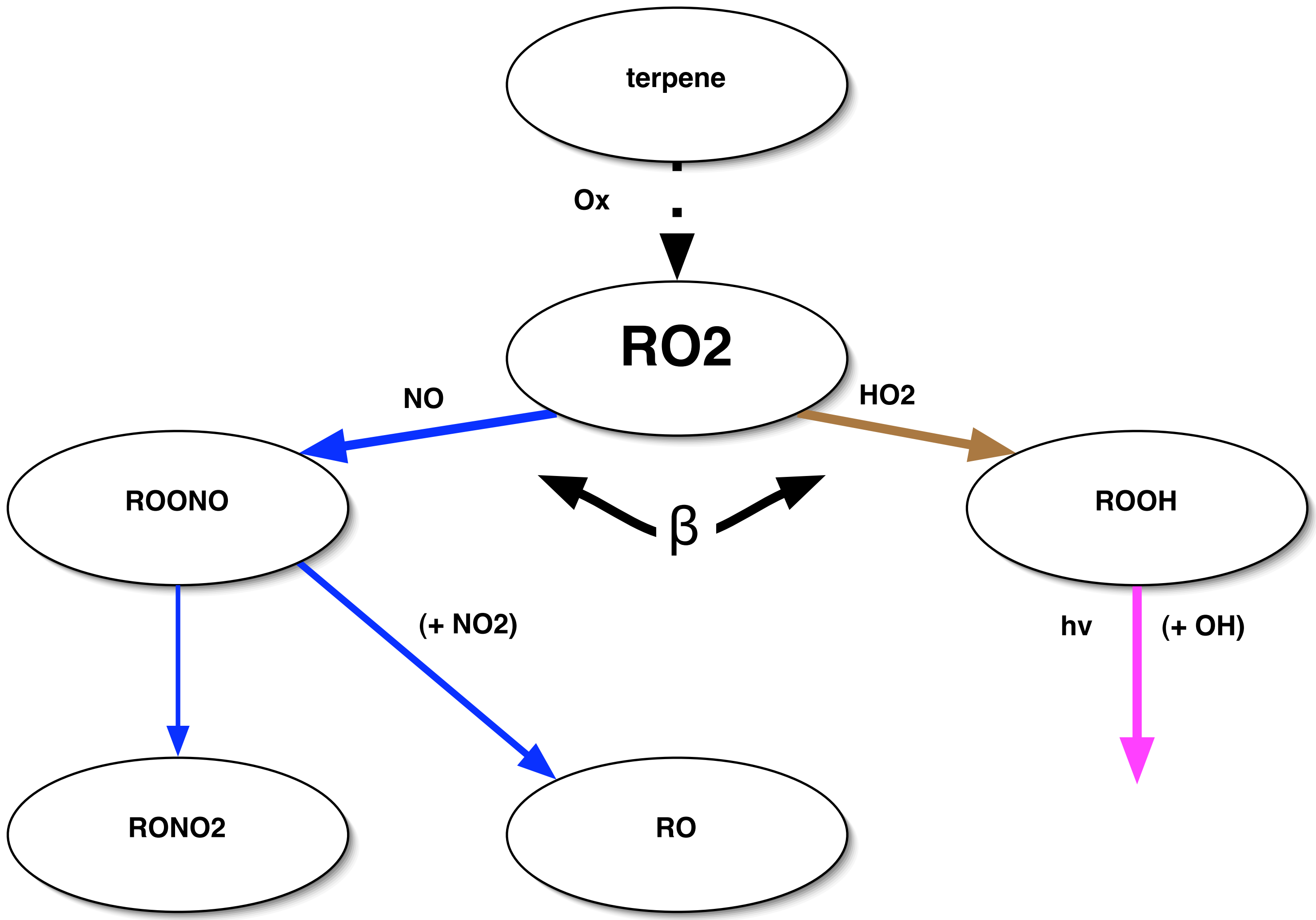
$$\alpha'_i(\mathrm{HO_2}) = \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, \ldots\}$$

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

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

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

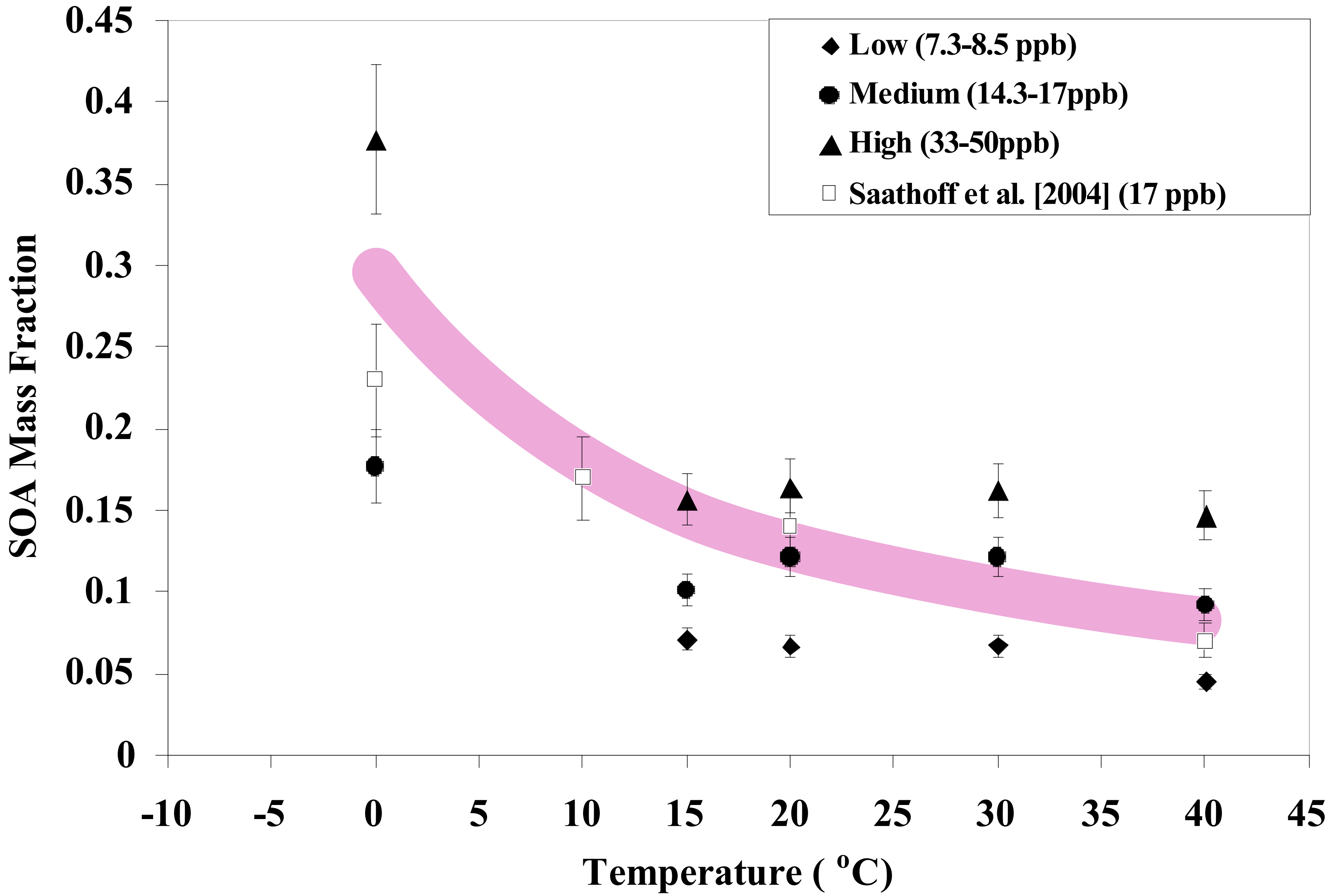
RO_2 Fate



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

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

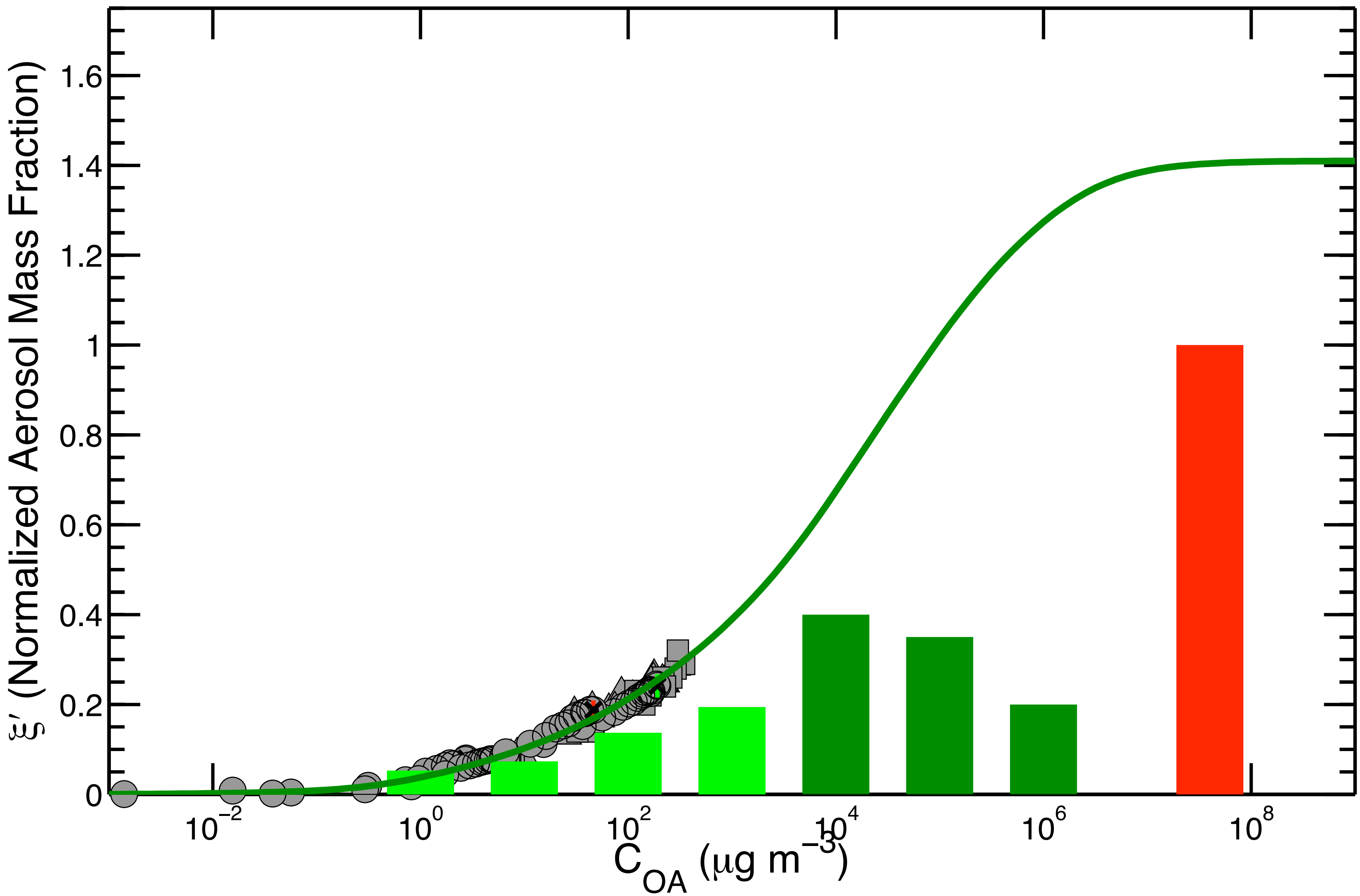
α-Pinene + Ozone T Dependence



Upturn in SOA between 15 and 0^{O}C.

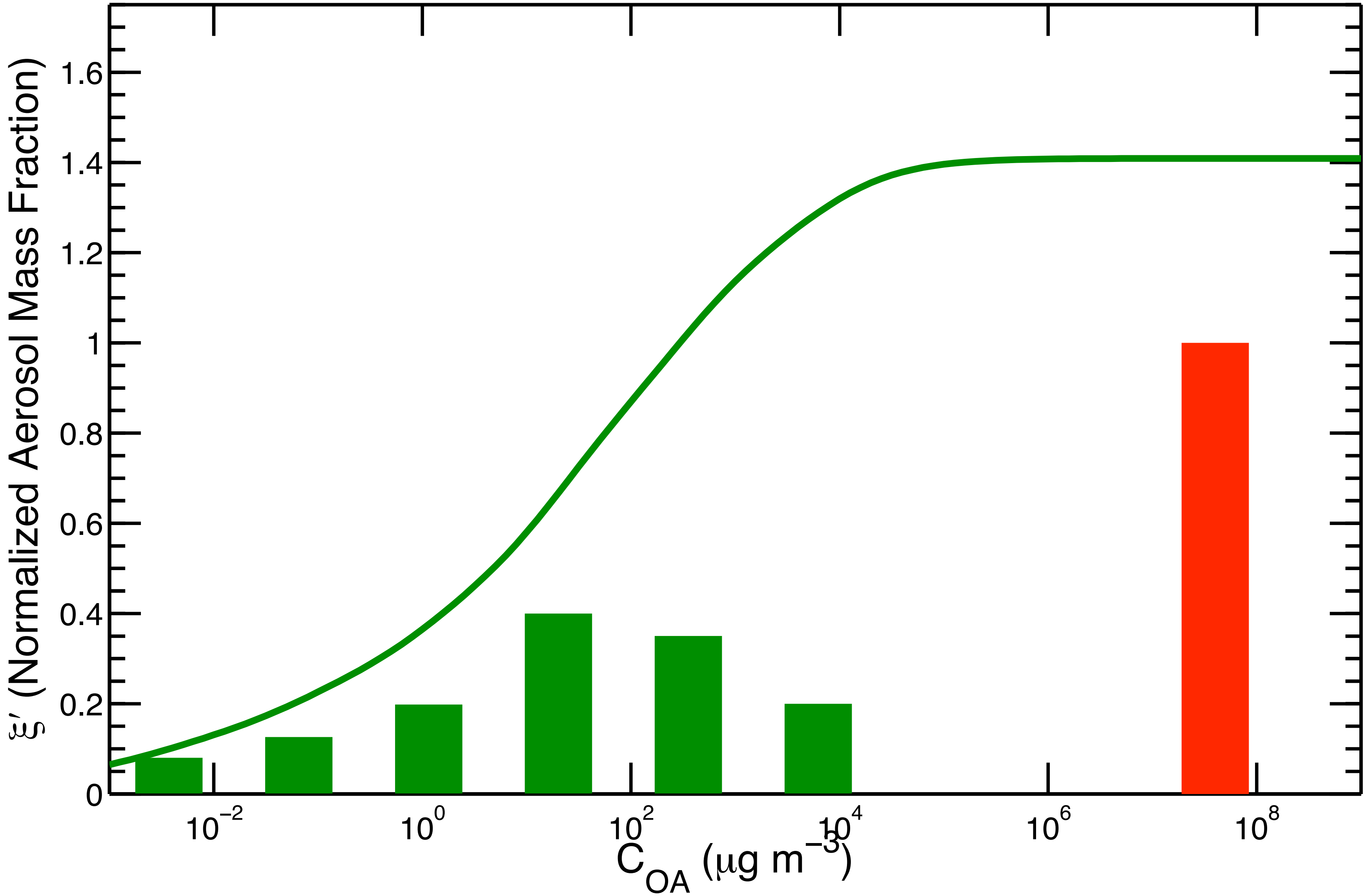
[Pathak *et al., JGR*, 2007], [Stanier *et al., ACPD*, 2007]

α-Pinene + Ozone Total Mass 300 K



Dark green yields are guesses – total is constrained.

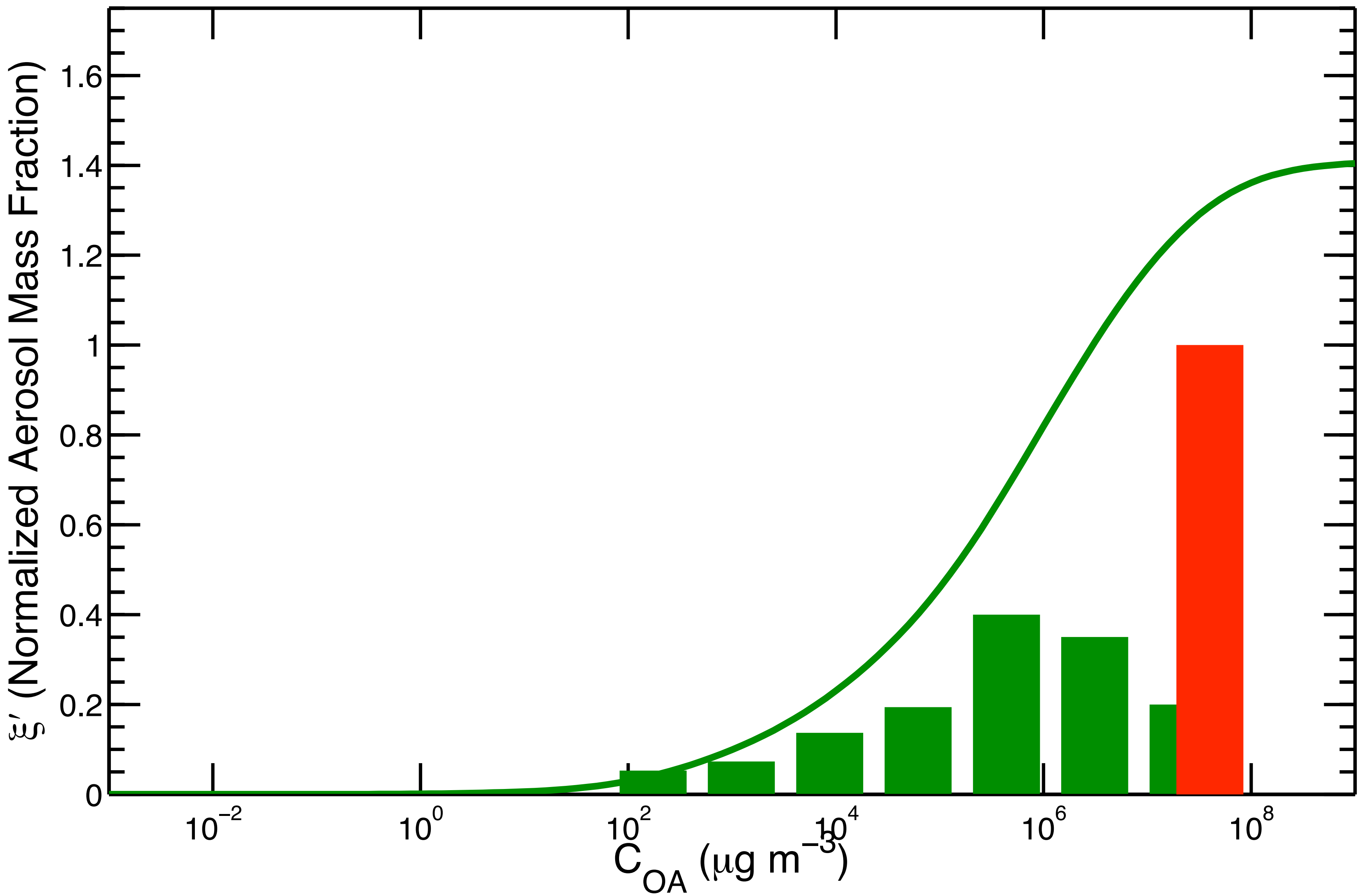
α-Pinene + Ozone Total Mass 243 K



Products shift left by 2.5 orders of magnitude.

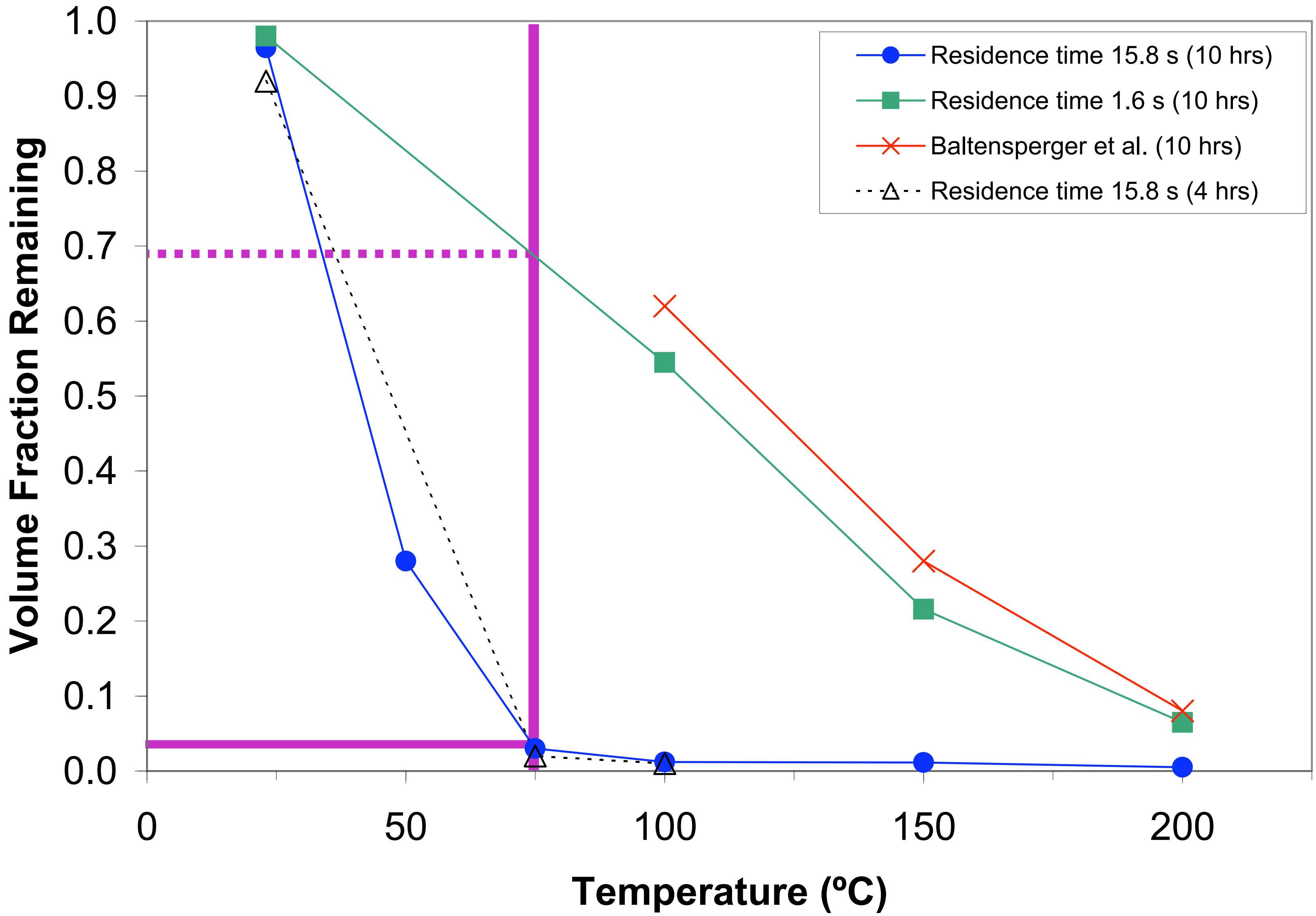
(Note – [Saathoff *et al.* IAC 2006] saw $\sim$1 AMF at 100-200 μg m^{-3} and 243 K.)

α-Pinene + Ozone Total Mass 350 K



Products shift right by 2.5 orders of magnitude.

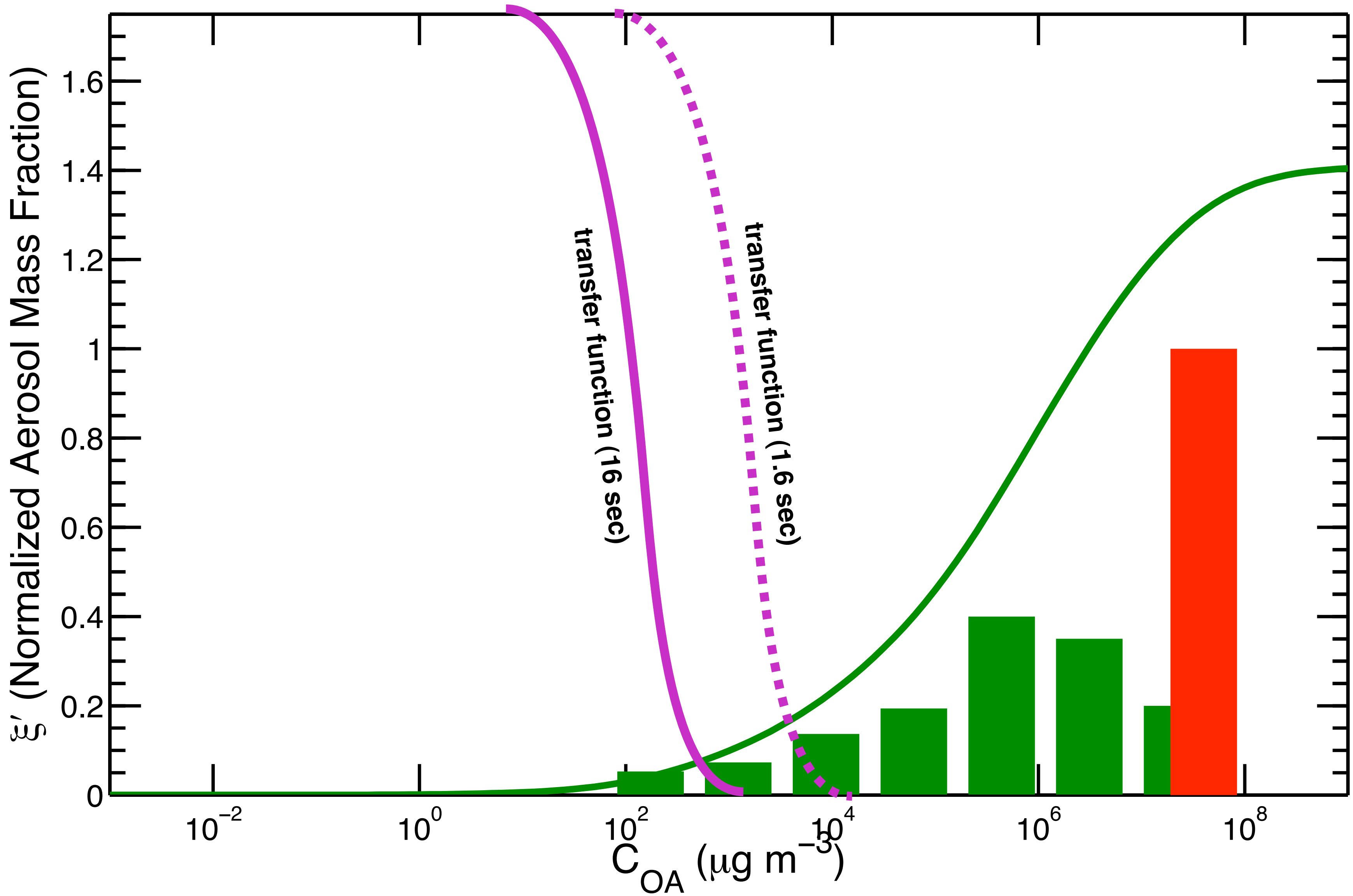
α-Pinene + Ozone Thermodenuder



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

[An *et al., Aerosol Sci.*, 2007]

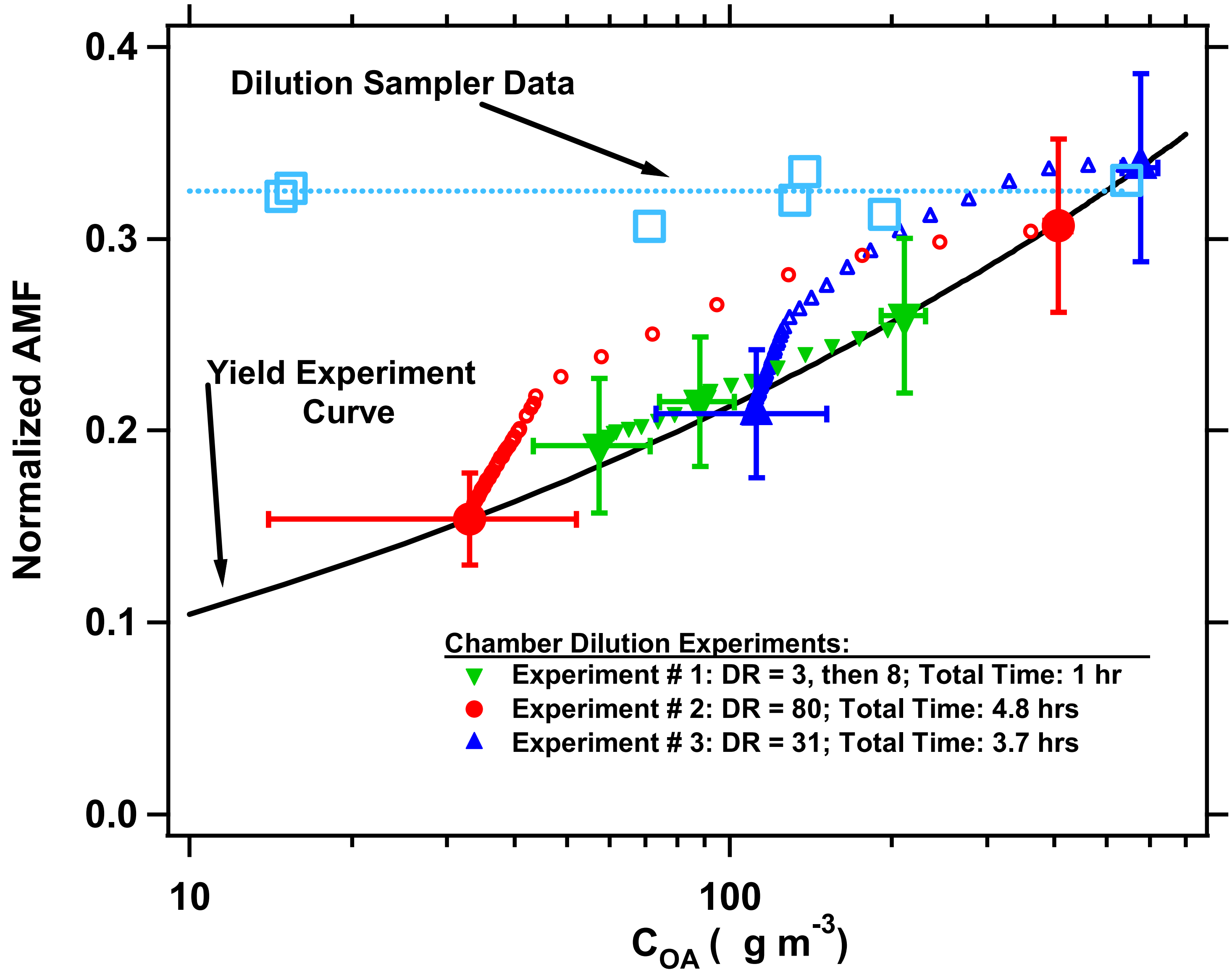
α-Pinene + Ozone Thermodenuder



Denuding is a function of evaporation timescales.

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

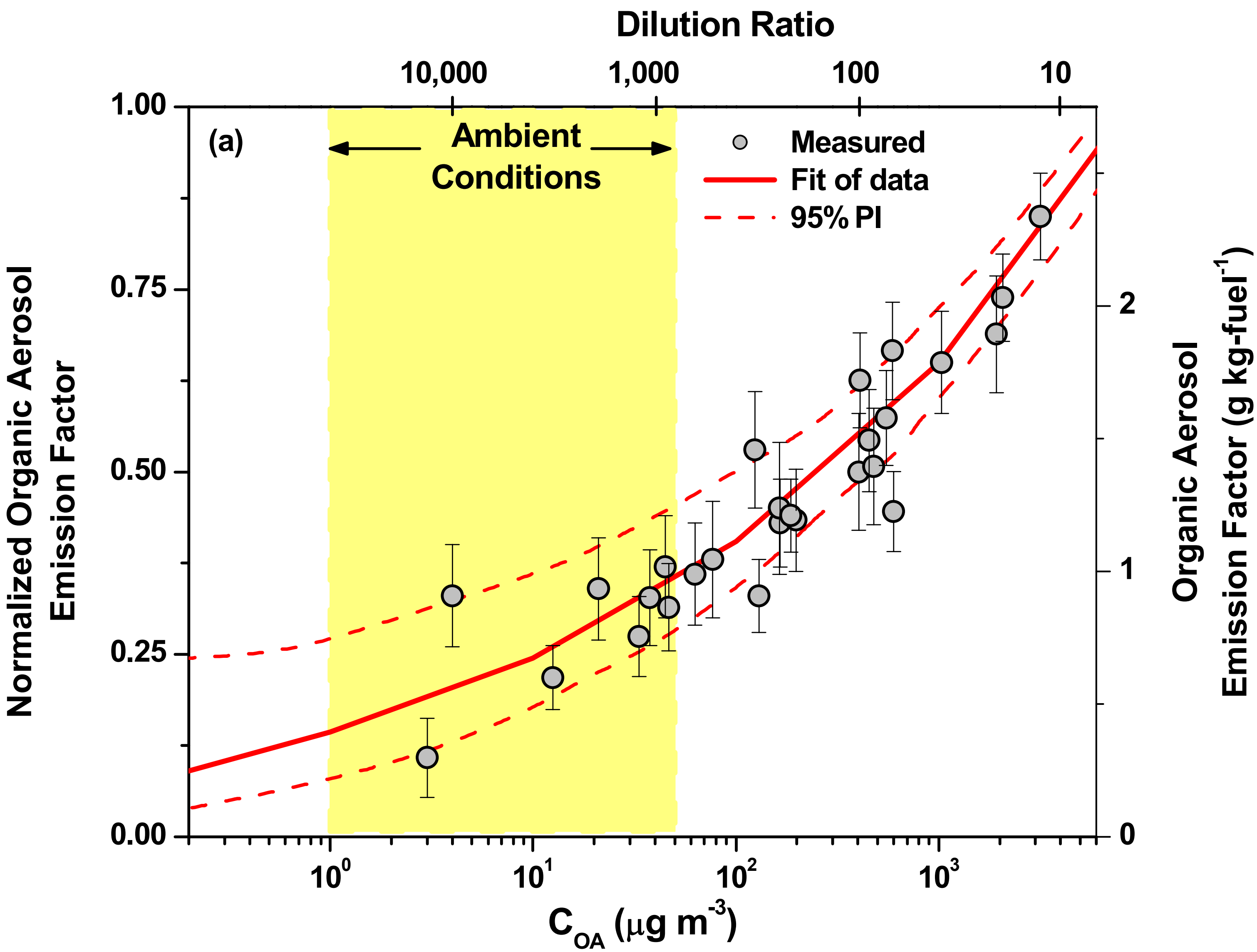
α-pinene + O_3 Dilution



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

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

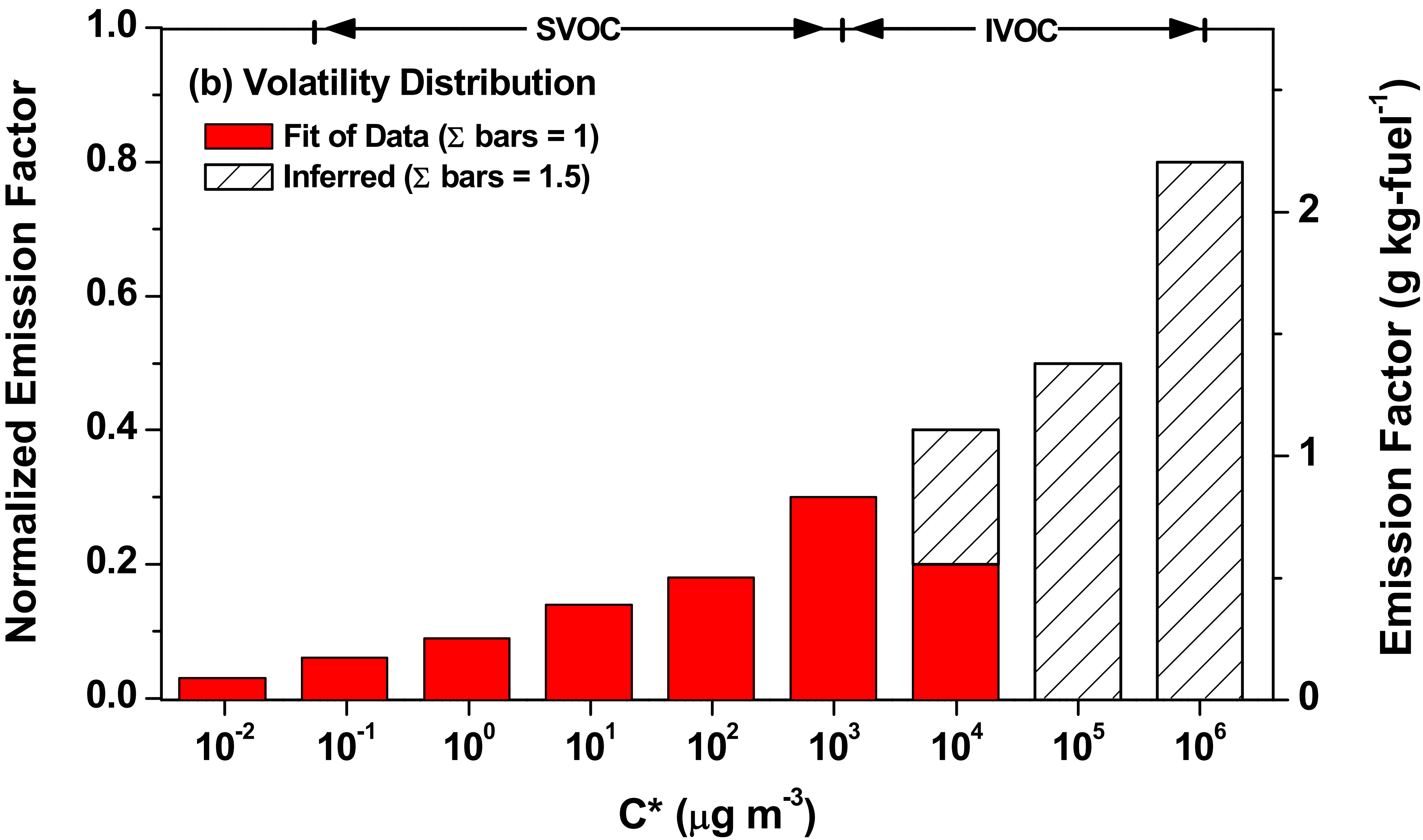
Dilution of Diesel Emissions



Dilution to smbient C_{OA} causes 67-90% evaporation of primary emissions.

[Shrivastava, Robinson, *et al., ES&T* [2006]

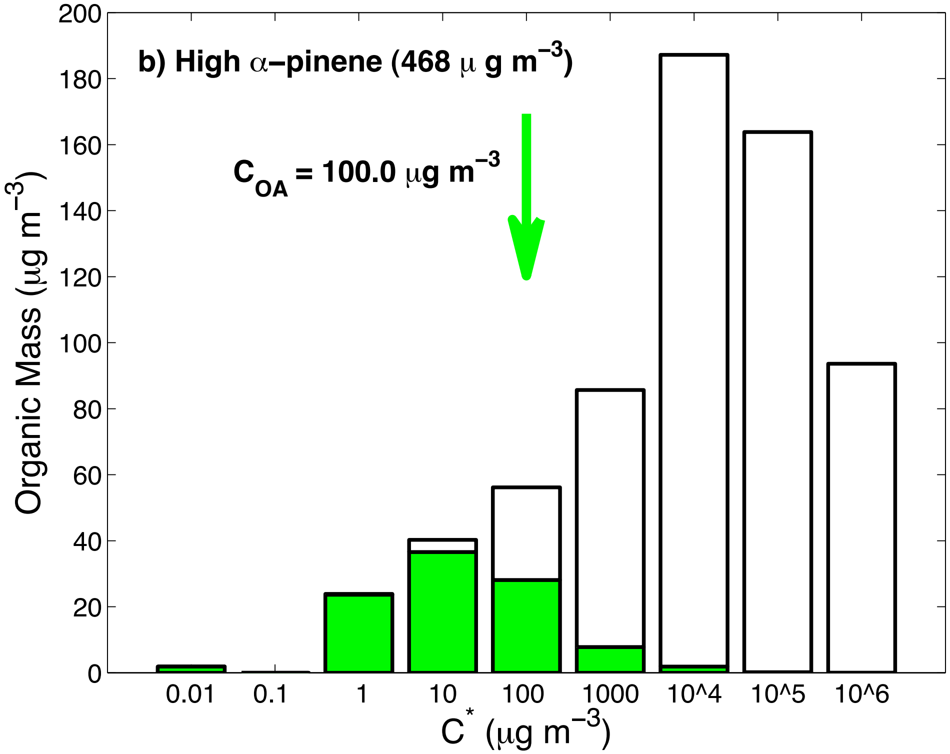
Basis Set Representation of Diesel Emissions

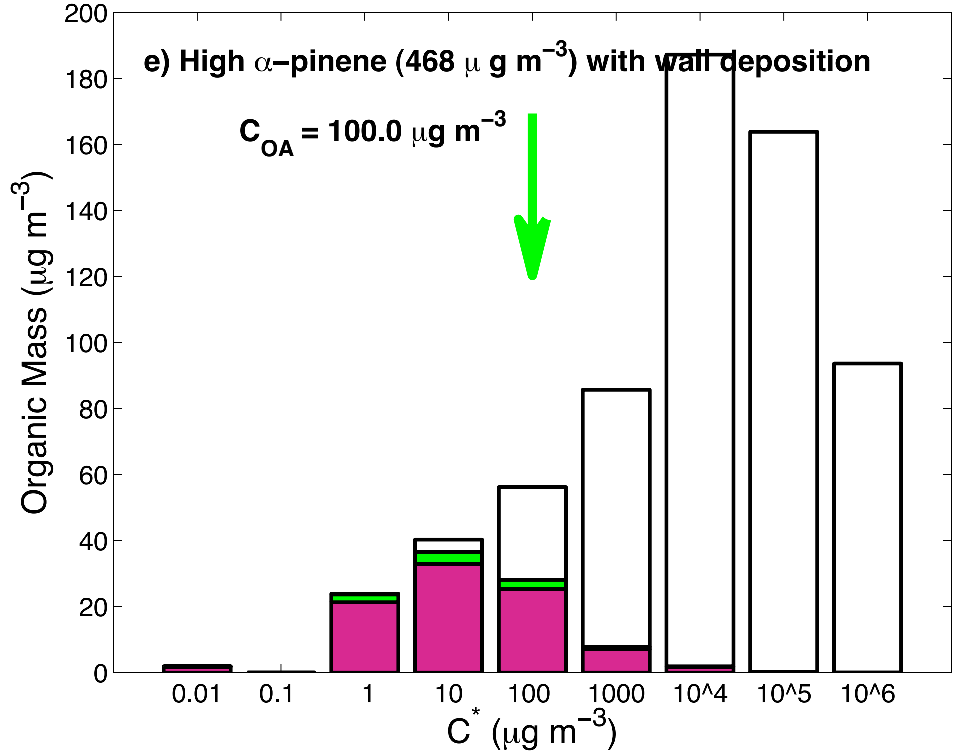


Emissions span volatility range, including 'IVOC'.

[Robinson, *et al., Science* [2007]

Basis-set 701: Advanced Basis





Consider *static* chamber experiments – i.e. 12 m^3 CMU chamber.

Generate $100\,\mu$g m^{-3} SOA and then let 90% deposit to the walls (purple).

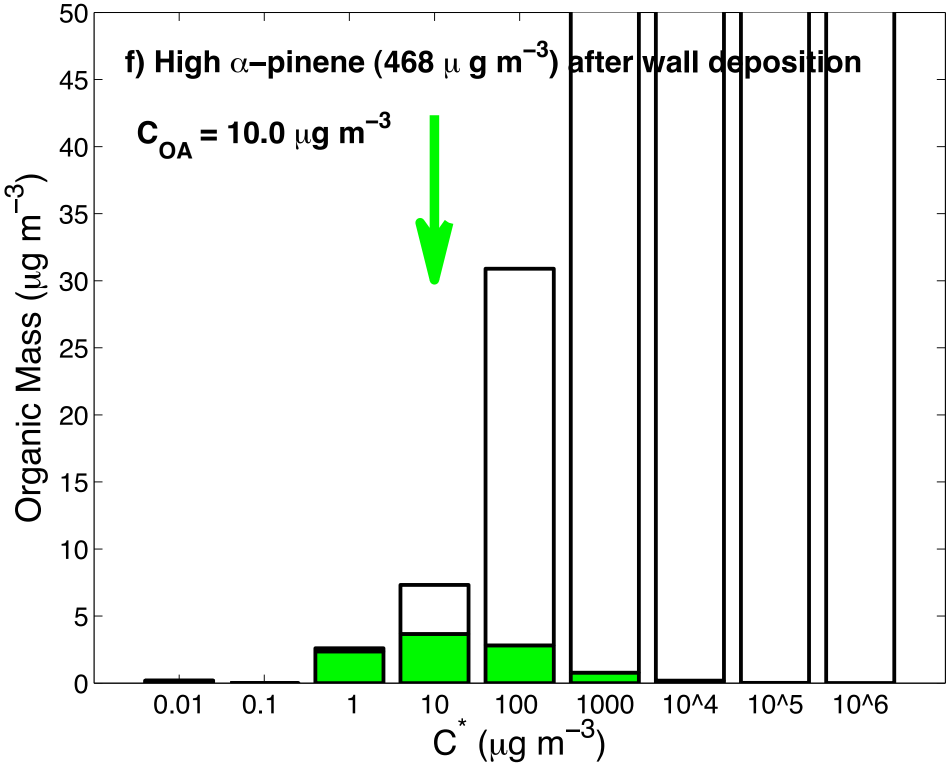
What is in equilibrium?

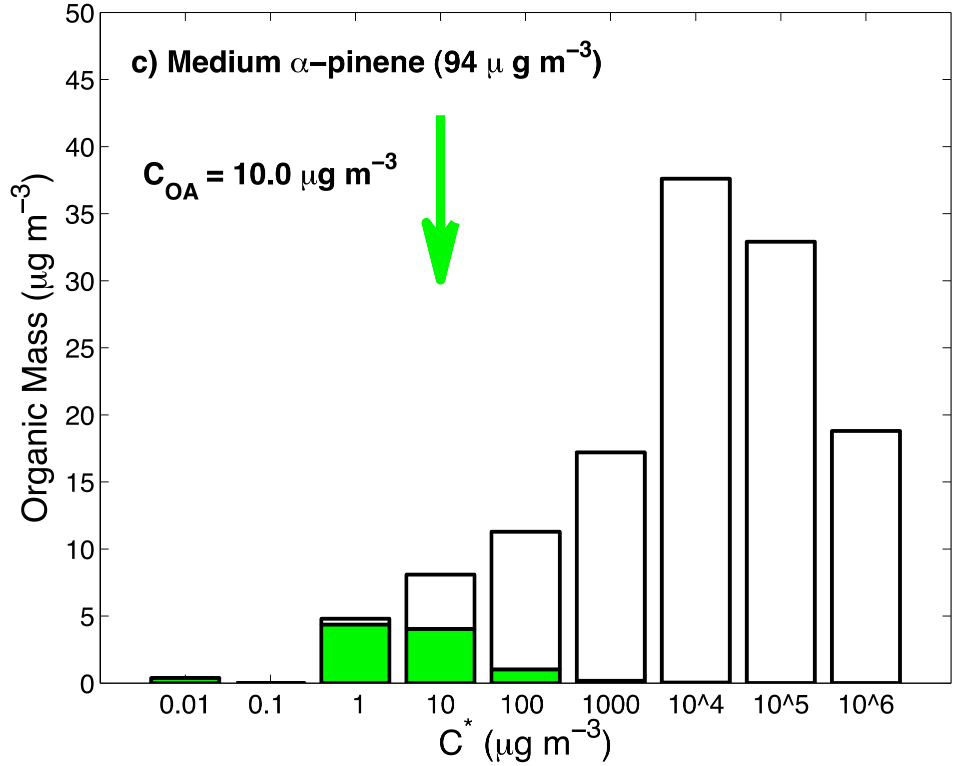
Vapors + suspended aerosol or Vapors + suspended aerosol + wall aerosol??

(work it out....)

[Donahue *et al.* in prep]

Basis-set 701: Wall Deposition



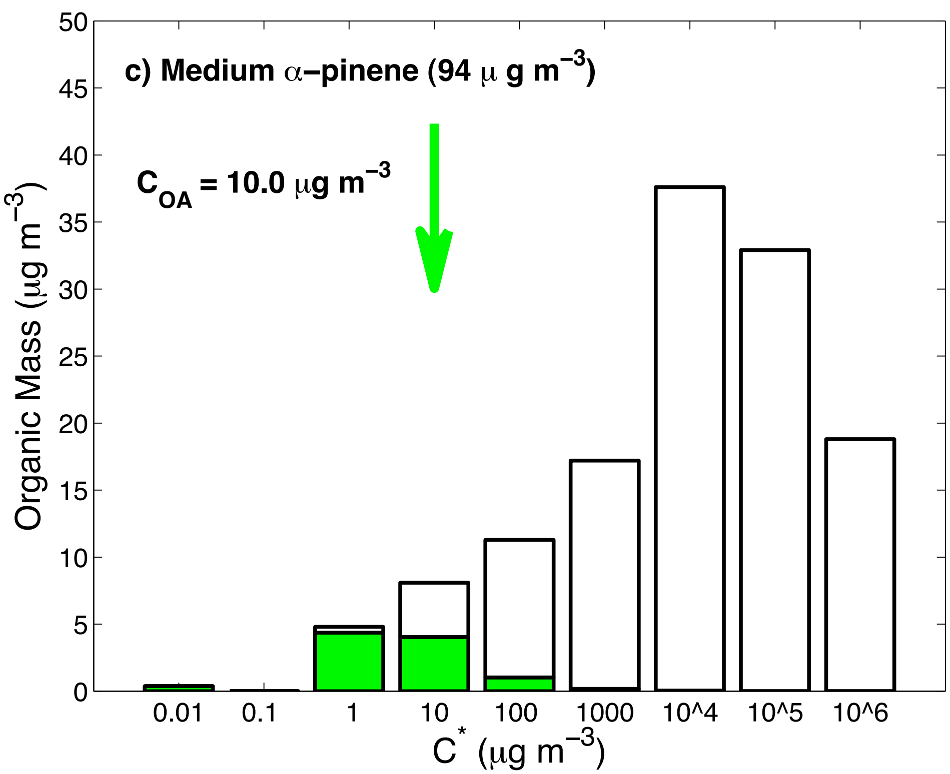


The answer is **BOTH!**

The suspended particles still represent the composition of $100\,\mu g\,m^{-3}$ SOA!

Deposition fractionates the total suspension toward the volatile products.

Basis-set 702: Steady-State Chambers



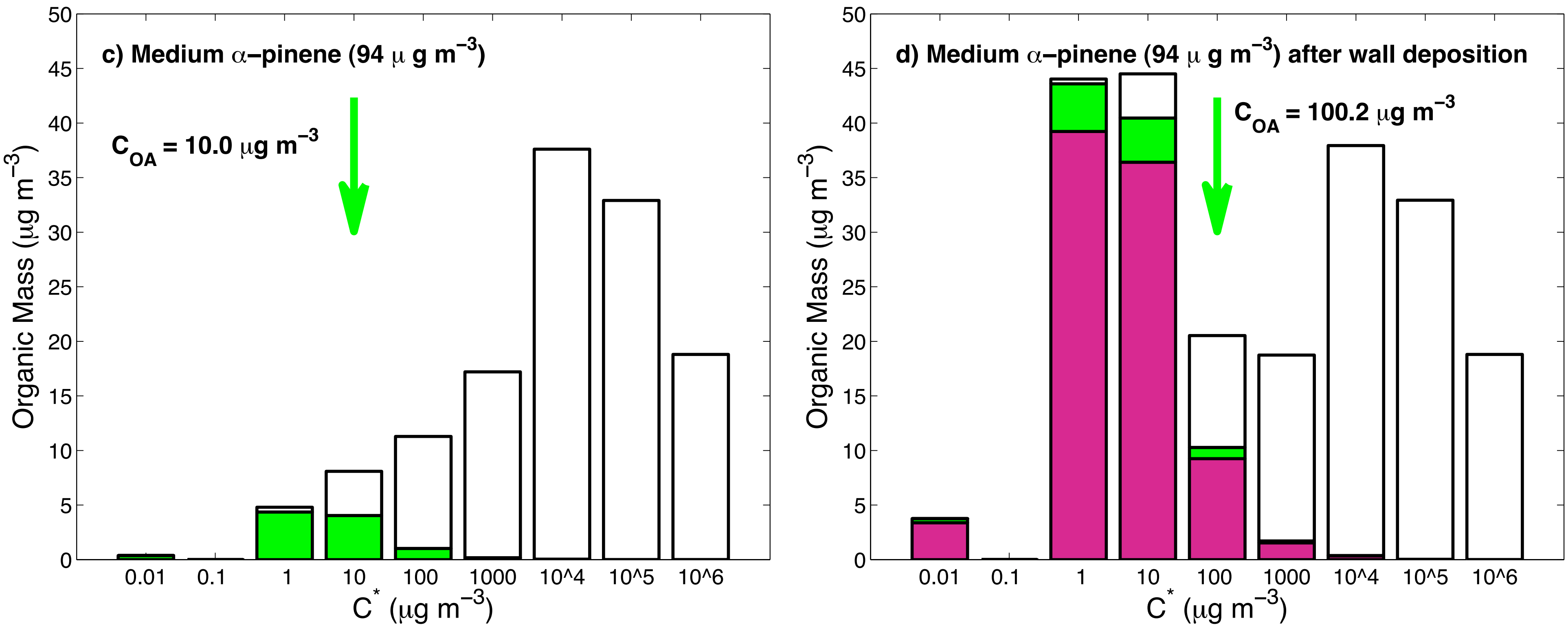
Now what happens in a 'steady-state' flow-through chamber?

Imagine an experiment with $10\,\mu\mathrm{g\,m^{-3}}$ suspended SOA that lasts 9 deposition lifetimes, so that

$C_{\mathrm{wall}} = 9\,C_{\mathrm{suspended}}$.

What happens to the distribution as particles collect irreversibly on the walls??

Basis-set 702: Flow-Through Wall Deposition



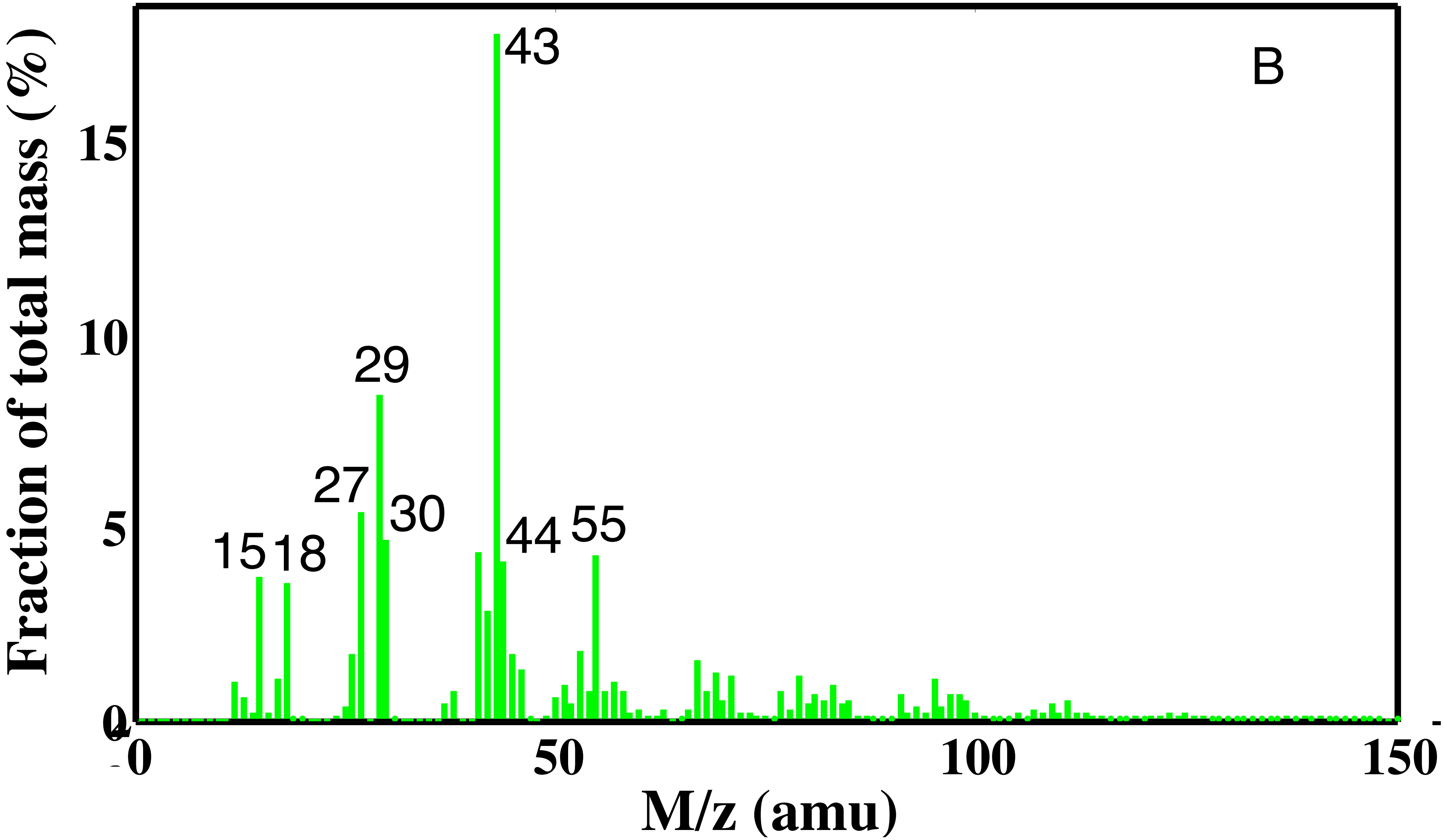
The suspended particles still represent the composition of $10\,\mu\mathrm{g\,m}^{-3}$ SOA!
However, the walls are covered with lower-volatility junk, total system at $100\,\mu\mathrm{g\,m}^{-3}$

Perturbing this system could have all kinds of strange consequences (it is buffered).
Bottom Line: Individual particles only know about the vapors.
Be very, very careful designing (and interpreting) experiments.

CONGRATULATIONS!

You are now a basis-set black belt.

Does Chamber SOA = OOA?



And now for the start of a lot of bad news... Chambers don't make OOA

AMS spectrum from limonene + O_3 is not OOA. [J. Zhang *et al. JPhysChem.* 2006]

α-pinene + O_3 just as bad – in fact *no* volatile precursors make OOA in chambers.

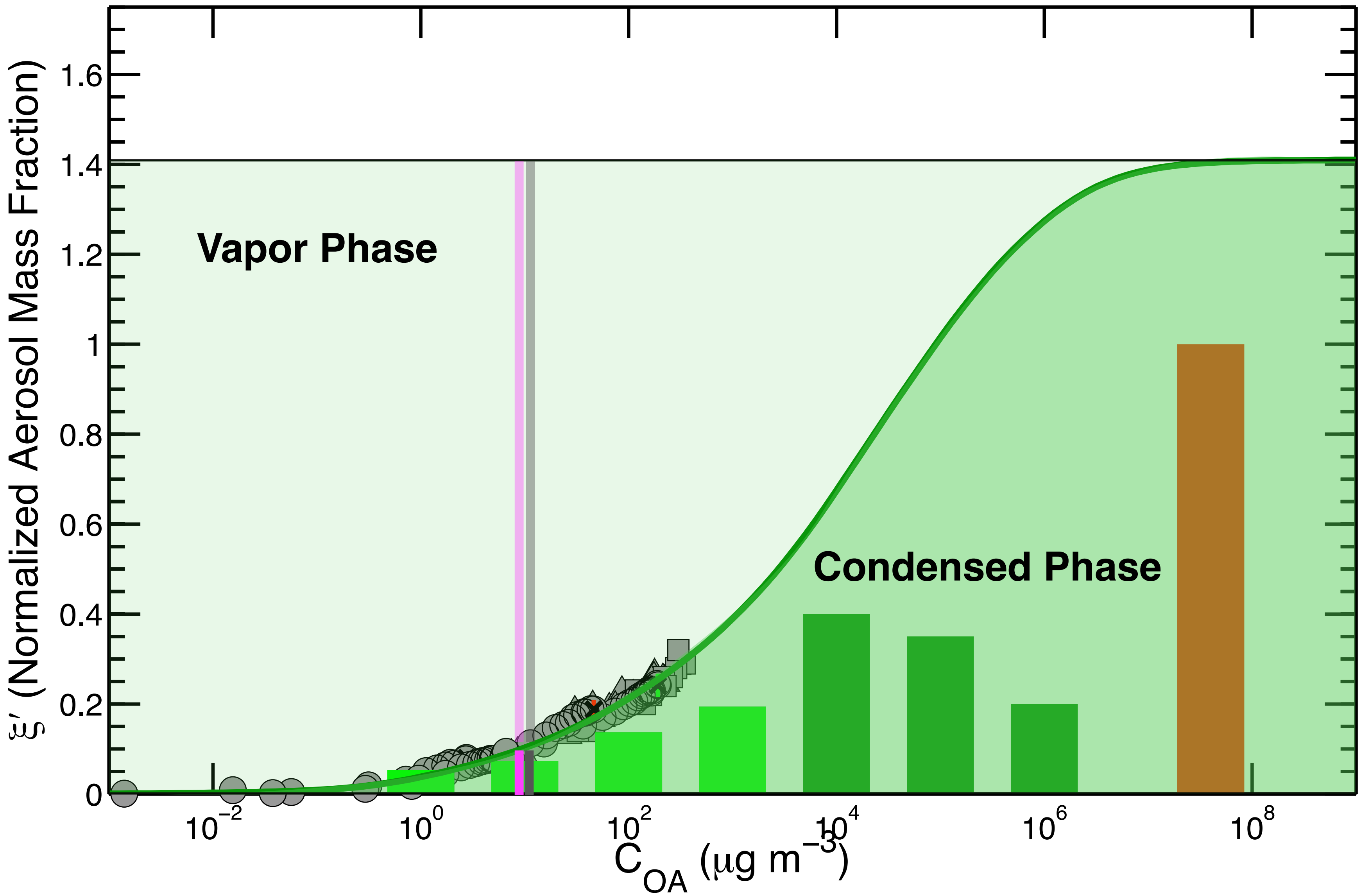
Where Are We?

- The existing picture – nonvolatile POA and semi-volatile SOA – is wrong.
  - SOA (as OOA) has relatively low volatility.
  - POA (as HOA) is quite volatile.

- At the same time, chamber SOA is not oxidized enough in the AMS.

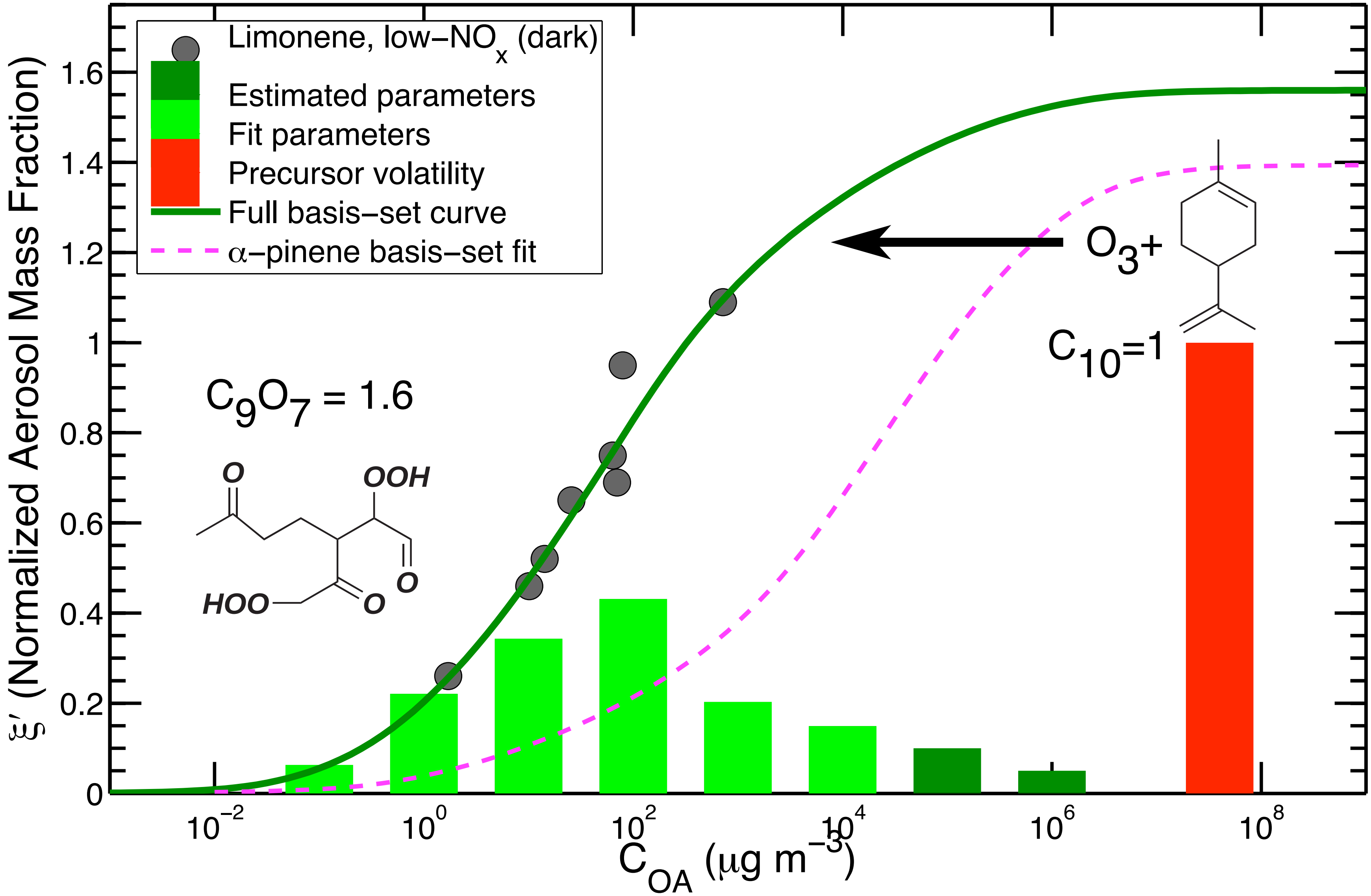
- The hypothesized solution is chemical aging:
  - Most mass, even low volatility emissions, is in vapor phase.
  - Gas-phase OH rate constant $\sim 3 \times 10^{-11}$: $\tau \sim 6$ hr.

Implications: Vapors



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

Limonene + Ozone Mass Balance

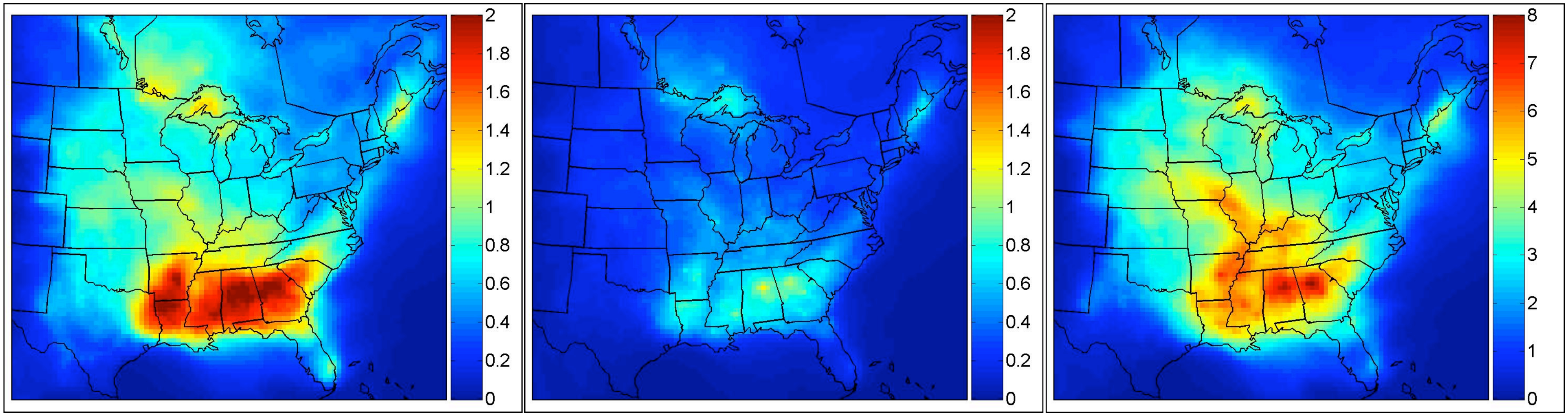


D-limonene + O_3 makes more SOA than α-pinene (2nd generation of oxidation).

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

Implementing Basis Set in PMCAMx

July 2001 Biogenic SOA

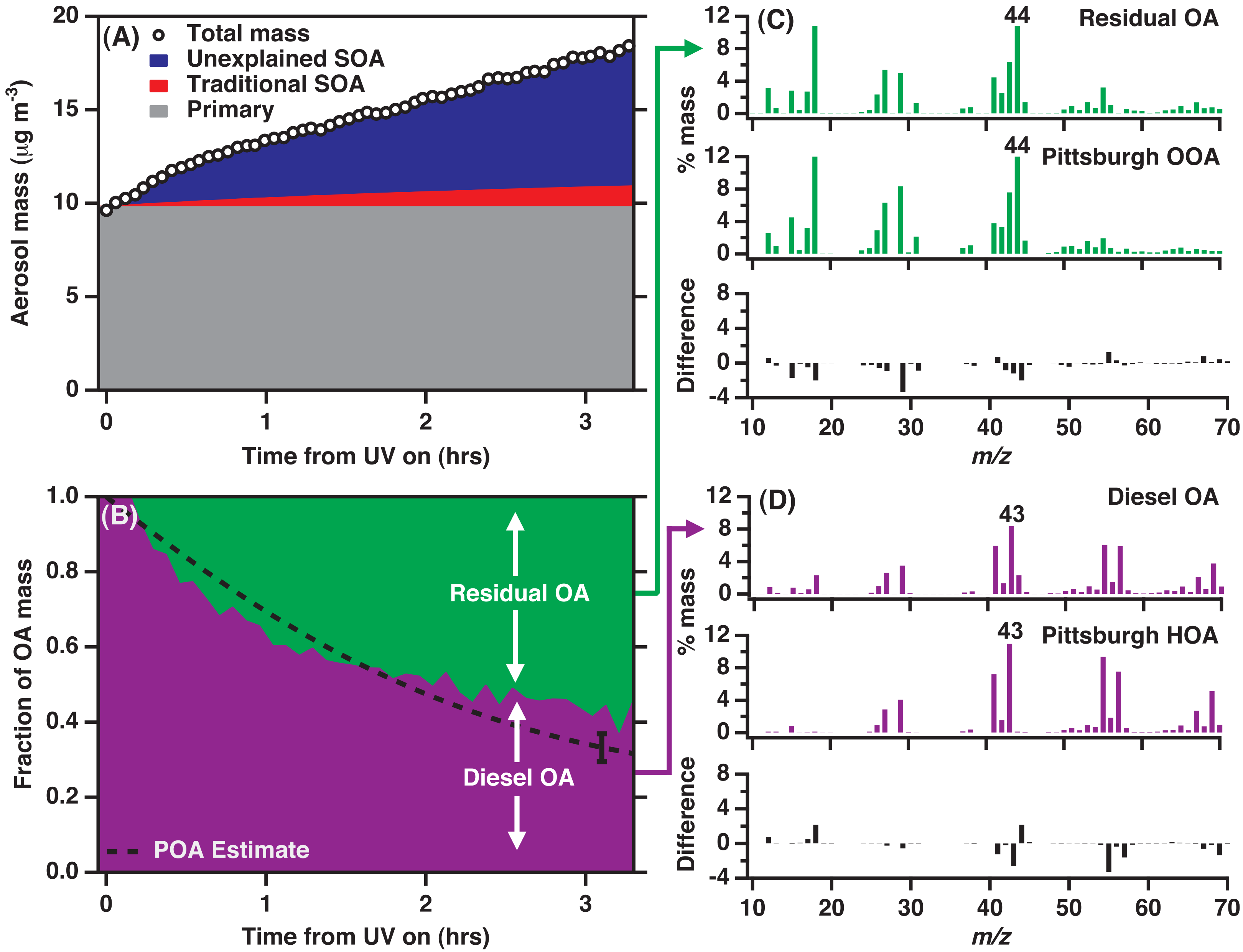


Old ∼constant yield — New Basis set yields — Multi-generation aging

- 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).

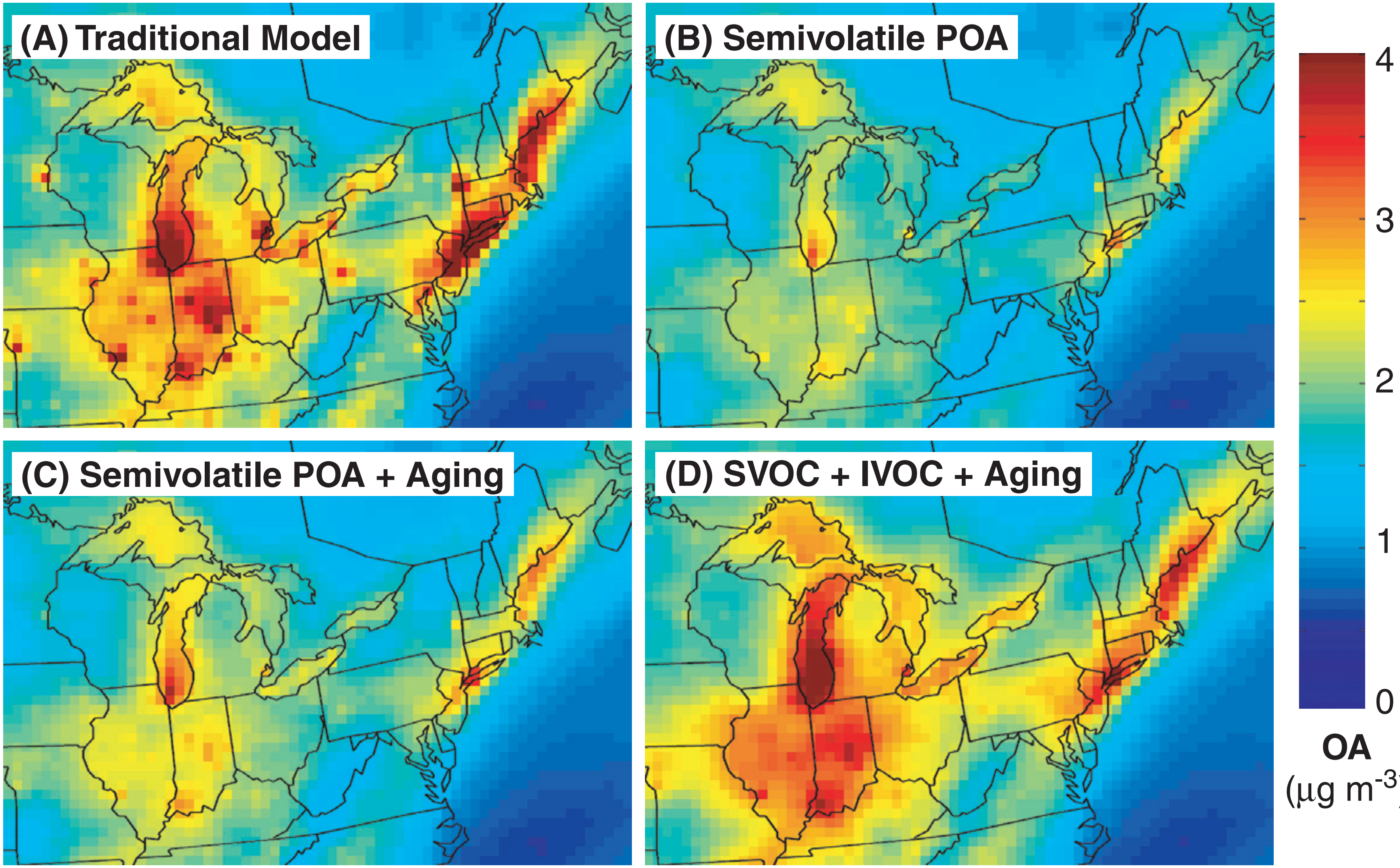
[Lane *et al.* in prep]

Photooxidation of Diesel Emissions



Oxidized fraction looks a lot like OOA.

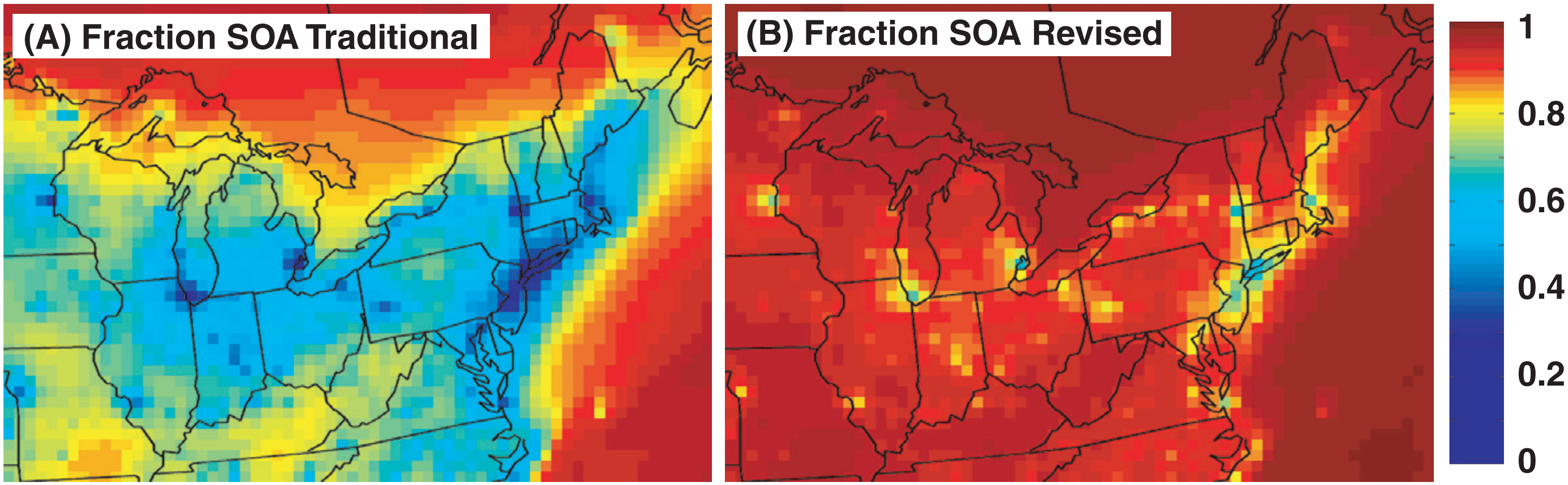
Implementation in PMCAMx



Oxidation of vapors produces regional organic aerosol.

Robinson et al. *Science* [2007]

SOA in PMCAMx



The aerosol is now 90% SOA in the region and 60% SOA in cities, just like AMS.

Robinson et al. *Science* [2007]

Conclusions Picture