Partitioning Theory
and
Smog-Chamber Measurements

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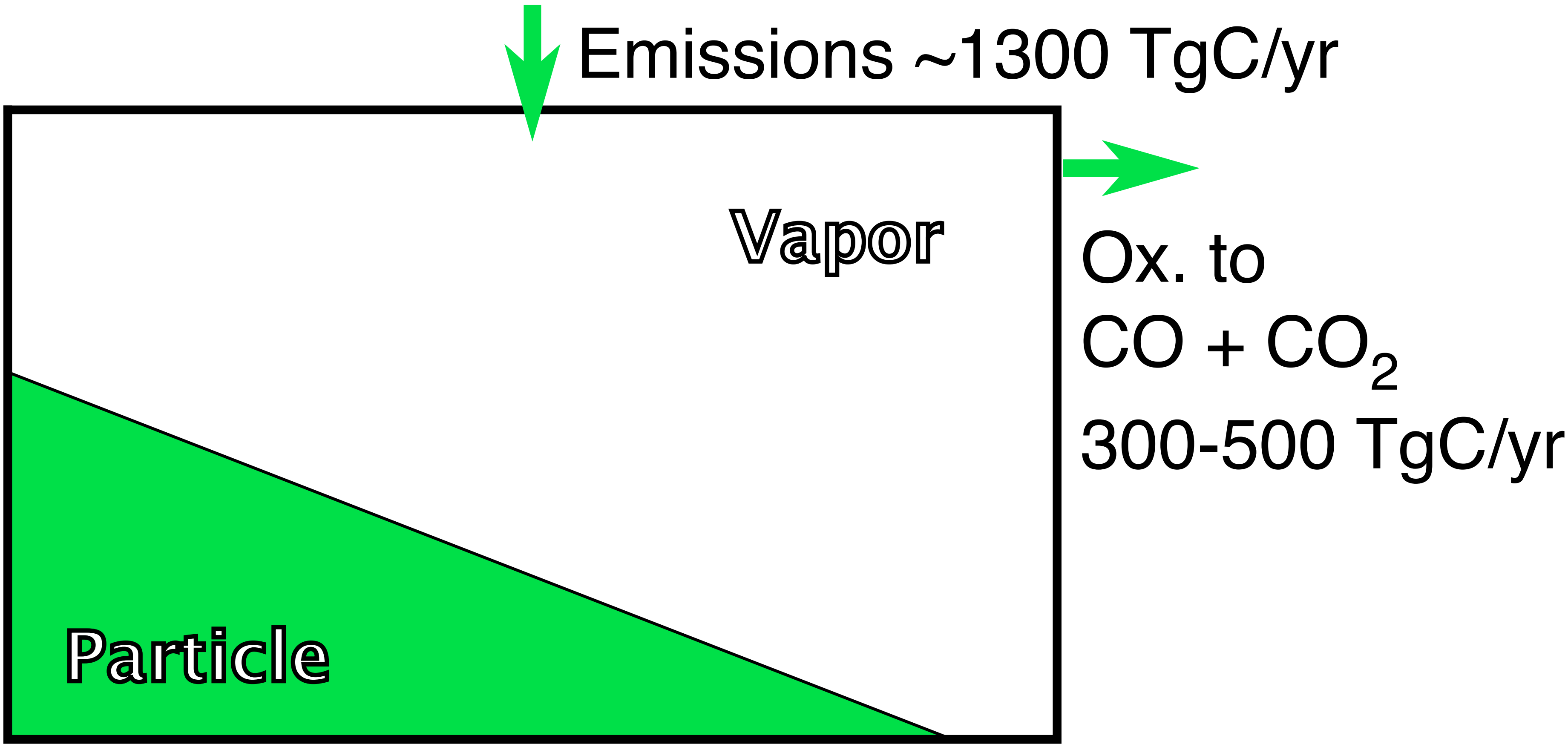
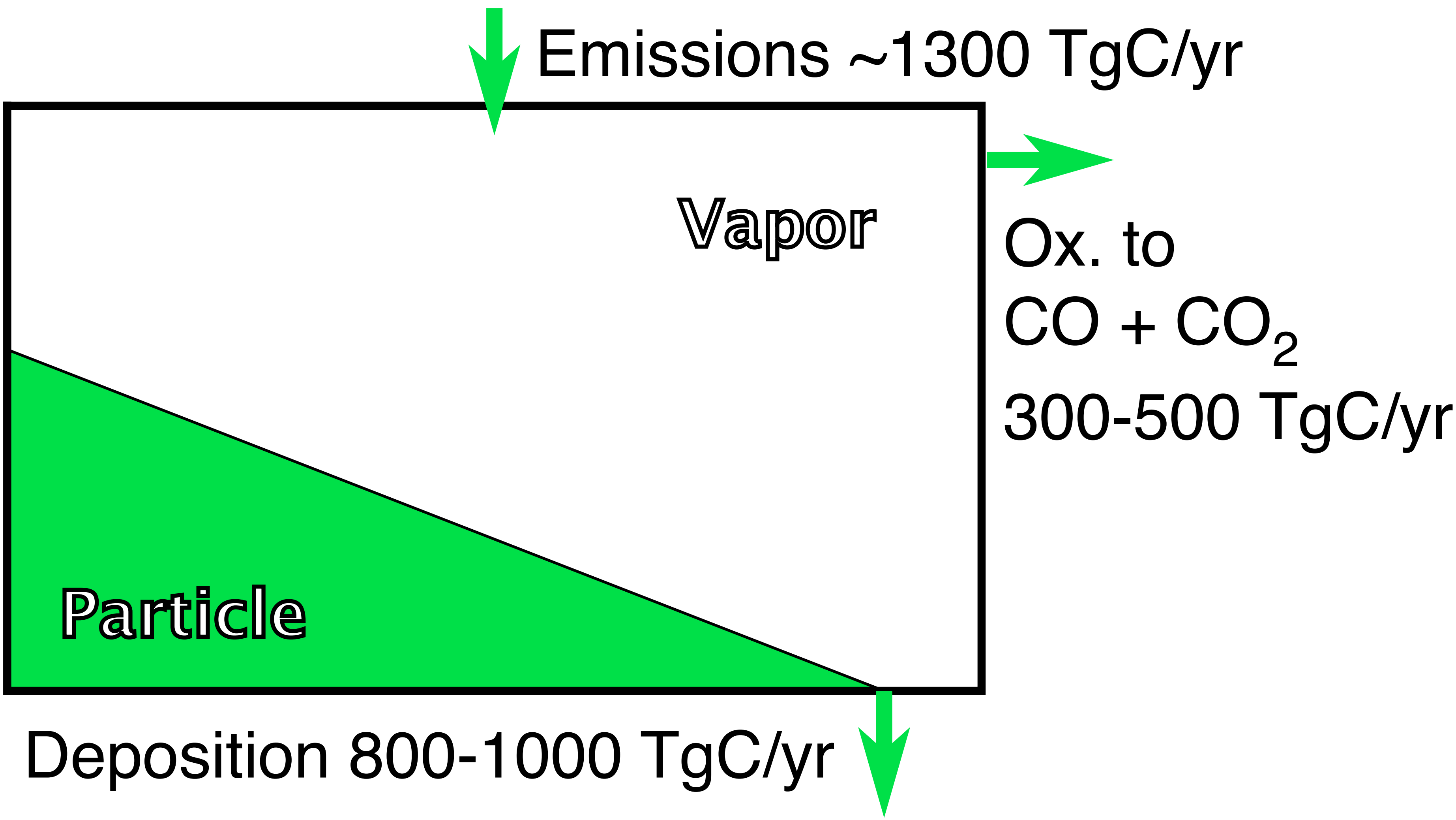
Global Non-methane Carbon Flux Balance



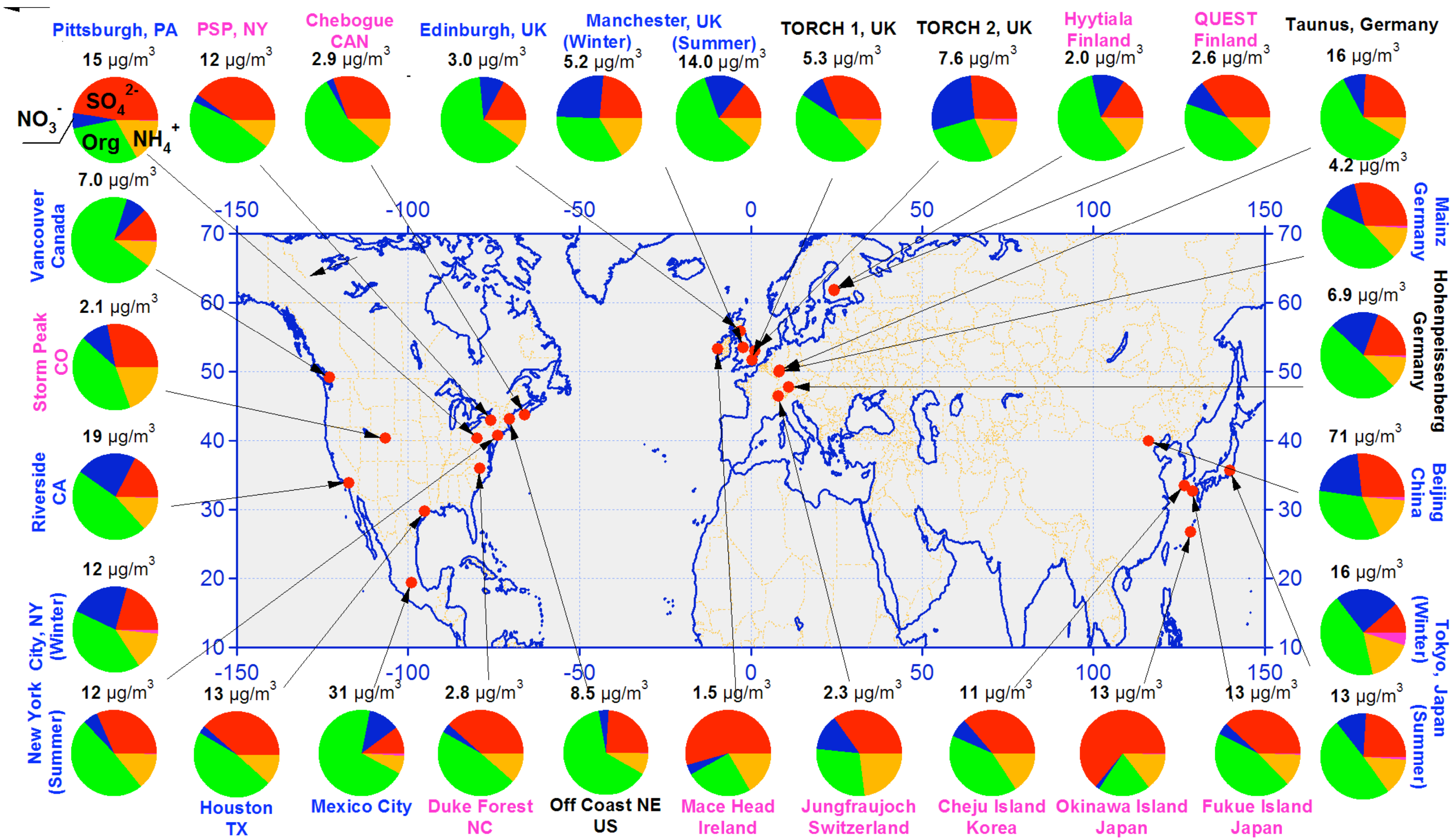
- Methane is another 500 Tg C yr^{-1}.
- Most of the NMHC does **not** get to CO_2 [Goldstein and Galbally *et al. ES&T* 2007]
  (Including methane, CO_2 formation is about 900 Tg C yr^{-1})
- Reduced carbon flux is thus about 2 Gt C yr^{-1}; 1 Gt C yr^{-1} to CO_2 in the atm
- Compare with 14 GY yr^{-1} CO_2 amplitude – $\sim 10\%$ of NPP goes into VOC fluxes!

Global Non-methane Carbon Flux Balance



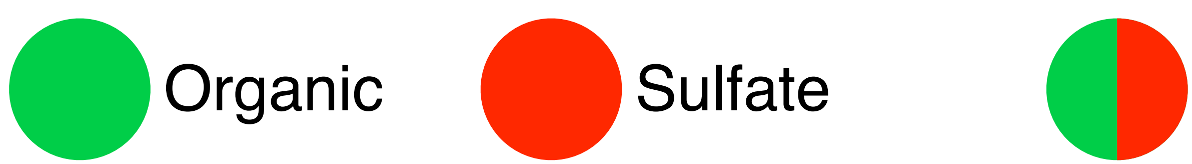
- Majority of carbon is removed by deposition. [Goldstein and Galbally *et al. ES&T* 2007]
- What phase??

Aerodyne AMS Surface Observations

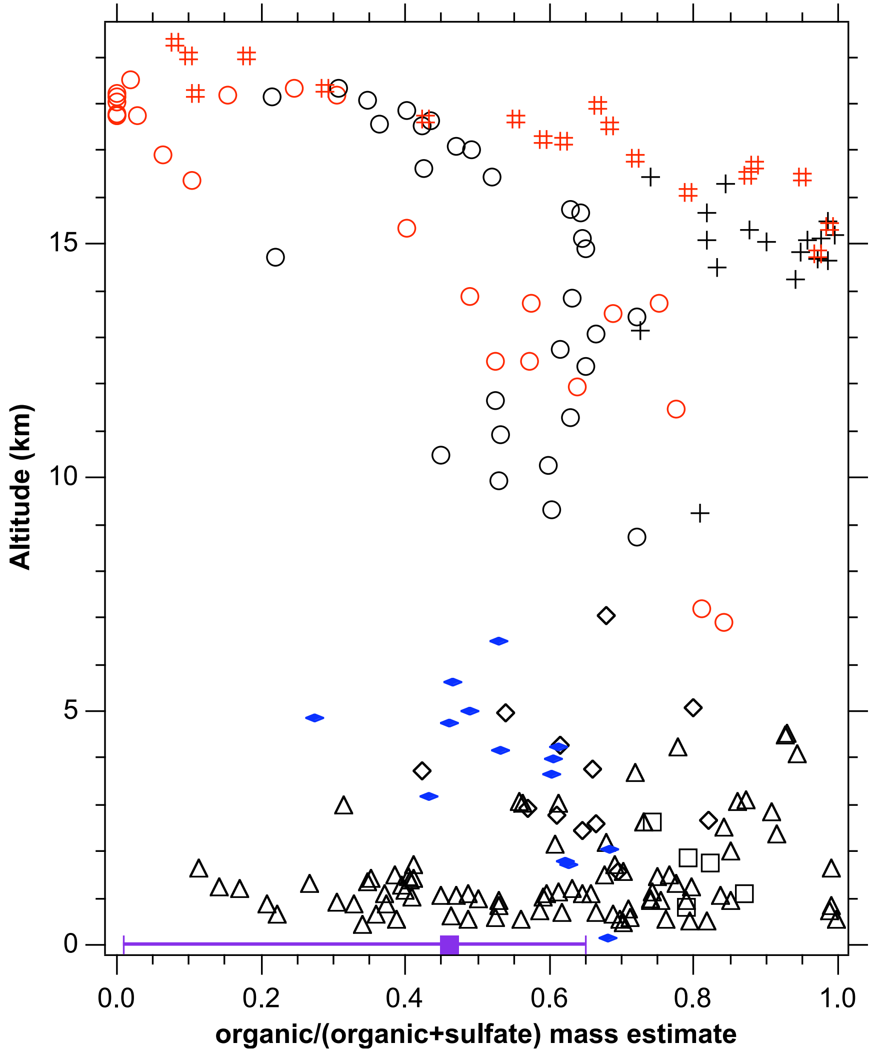


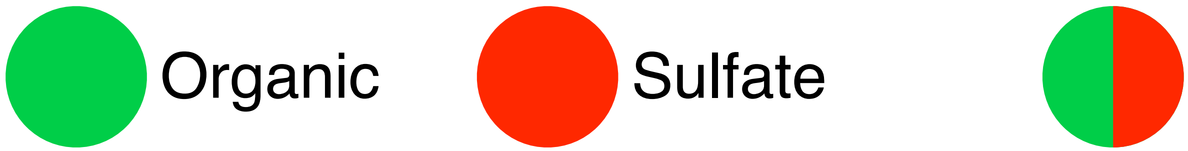
Zhang, Jimenez et al., *GRL*, 2007

- Surface 33 - 67% OA:



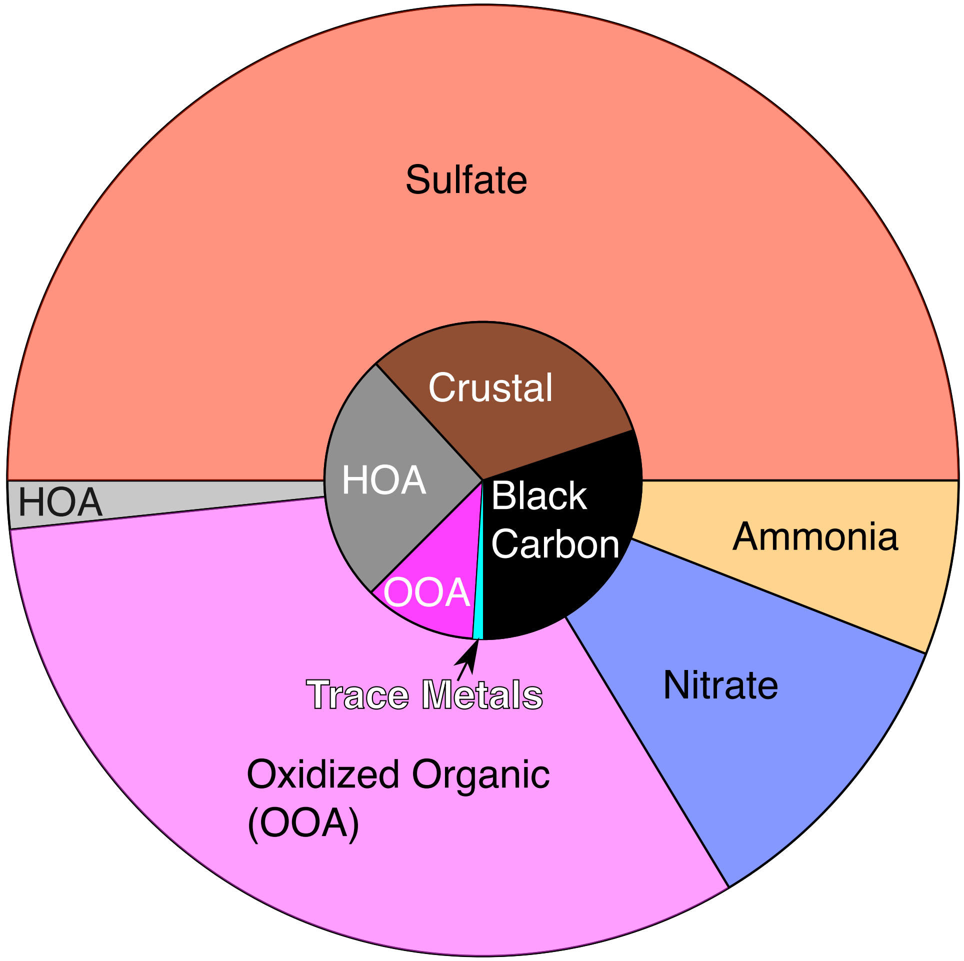
Particle Ablation Laser Mass Spec. (PALMS)





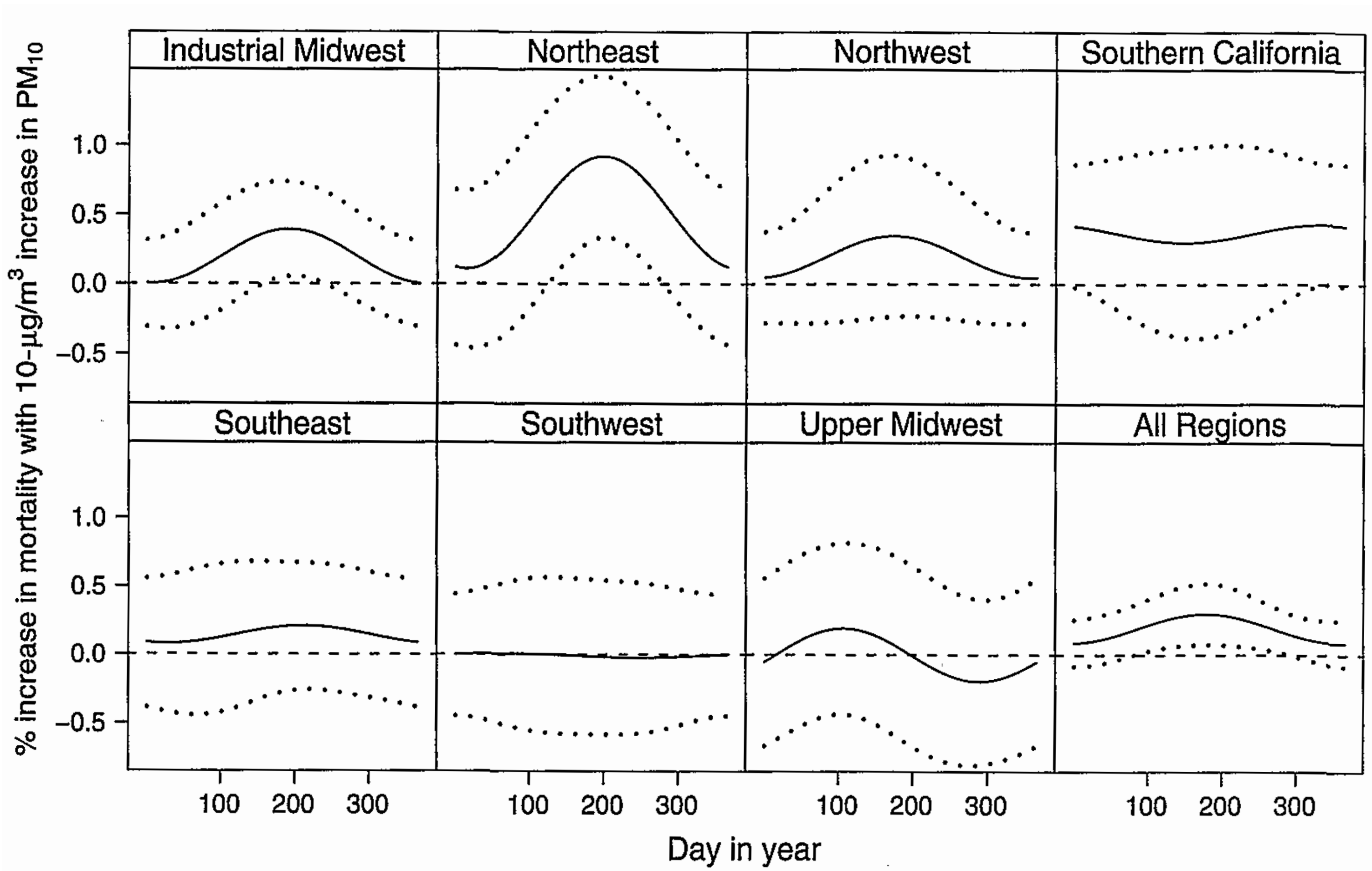
- Most of the troposphere ∼50% OA (1:2 < OA:Sulfate < 2:1) [Murphy *et al.*, 2007]

What do Individual Particles Look Like?



- Most particles are an internal mixture dominated by condensation.
  - **Core** is primary (i.e., no core for nucleated particles),
  - **'Coating'** is a mixture, may be several distinct phases.

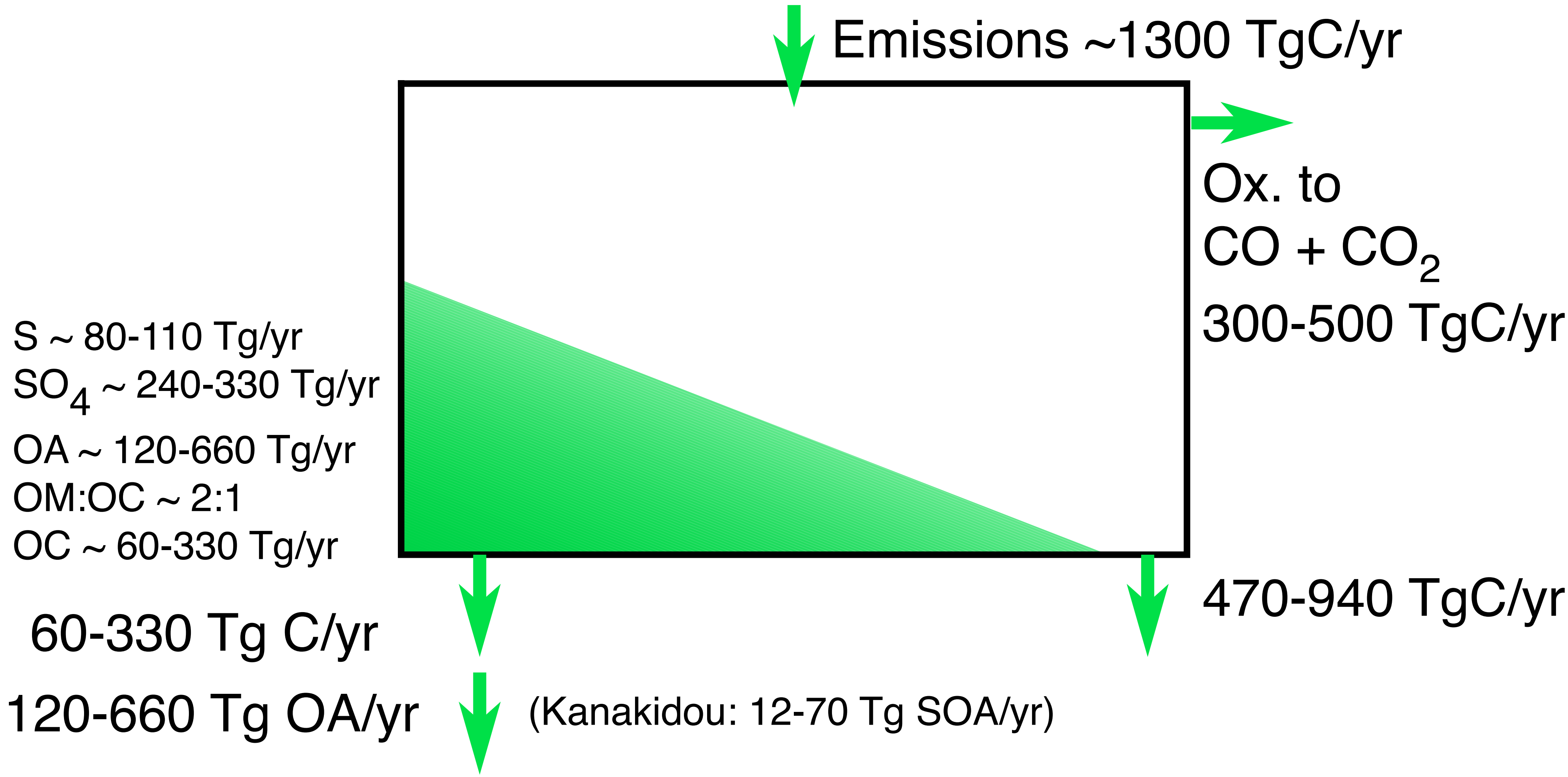
Where are the Health Effects?



[Peng *et al.*, 2005]

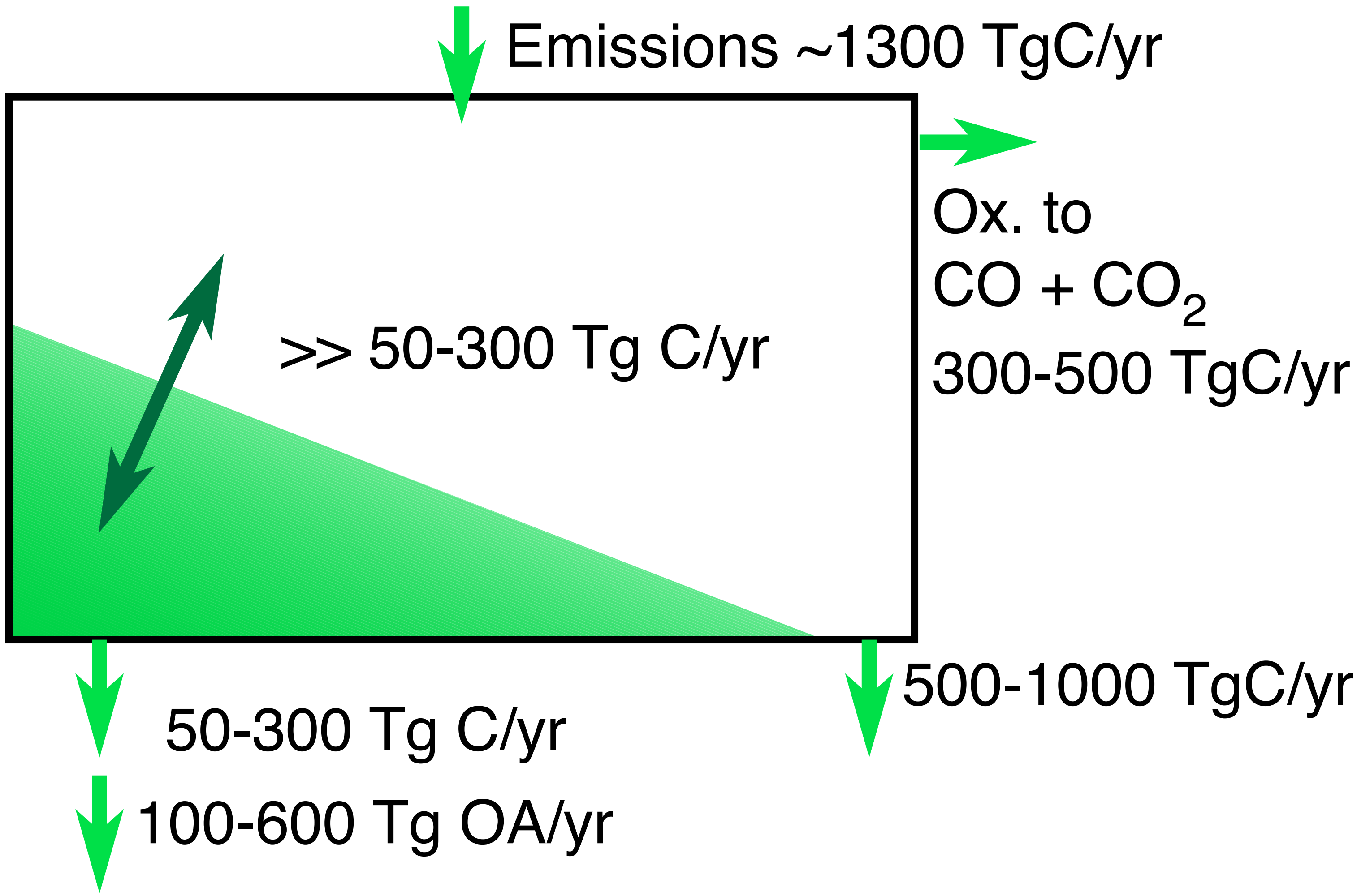
- Health effect from PM_{10} (also $PM_{2.5}$) regional and seasonal.
  - $SO_4^{=}$ peaks in N.E. Summer,
  - However, so does OOA1! (OOA:$SO_4^{=}$).

Organic Aerosol Flux Balance



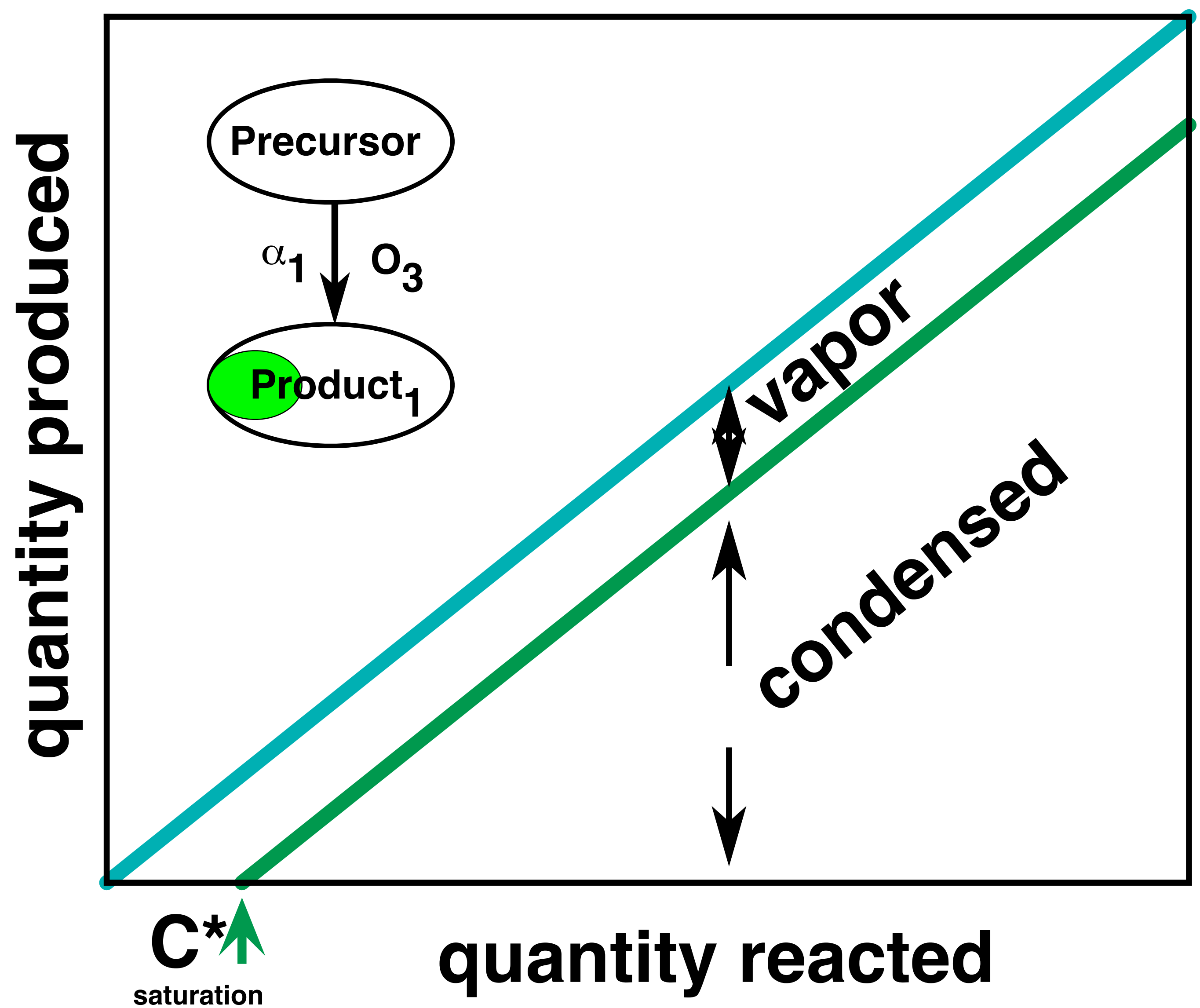
- Really large number for OA flux! *Consistent* with global budgets.
- About 4x more OA than models predict (wide error).
  - Note large residual vapor deposition term. Few constraints.

Net Fluxes are not Gross Fluxes!



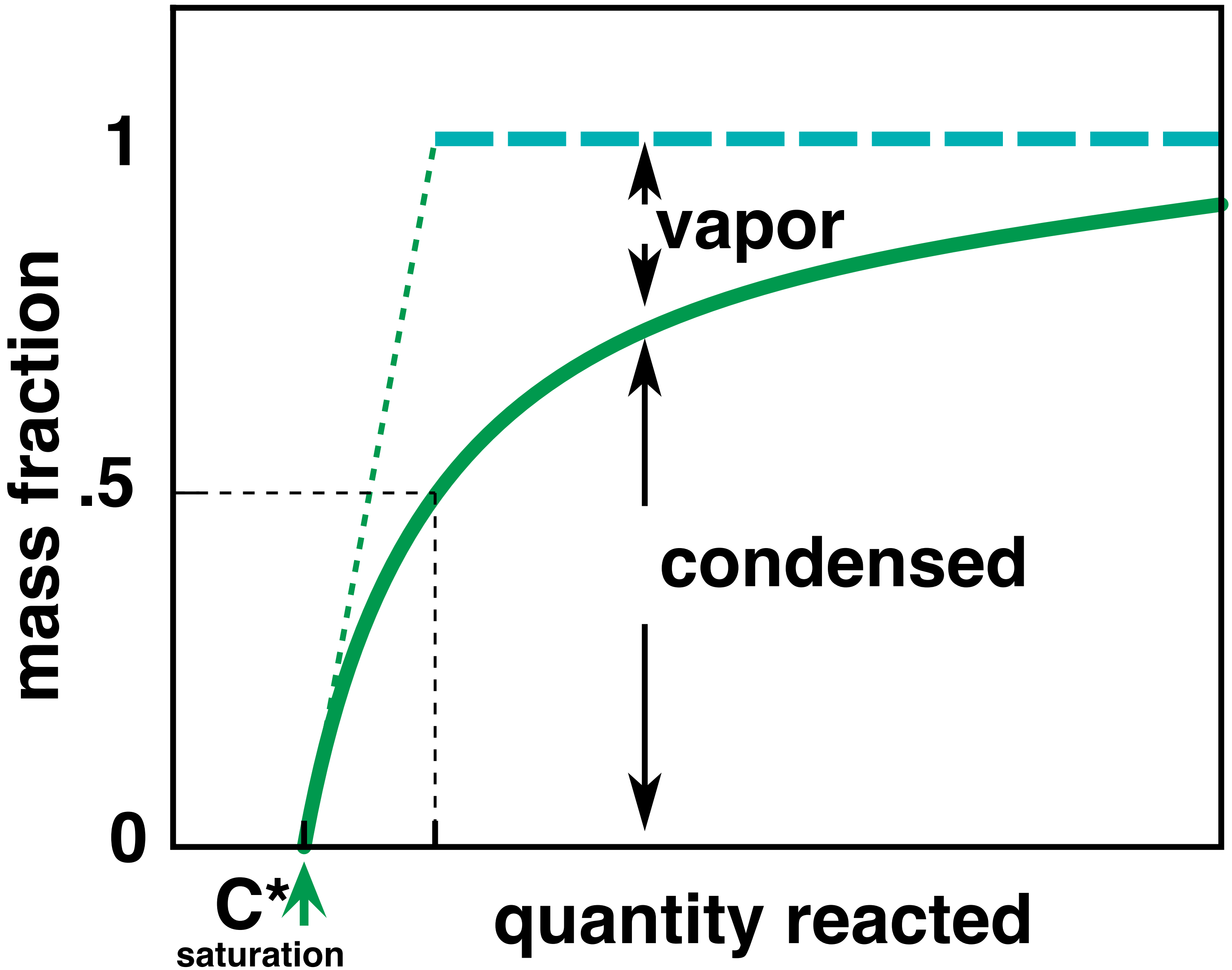
- What is the gross flux into and out of OA?
- There are several **major** questions relating to **assumed** organic vapors.
    - Oxidation state, as we will see, is a critical part of this.
        - HR-ToF PTRMS!!

Phase Behavior of a Semi-Volatile Compound

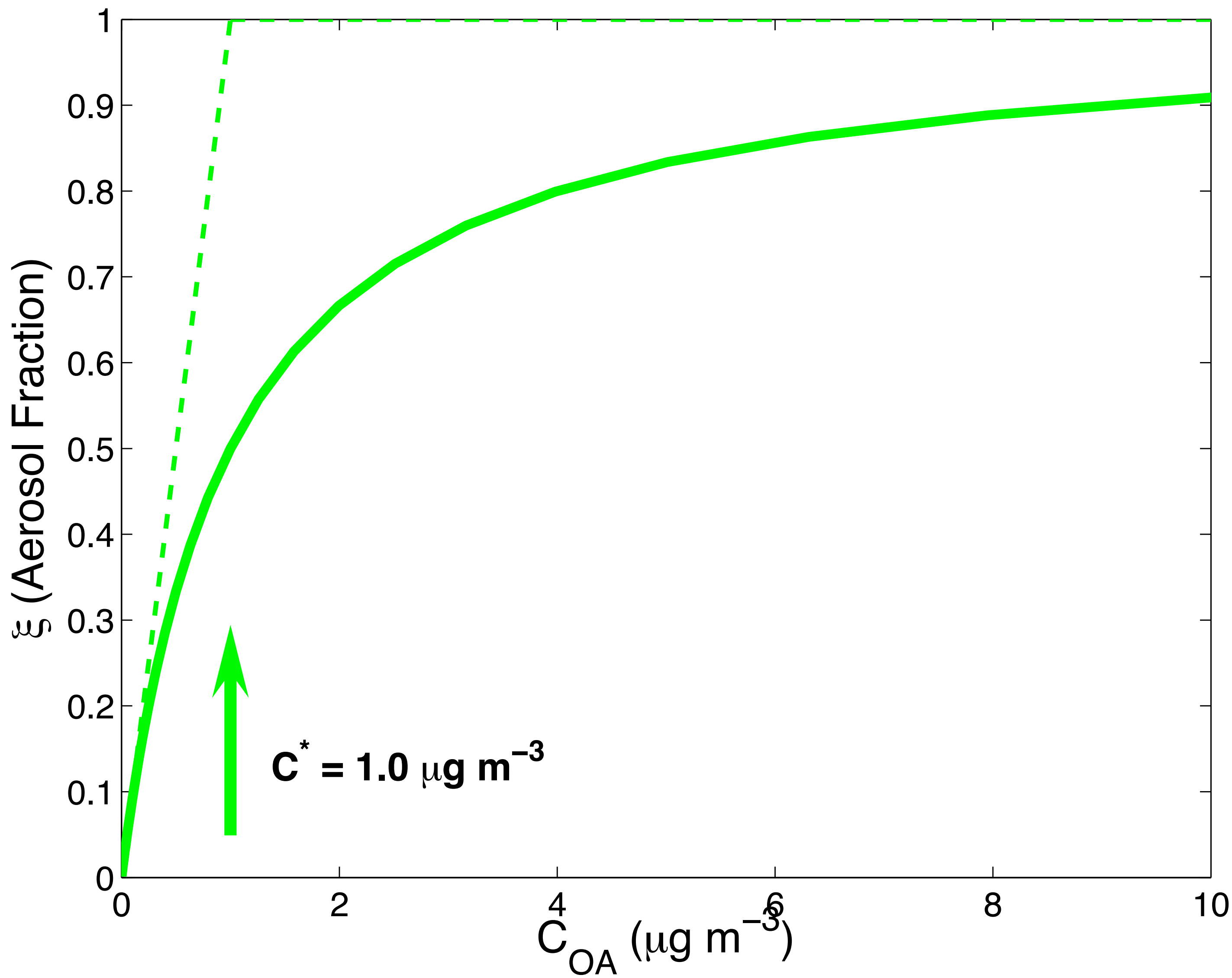


• Note that we tend to work on a mass basis in particle world.
Instead of vapor pressure, we use saturation mass concentration C*.

Semi-Volatile Mass Fraction



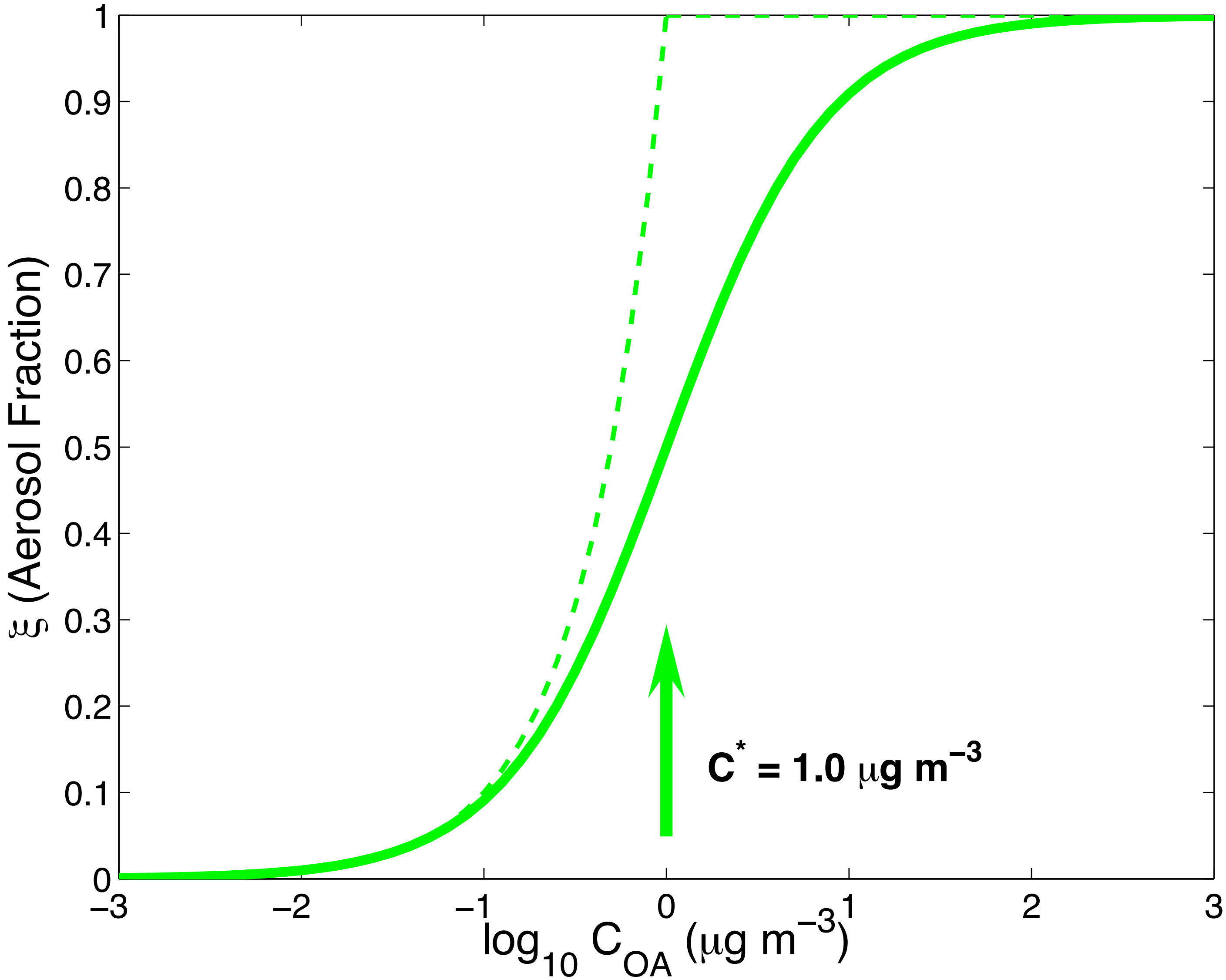
Partitioning of Single Component



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

Standard Hinshelwood-type saturation curve.

Partitioning of Single Component (log X Axis)

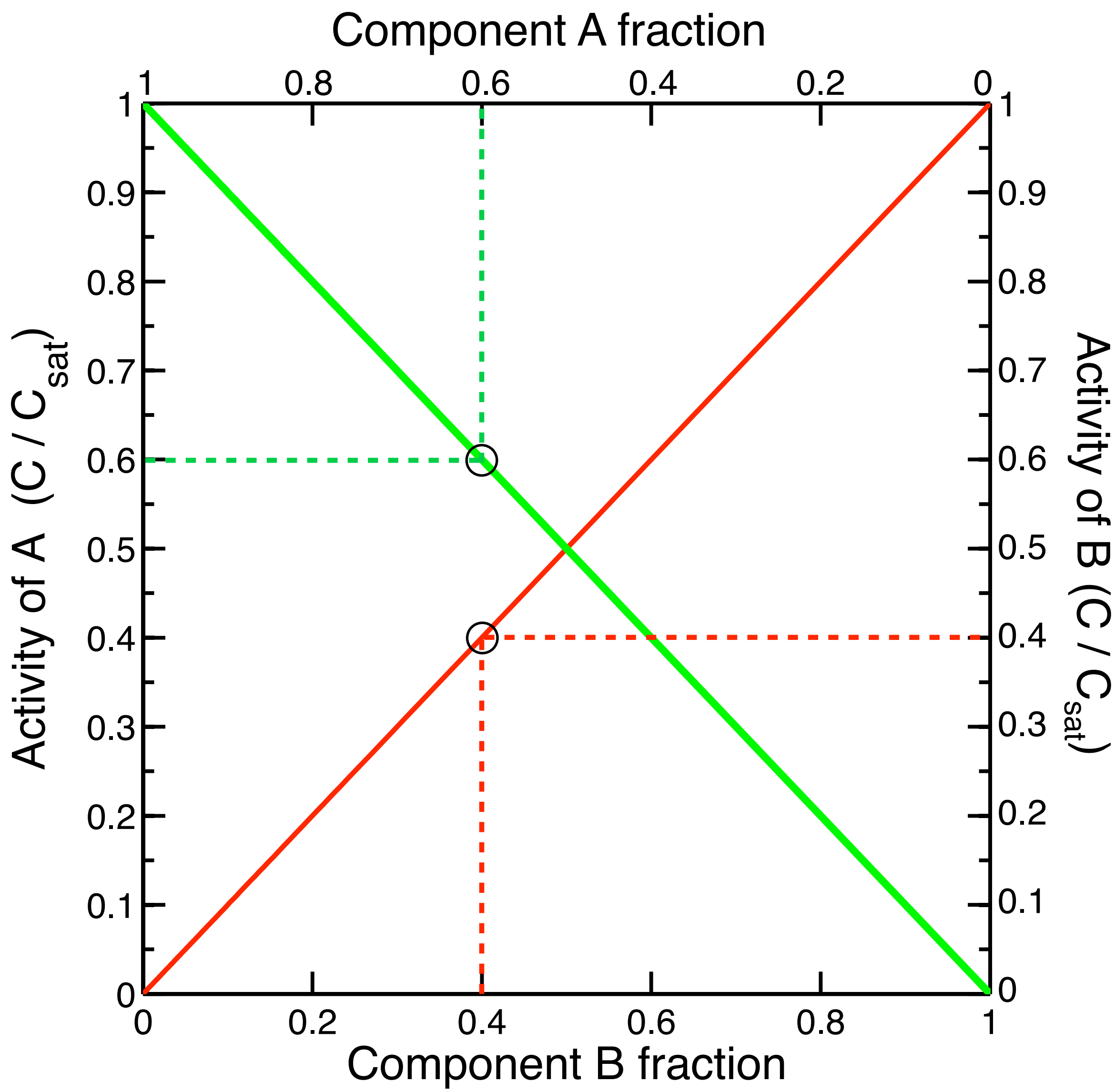


$$\xi_{\mathbf{i}} = \frac{1}{1+\frac{C^*_{\mathbf{i}}}{C_{\mathbf{OA}}}}$$

Now it looks like a gain curve! 1 decade linear region.

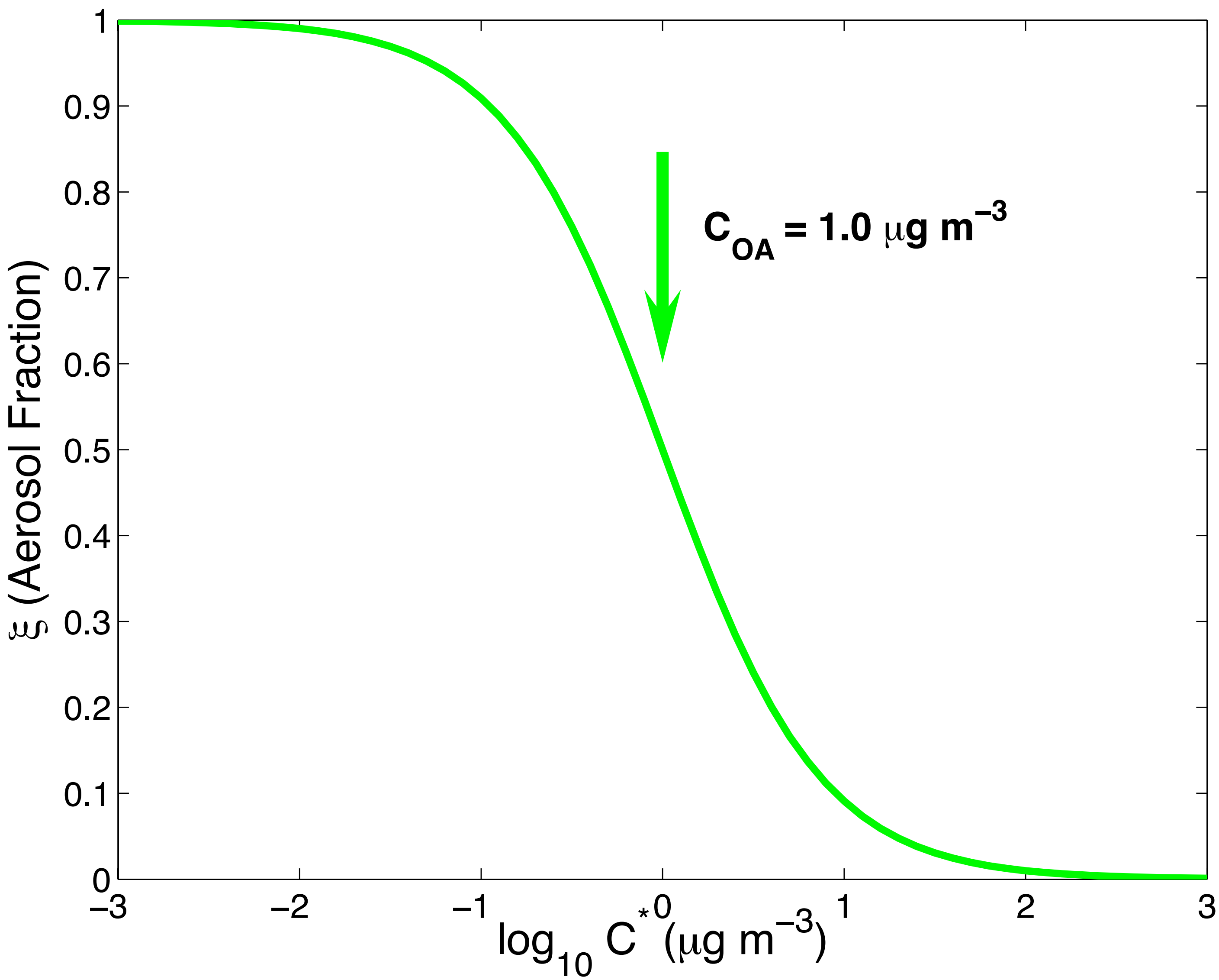
Raoult's Law

$C_{eq} = k_{off} / k_{on}$



$$C_i^* = \frac{10^6}{R\,T}\,\frac{W_i\,\zeta_i}{\overline{W}}\,p^\circ_{L,i}$$

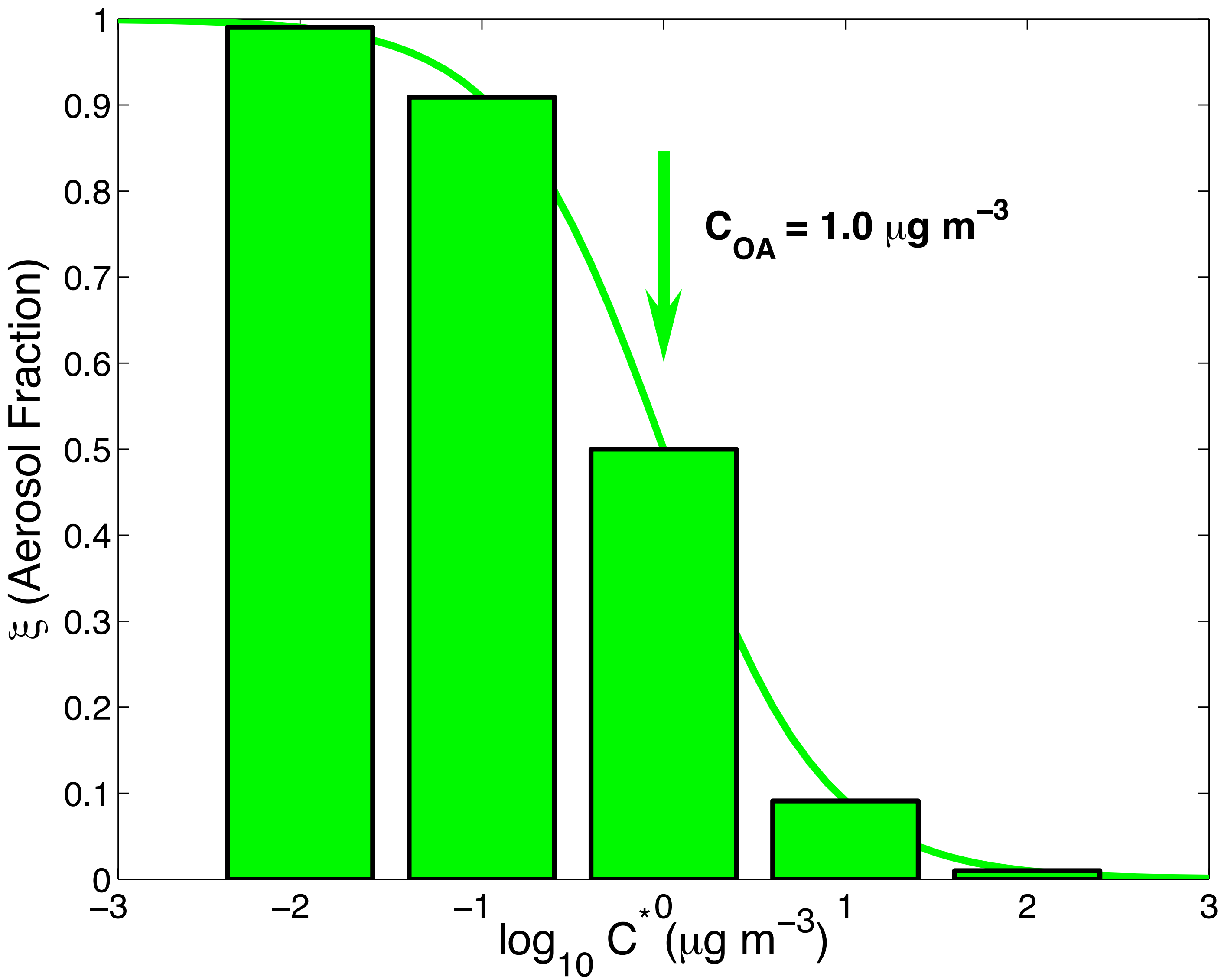
Partitioning at Specified C_{OA} in Solution



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

Raoult's law; really semi-ideal soln. with const. activity coeff.

The Volatility Basis Set



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

The Volatility Basis Set: Nomenclature

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

$C_i^* = \{0.01, 0.1, 1\}\ \mu\mathrm{g\,m^{-3}}$ **Low Volatility Organic Compounds (LVOC).**
Mostly in aerosol.

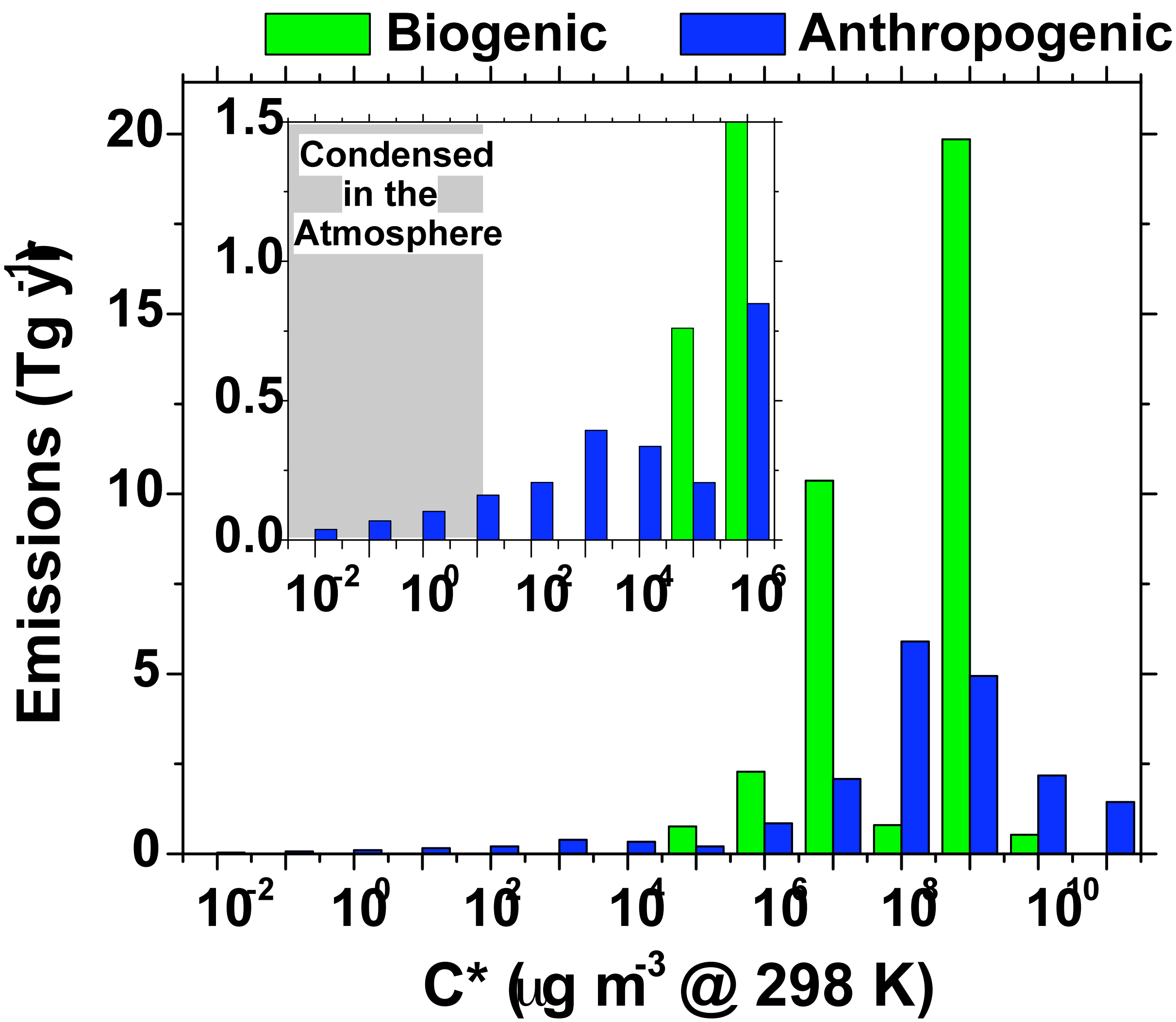
$C_i^* = \{10, 100, 1000\}\ \mu\mathrm{g\,m^{-3}}$ **Semi Volatile Organic Compounds (SVOC).**
Both vapor and aerosol, depends a lot on local conditions.

$C_i^* = \left\{10^4, 10^5, 10^6\right\}\mu\mathrm{g\,m^{-3}}$ **Intermediate Volatility Organic Compounds (IVOC).**
Entirely vapor, but untold numbers and hard to measure.

$C_i^* > 10^6\ \mu\mathrm{g\,m^{-3}}$ Pretty much anything you can name (the **VOCs**)

It is not that I don't know the identity of all these xVOCs: I have absolutely no idea what I would do with the information even if I knew it!!

Direct Emissions in the Continental U.S.

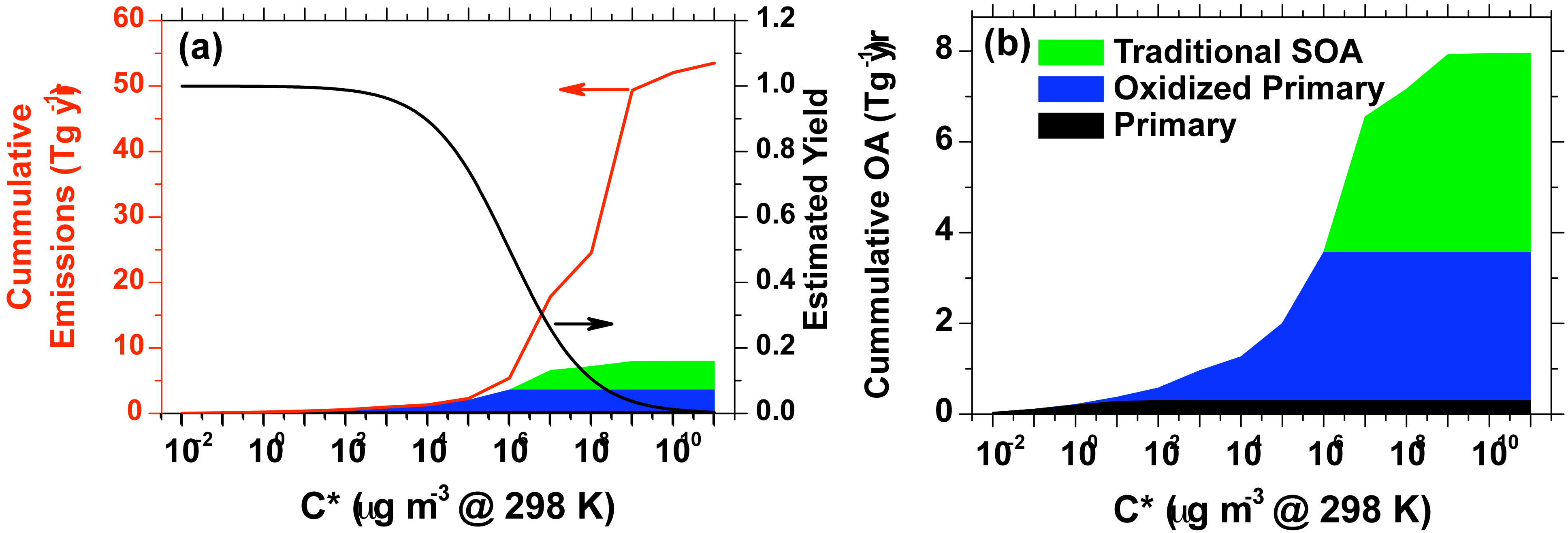


- Biogenic emissions (green) dominate.
  - They are much more volatile than anthropogenic emissions (blue).

THIS DOES NOT INCLUDE WILDFIRES! ($\simeq$ ANTHROPOGENIC?)

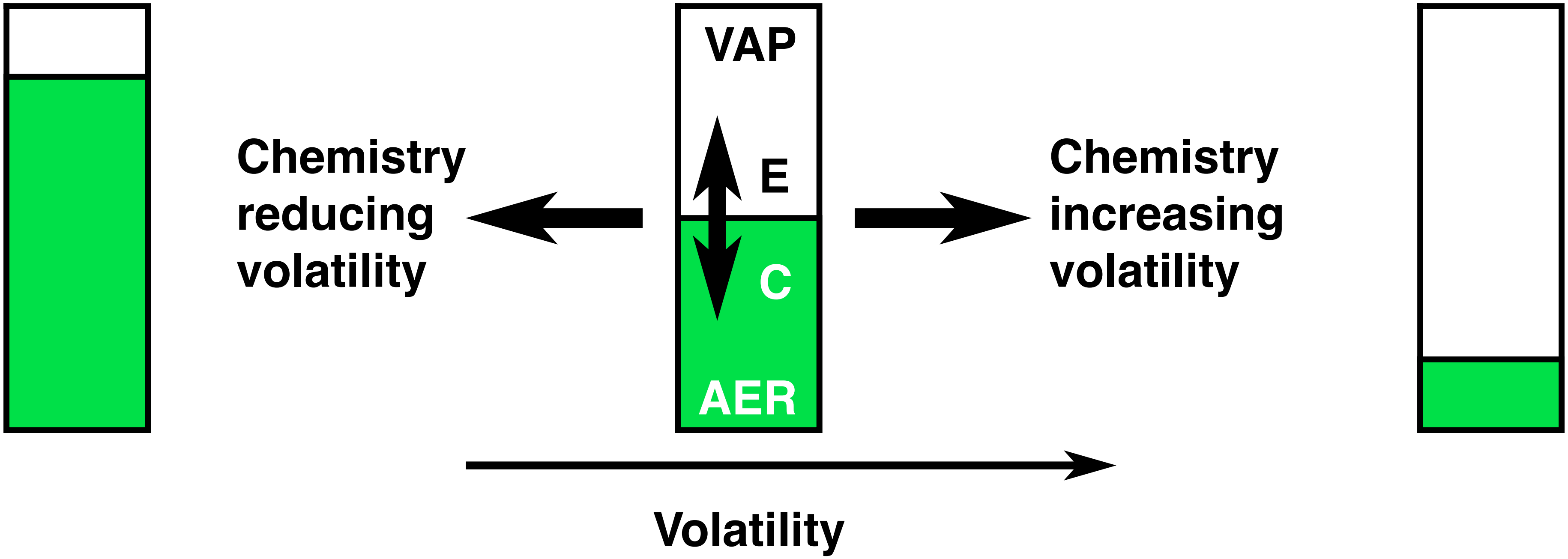
Shrivastava, *et al., JGR submitted* [2008], Millett [MEGAN biogenic fluxes]

Cumulative Emissions in the Continental U.S.



- Cumulative fluxes in red, xfer function to OC in black, cumulative OC in:
  - **Black** is primary OA (condensed ∼ always in atmosphere),
  - **Blue** is 'non-traditional' SOA (less volatile precursors now usually POA),
  - **Green** is traditional SOA.
- Less volatile precursors should have a higher probability of contributing to OC.
- About half of the SOA comes from 'non traditional' precursors.
- This transfer fcn. is an educated guess (like almost everything!).
  - What is it for real?

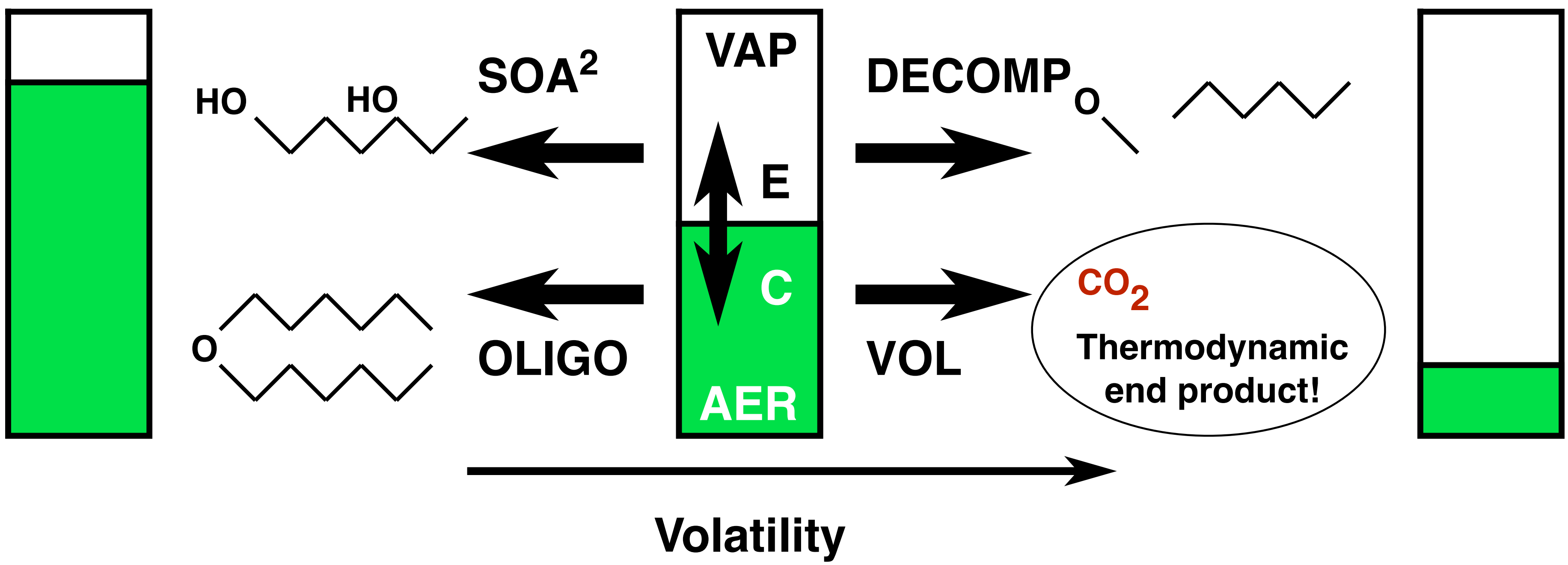
The Essential Issue



- Volatility is everything (well, no), and we have to conserve mass.
- When chemistry happens, products either:
  - Move to lower volatility, in which case aerosol mass will go up, or
  - Move to higher volatility, in which case aerosol mass will go down.

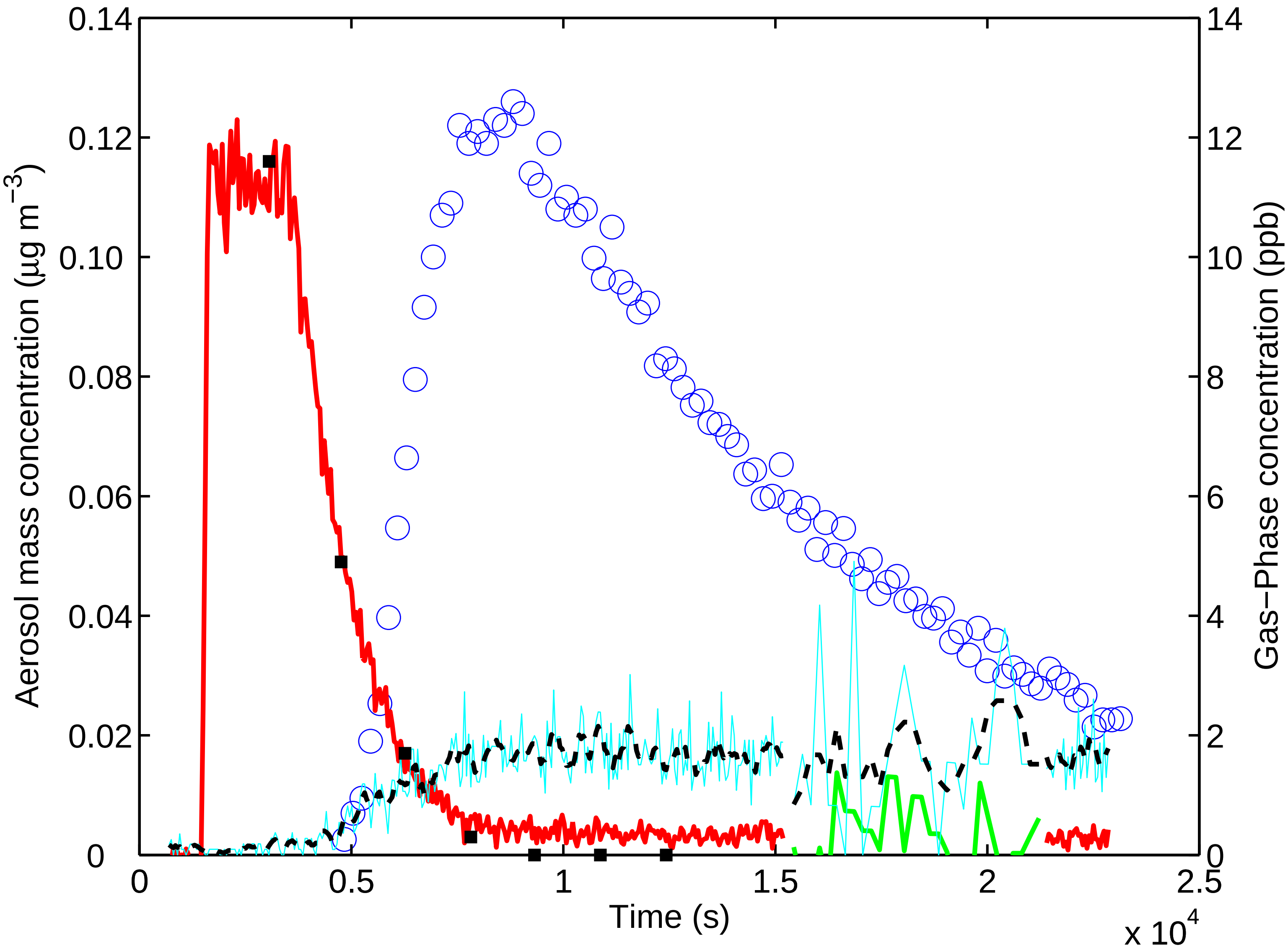
- Is SOA/OOA a major product of a minor species
  or a minor product of a major species?

What Does Chemistry Do?



- SOA chemistry = decreasing volatility.
- CO_2 formation is thermodynamic imperative, *given sufficient time*.
- Which phase the reaction occurs in clearly matters.
  - We will focus on the gas phase here.

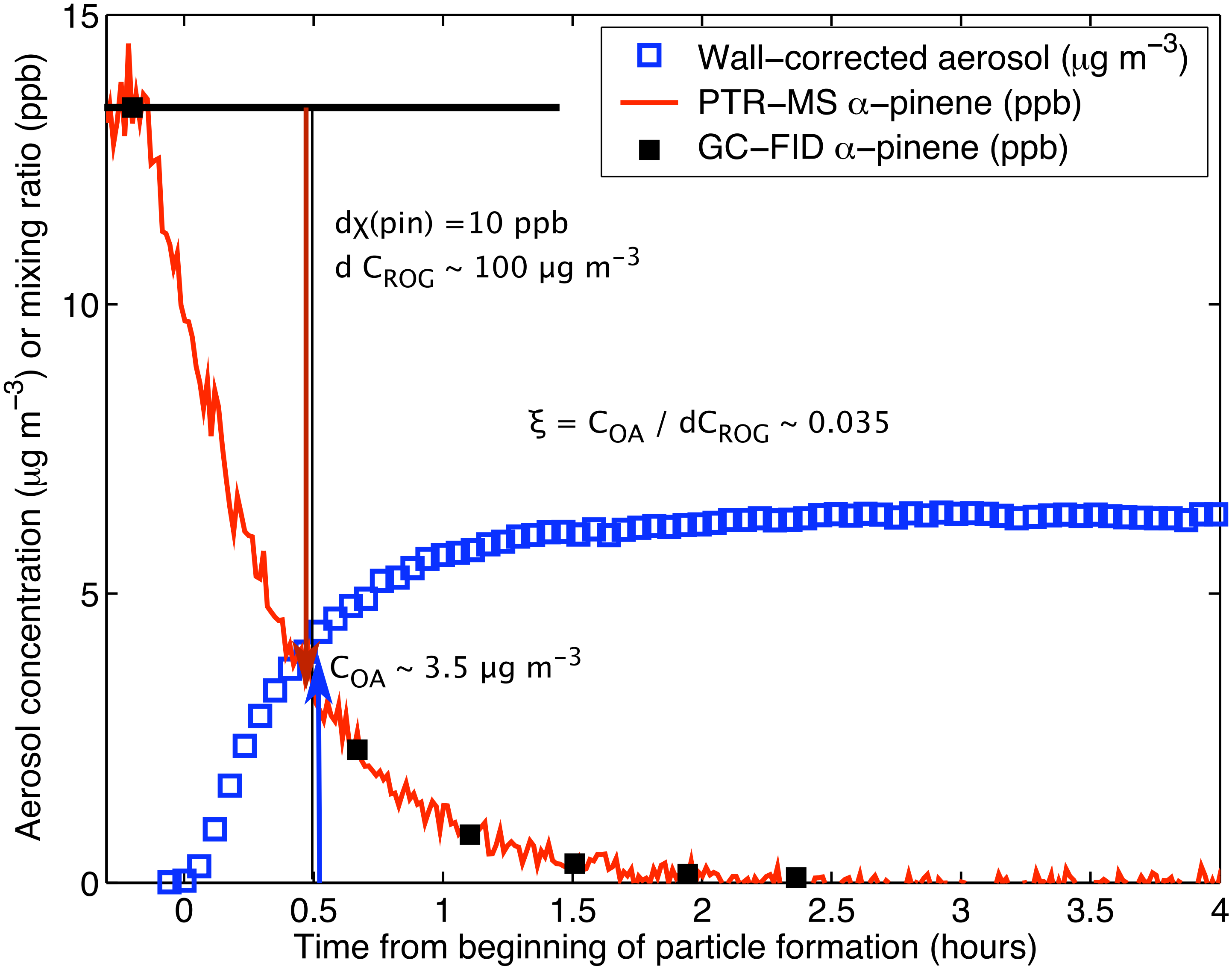
α-pinene + Ozone



- Cyan line is pinonaldehyde? m/z 151 + 169.
- Small interference for α-pinene at 137 – we subtract this out $\propto$ pinonaldehyde.

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

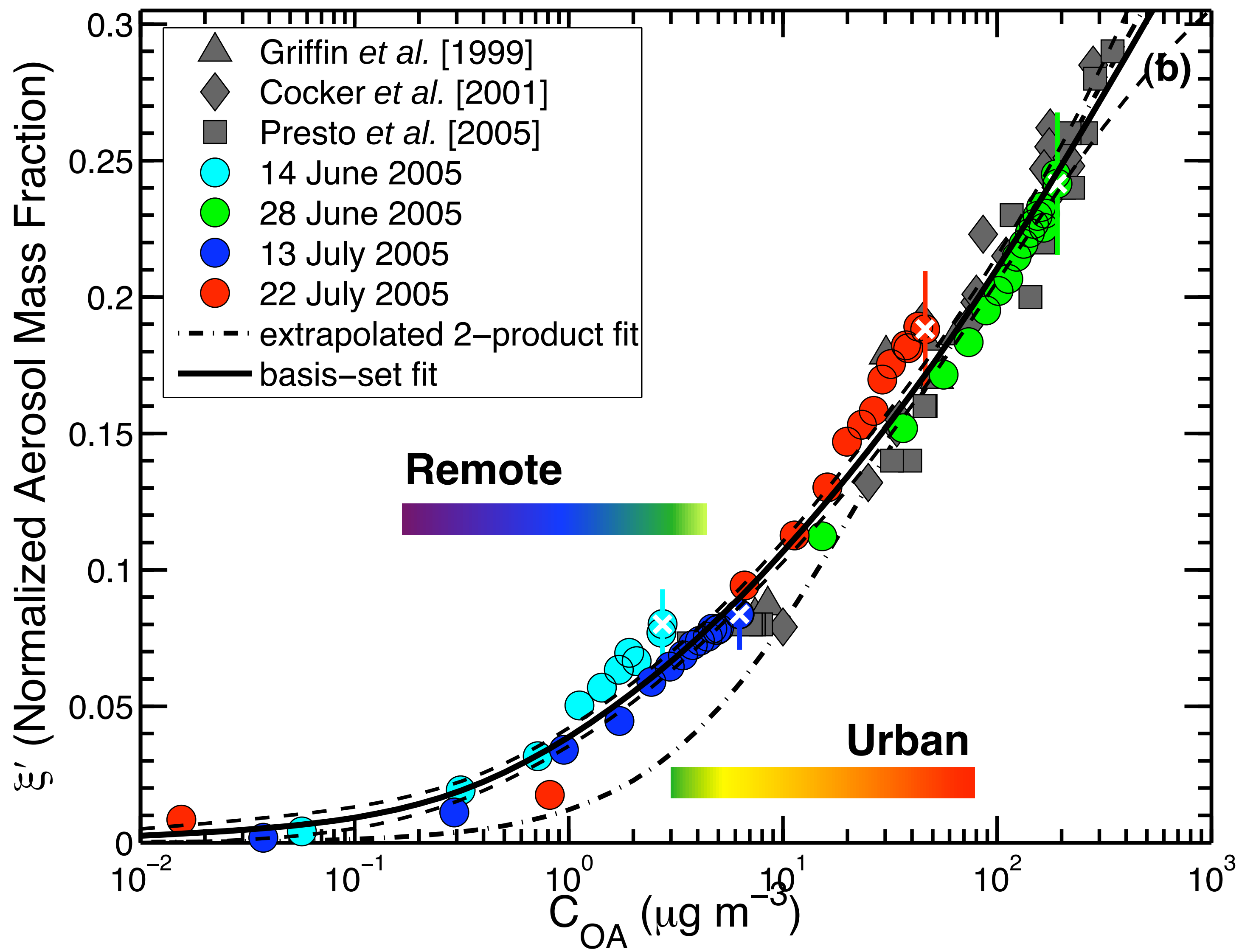
Aerosol Mass Fraction



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

[Odum, *et al ES&T*, 1996]

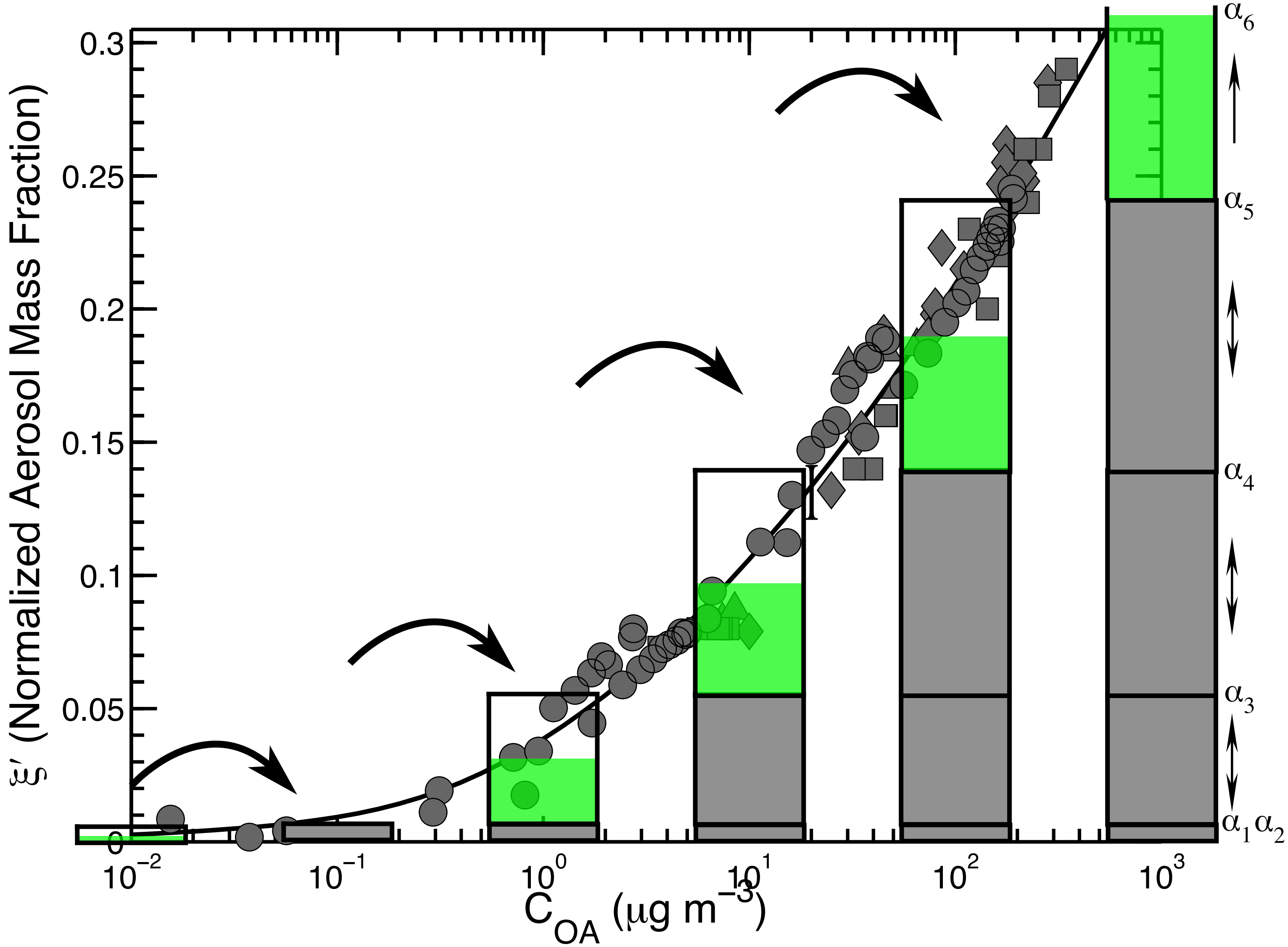
α-pinene + Ozone



∼ 2x SOA under remote atmospheric conditions vs. extrapolation.

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

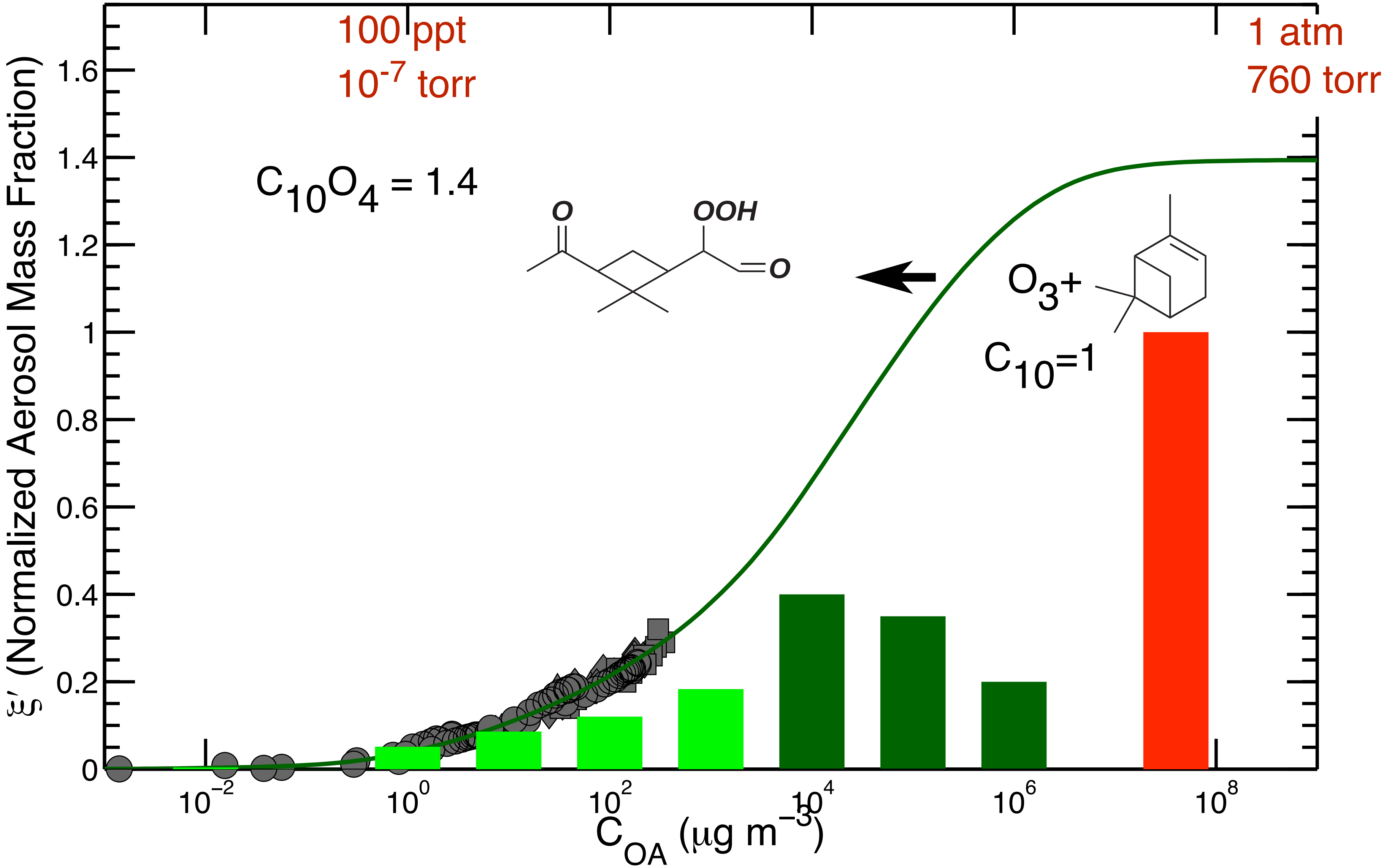
α-pinene and the Basis Set



(mass yields α')

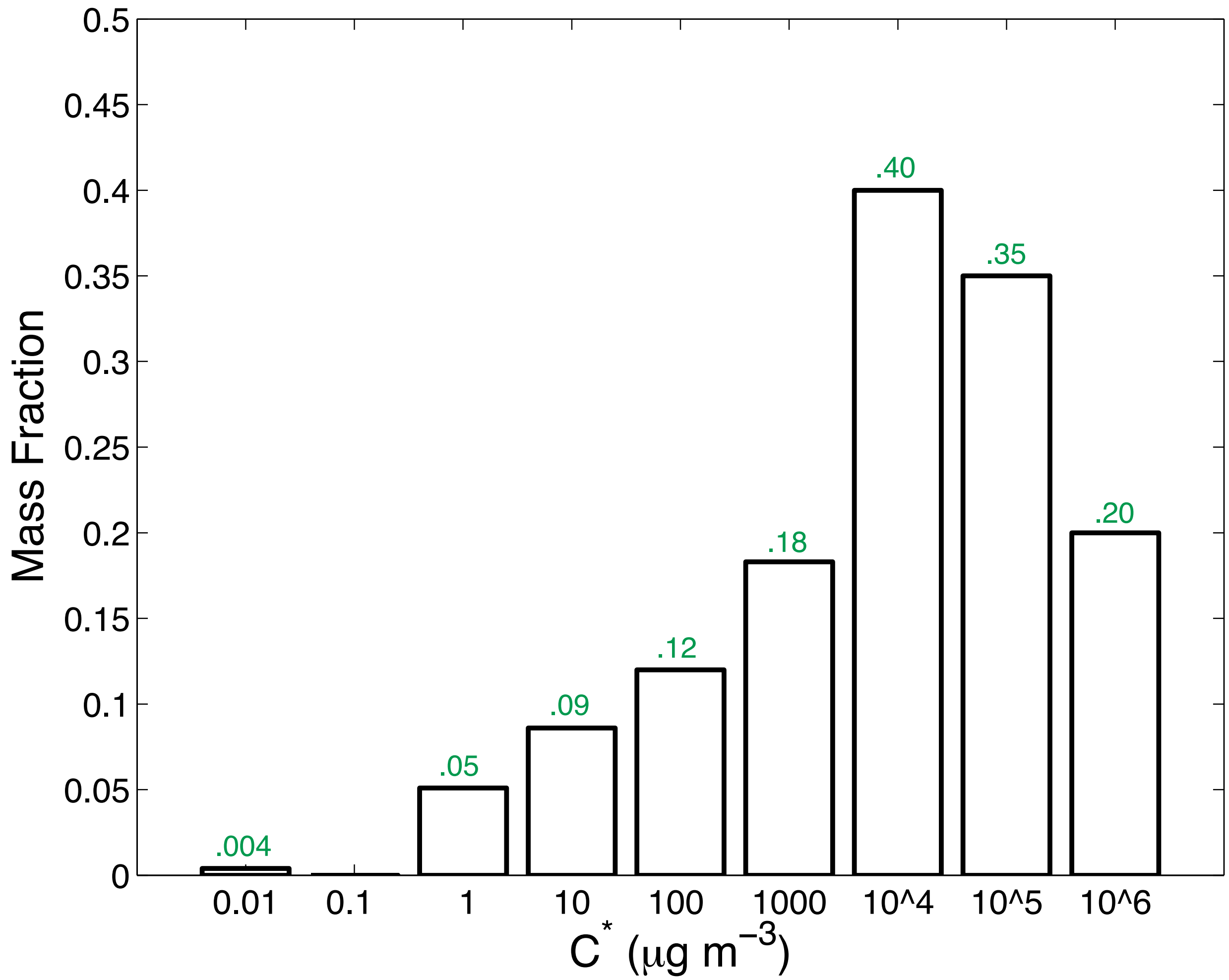
$$\alpha'_{\mathrm{i}} = \{.004, \quad 0, \quad .05, \quad .09, \quad .12, \quad .18, \ldots\}$$

α-Pinene + Ozone Mass Balance



- Mass yields $\alpha_i' = \{.004, 0, .05, .09, .12, .17, .29, .29, .20\}$
- Only around 0.055 SOA formation from α-pinene in the LVOC range at low NO$_x$.
- Mass balance for ‘nominal product’ demands $\xi_{\mathrm{max}} = \sum_i \alpha_i \simeq 1.2 - 1.4$.

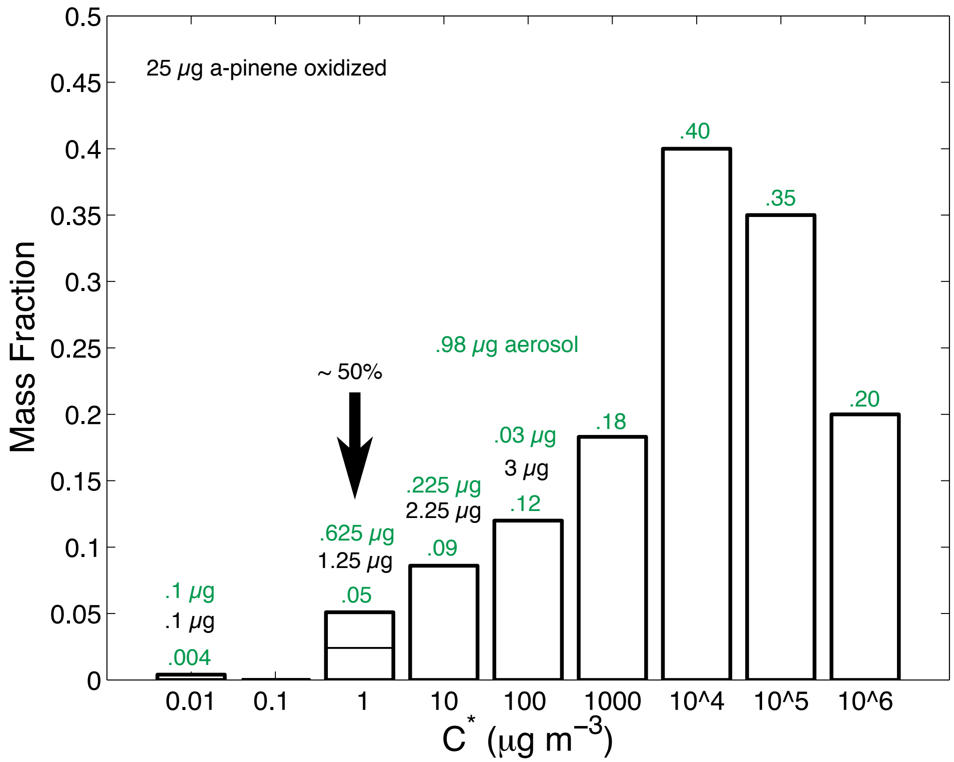
α-Pinene + Ozone Product Distribution

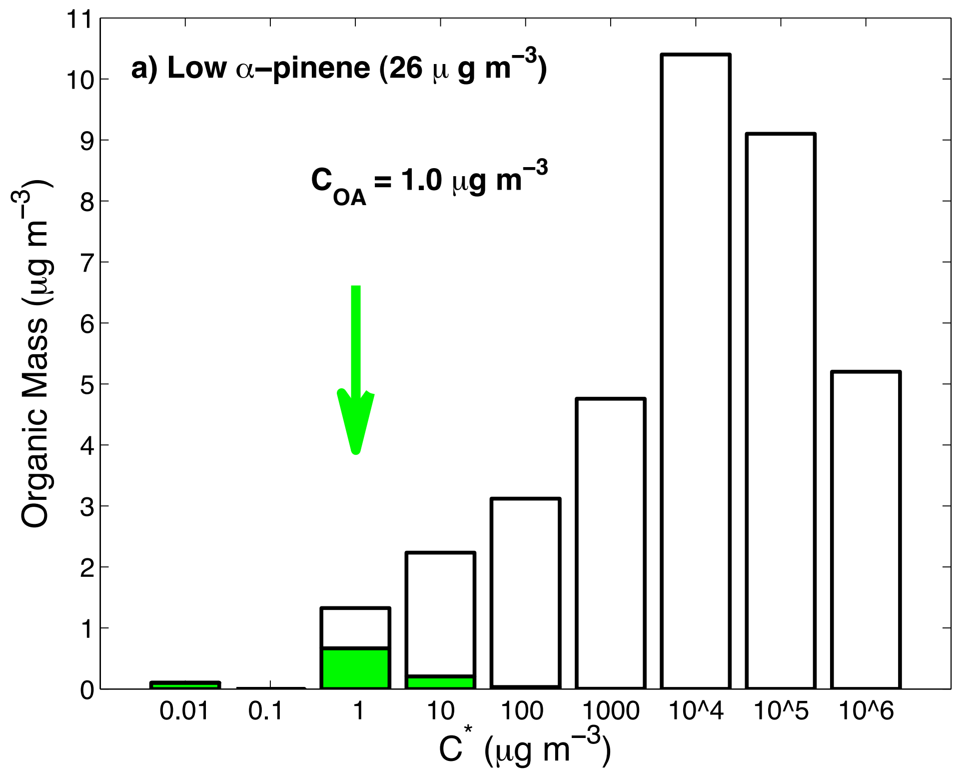


Products distributed over volatility space (a transformation vector)
Note very small yield of 'nucleator', consistent with [Burkholder *et al.* 2006]
Multiply yields by mass of α-pinene consumed to get product masses.

[Donahue *et al.* in prep]

Basis-set 101: Basis Basics

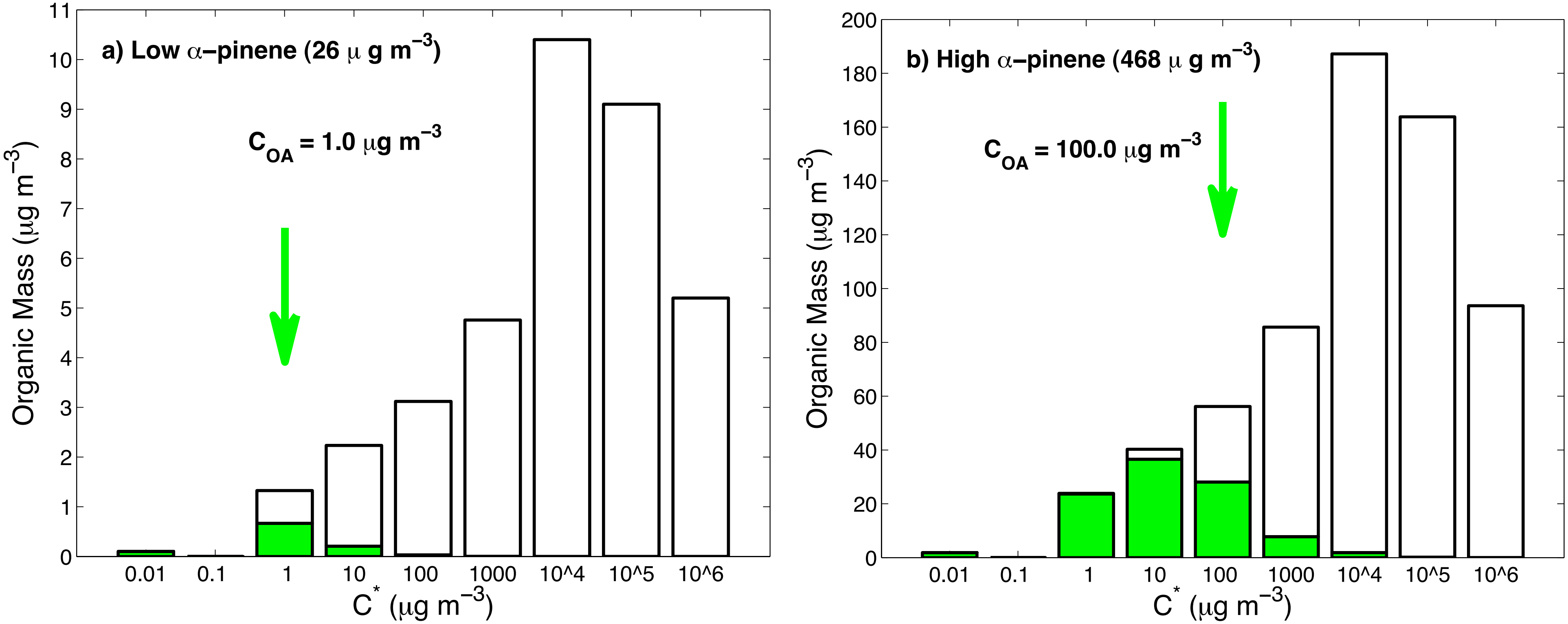




Oxidize some amt. of precursor, say 25 μg m^{-3}, and distribute products.
Start adding from left and see which bin is roughly saturated.
Partition that bin 50:50, others accordingly. Add salt to taste. Adjust accordingly.

[Donahue *et al.* in prep]

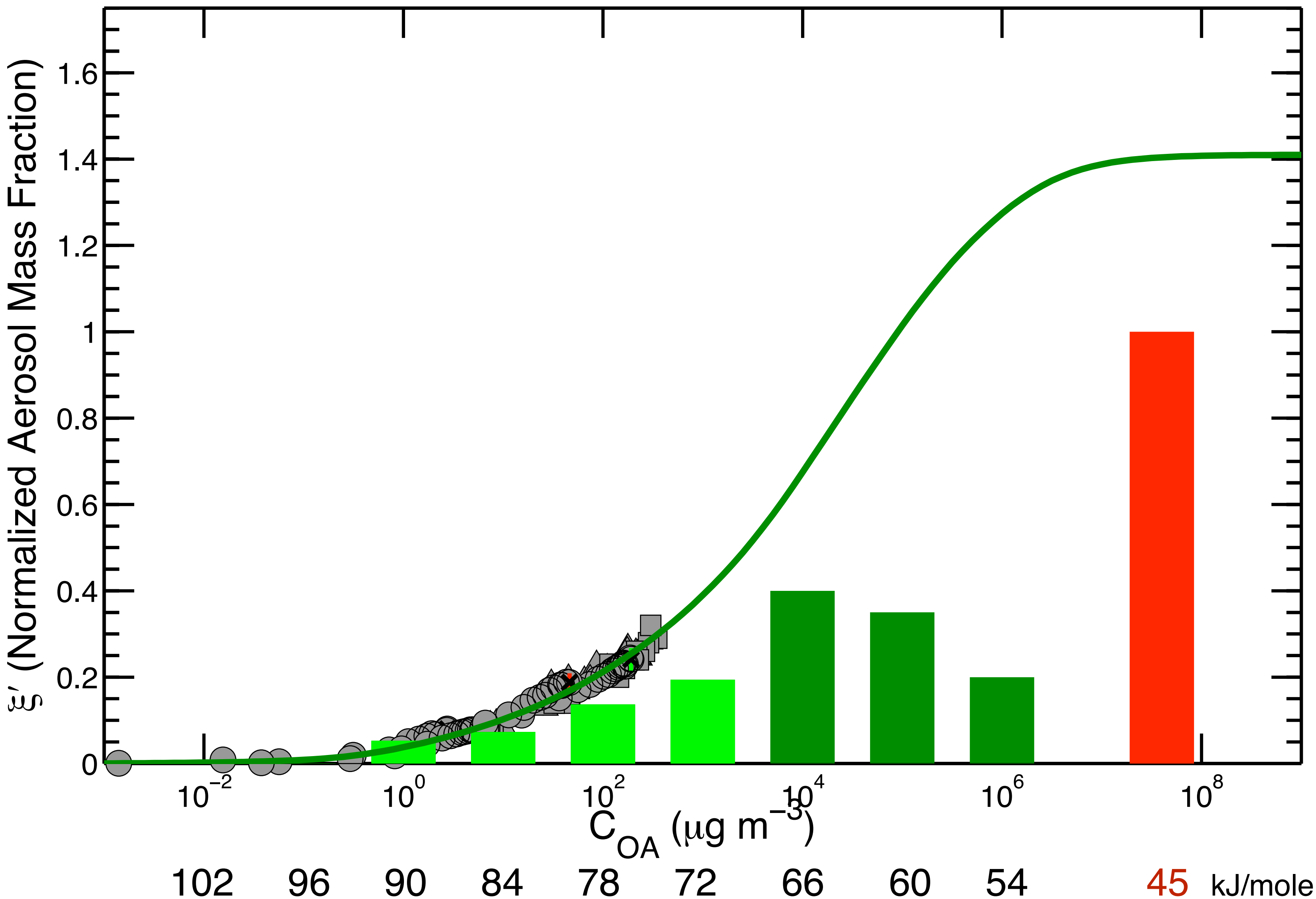
α-Pinene + Ozone Partitioning



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.

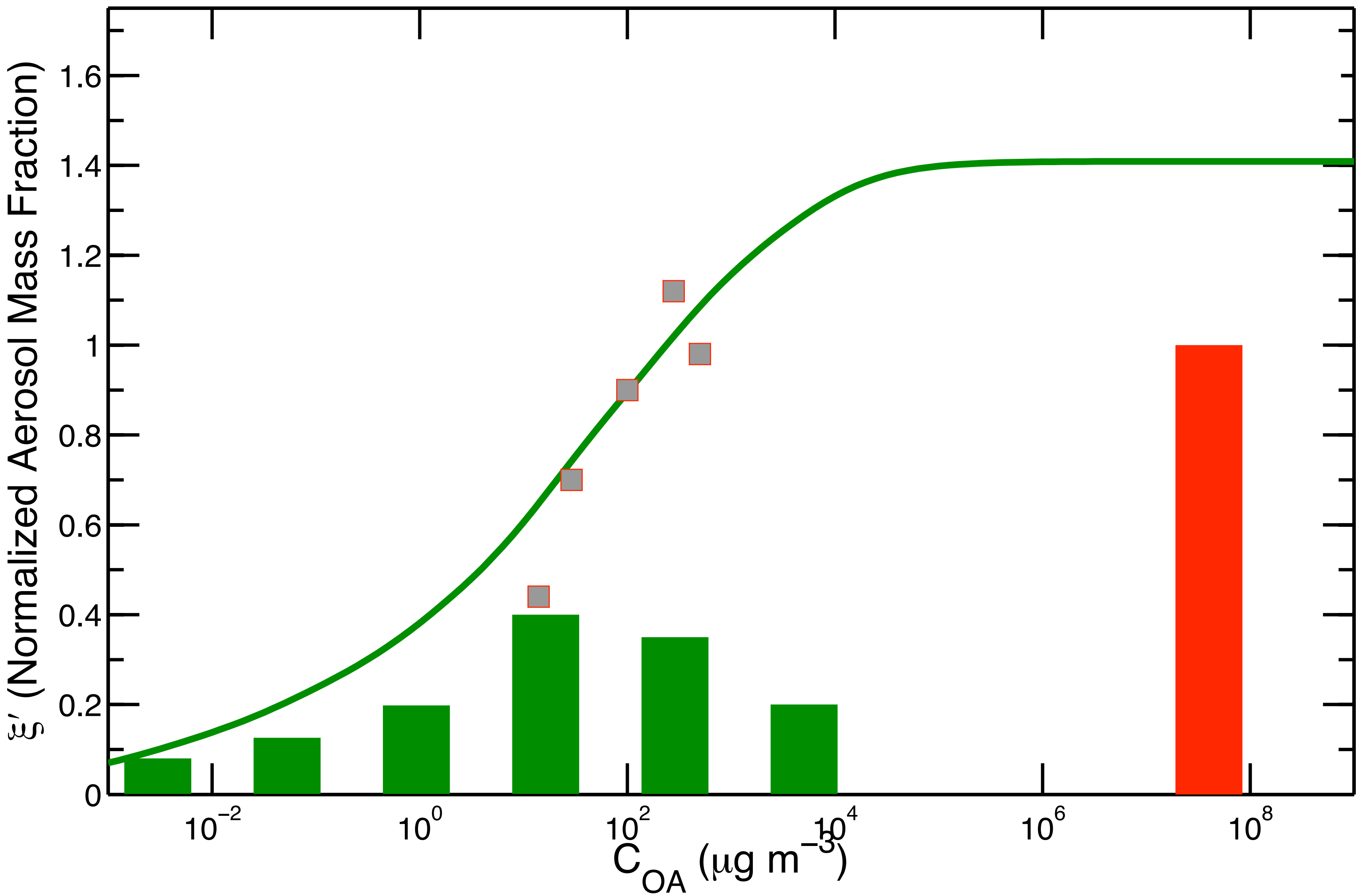
[Donahue *et al.* in prep]

α-Pinene + Ozone ΔH_V 300 K



$$C^*(T) = C^*(300)\,\frac{300K}{T}\,\exp\left[-\frac{\Delta H_V}{R}\left(\frac{1}{T}-\frac{1}{300K}\right)\right]$$

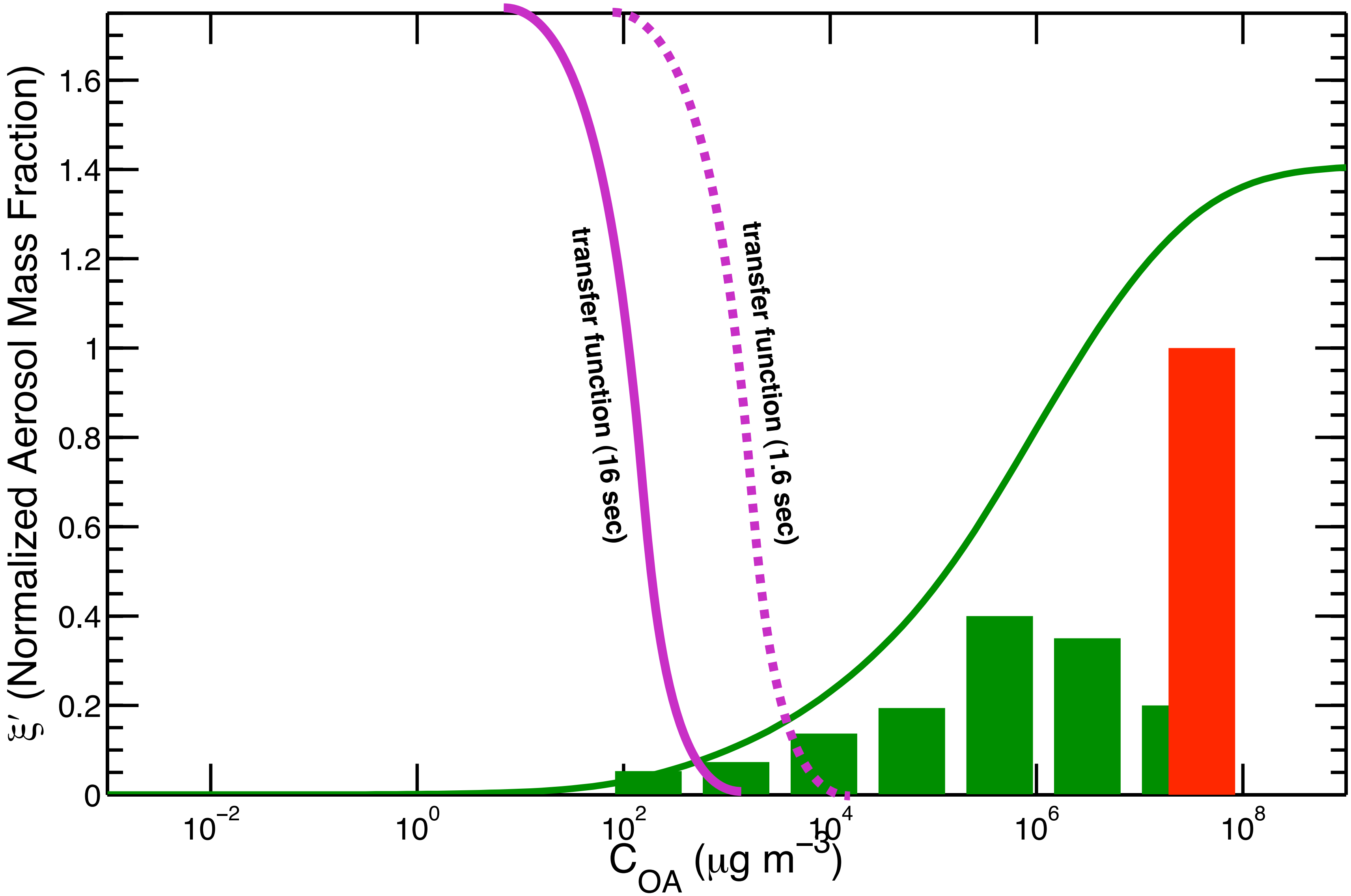
α-Pinene + Ozone Products 243 K



- Products shift left by 2.5 orders of magnitude with a 60 K temperature shift.

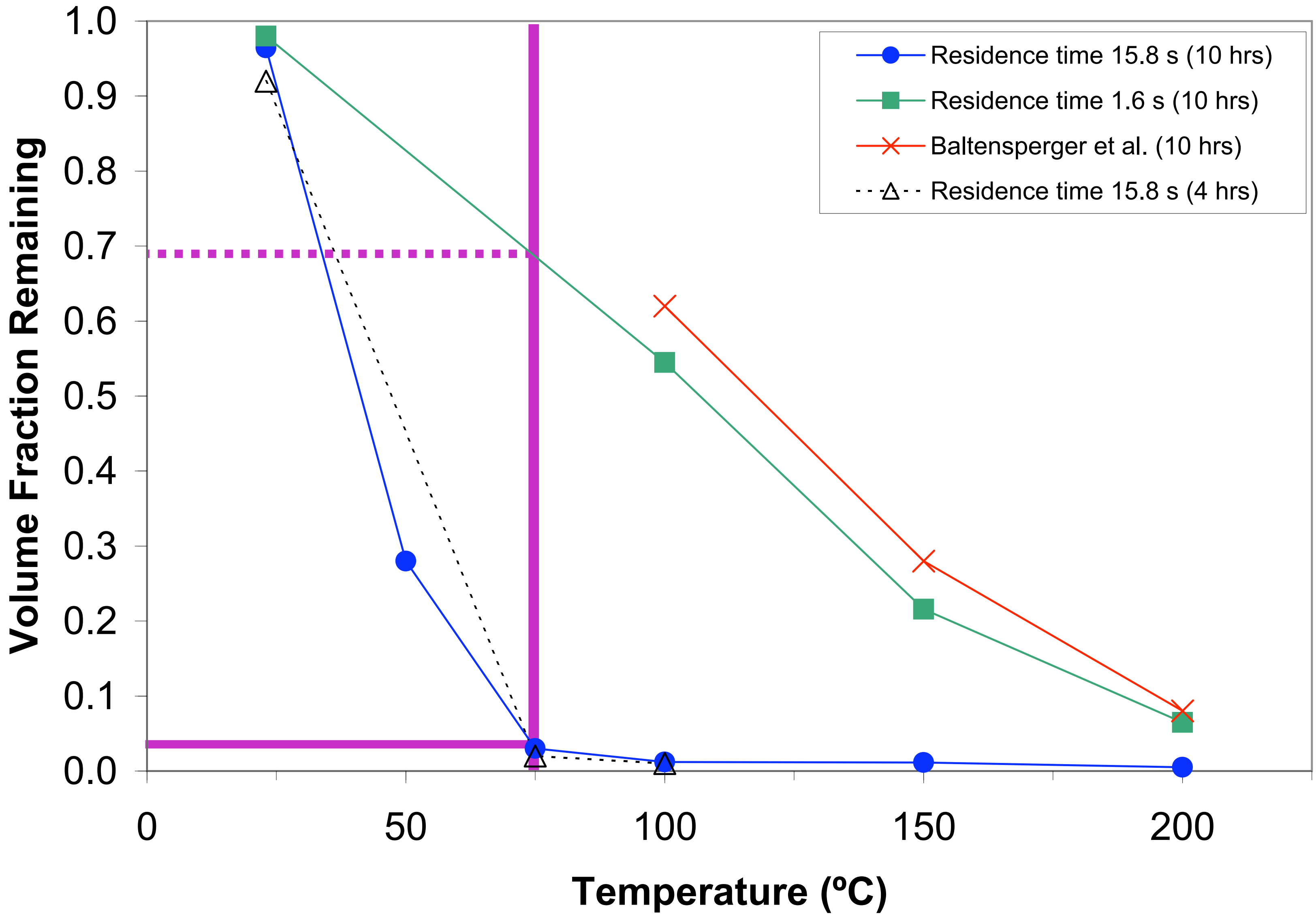
(**Preliminary** data from Saathoff *et al.* $\sim$1 AMF at 100-200 μg m^{-3} and 243 K in AIDA.)

α-Pinene + Ozone Products 350 K (Denuder)



- Products shift right by 2.5 orders of magnitude with a 60 K temperature shift.
- Mass loss depends on mass-transfer kinetics, but it should be substantial.

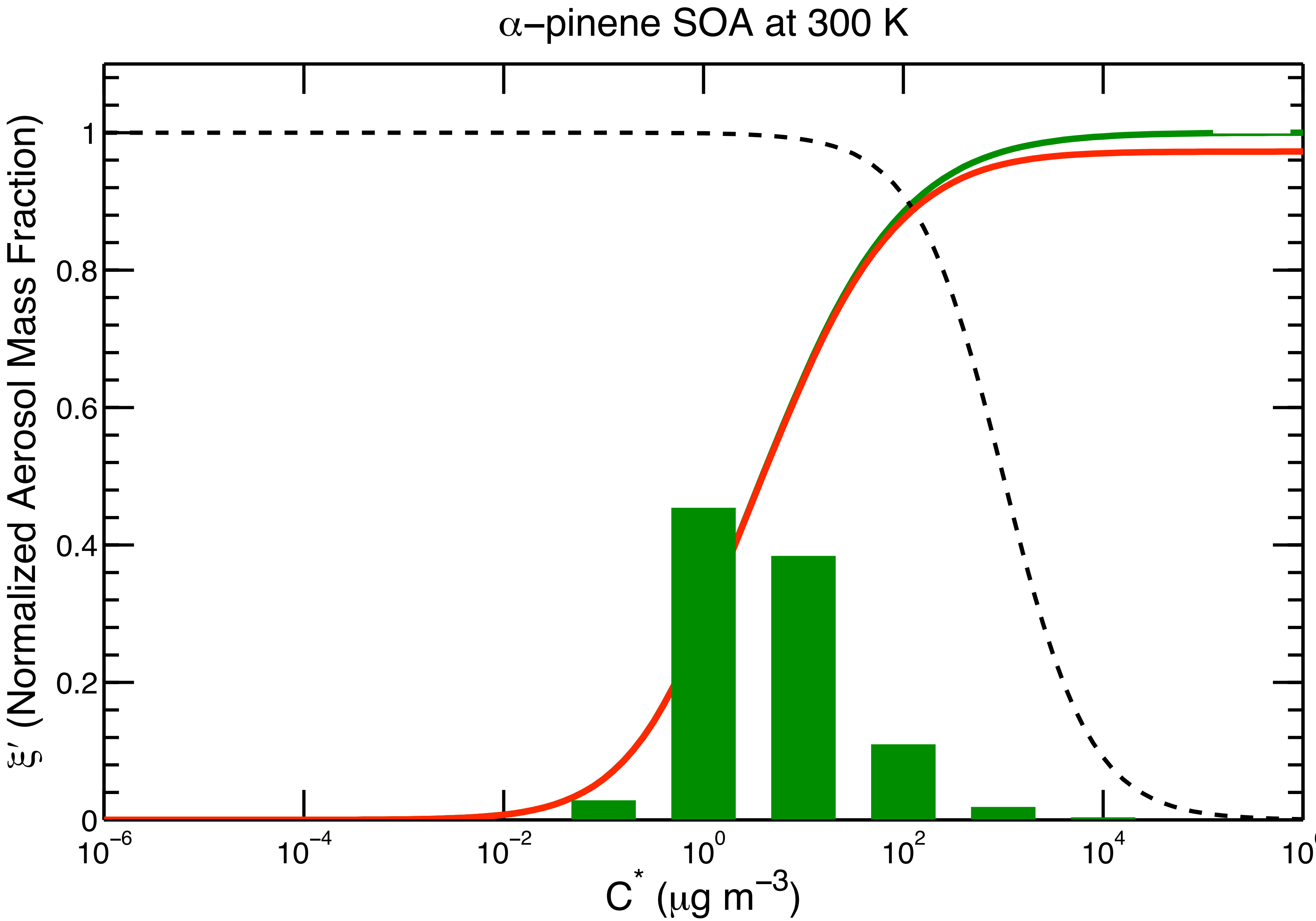
α-Pinene + Ozone Thermodenuder



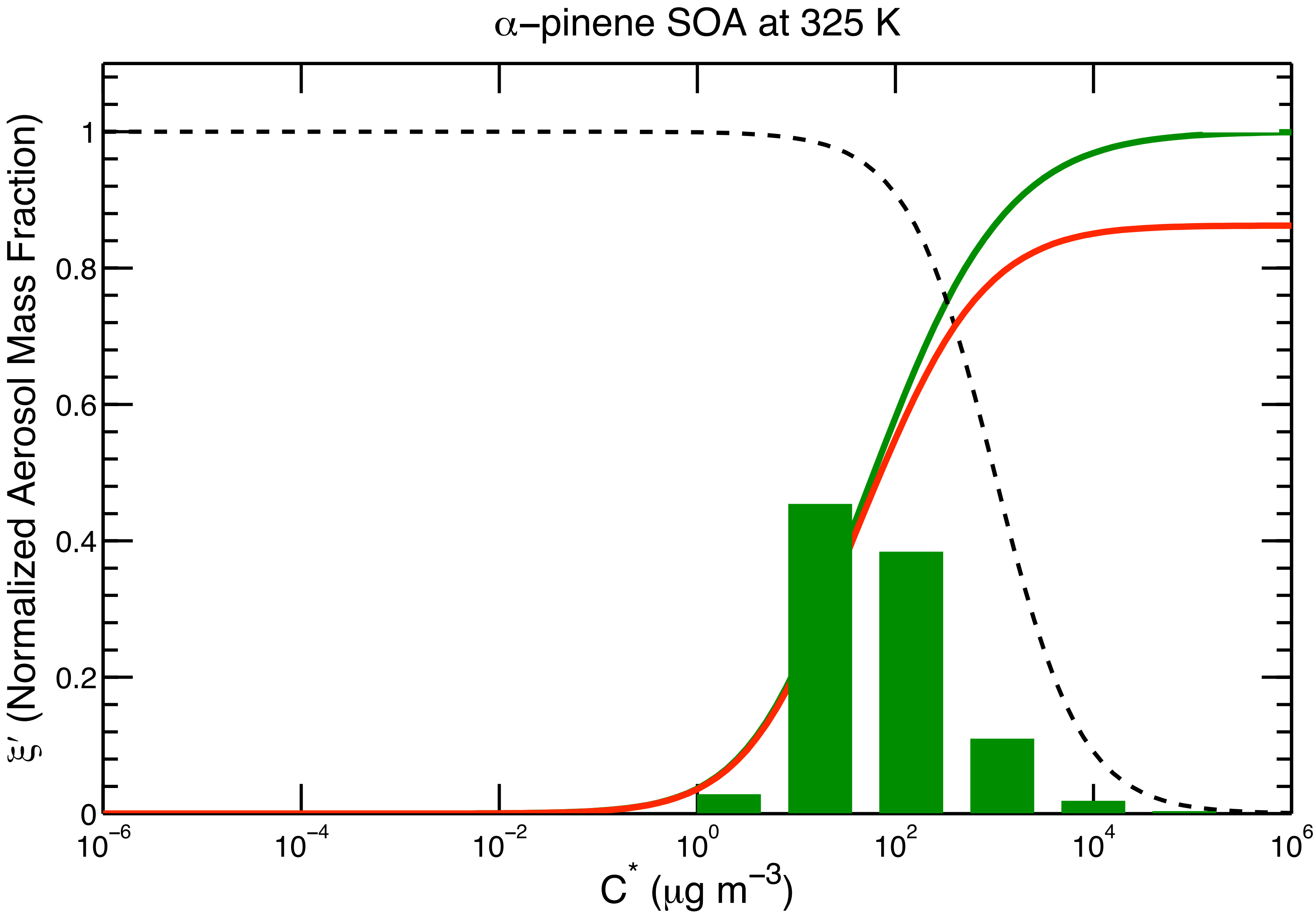
- Given time, *all* α-pinene SOA evaporates at 70 ^{o}C.

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

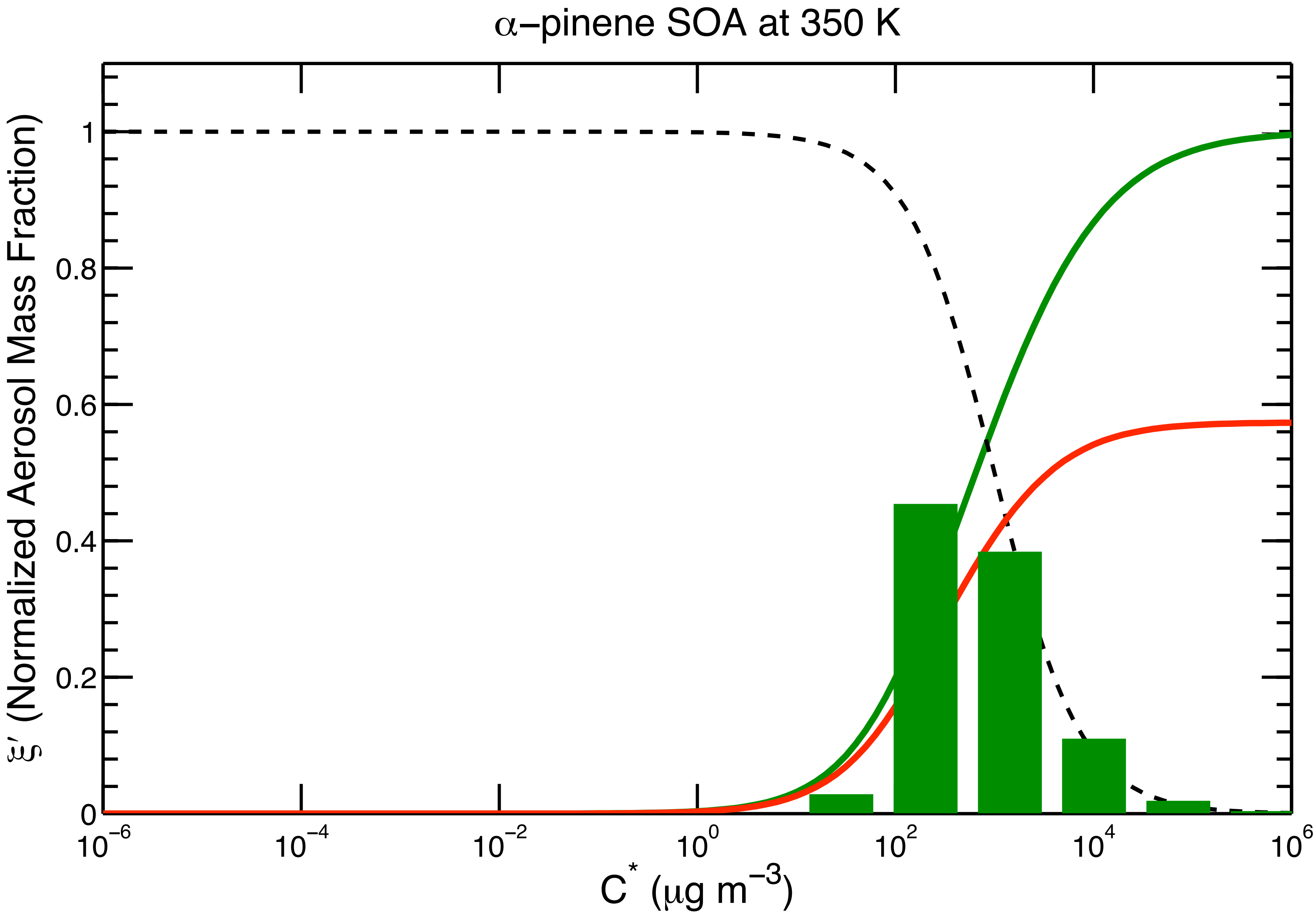
α-Pinene + Ozone Denuder Model



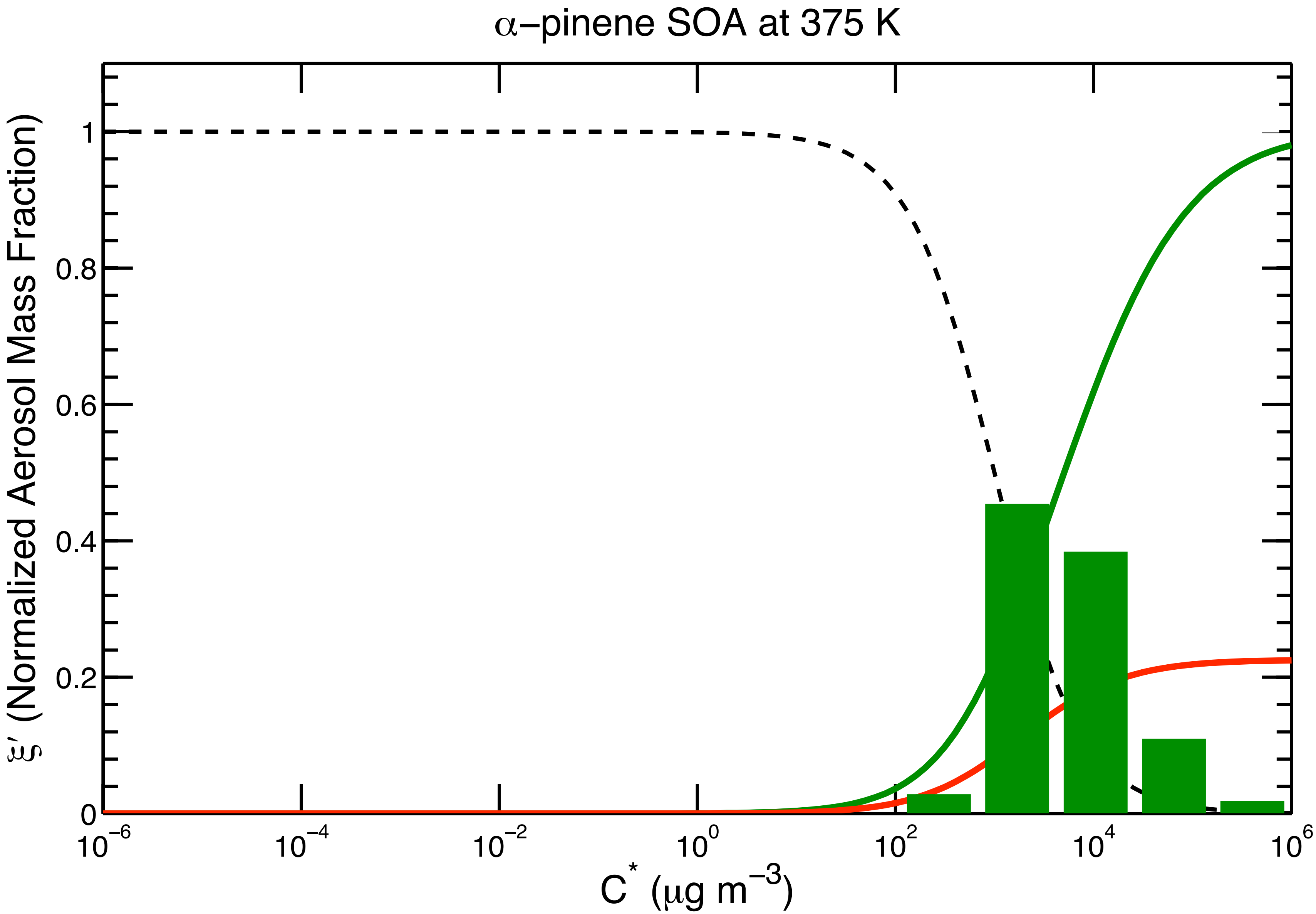
α-Pinene + Ozone Denuder Model



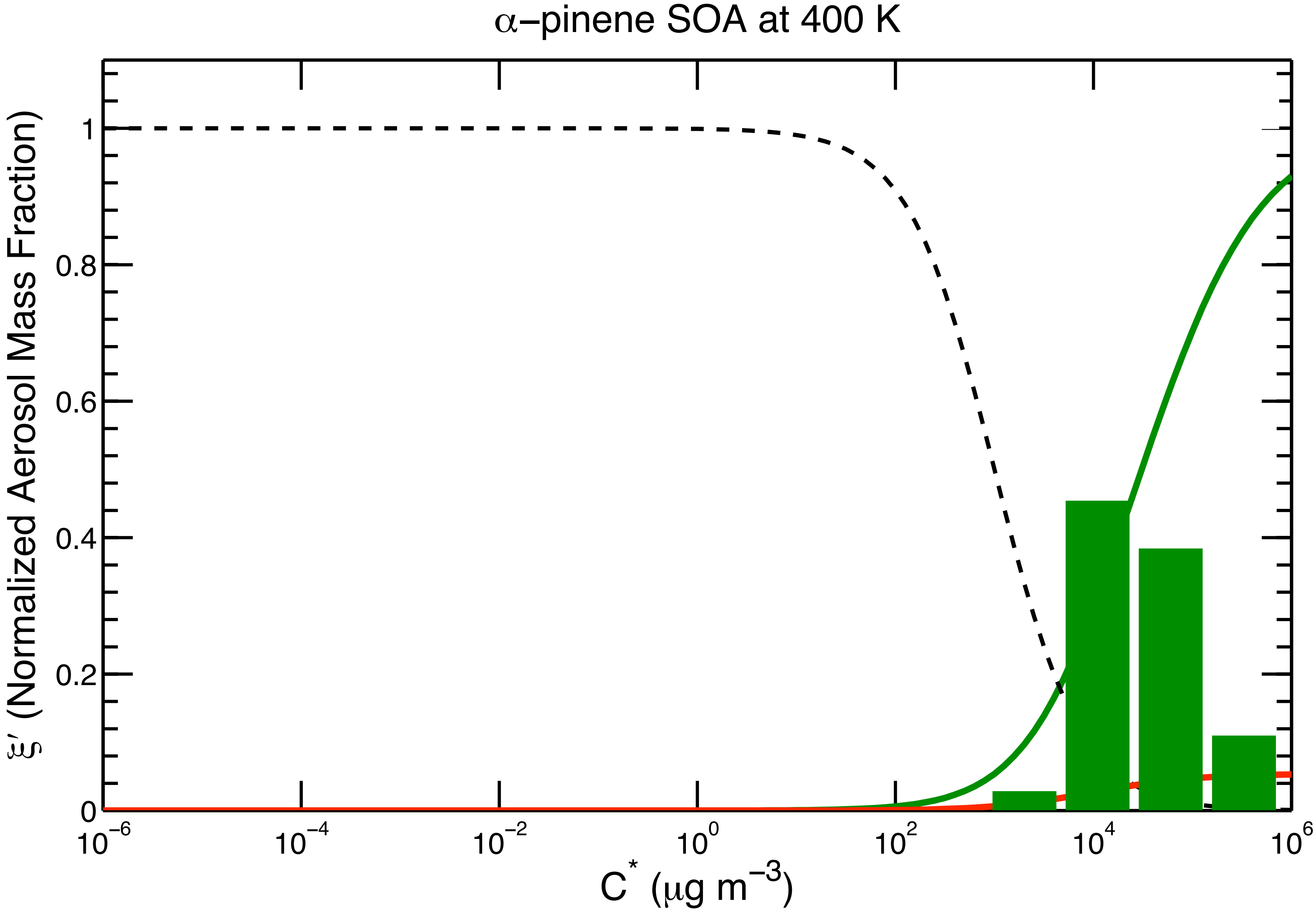
α-Pinene + Ozone Denuder Model



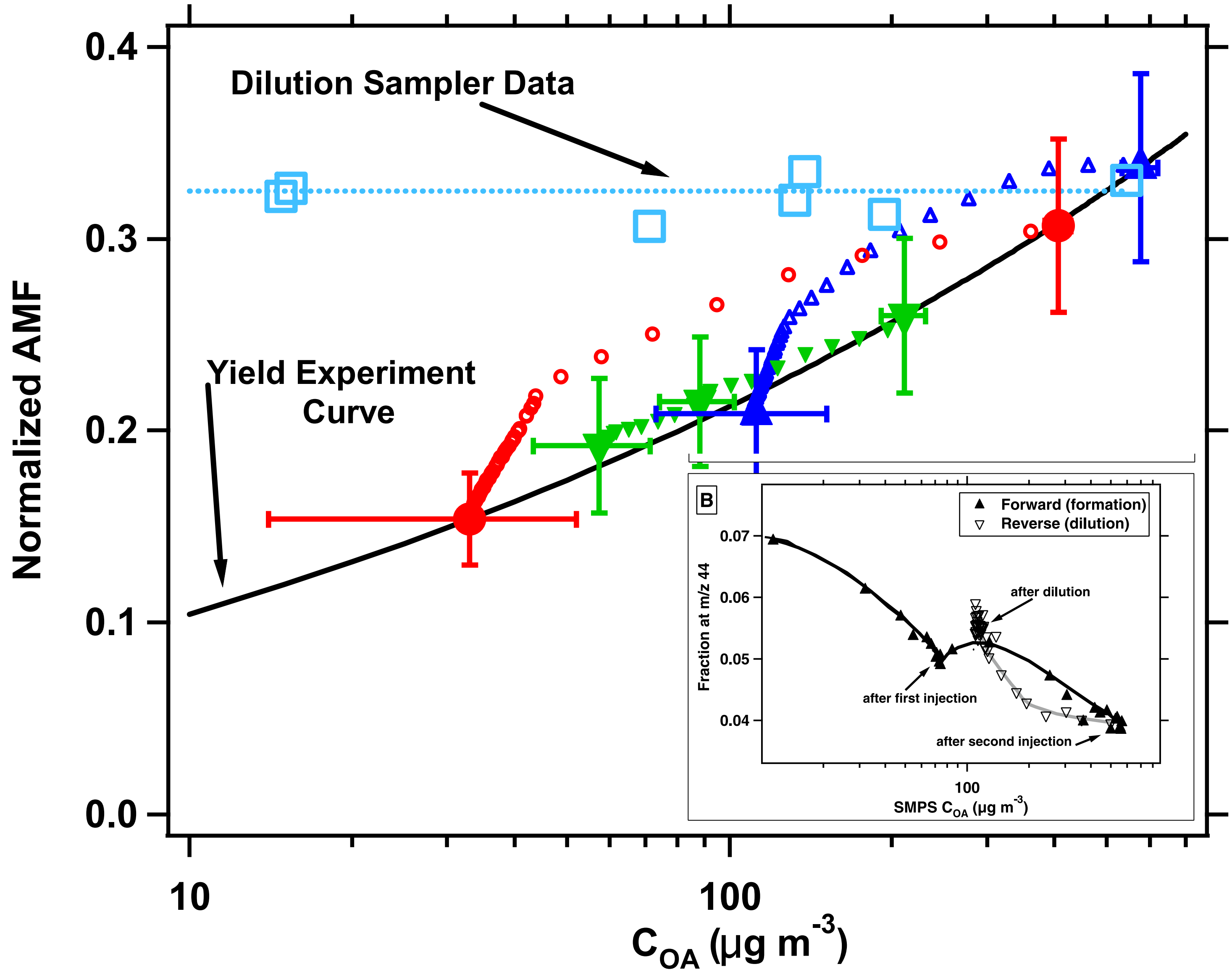
α-Pinene + Ozone Denuder Model



α-Pinene + Ozone Denuder Model



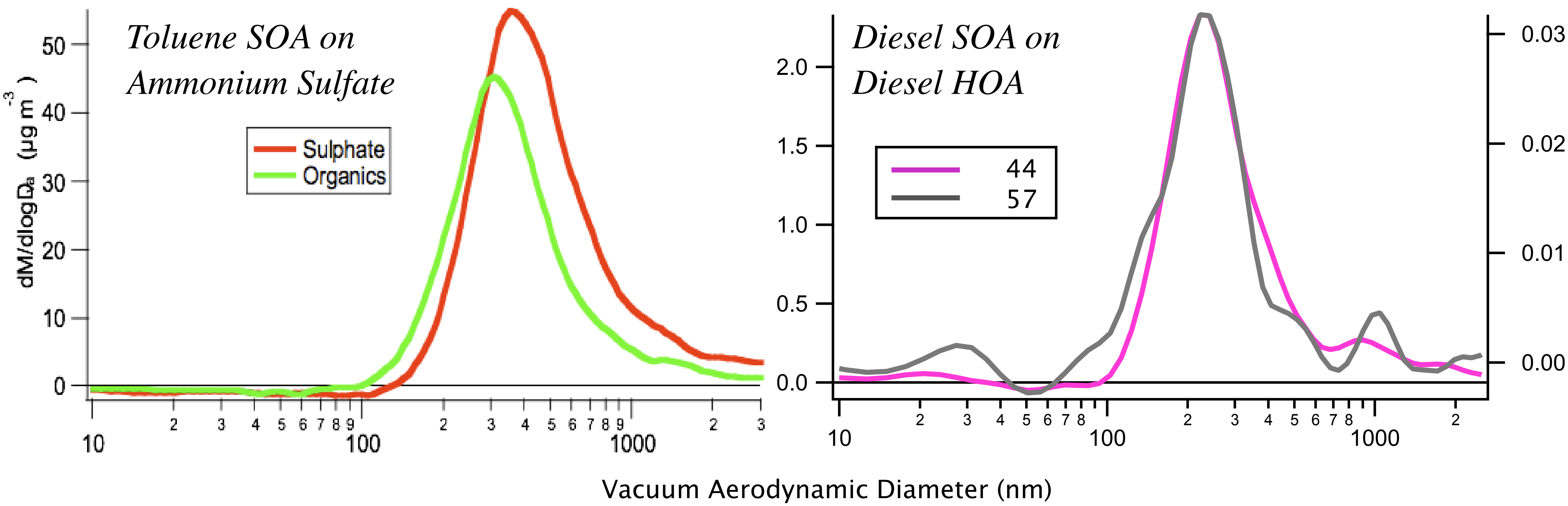
α-pinene + O_3 Dilution



- Generate high SOA and then flush 90% of chamber air.
- Particles shrink *slowly* to expected size.

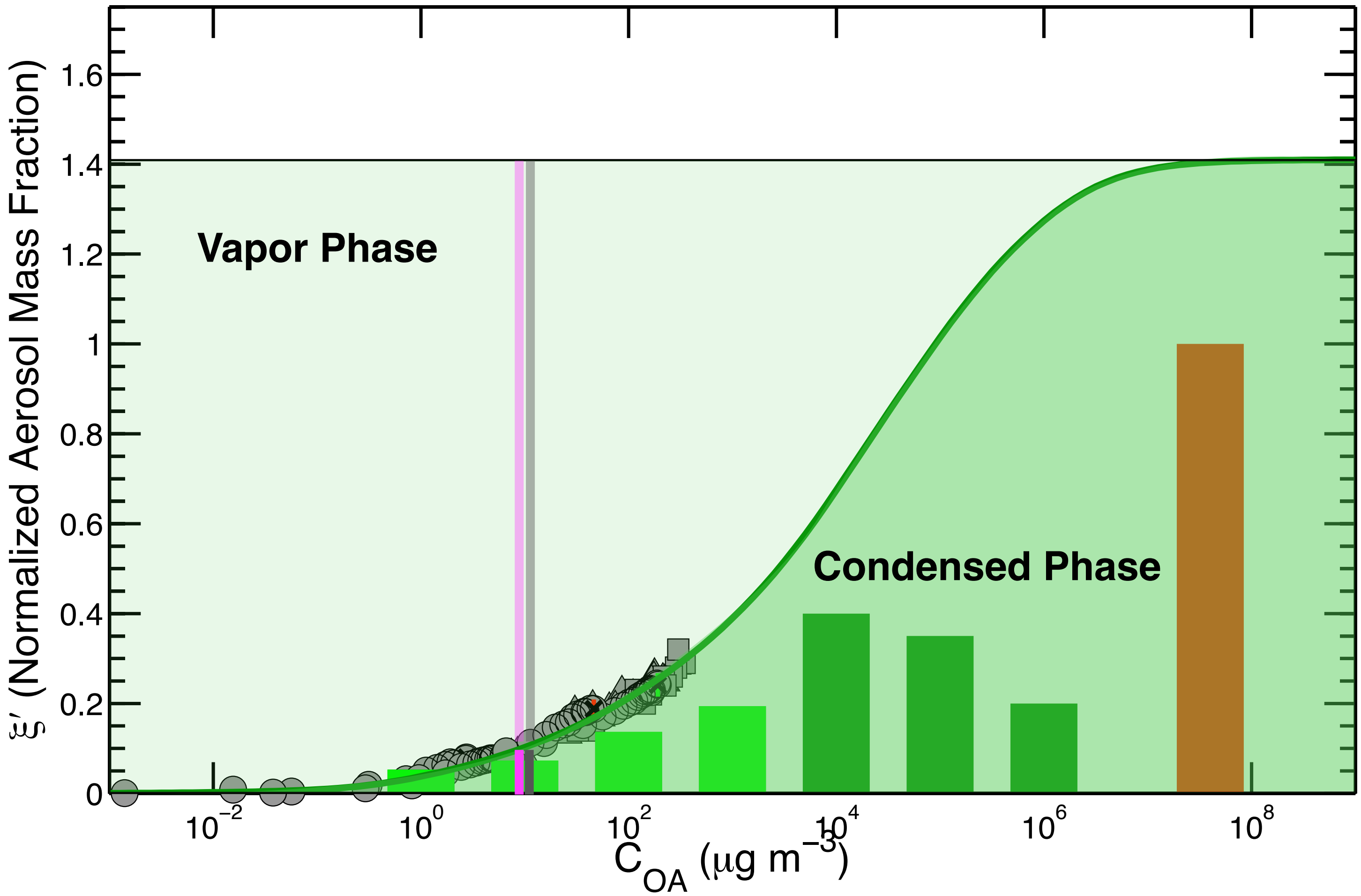
[Grieshop *et al.*, *GRL* 2007]

Mixtures of Organic Fractions



- Toluene SOA associates with sulfate seed *area*.
- New OOA associates with HOA mass on diesel (more about this later).
- This is the difference between 2 separate phases (on one particle) and a mixture.
  - The SOA/AS separation remains at 90% RH. They don't mix!

Implications: Vapors



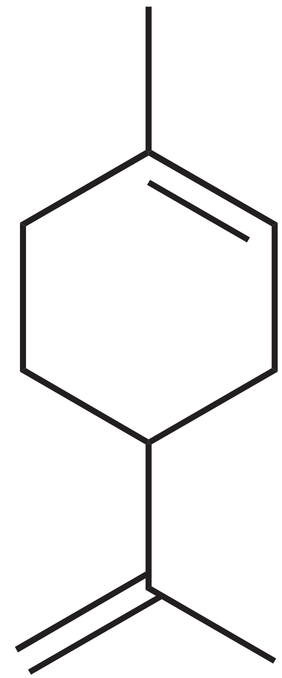
- The mass not seen in the particles is in the gas phase, very low vapor pressure.
- Measuring the partitioning of well-chosen compounds (volatility tracers).

Accurate, precise measurements in both phases is a first-order need.

Generations in Terpene + O_3

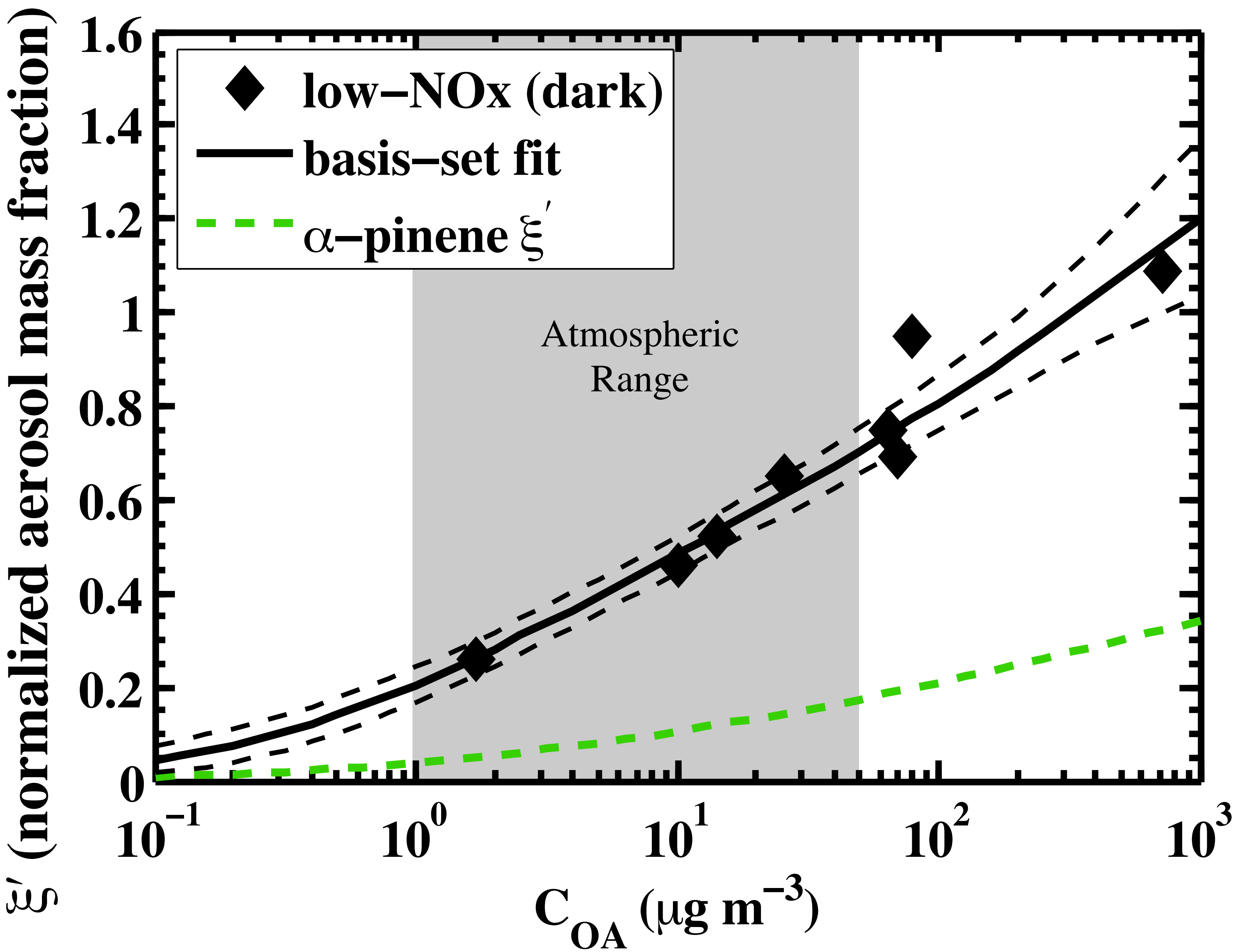
- Multiply unsaturated terpenes like d-limonene should suffer multiple ozonation.
- Which double bond goes first, and what phase is the second reaction in???

$k \simeq 3 \times 10^{-16}$



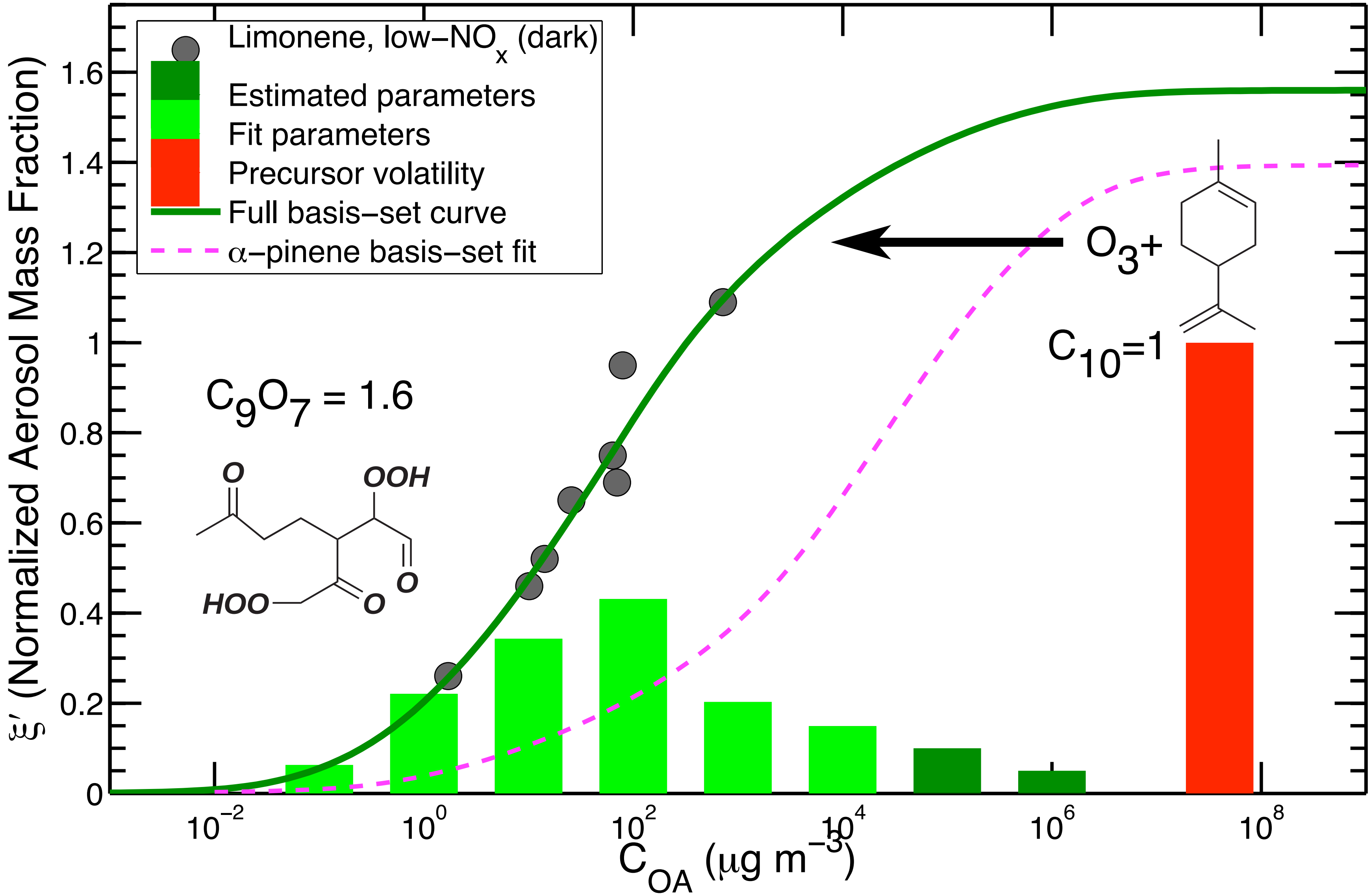
$k \simeq 8 \times 10^{-18}$

Limonene and the Basis Set (1 ppm O_3)



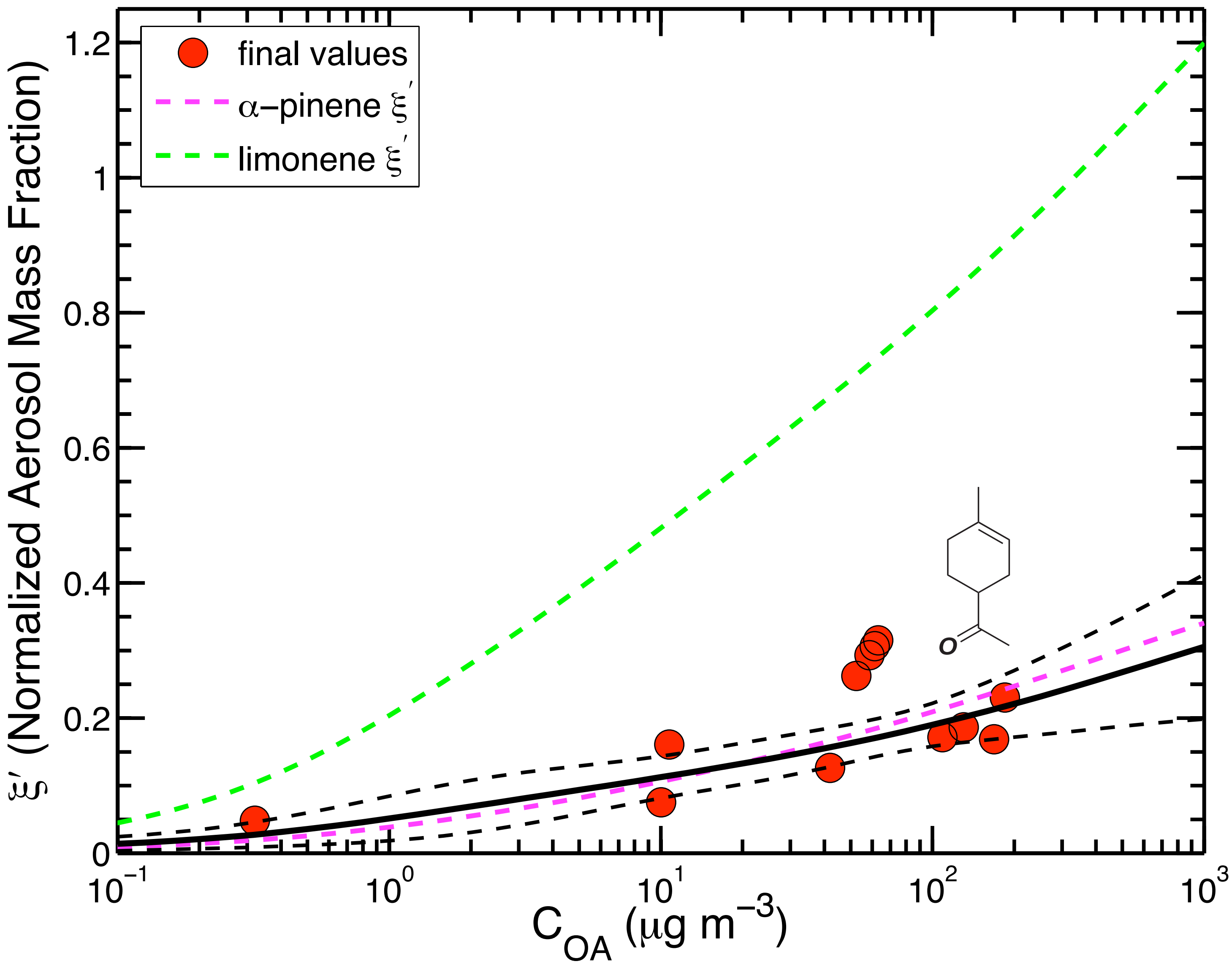
$\alpha'_i = \{.0, \quad .06, \quad .22, \quad .34, \quad .43, \quad .20, \quad .14, ...\}$

Limonene + Ozone Mass Balance



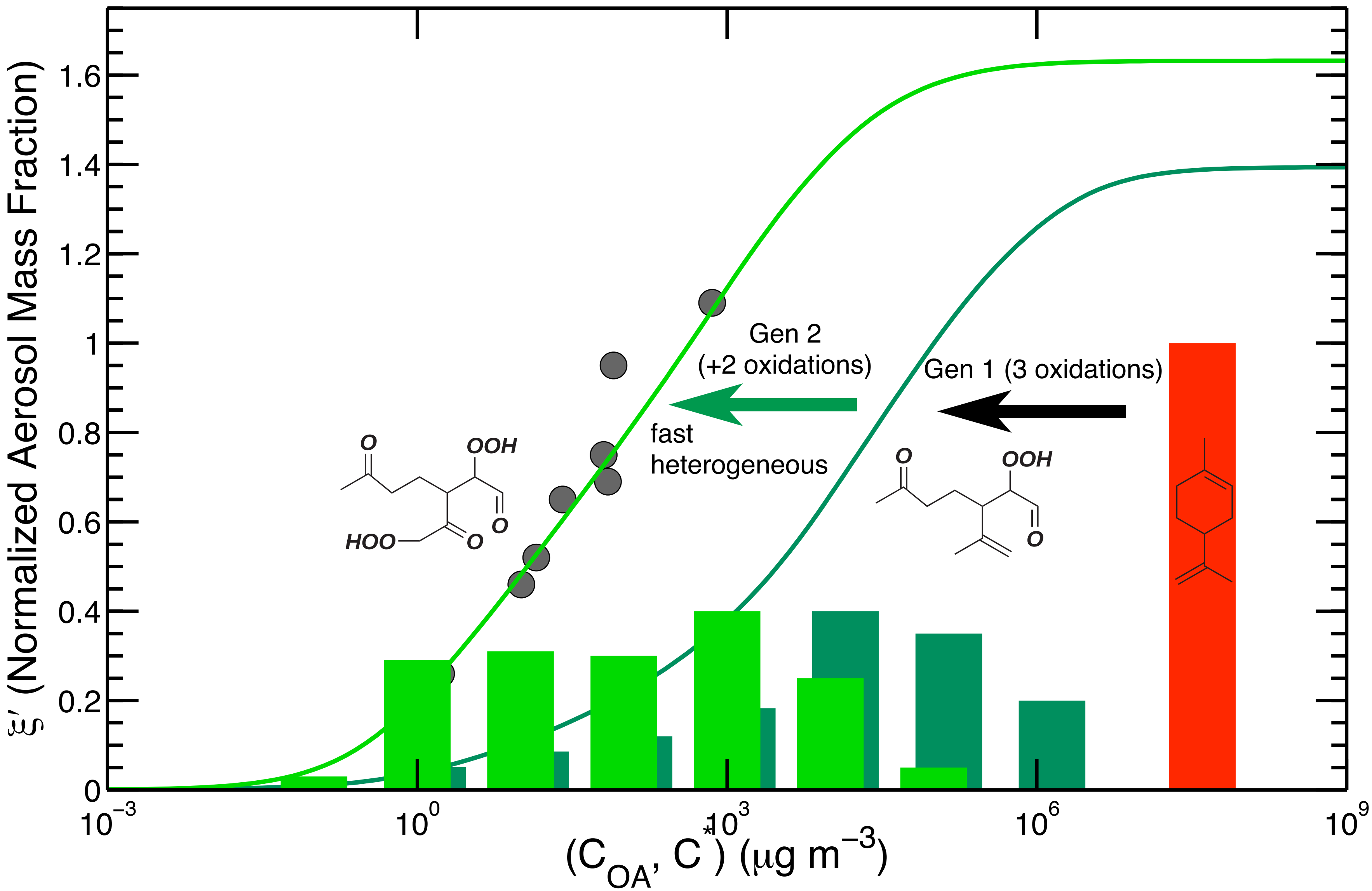
D-limonene + O_3 makes more SOA than α-pinene.

Limonaketone + Ozone



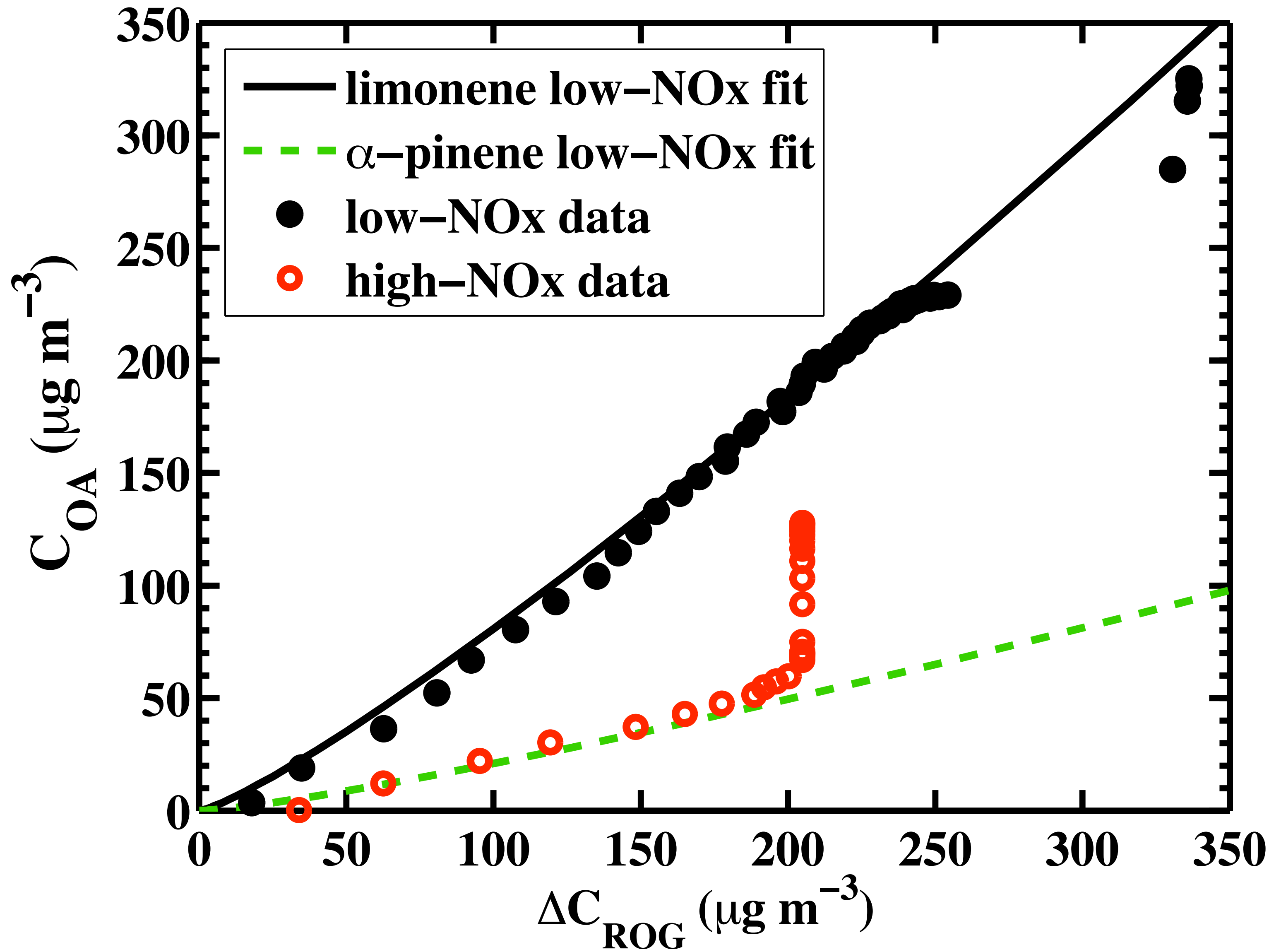
But limonoketone is just like α-pinene.

Generations of Limonene Oxidation



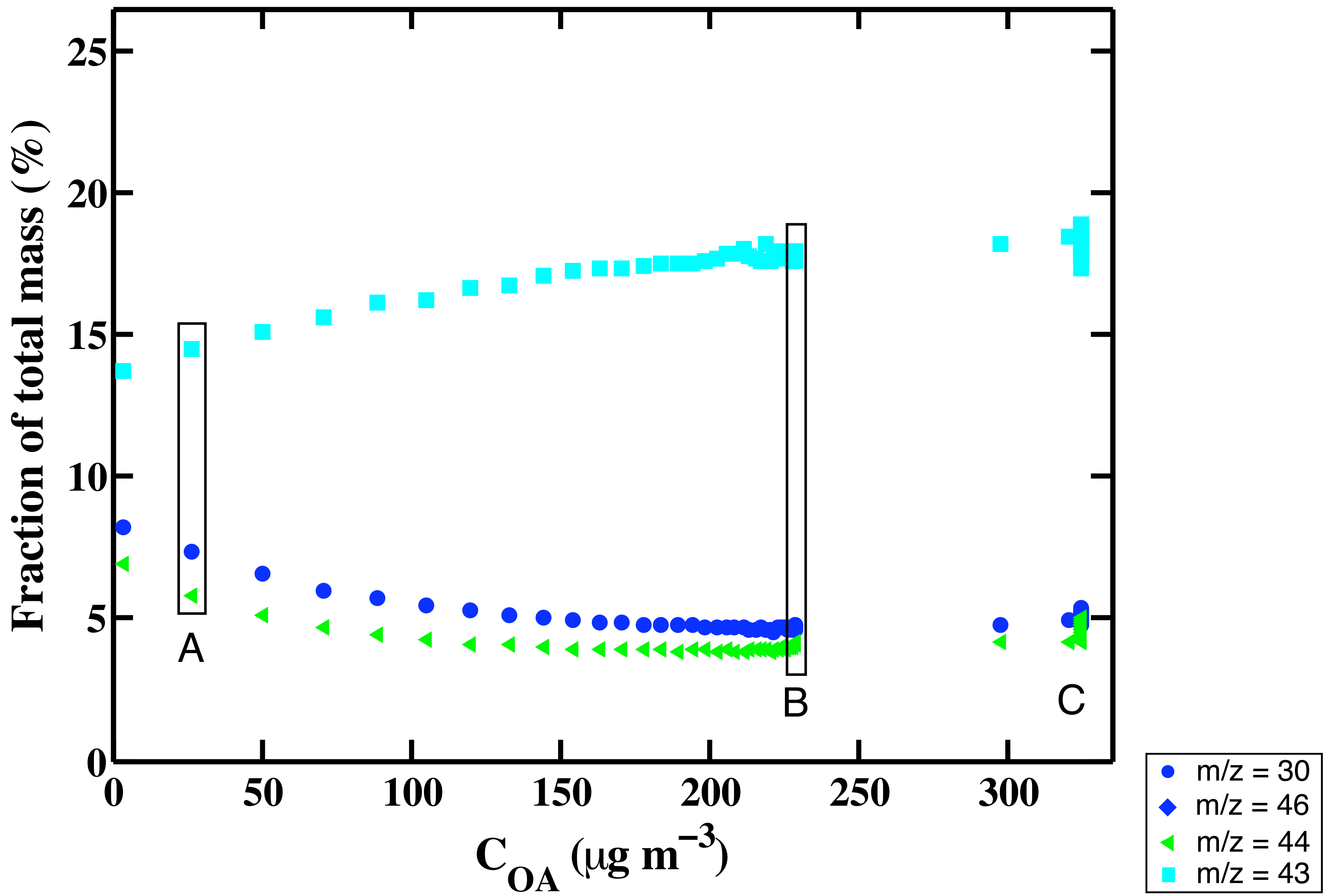
What happens with 2nd oxidation on real aerosol??.

Limonene + Ozone (100 ppb ozone)



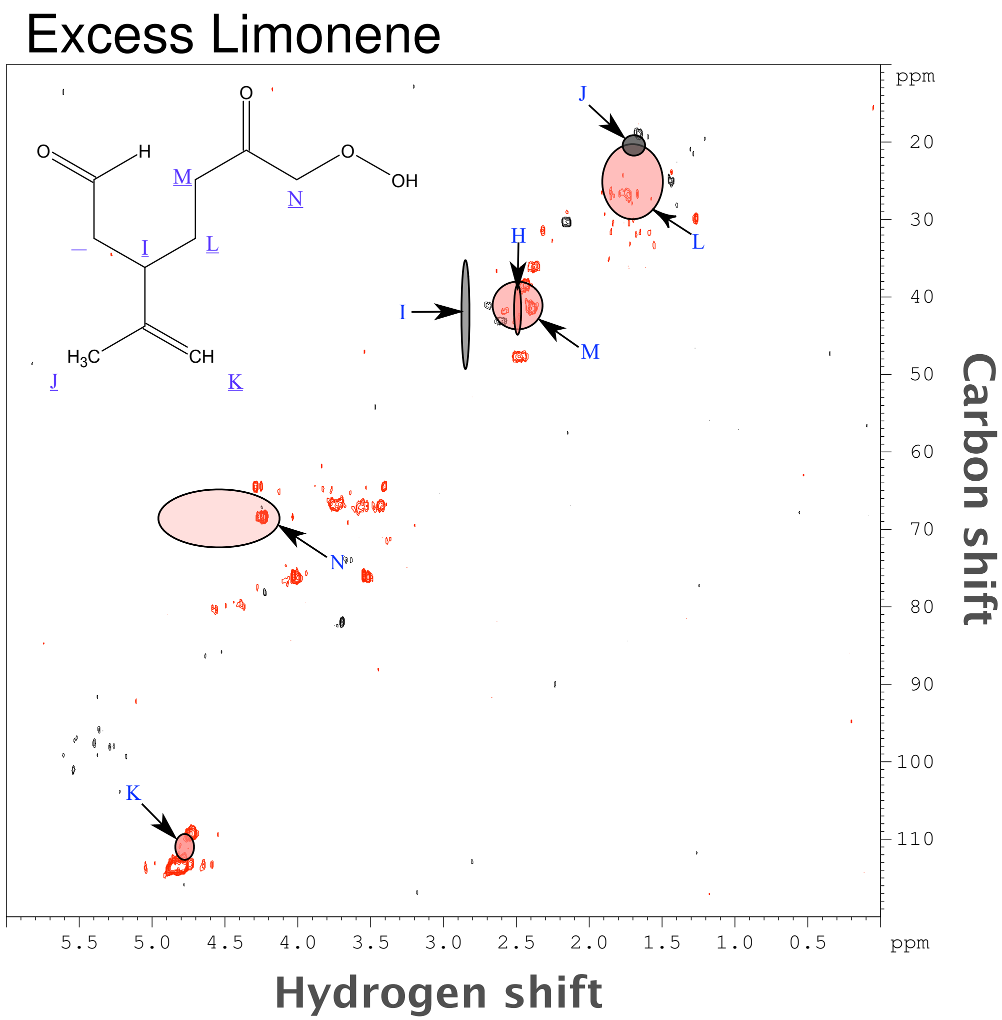
Low-NO$_x$ data on complete oxidation line as limonene oxidized!

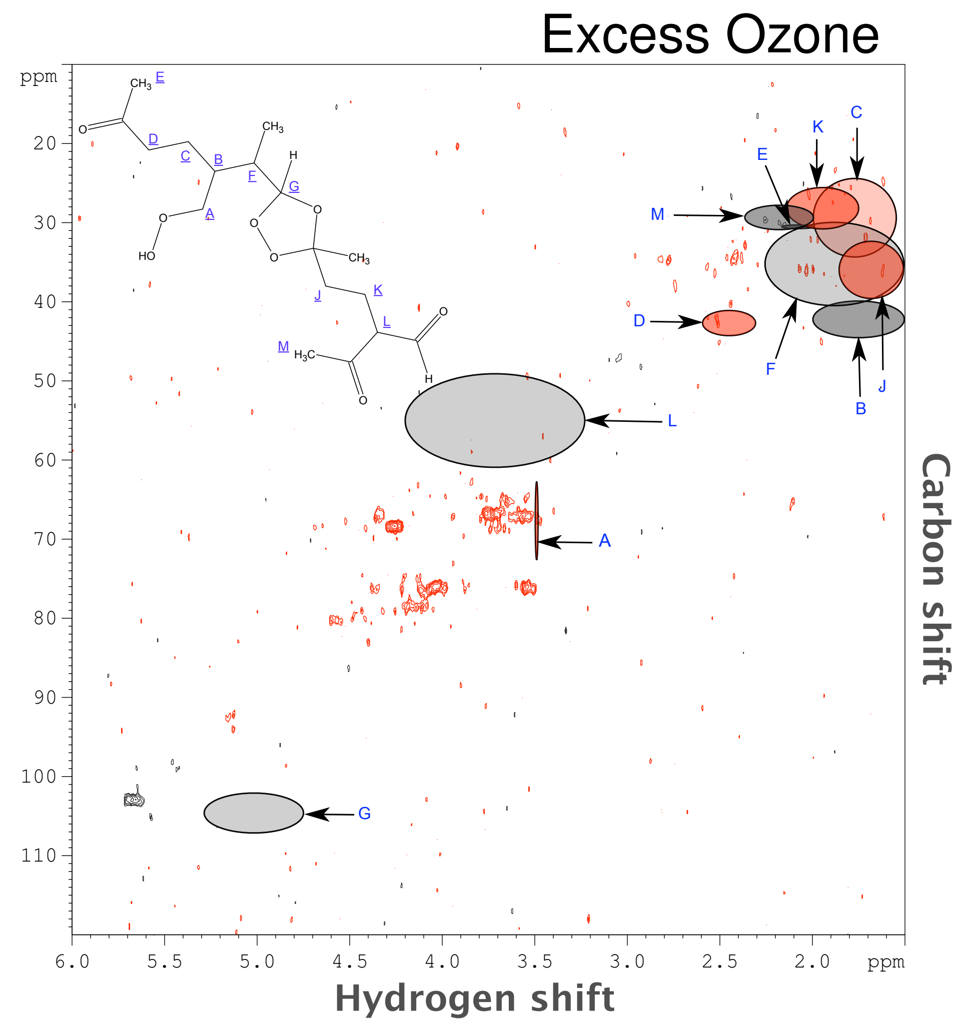
Low-NO_x limonene Q-AMS Data vs C_{OA}



· More oxidized material favored at low C_{OA} has lower C* (lower vapor pressure).

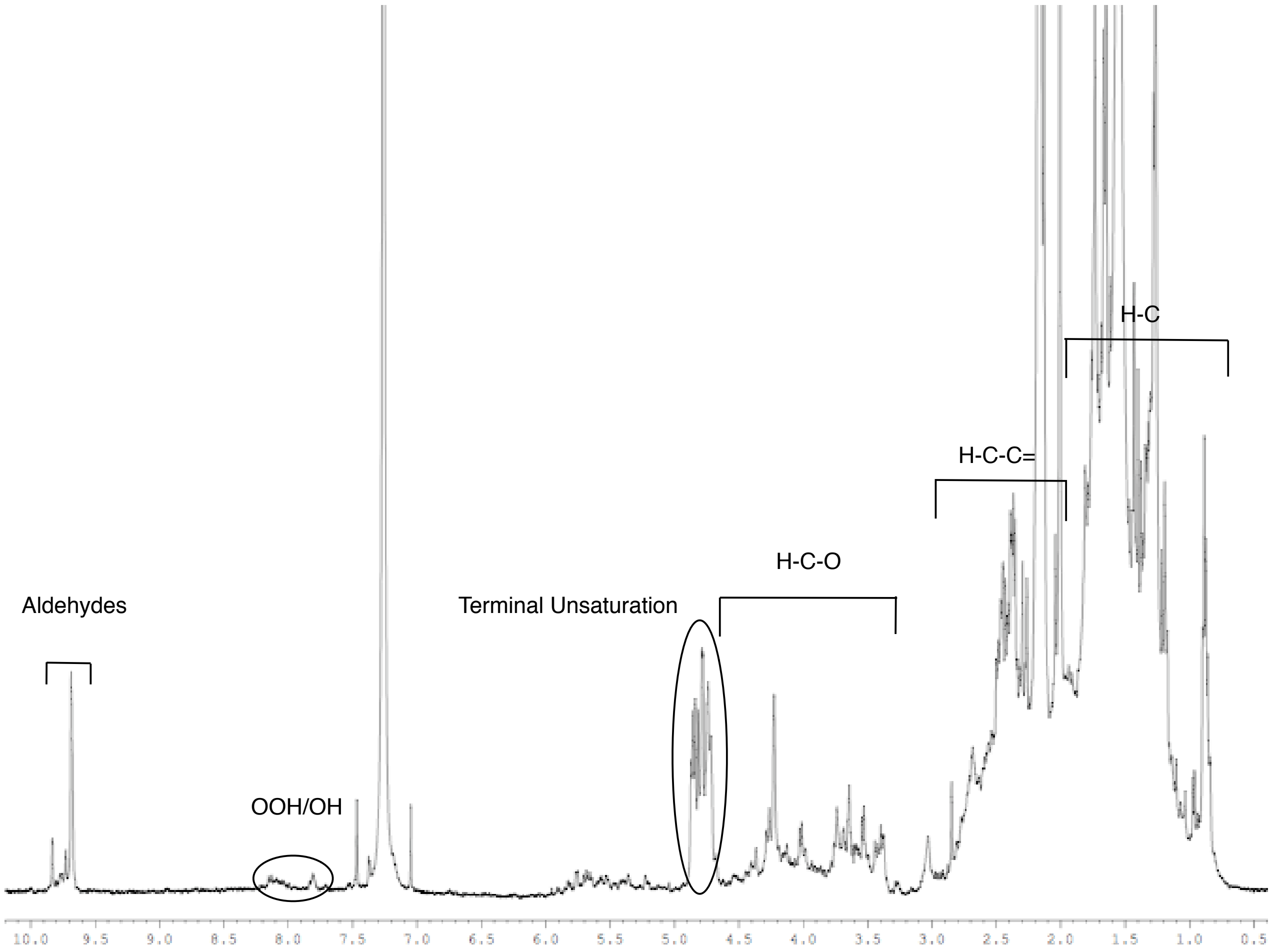
Limonene + Ozone 2-D NMR (HSQC)





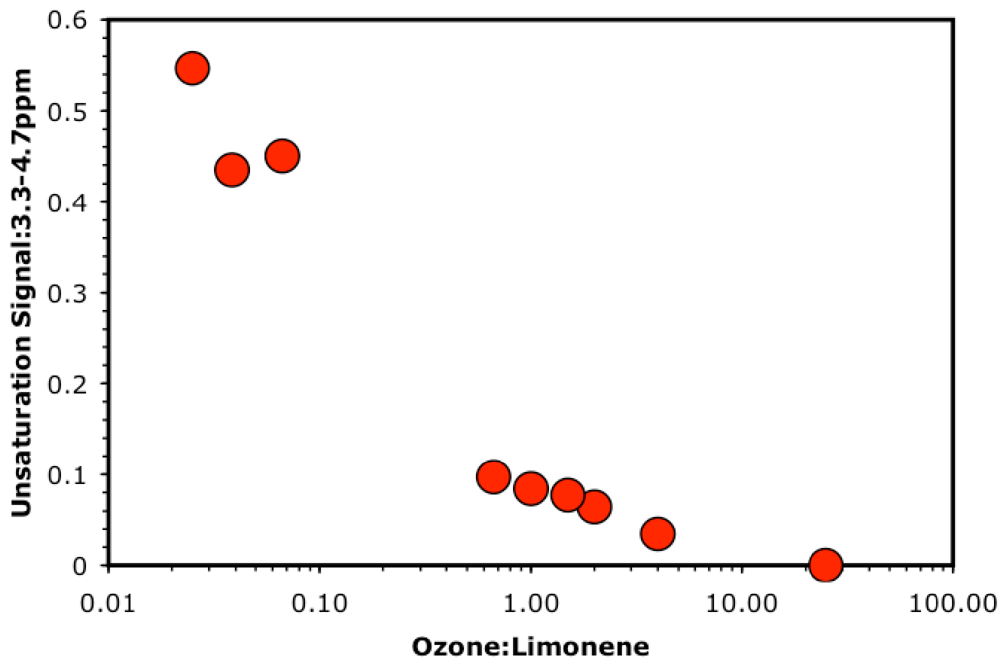
- Double bond at 4.8 ppm H and 115 ppm ^{13}C totally gone for excess ozone.
- Persistent down-field 'box' at 3.5-4.5 ppm H is multi-functional ROOH and ROH.

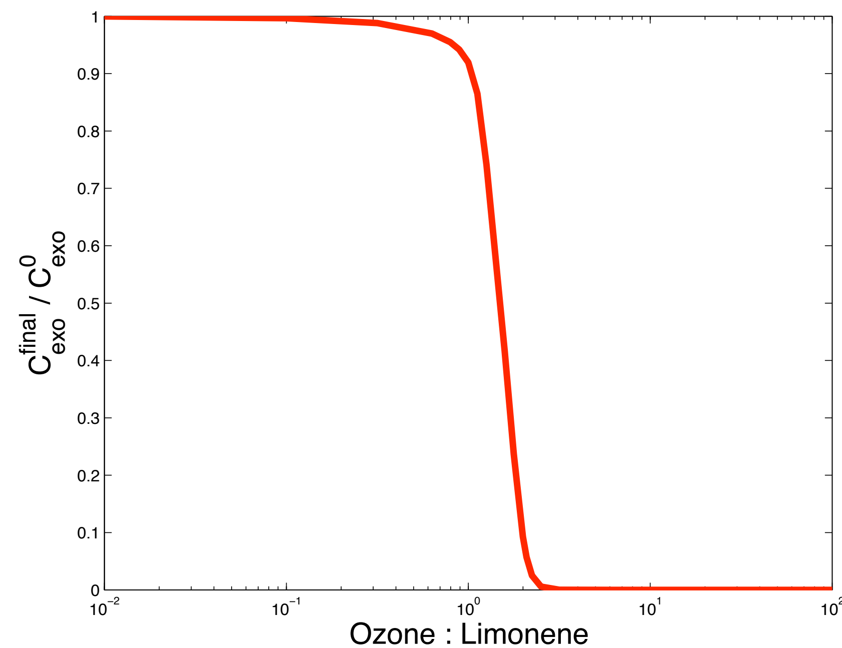
Limonene + Ozone H-NMR (Quantitative)



- Quantify unsaturation vs something else (we use 3.3-4.7 H-C-O, can use other).

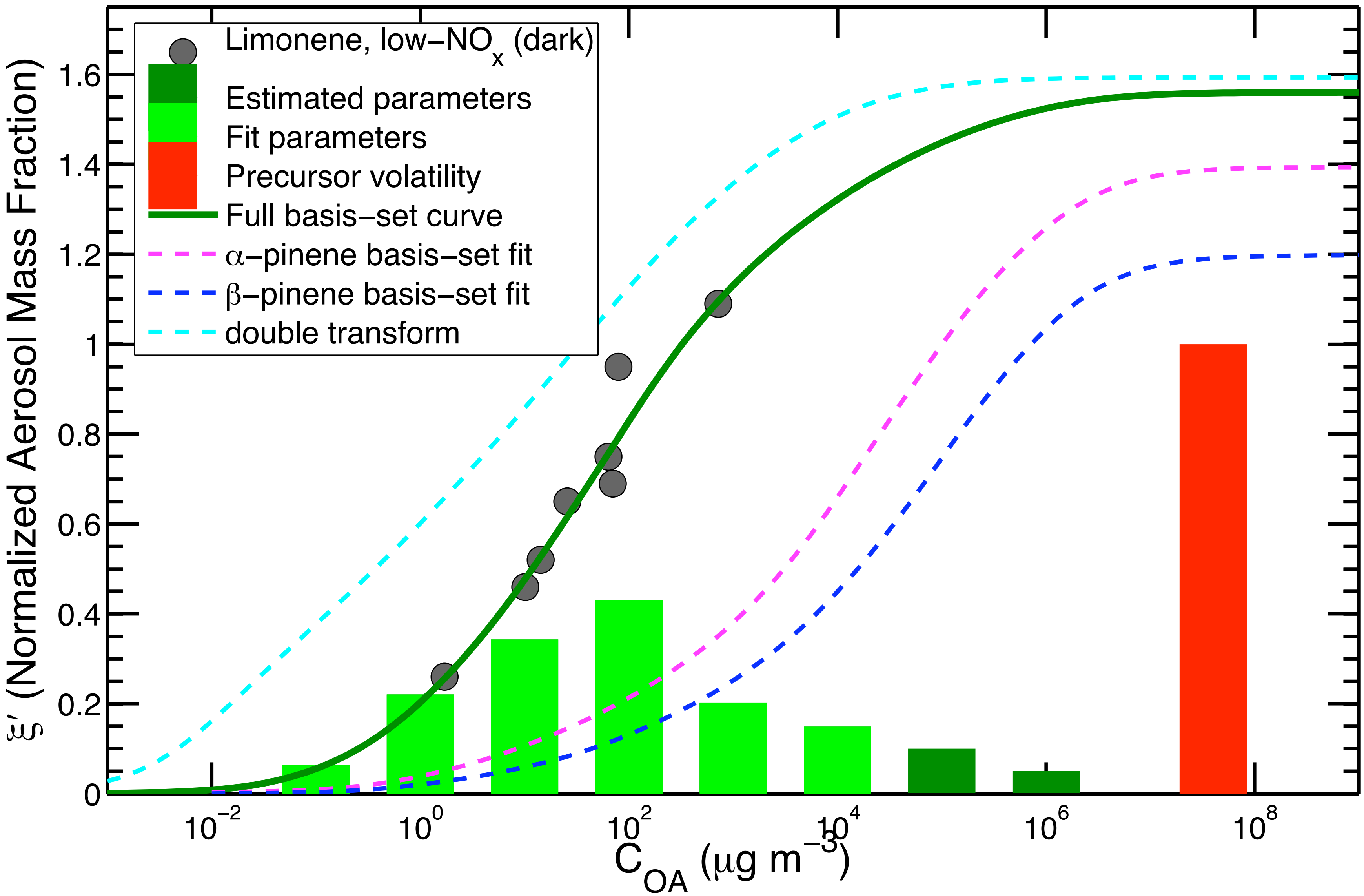
Limonene + Ozone Titration





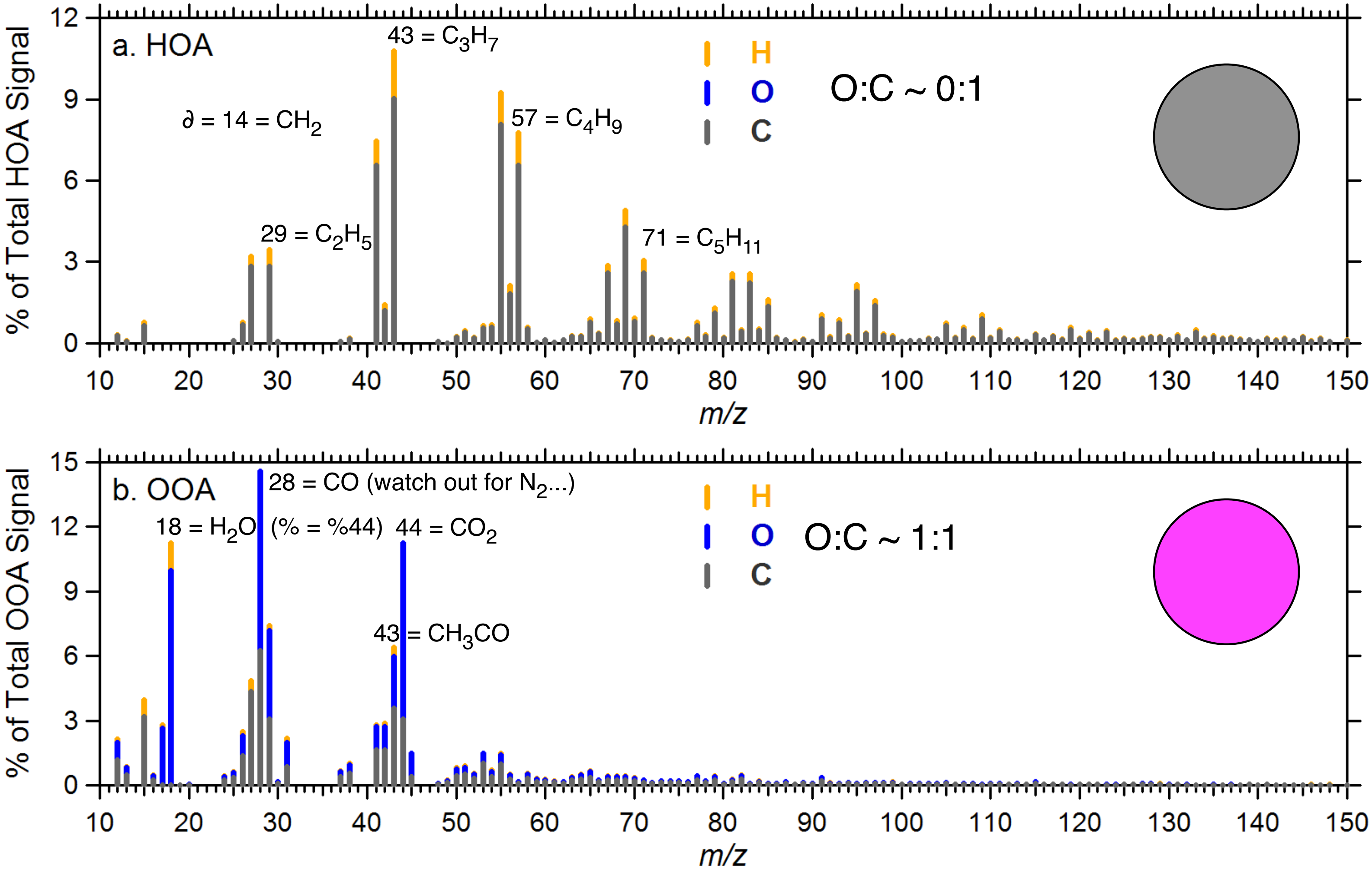
- Loss of unsaturation is much more gradual than homogeneous prediction.
- Consistent with uptake of O_3 as we hypothesized.

Limonene SOA as $\alpha \cdot \beta$-pinene (Operator)



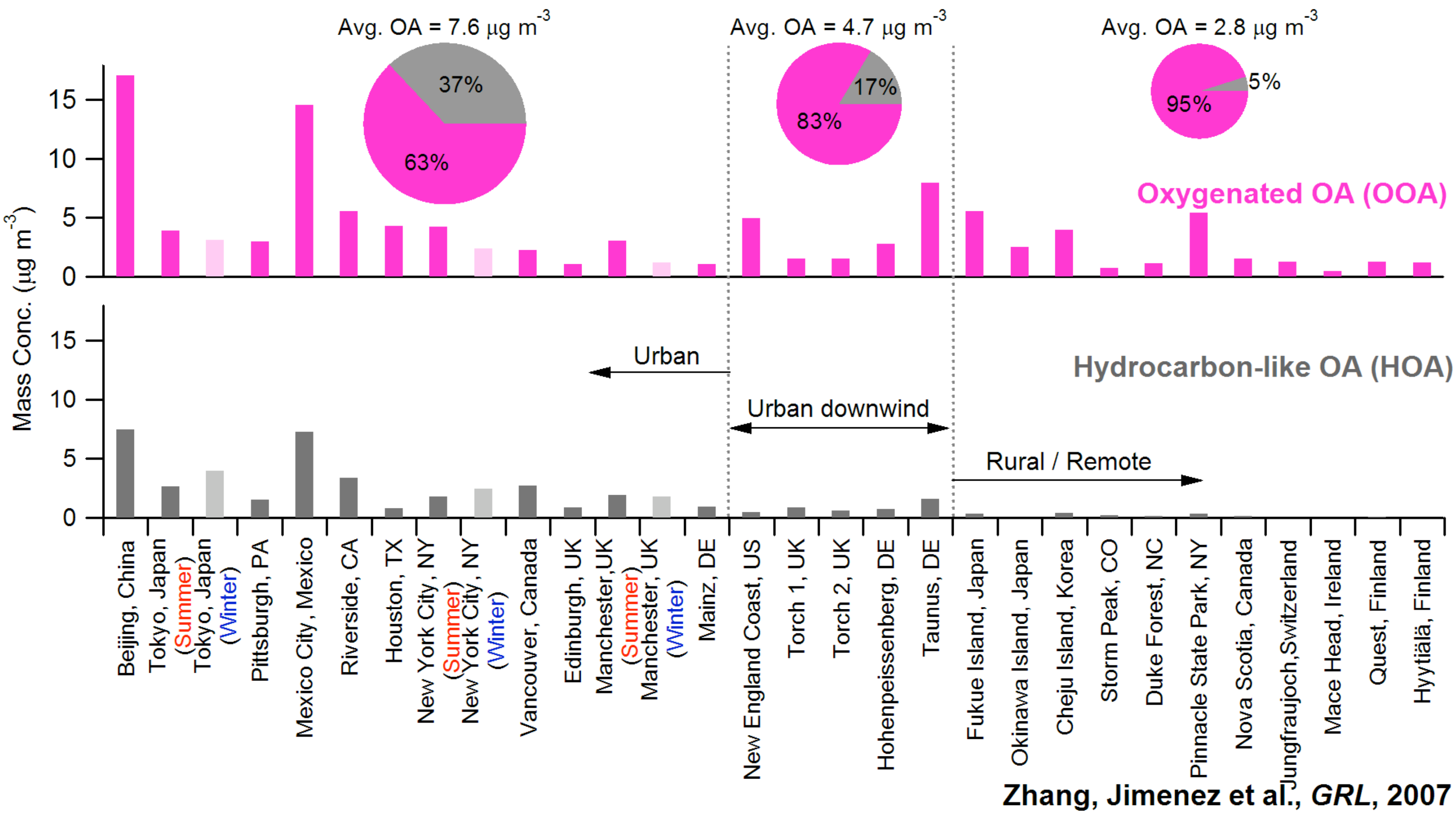
- Limonene can be characterized by an 'aging operator'.
- Can we formalize this?

Aerosol Mass Spectrometer Data



- Ambient organic aerosol *in AMS* resolve into factors (these from Pittsburgh). (From many thousands of compounds!!!)
  - HOA looks like diesel and has little oxygen.
  - OOA looks highly oxidized. [Qi Zhang *et al. ACP* 2005]
  - More factors give OOA1 (O:C∼1), OOA2 (O:C∼ 0.5), BBOA, ...

AMS OOA

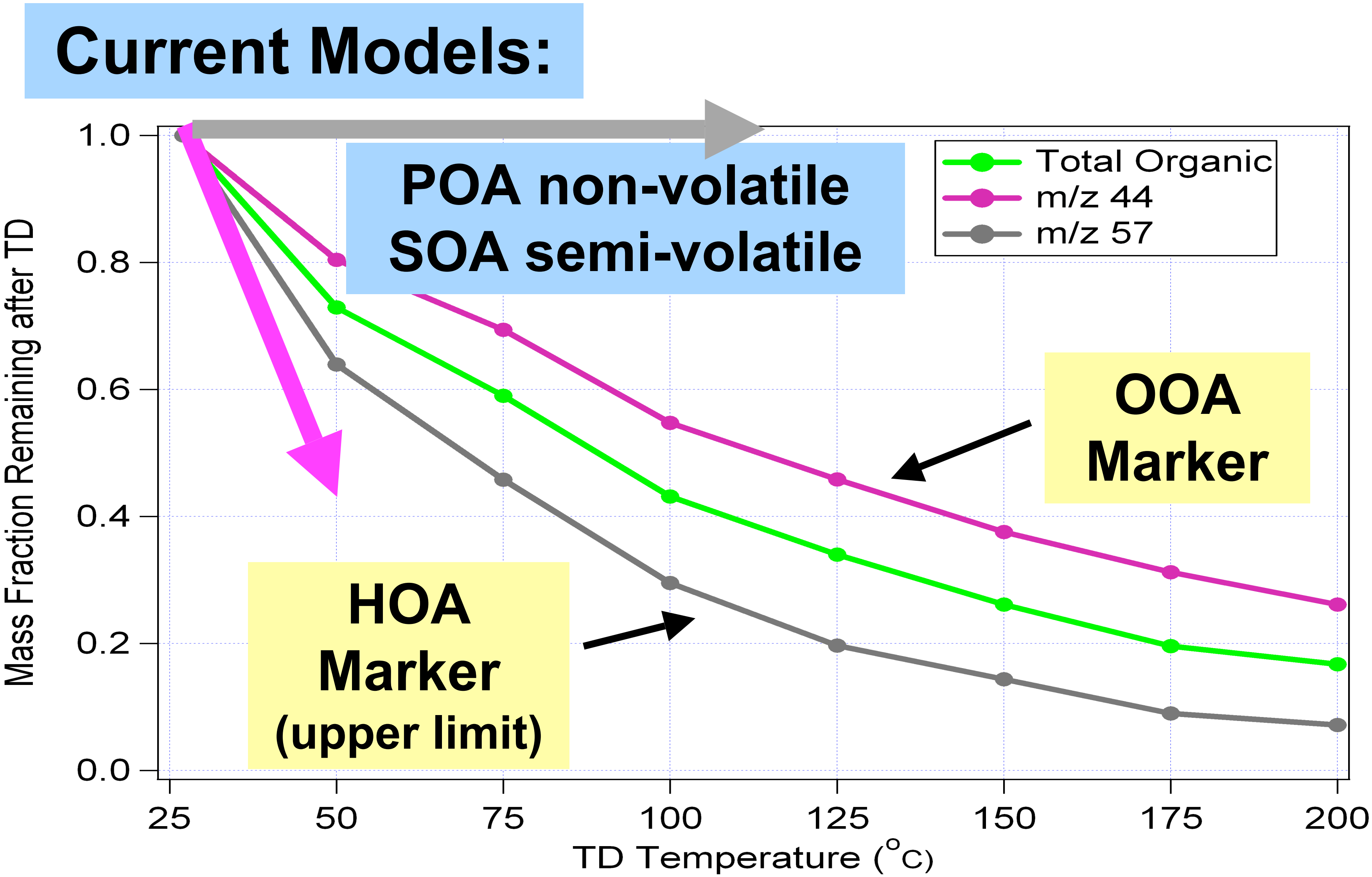


- Cities mixed, more than 50% OA
- Remote sites almost all OOA

[Qi Zhang *et al. GRL* 2007]

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

OA Volatility in the Atmosphere

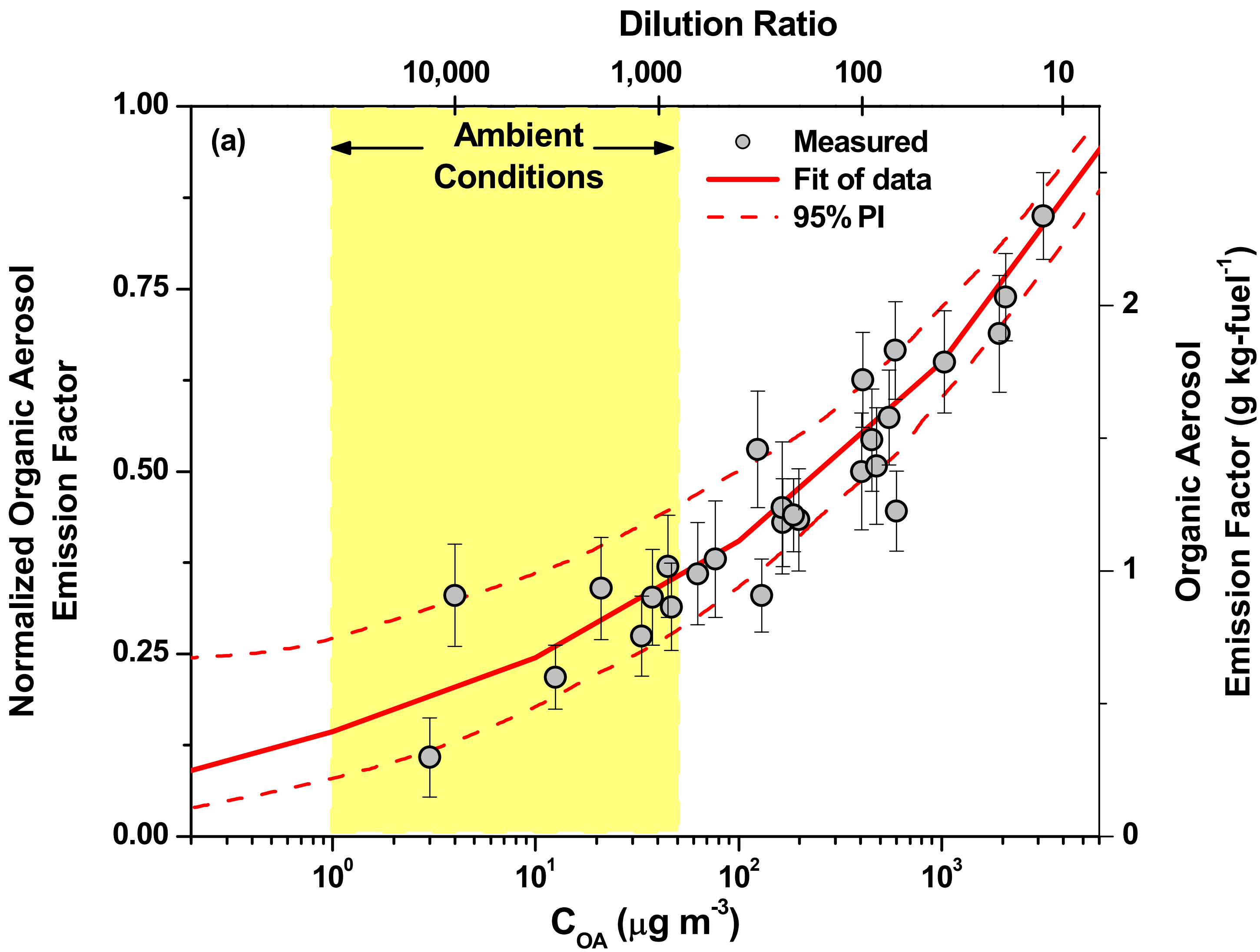


More 'bad' news...

[Huffmann, Jimenez *et al. ES&T*, submitted]

- Ambient (Mexico City) OOA is **LESS** volatile than HOA!!
- THIS COMPLETELY REVERSES THE CURRENT PARADIGM!!!!

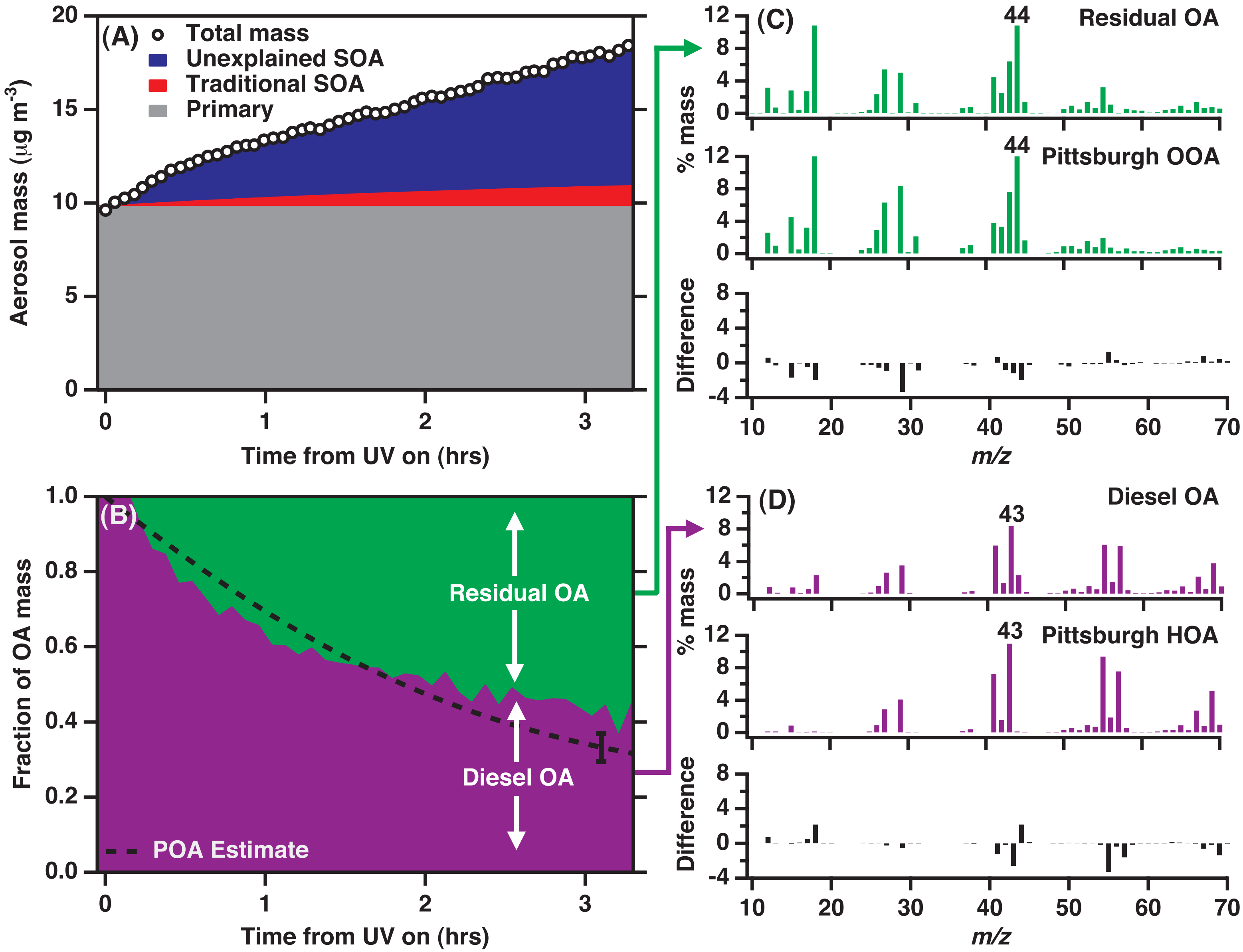
Dilution of Primary Emissions



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

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

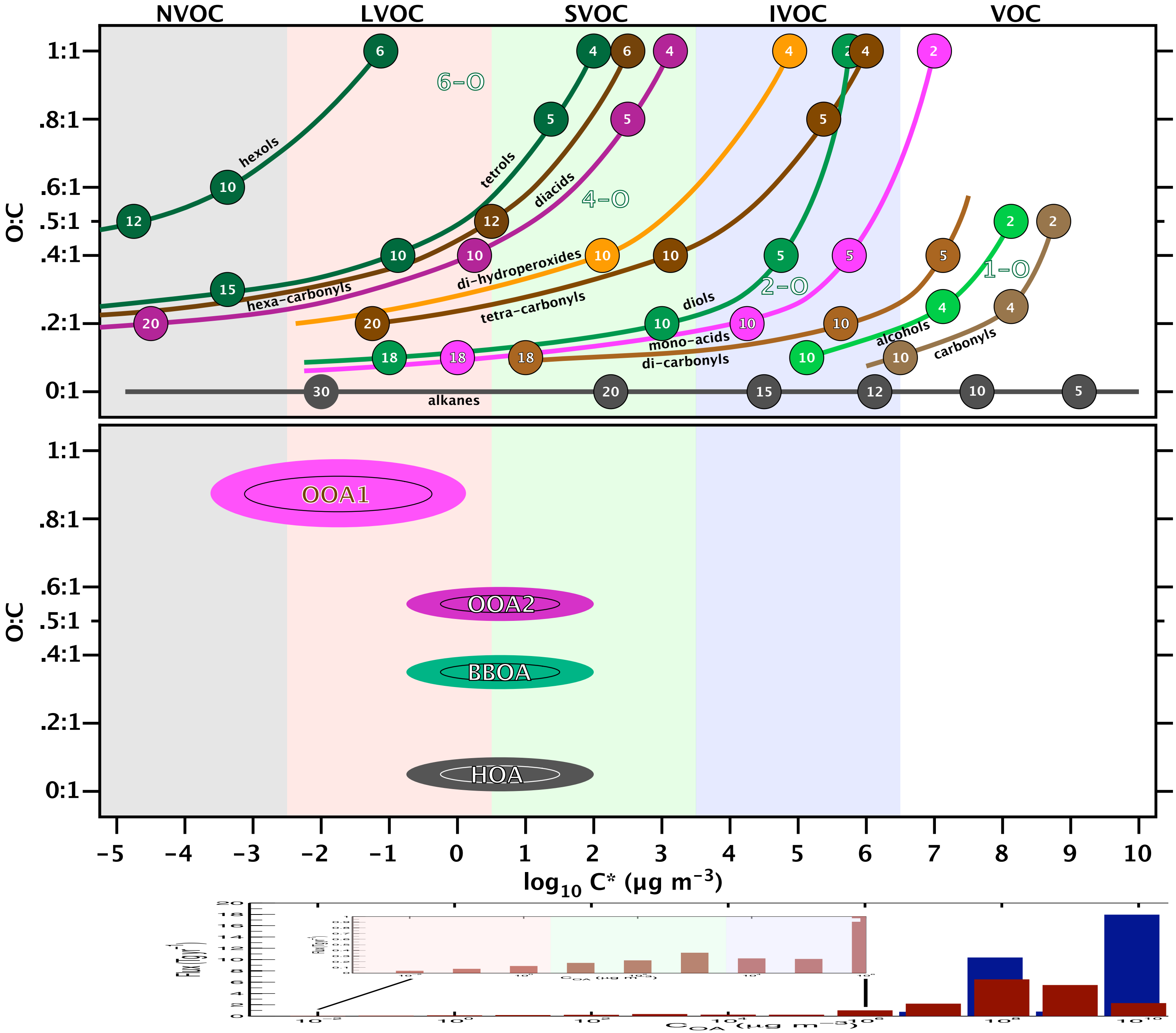
Photooxidation of Diesel Emissions



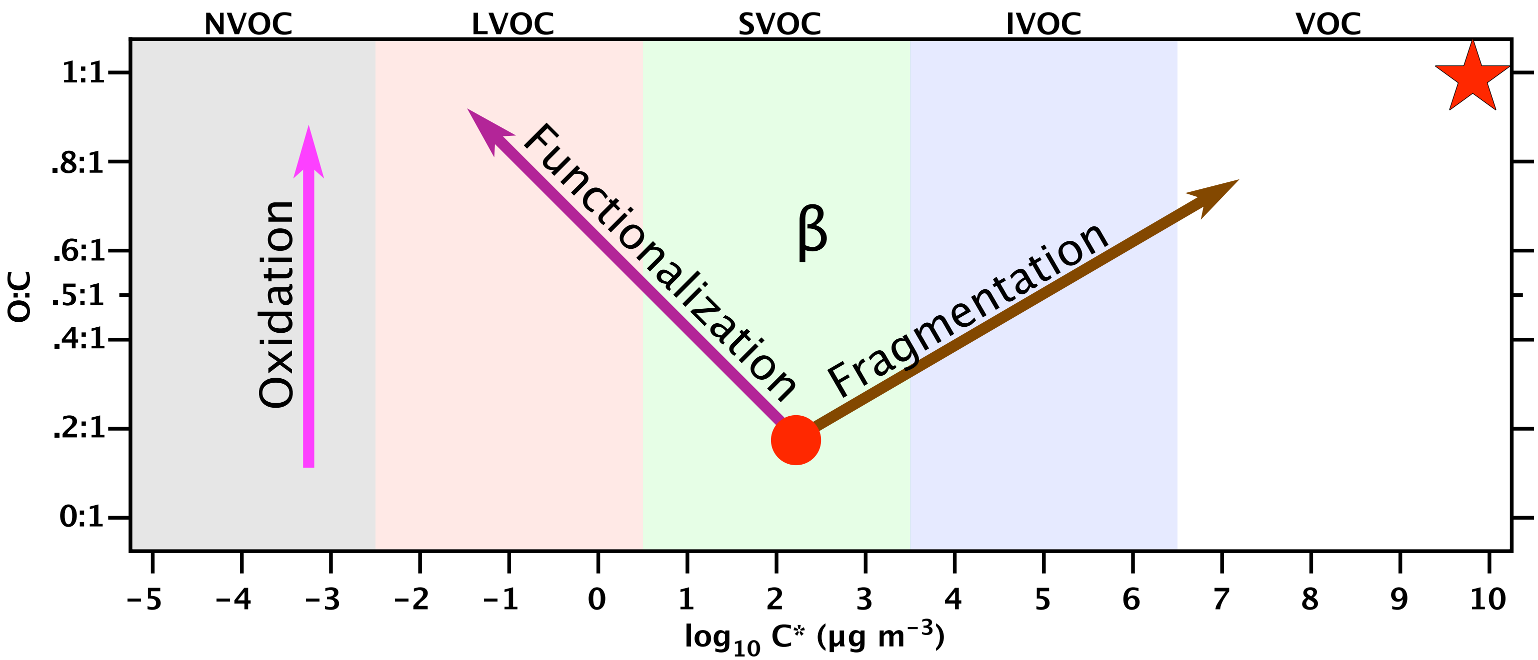
- Oxidized diesel fraction looks a lot like OOA.

Robinson *et al., Science* [2007]; Sage *et al., ACP* [2008]

A 2-Dimensional VBS: Add Oxygen:Carbon

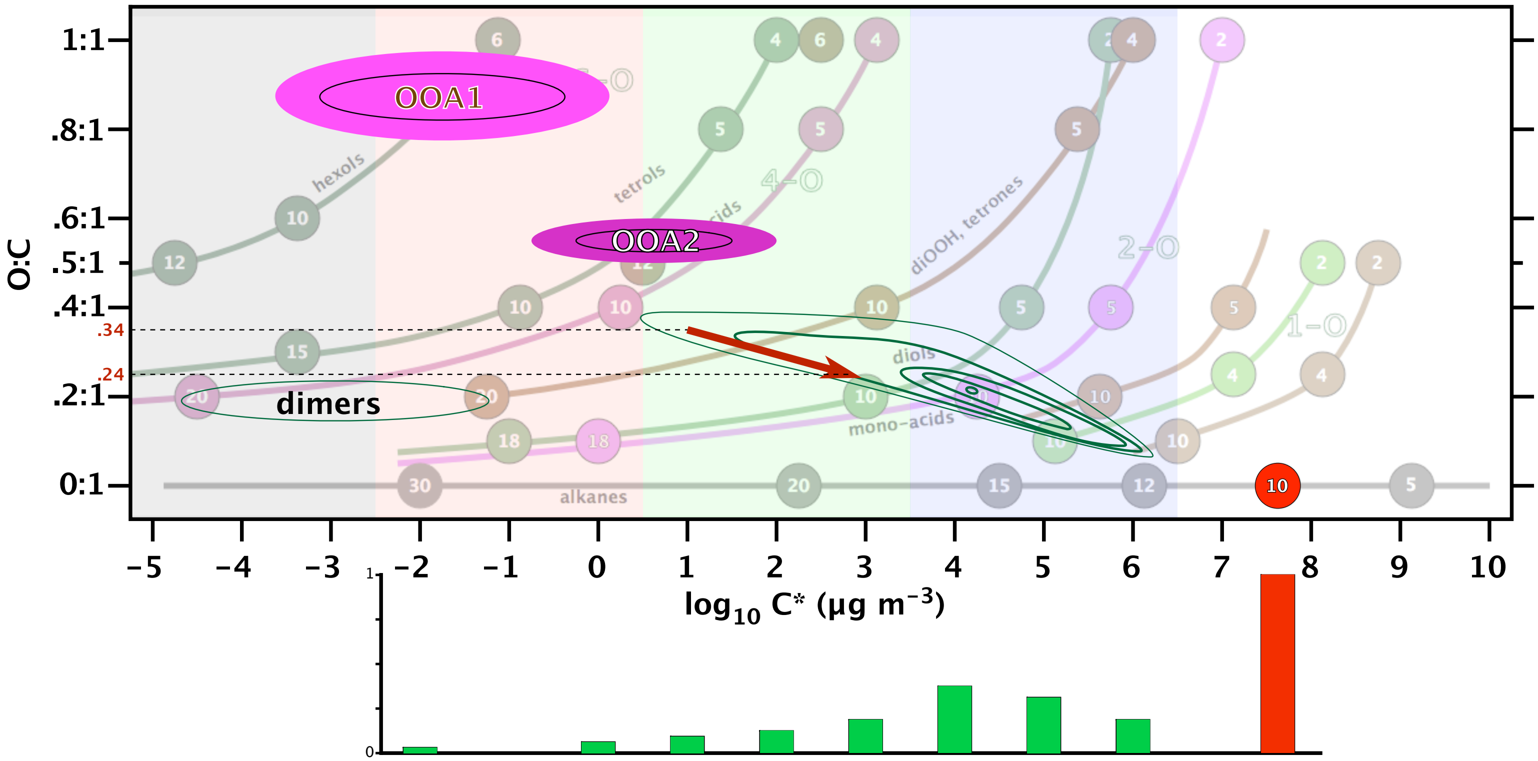


Fundamental Oxidation Processes



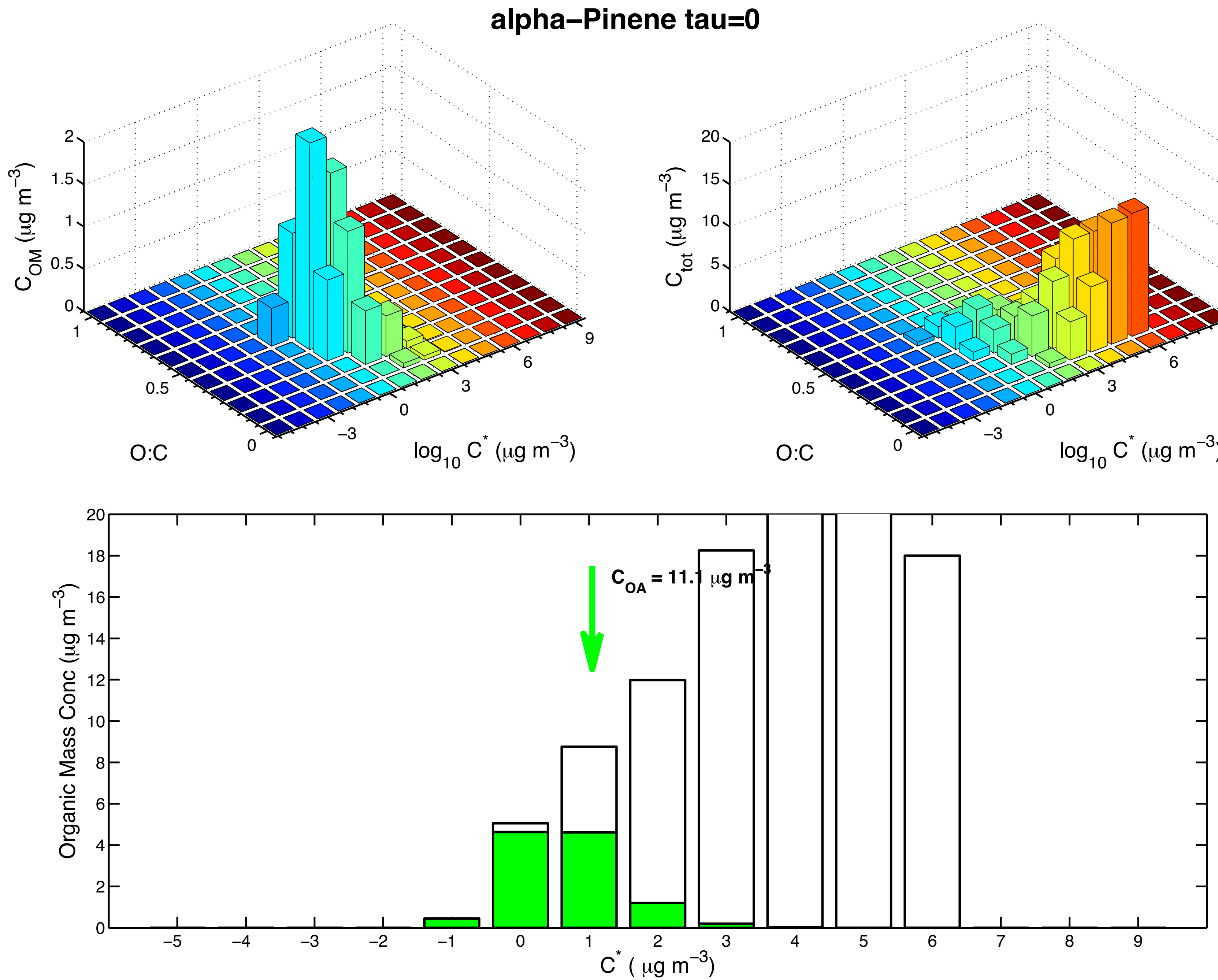
- Competition between functionalization and fragmentation (branching ratio = β).
- Given time, fragmentation will win (CO_2 formation).
- **Assume $\beta \propto$ O:C^n; $\quad n = 0.5$.**

α-pinene SOA

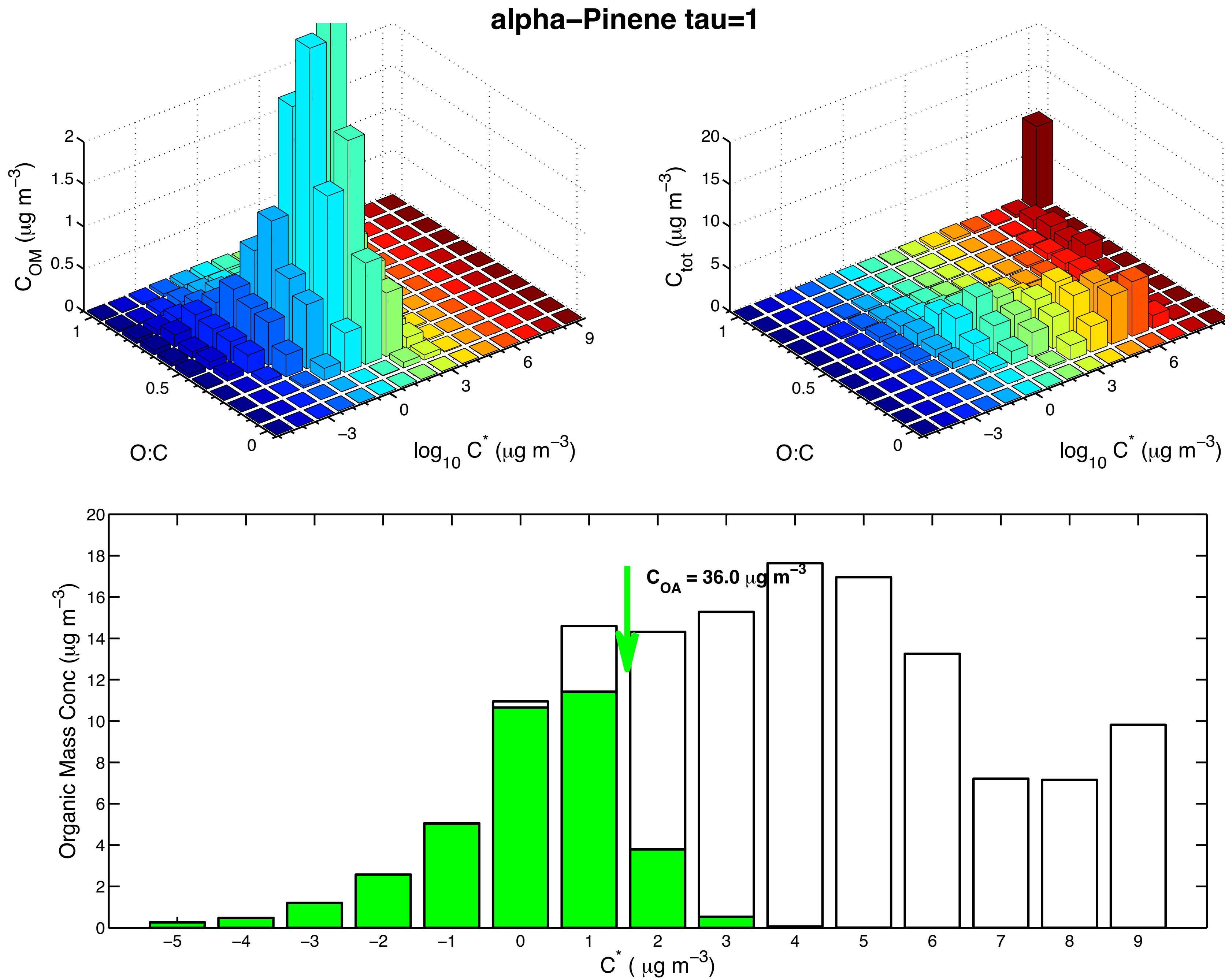


- α-pinene SOA in chambers heading *toward* OOA, but it is not there yet.

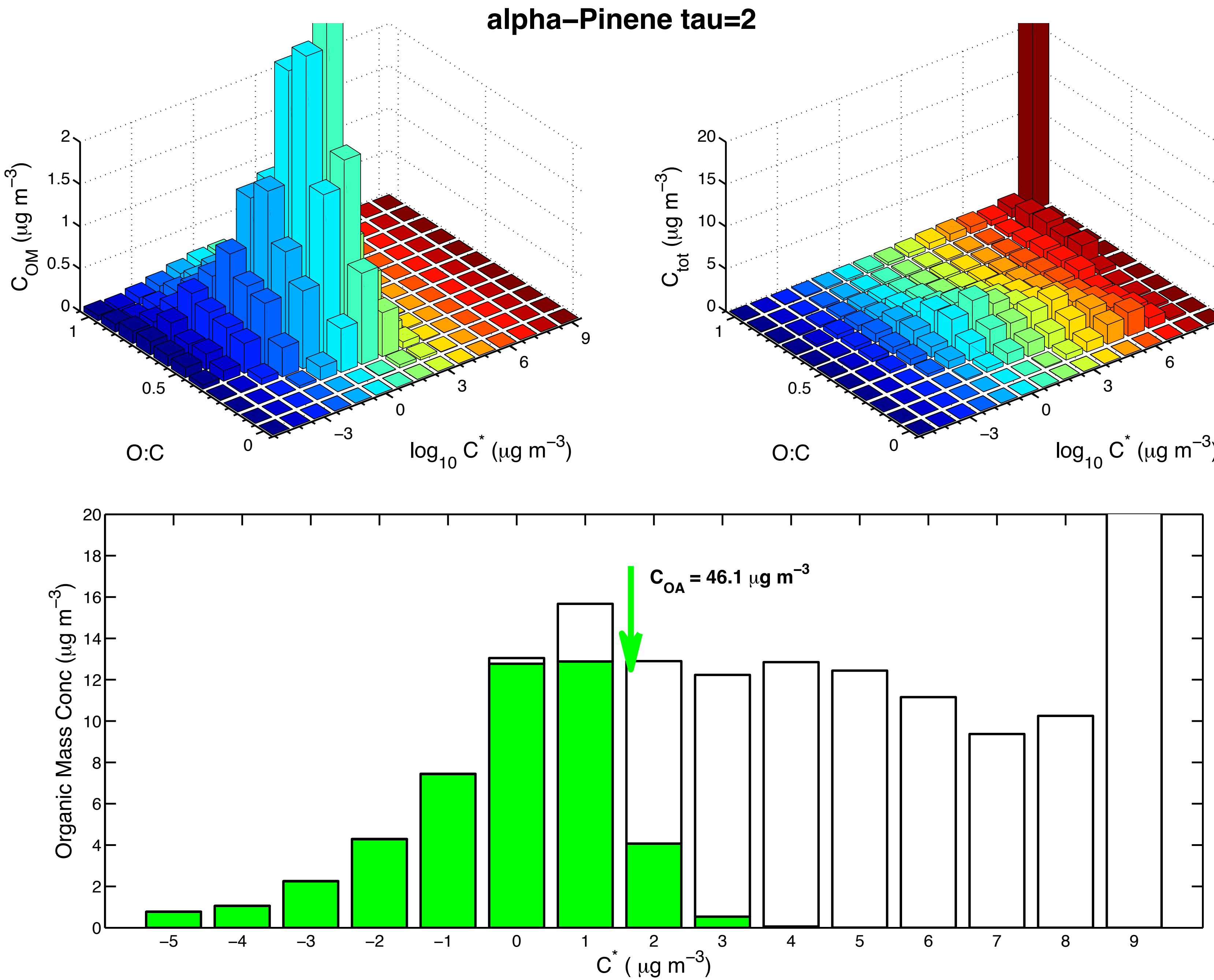
α-pinene SOA Aging



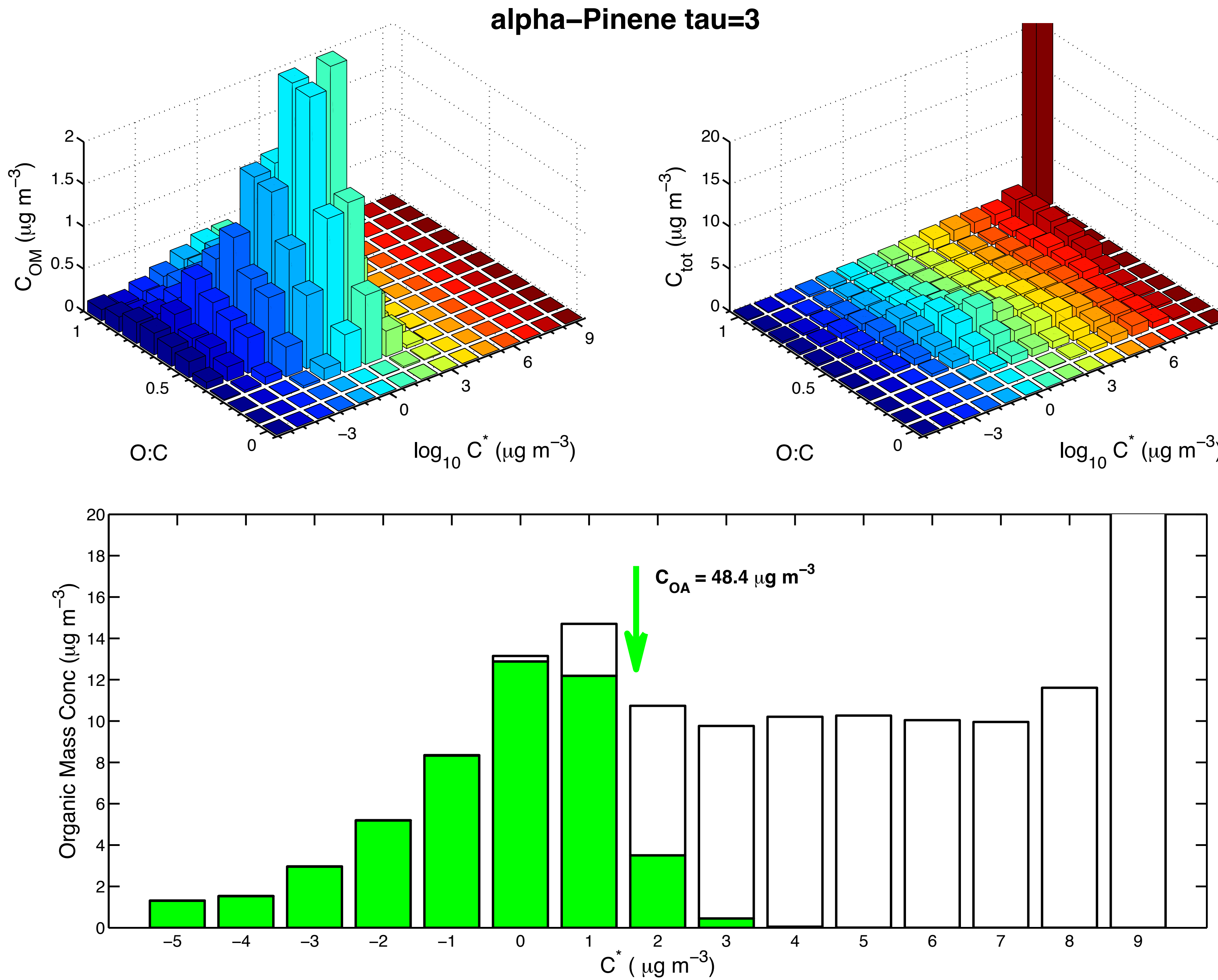
α-pinene SOA Aging



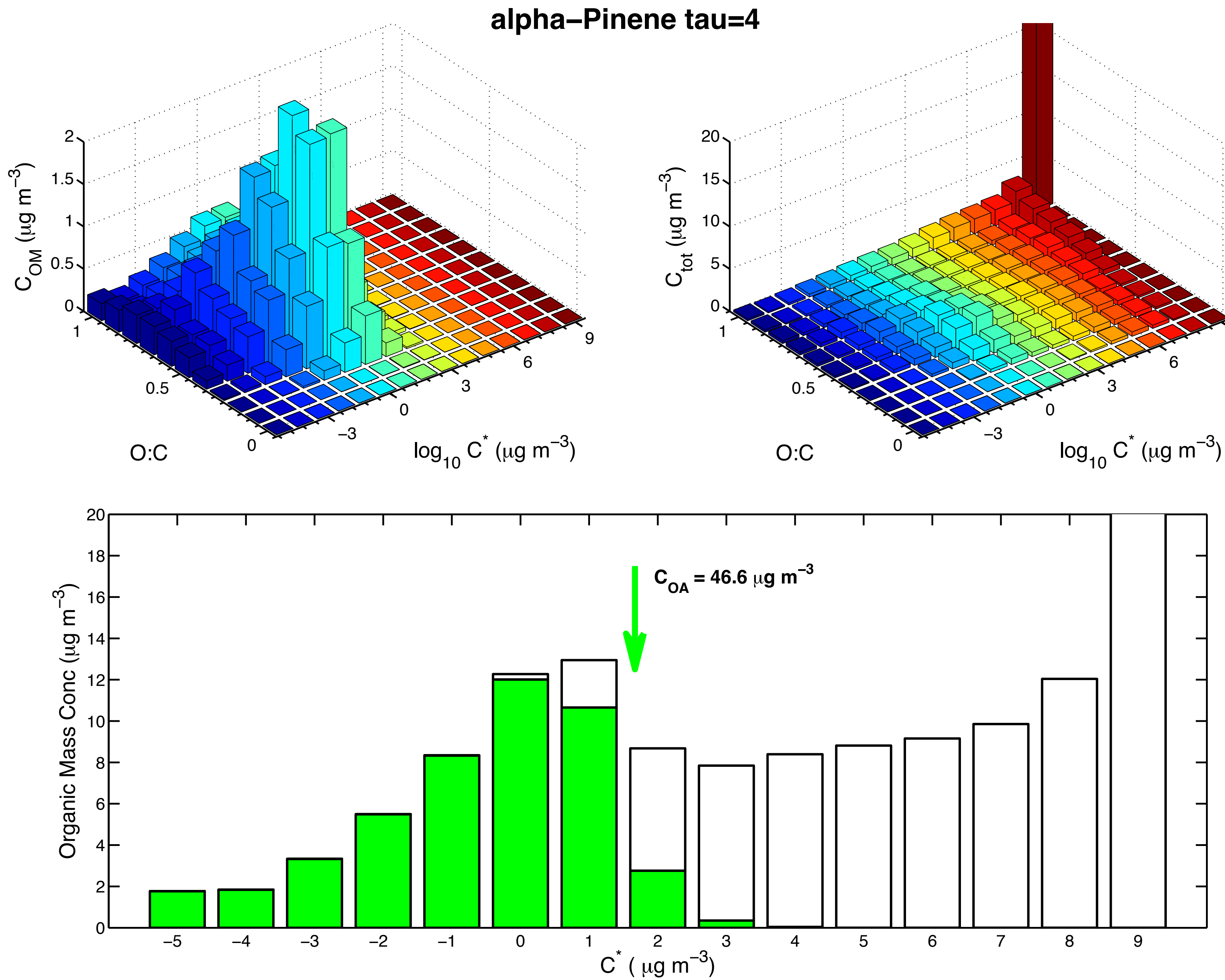
α-pinene SOA Aging



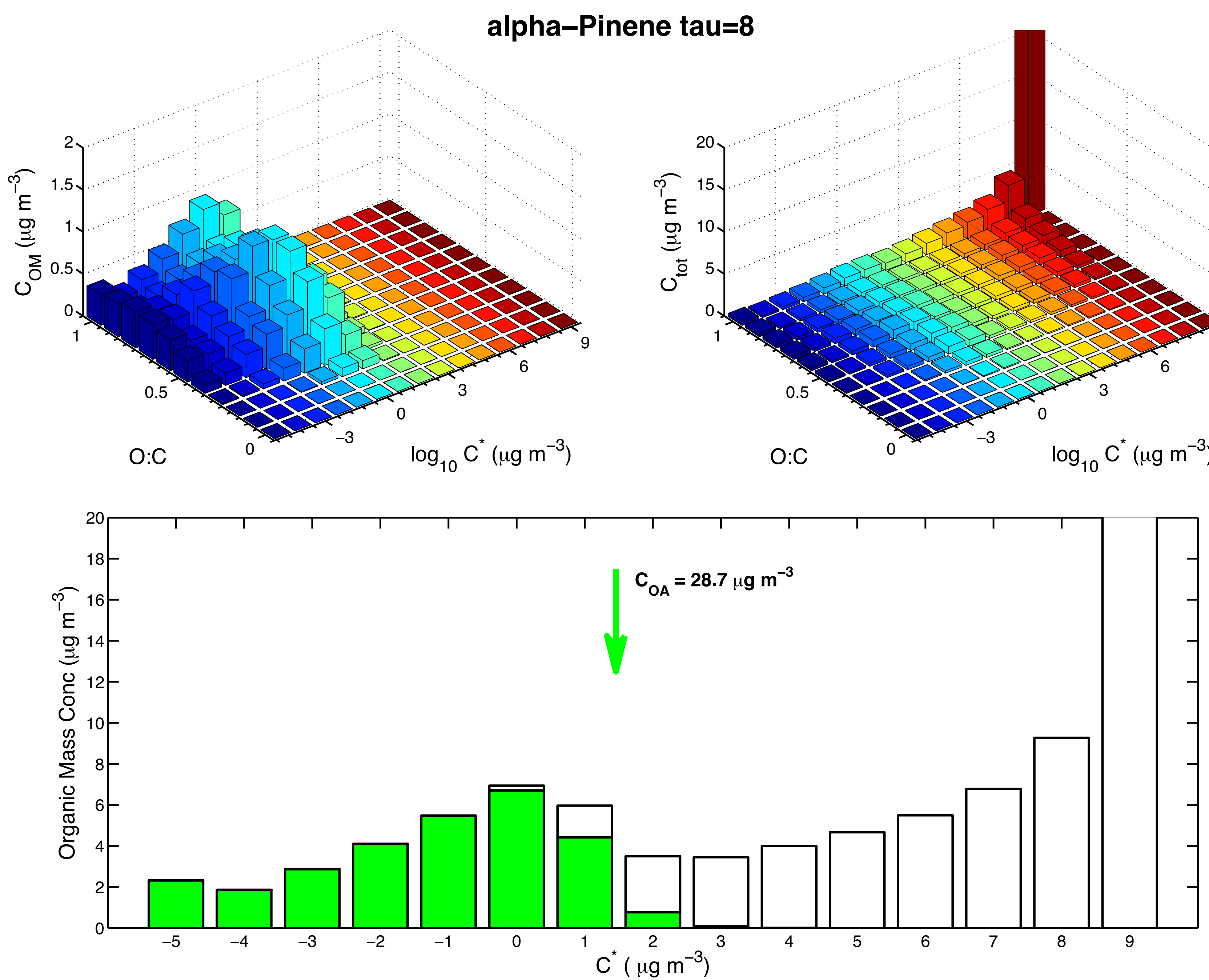
α-pinene SOA Aging



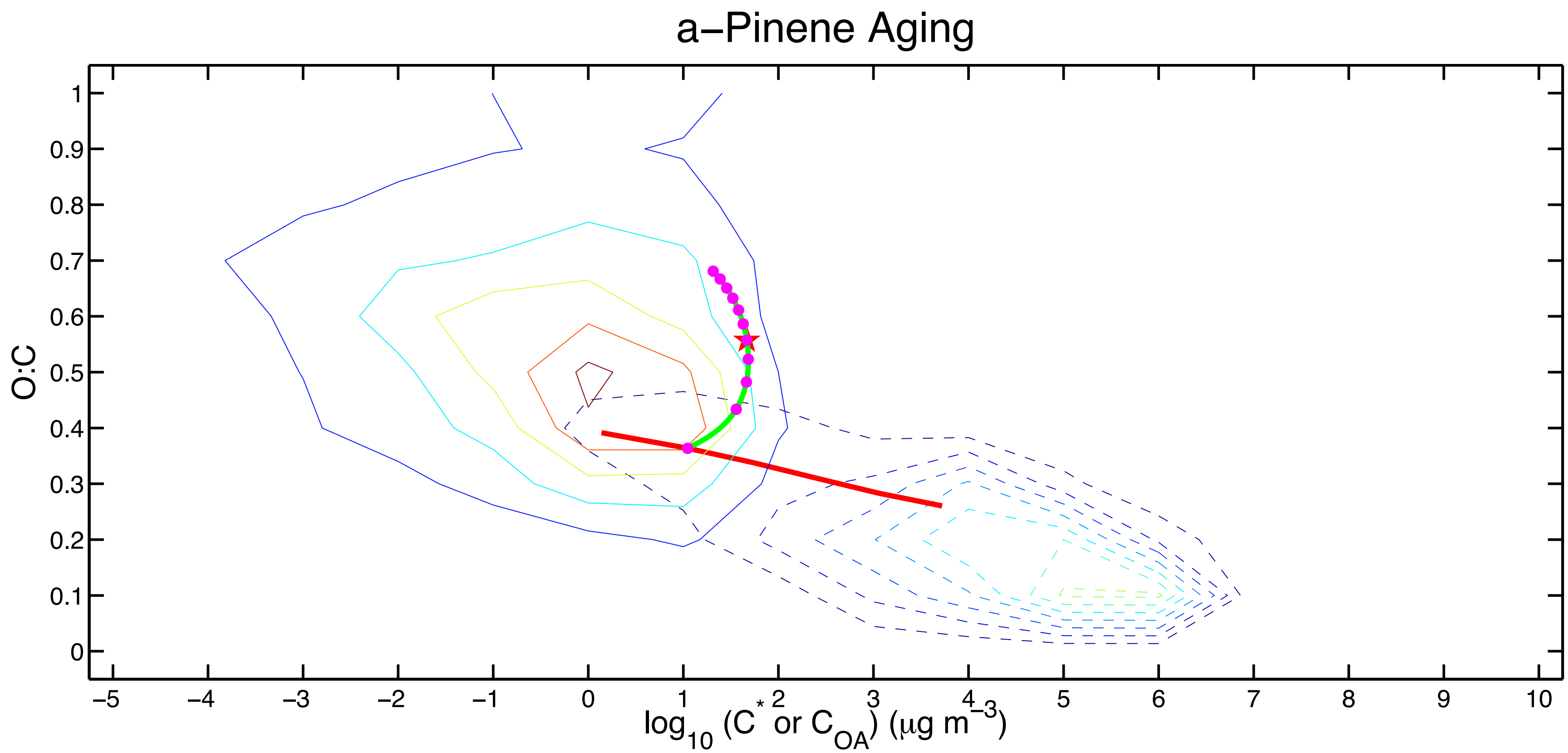
α-pinene SOA Aging



α-pinene SOA Aging

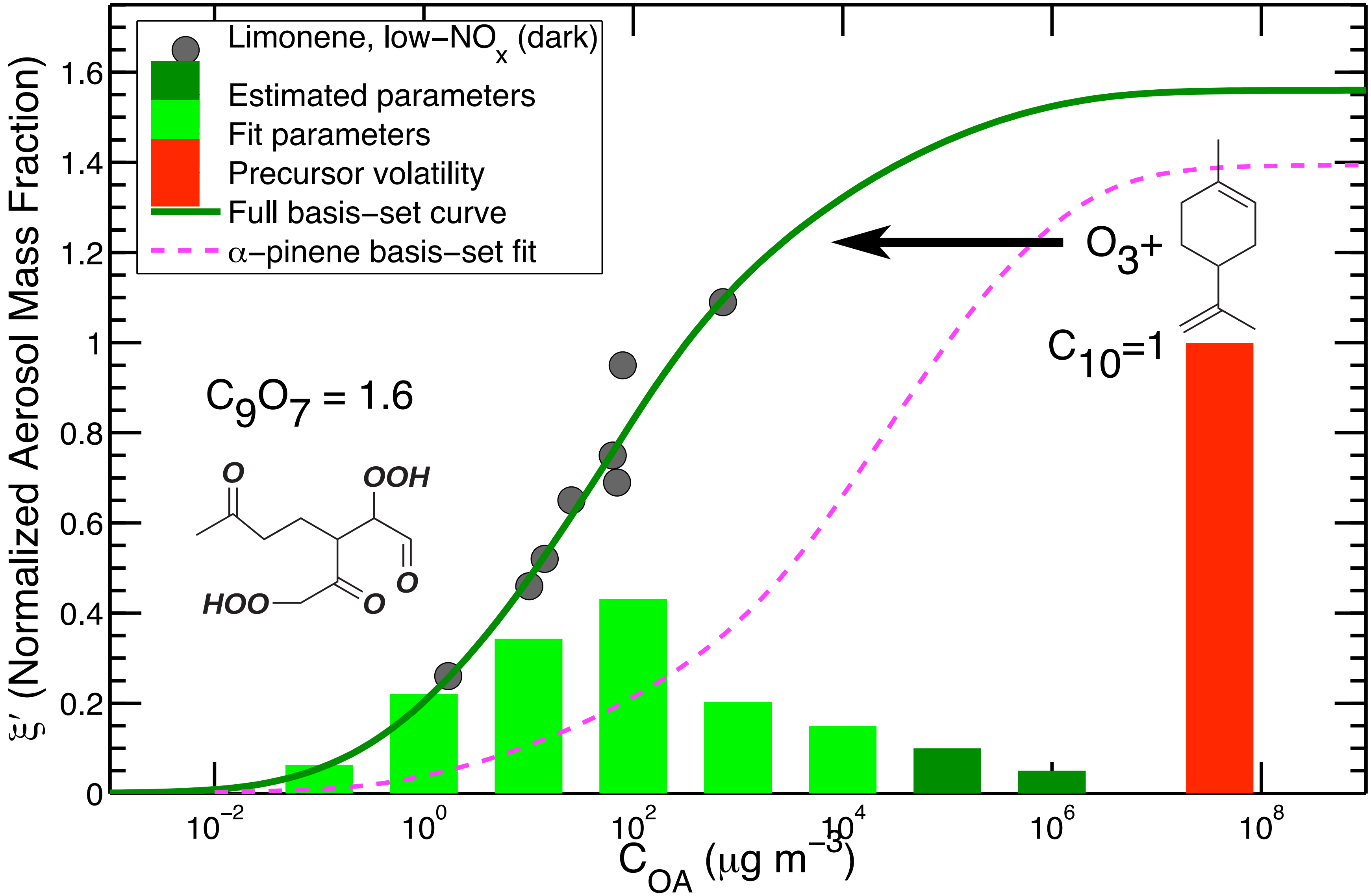


α-pinene SOA Aging



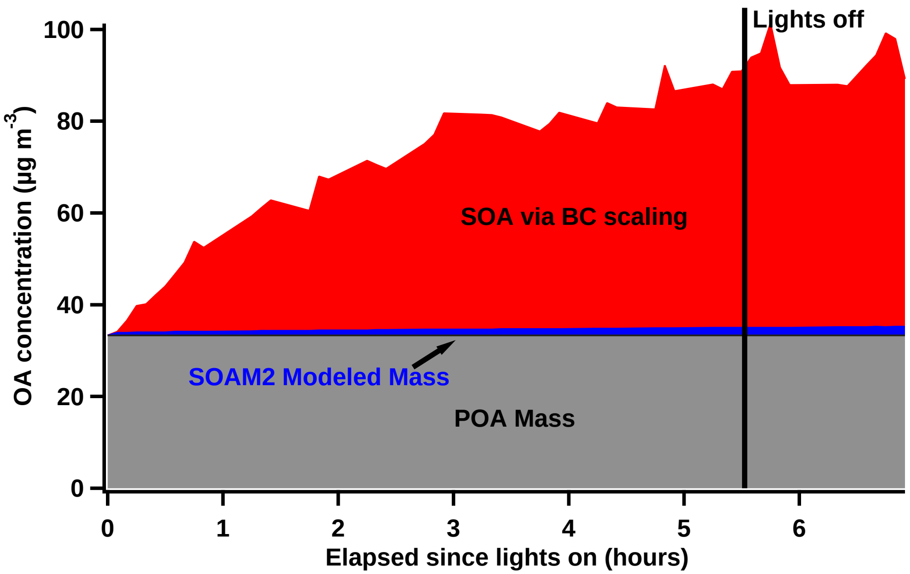
- 1-4 Generations of aging makes OA that looks a lot like OOA2!

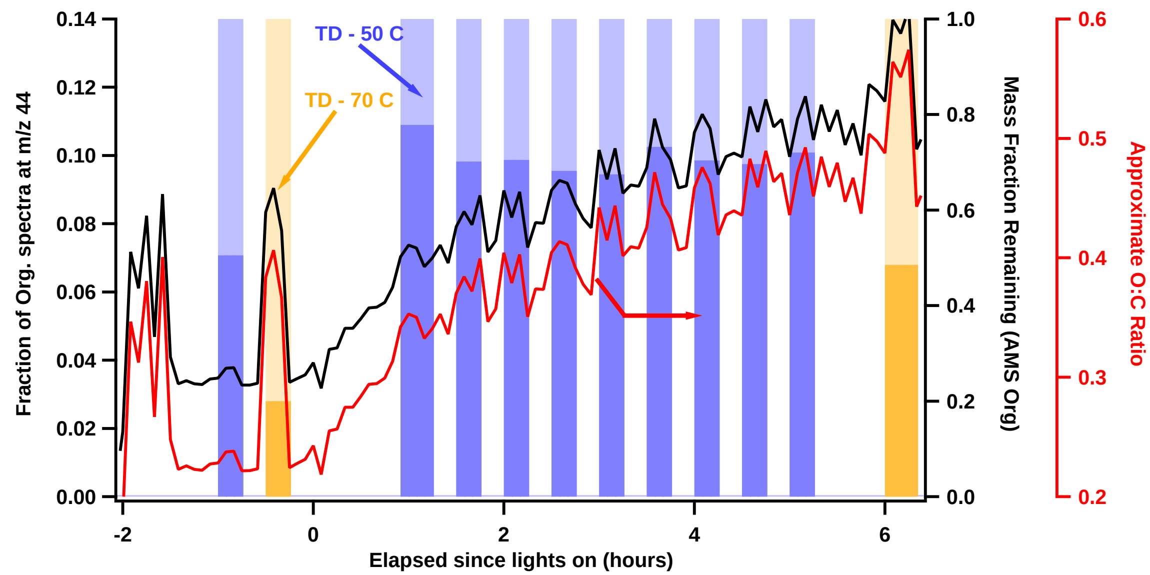
Limonene + Ozone Mass Balance



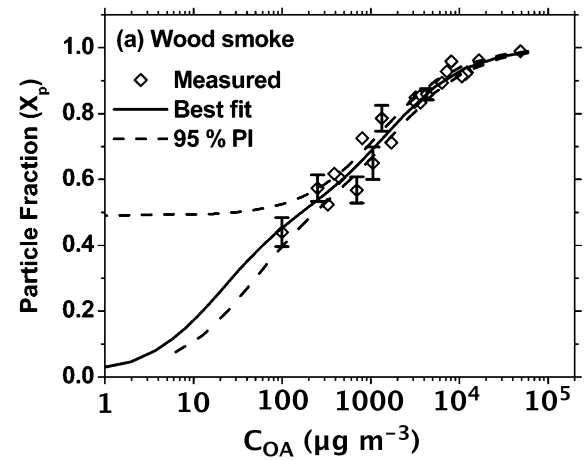
- Makes much more SOA than α-pinene because 2nd double bond is 'aged'

Biomass Burning SOA and Thermo Denuder



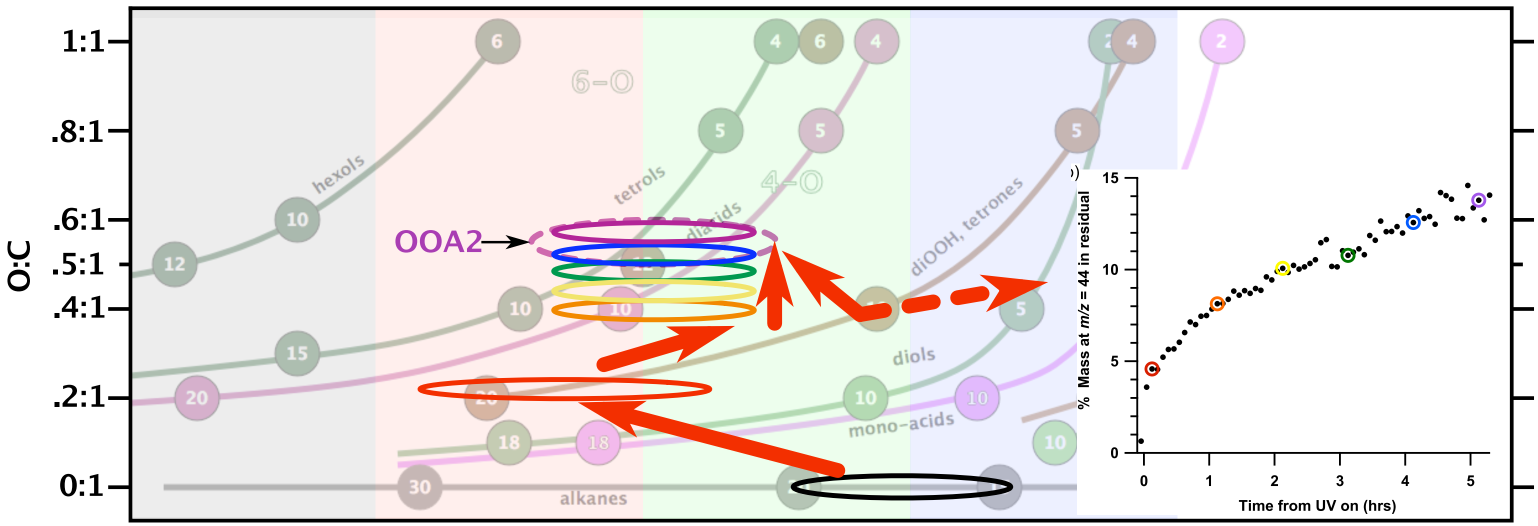


- Dilute smoldering yellow pine POA to ambient levels ($\sim 40\, \mu$g m^{-3}, 1:10 EC:OC).
- Hit lights (black lights). NO_x present, photochemistry ensues.
- Monitor with AMS and 15s TD at 50°C (70° C for 2nd and last cycles).
- Sharp OA increase, % m/z = 44 rises sharply. TD volatility drops, 44 correlates.



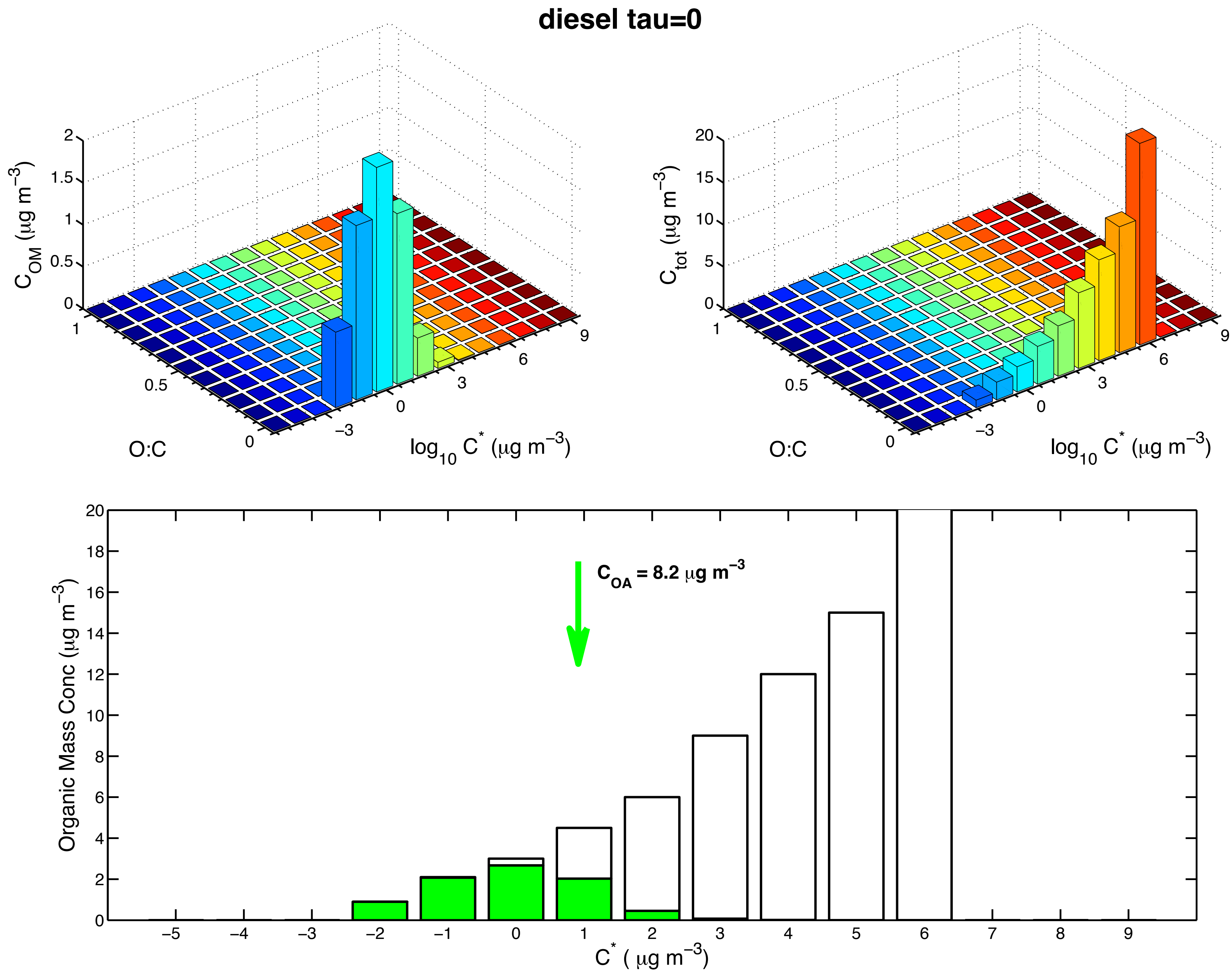
- **Bottom line: BBPOA evaporation and oxidation makes lots of BBSOA.**

Diesel SOA

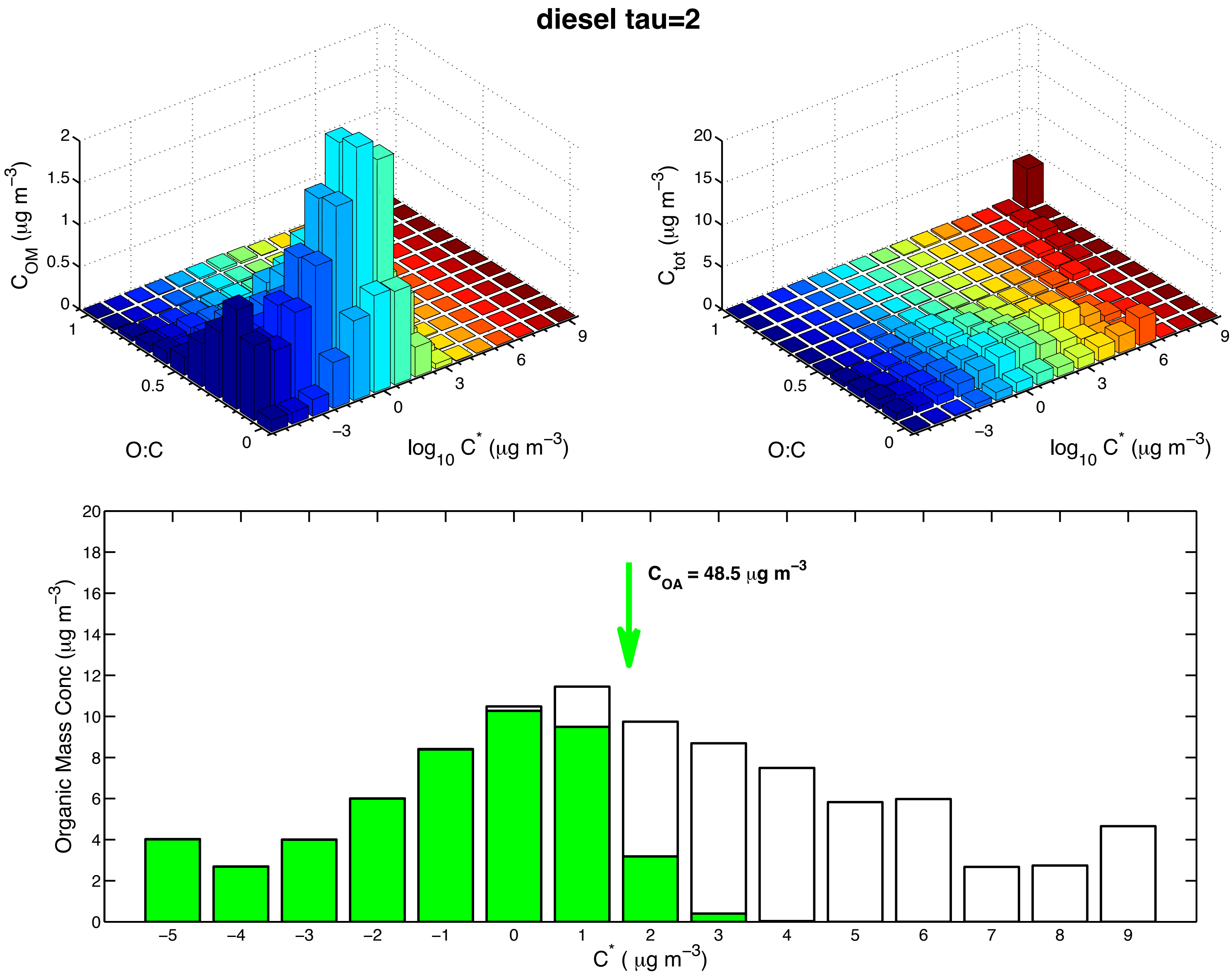


- Diesel aging DOES look like OOA!
- O:C increases progressively with modest (2x) increase in C_{OA}.

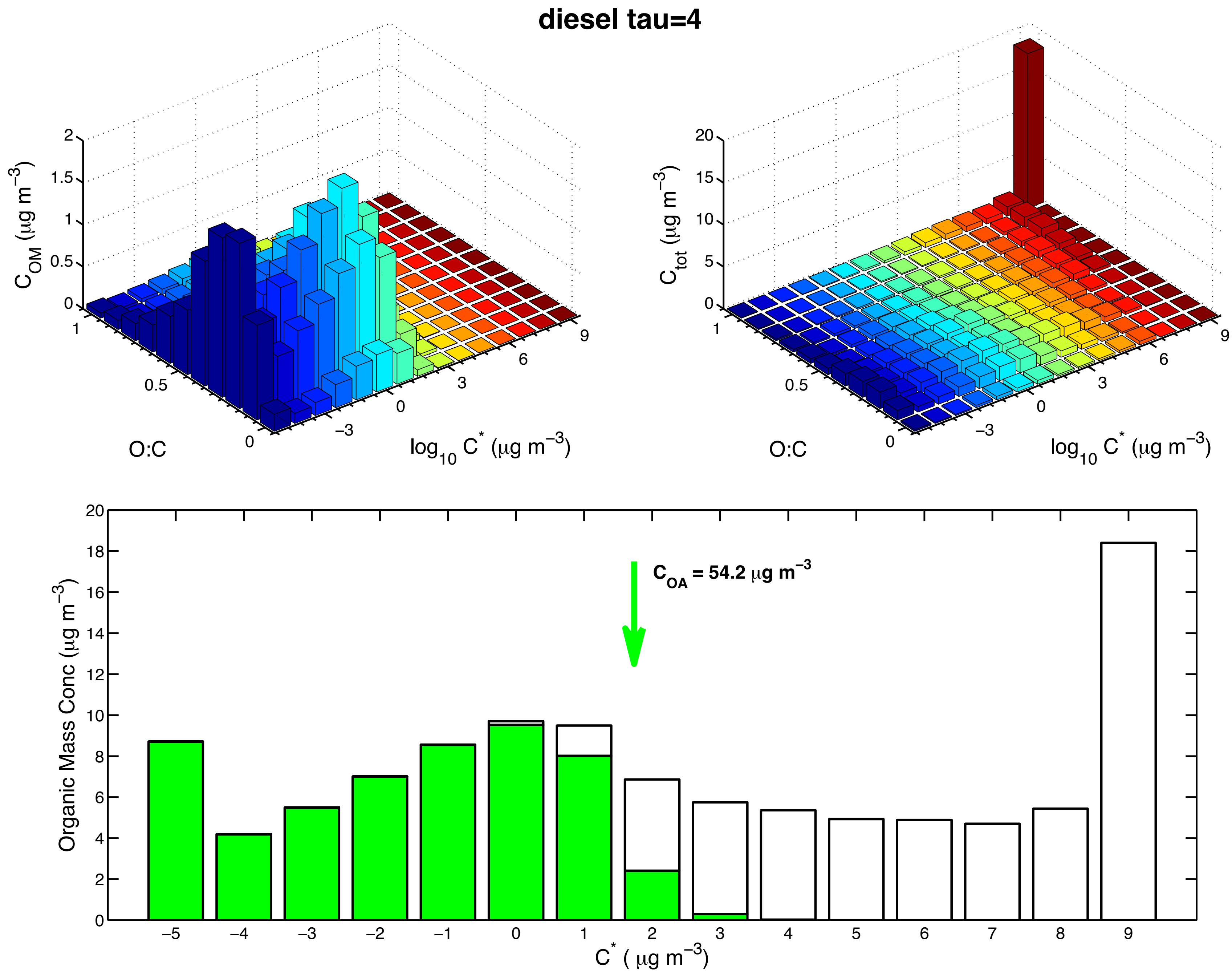
Diesel SOA Aging



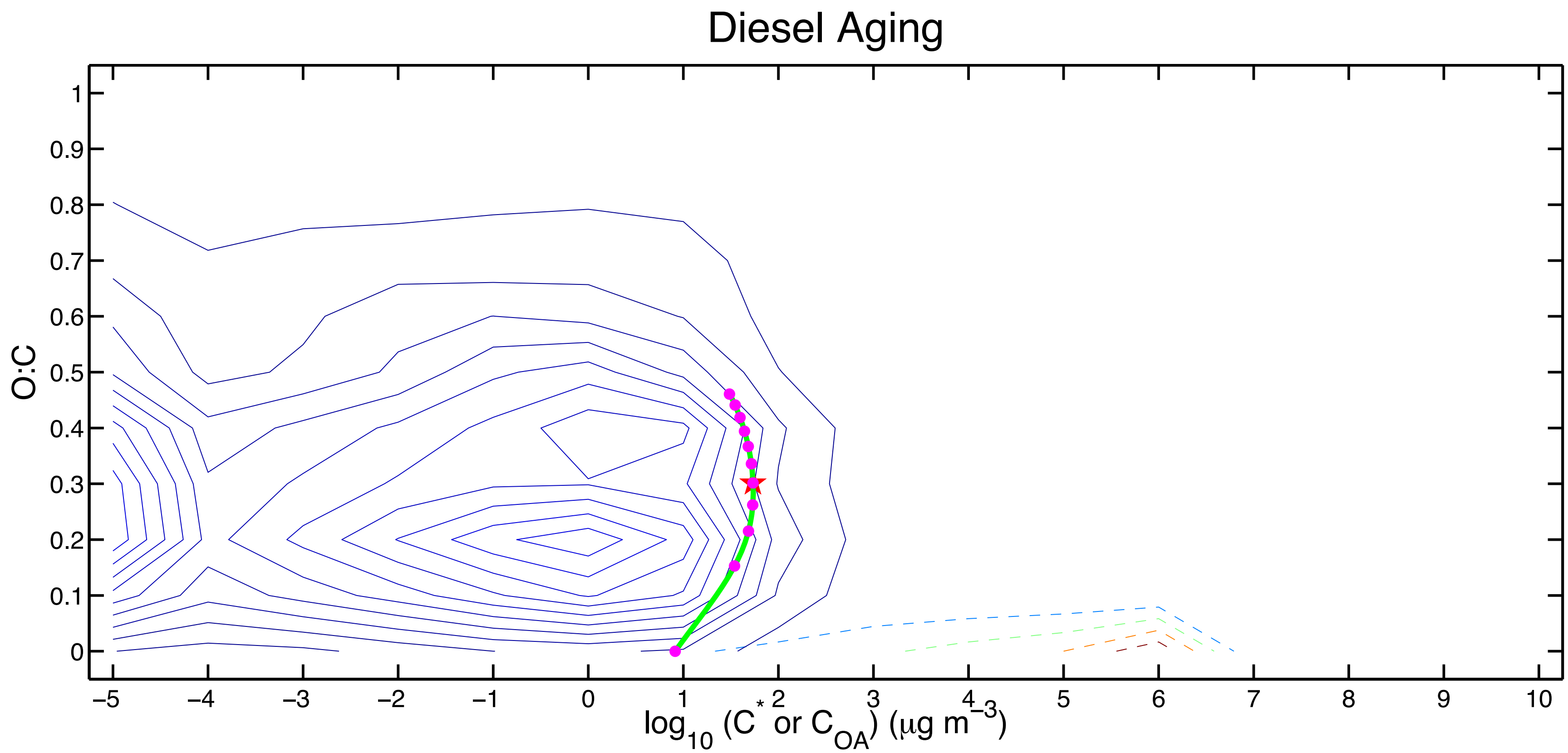
Diesel SOA Aging



Diesel SOA Aging

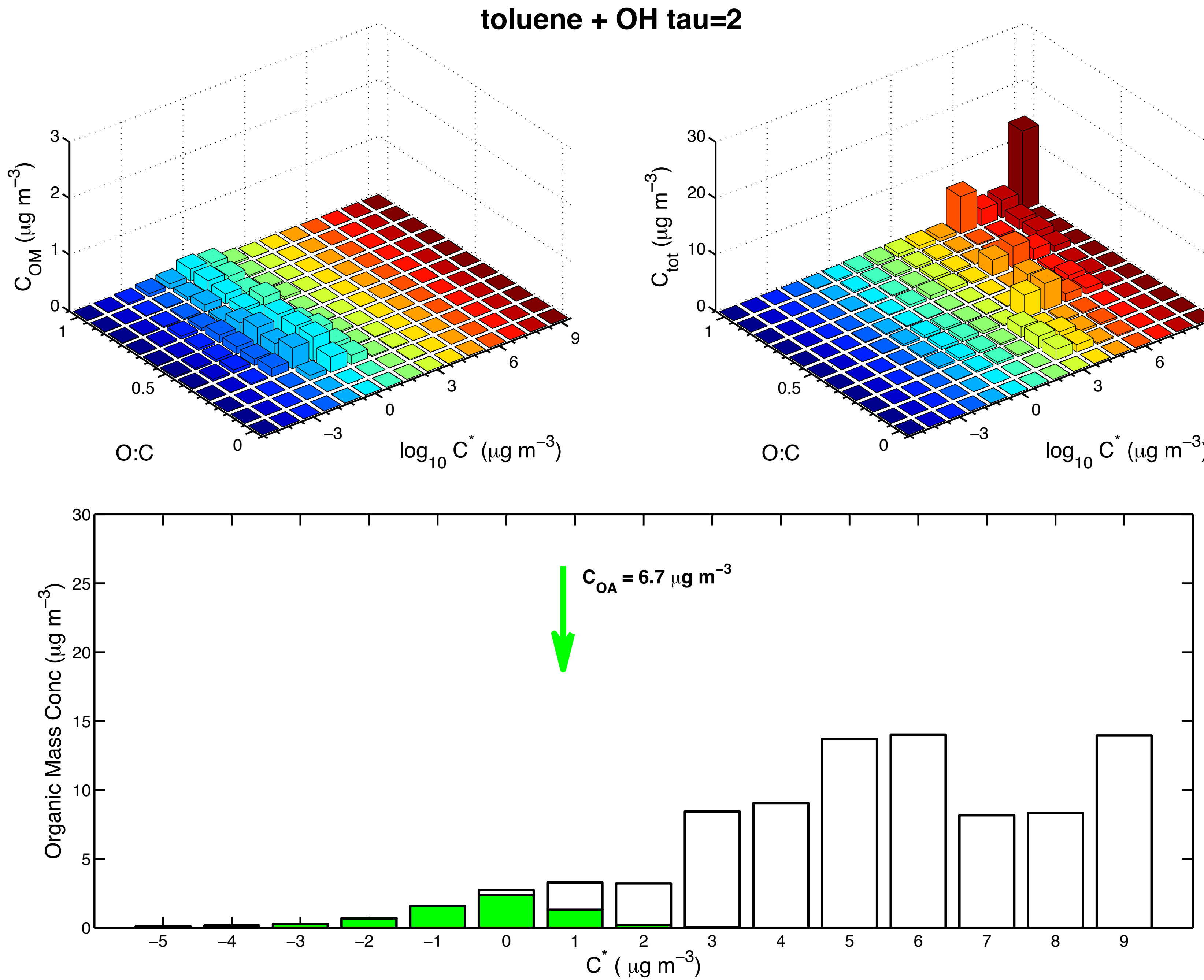


Diesel SOA Aging

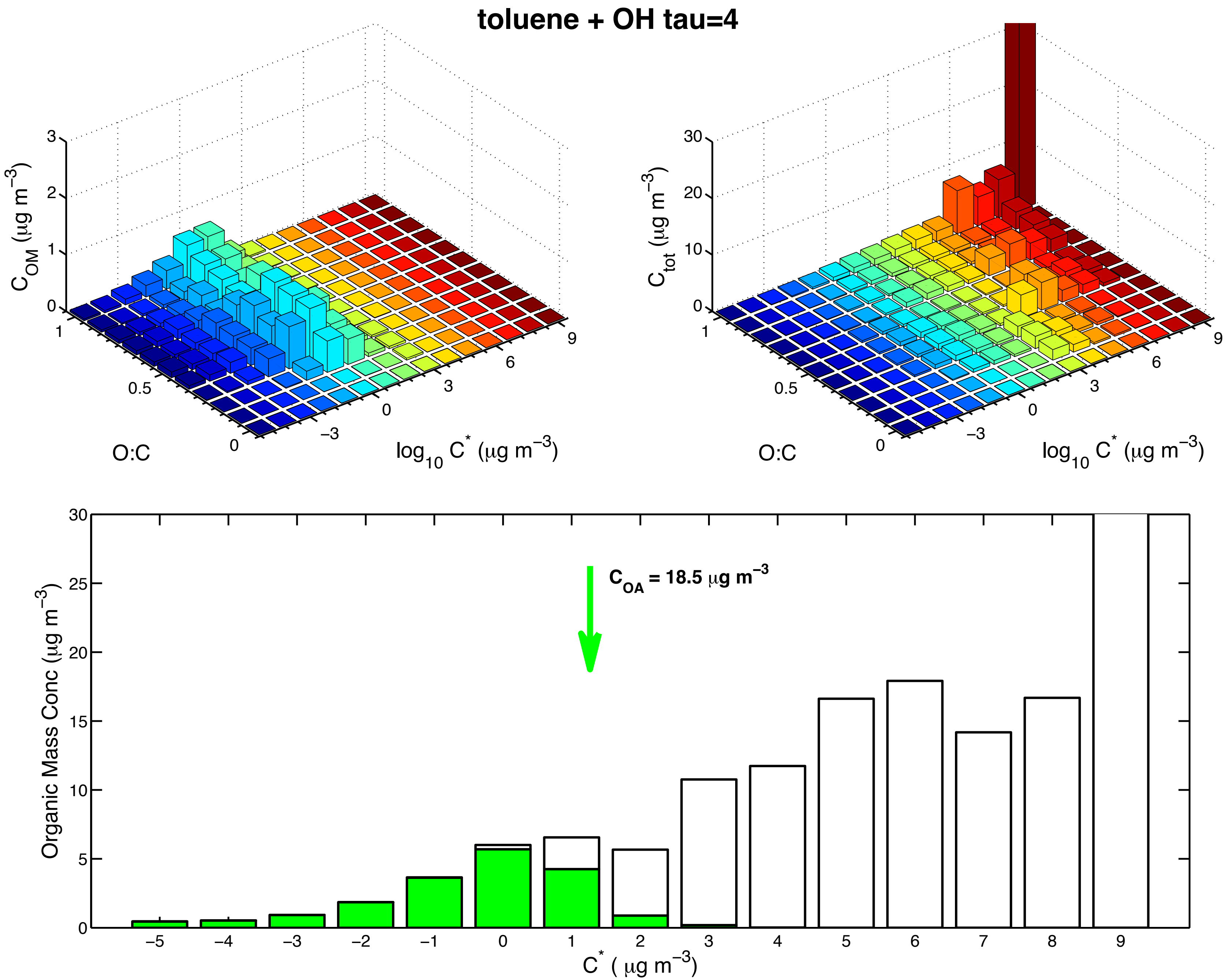


- 10? generations of aging makes OA that looks a lot like OOA2!

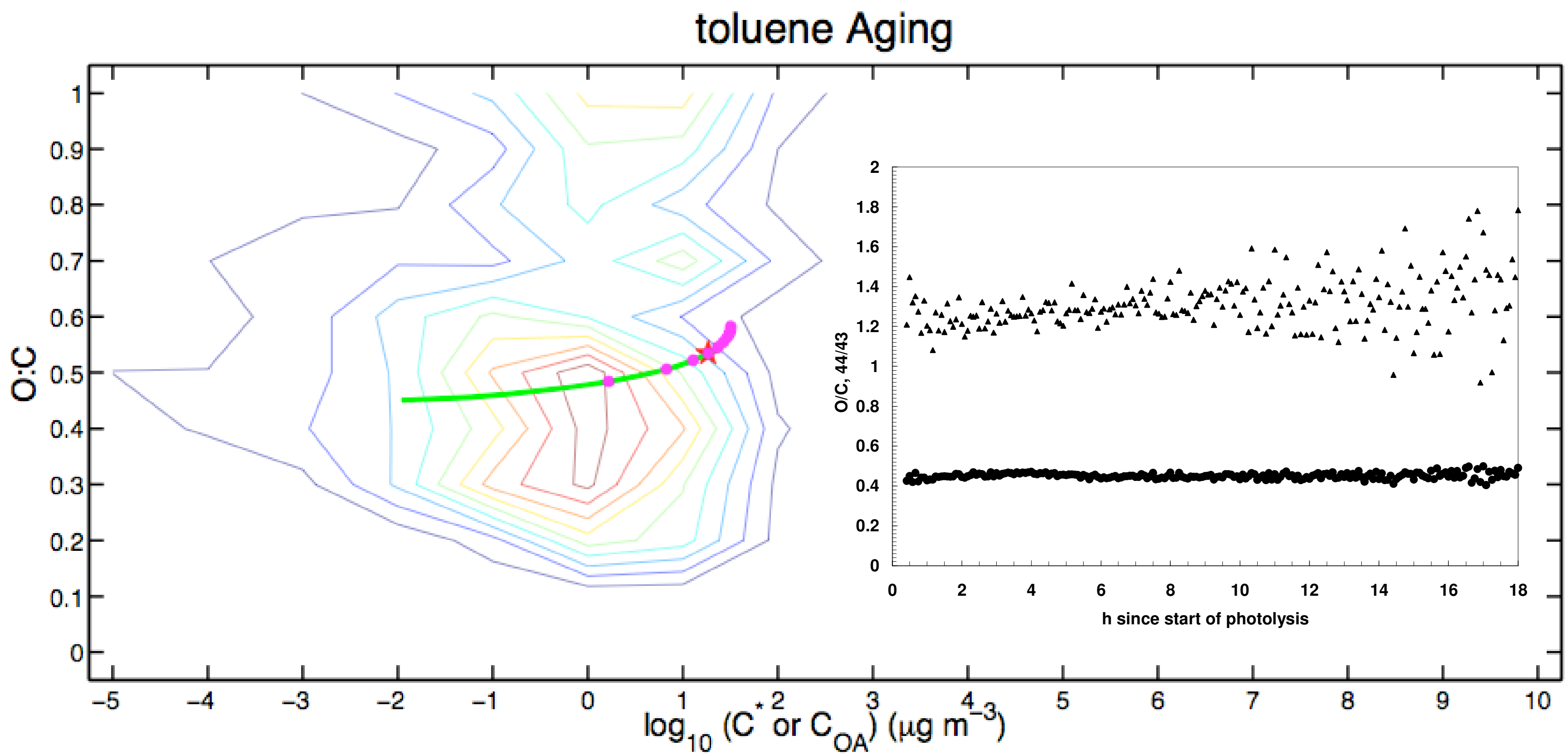
Toluene SOA Aging



Toluene SOA Aging

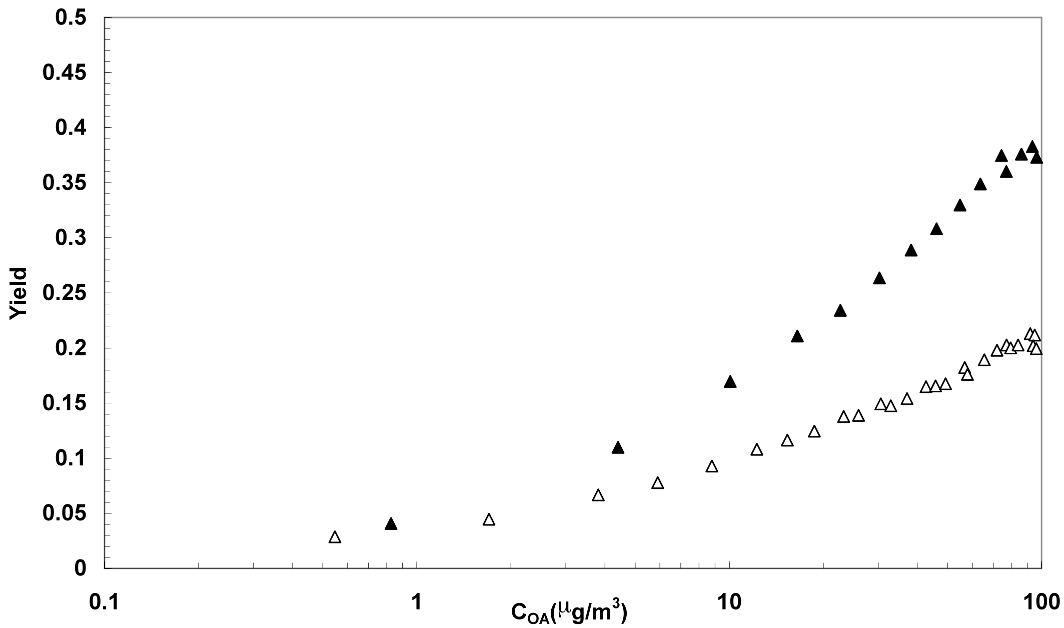


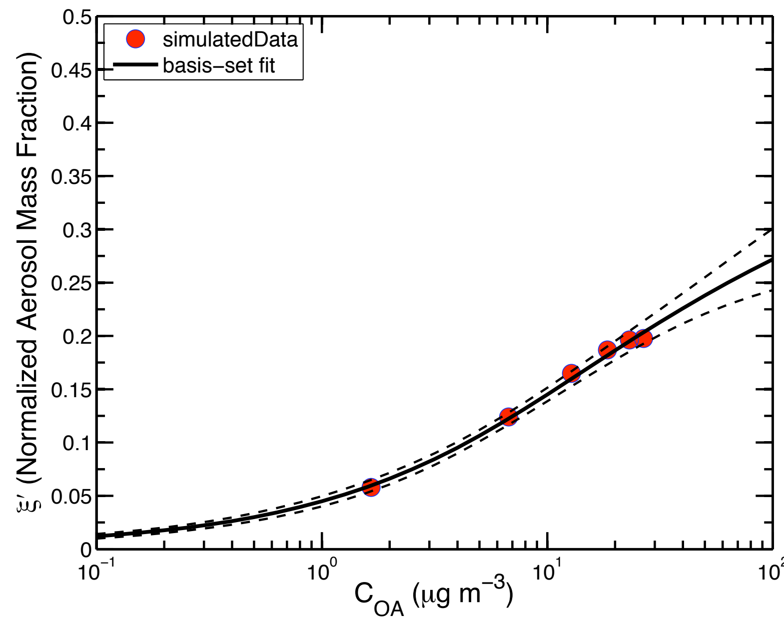
Toluene SOA Aging



- Continuous aging of long-lived toluene holds O:C roughly constant.
- Large changes in C_{OA} because of multi-generational products.
- Once again a lot like OOA2!

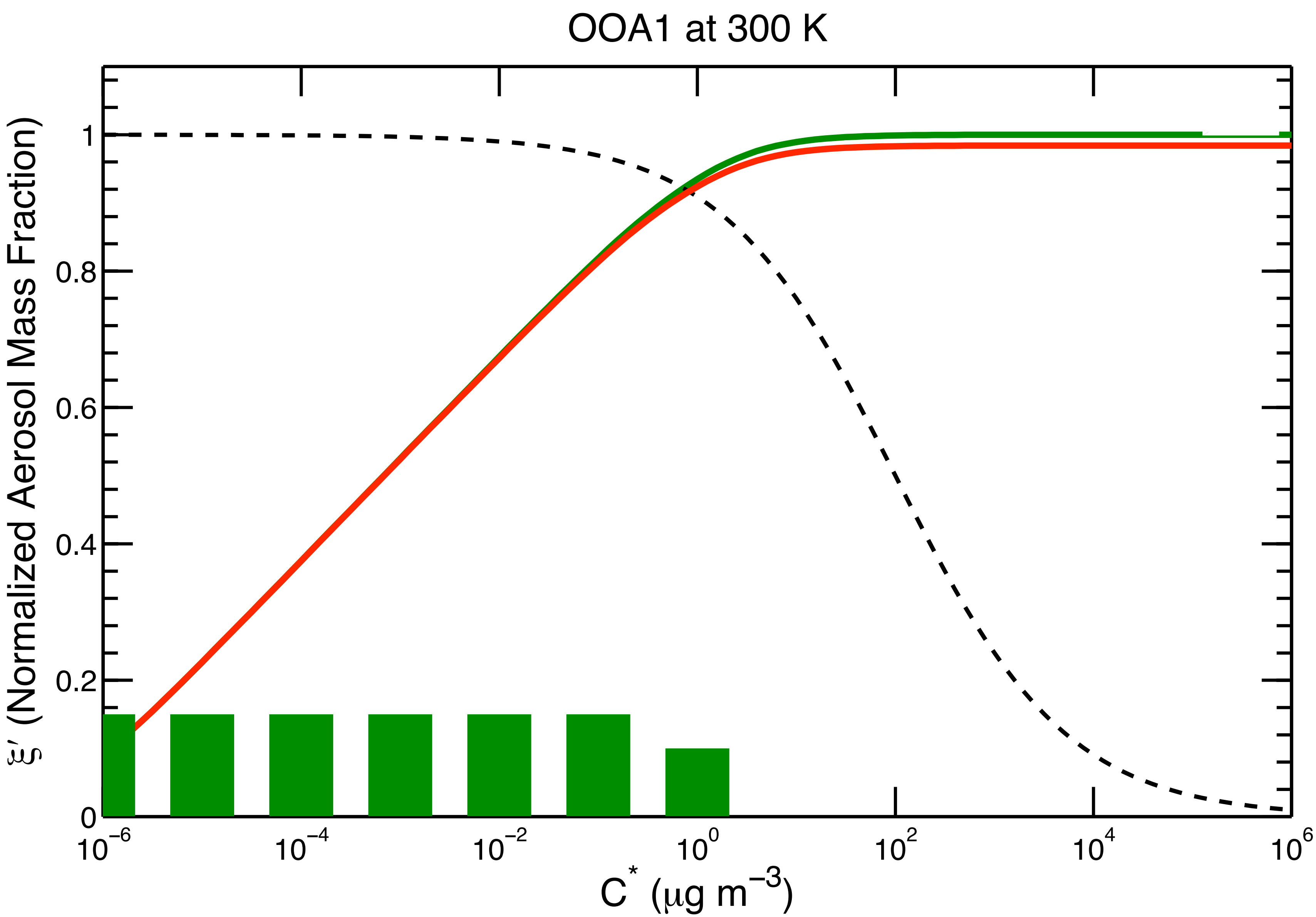
Toluene SOA



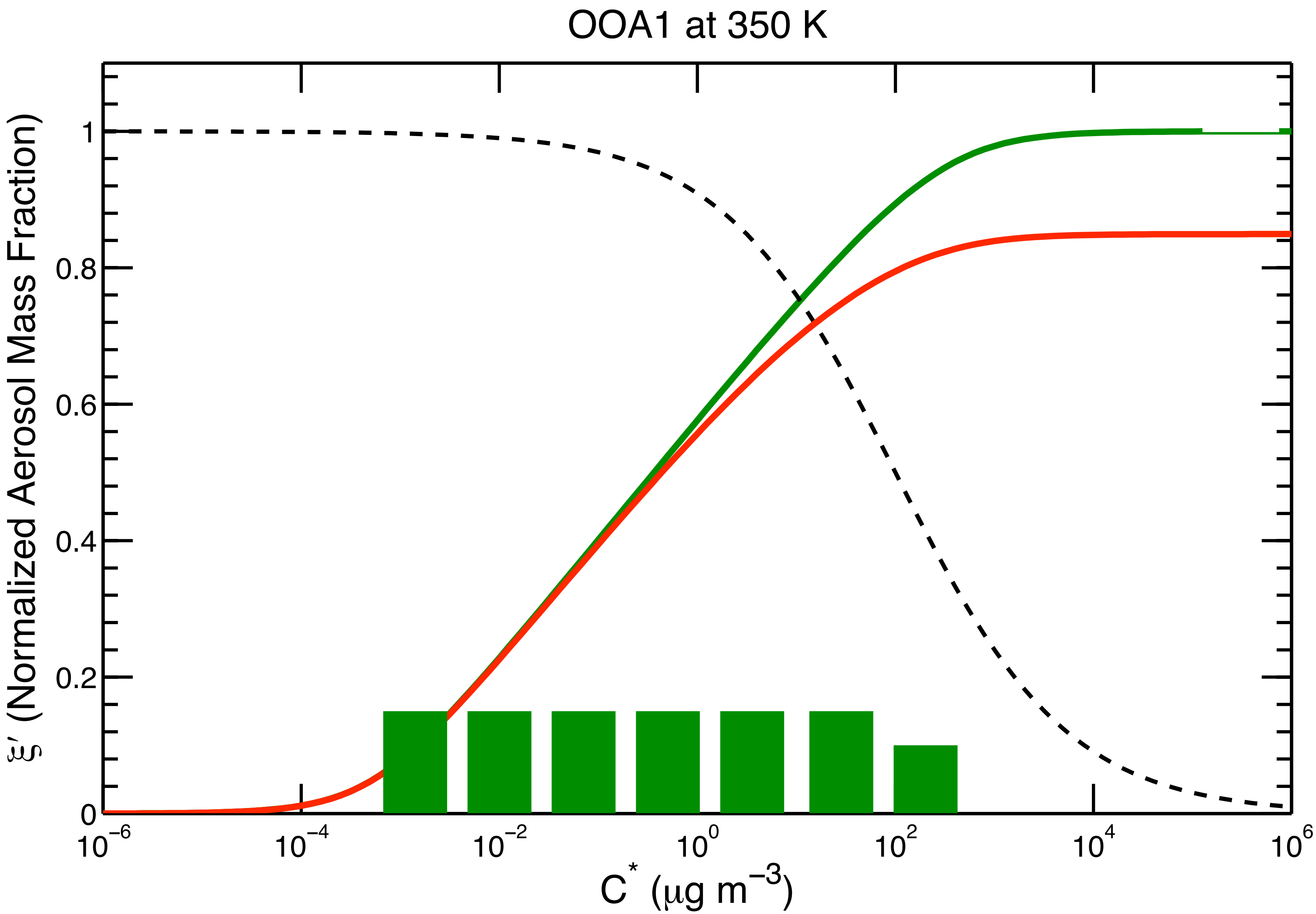


- 3x increase in UV intensity increases SOA formation.
- General levels consistent with aging model.
- Once again a lot like OOA2!

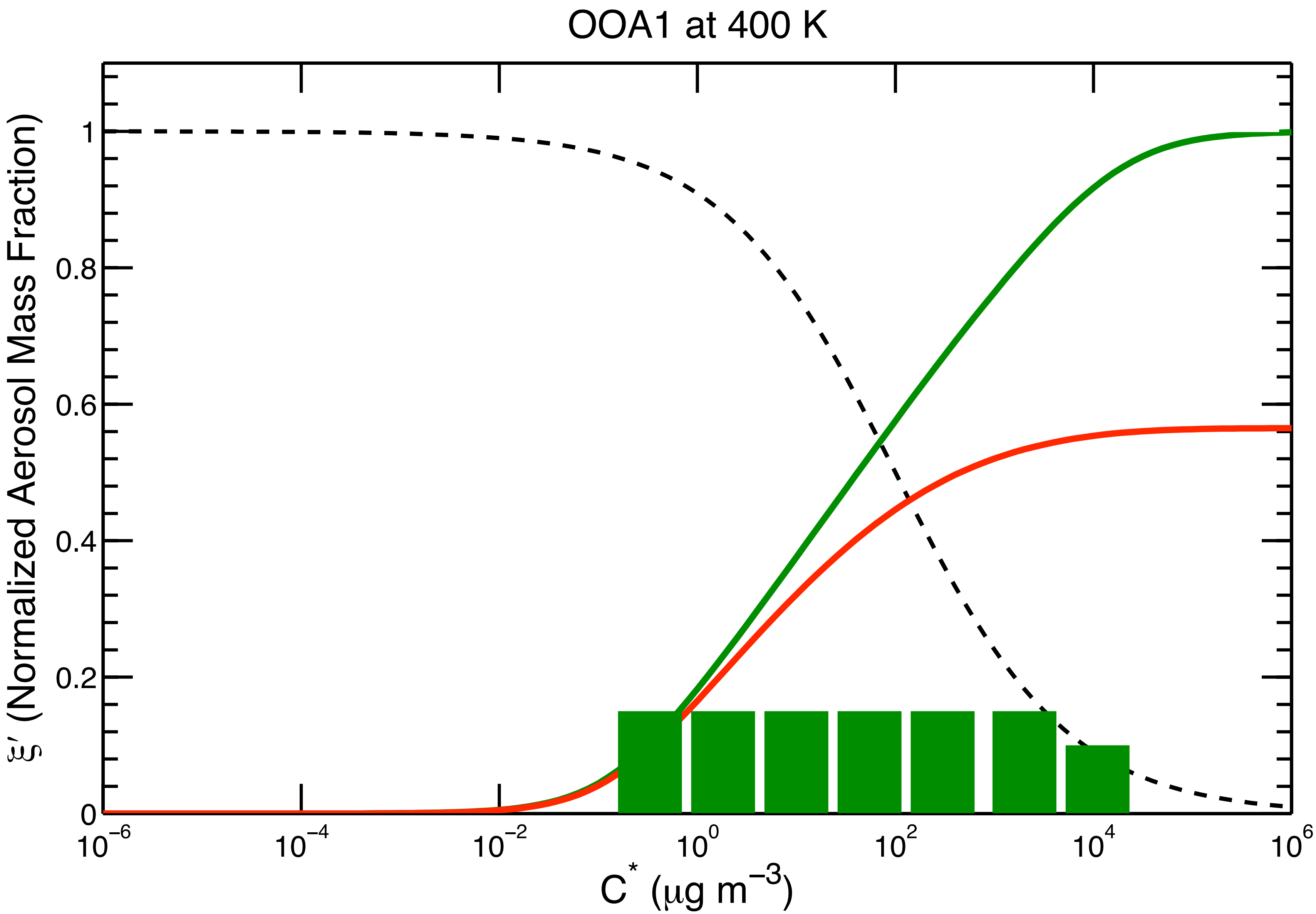
OOA1 Denuder Model



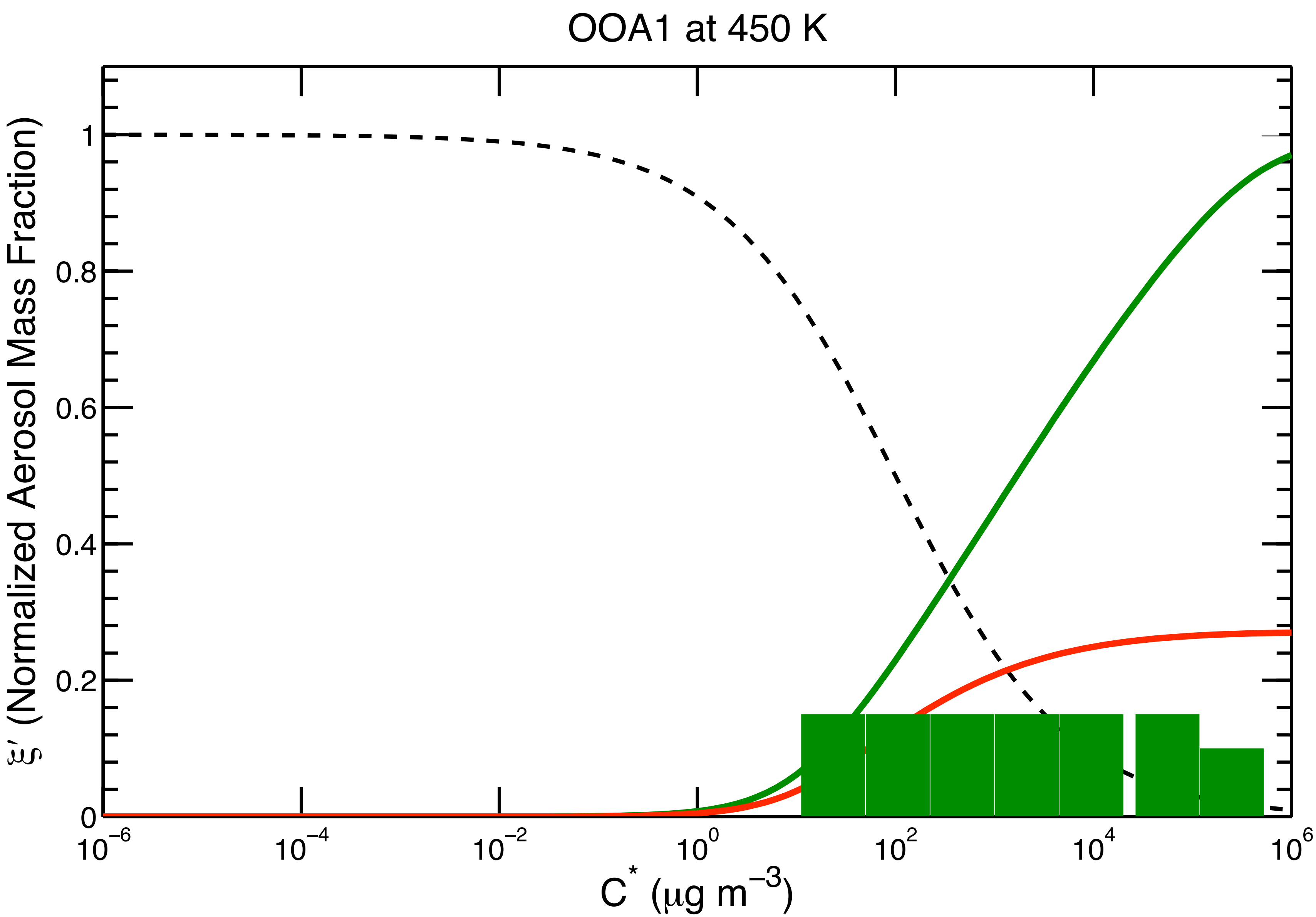
OOA1 Denuder Model



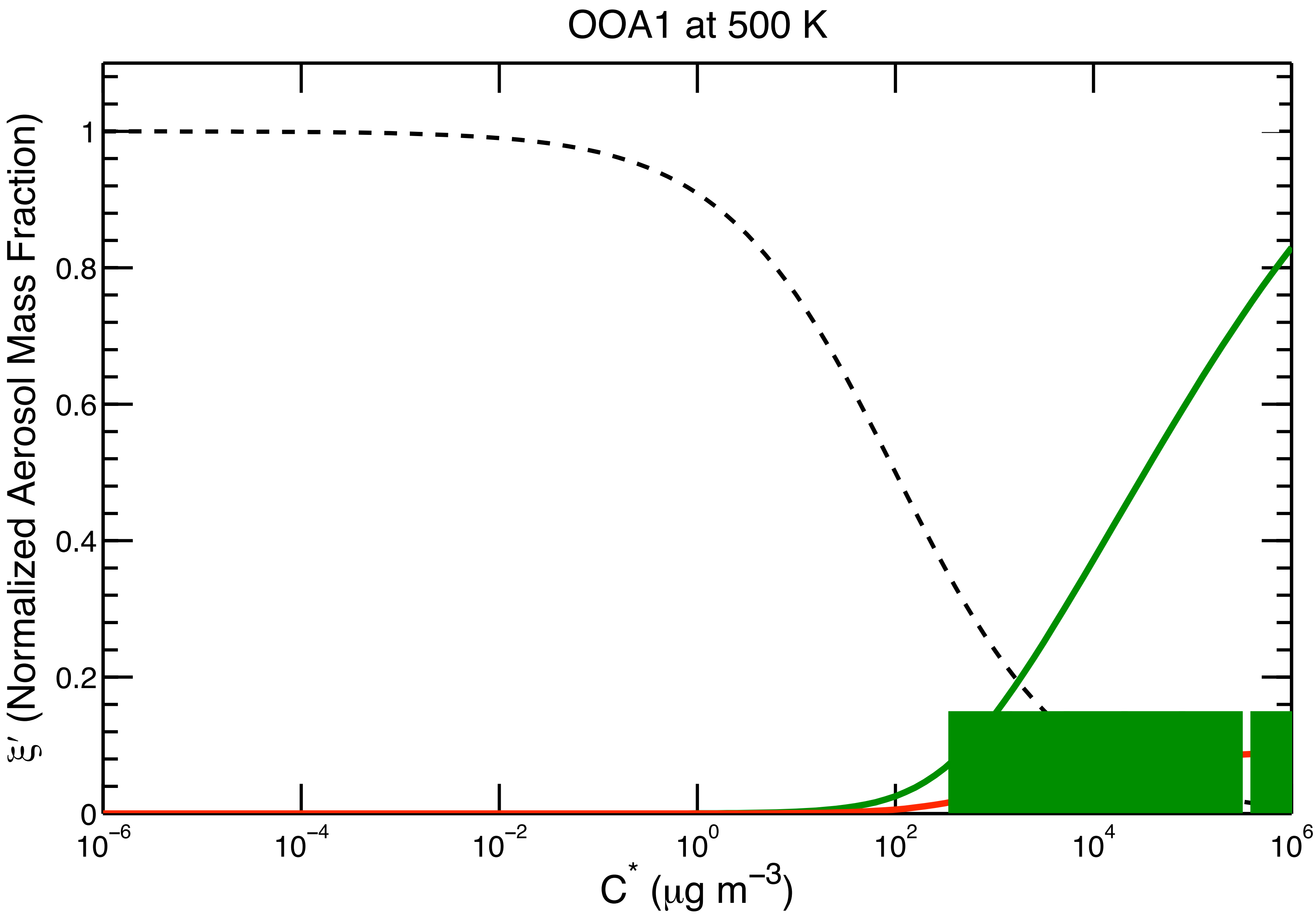
OOA1 Denuder Model



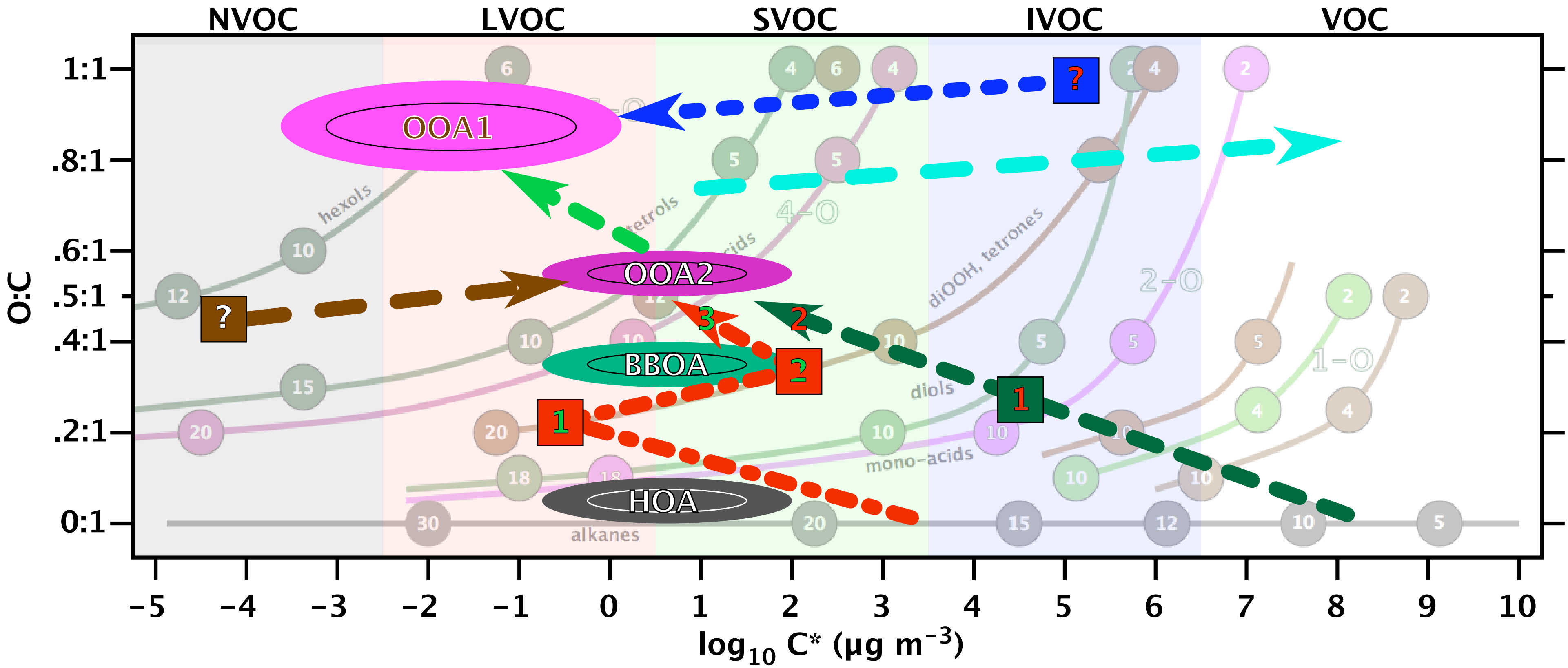
OOA1 Denuder Model



OOA1 Denuder Model



OOA Production Mechanisms



- There are many routes to OOA; all probably matter.
- Aging dominates OA levels in the global atmosphere.