Sources and Atmospheric Formation of Organic Particulate Matter

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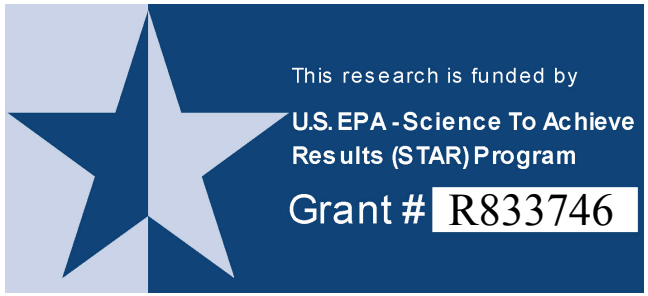
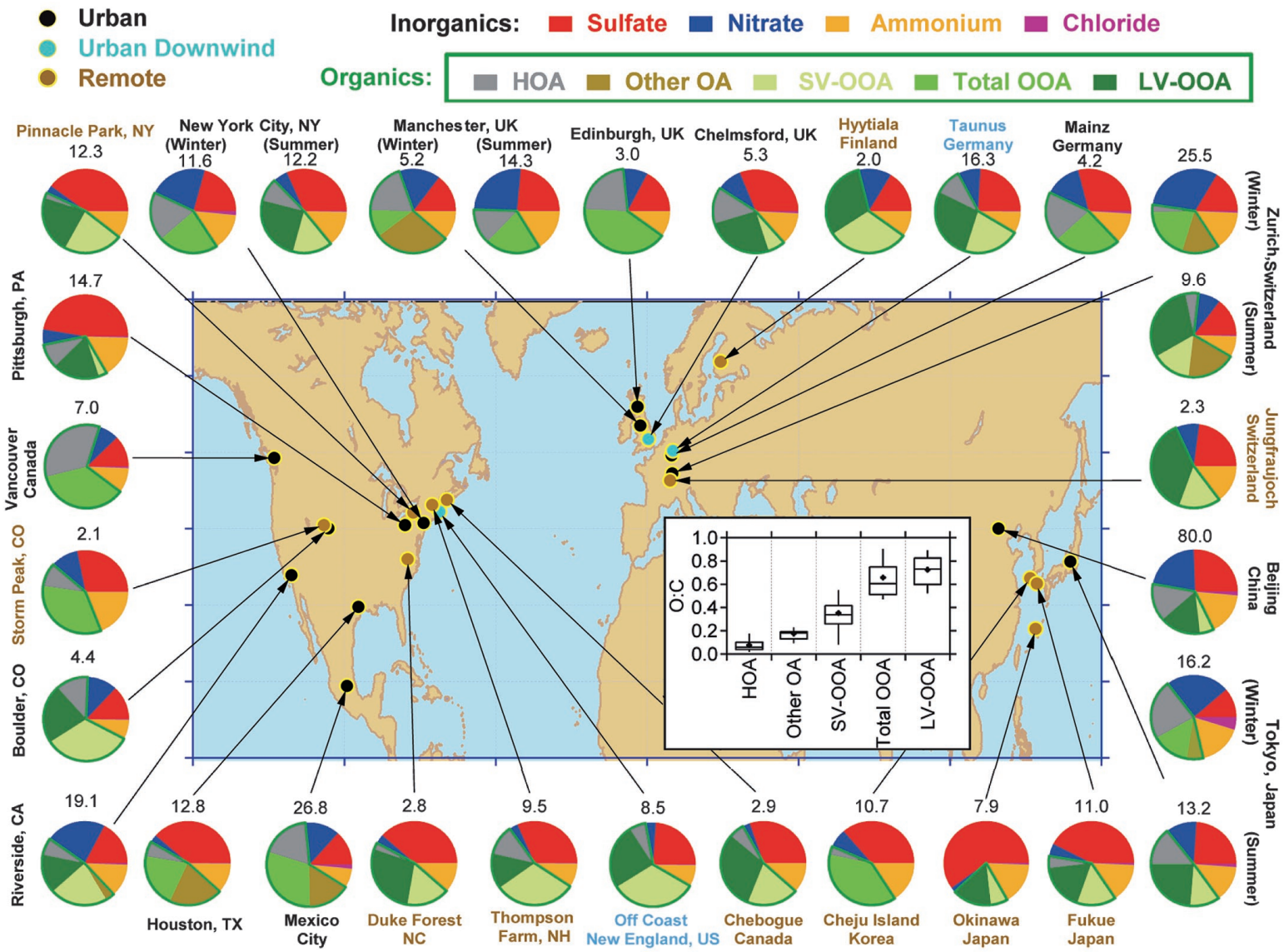
STAR Grant Meeting
21 Sep 2011
RTP, North Carolina



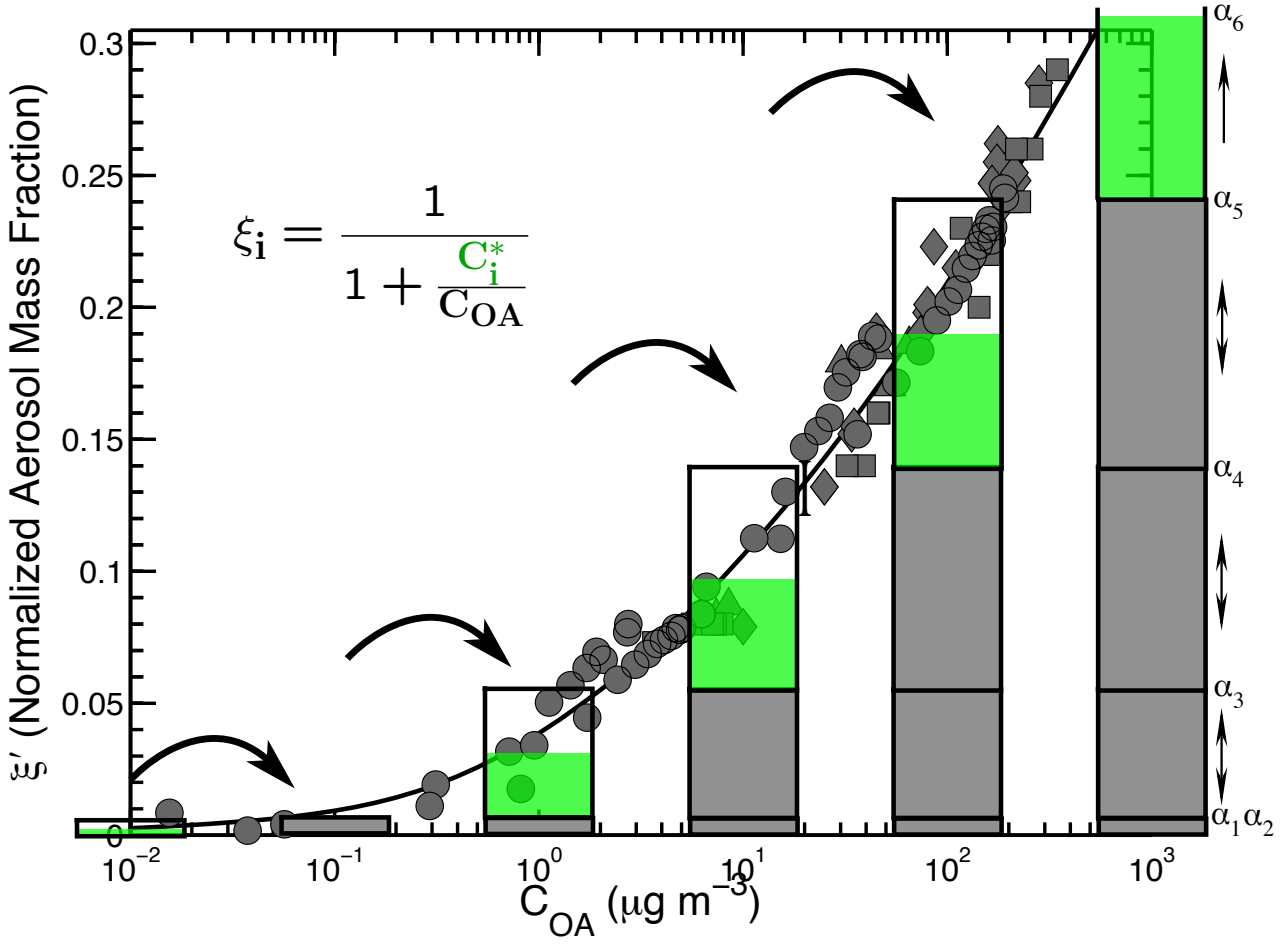
Motivation



- Highly oxidized organic aerosol incredibly important around the globe.

[Jimenez, *et al., Science* **2009]**

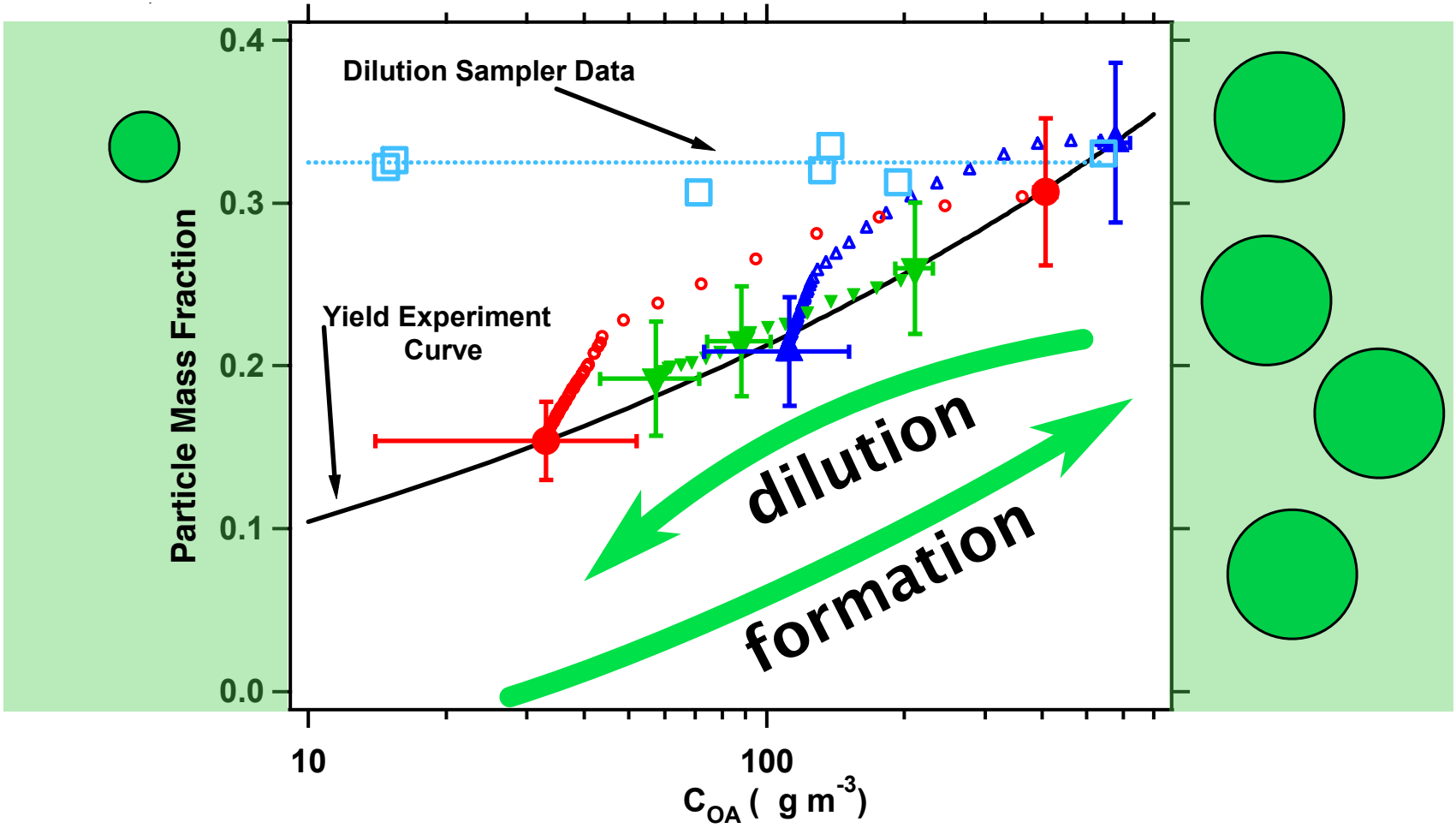
Motivation



- SOA mass yields increase with increasing SOA mass.
- Odum showed this means SOA is semi-volatile.

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

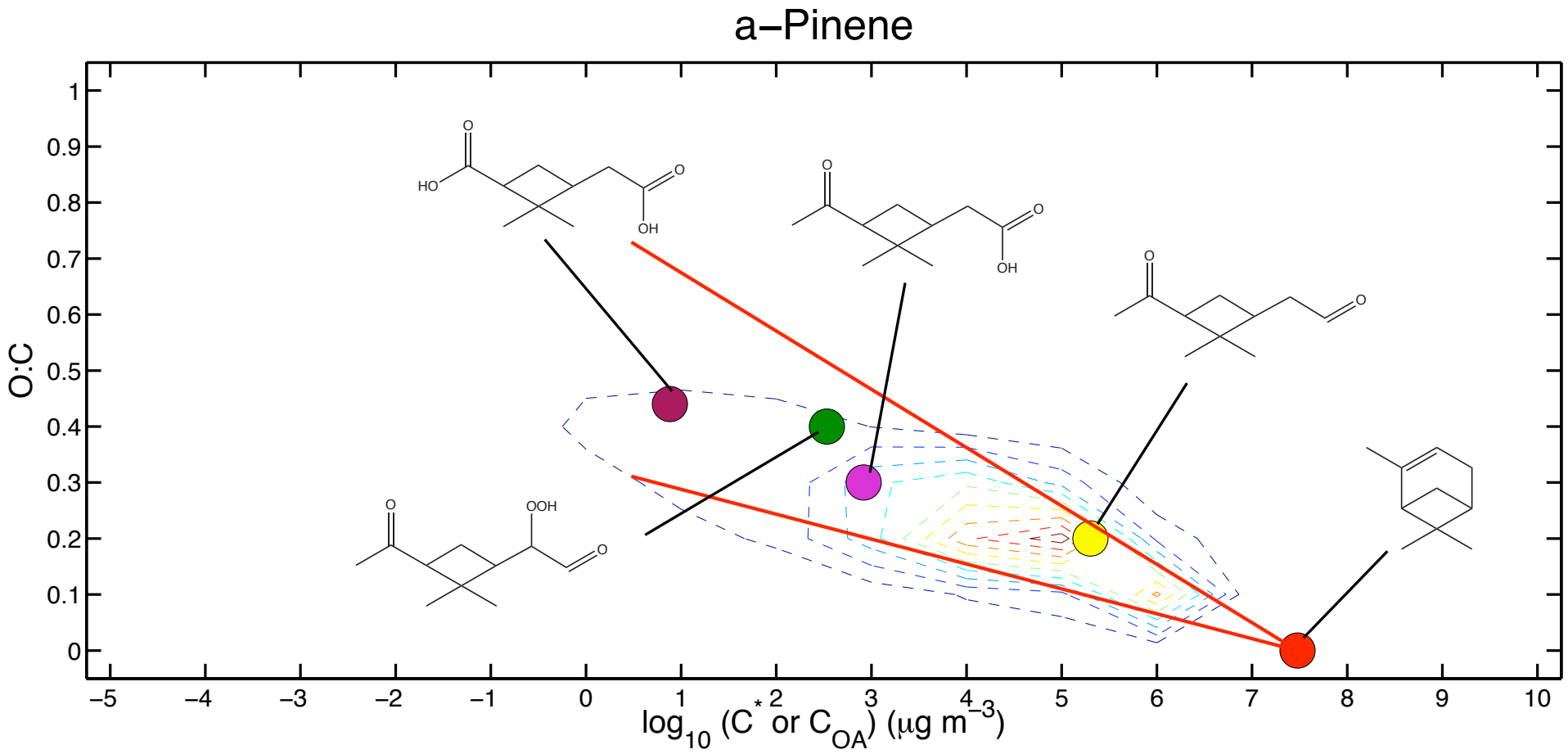
Motivation



- α-pinene SOA evaporates after dilution.
- SOA remains semi-volatile after formation (in chambers).

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

α-pinene SOA Interpretation

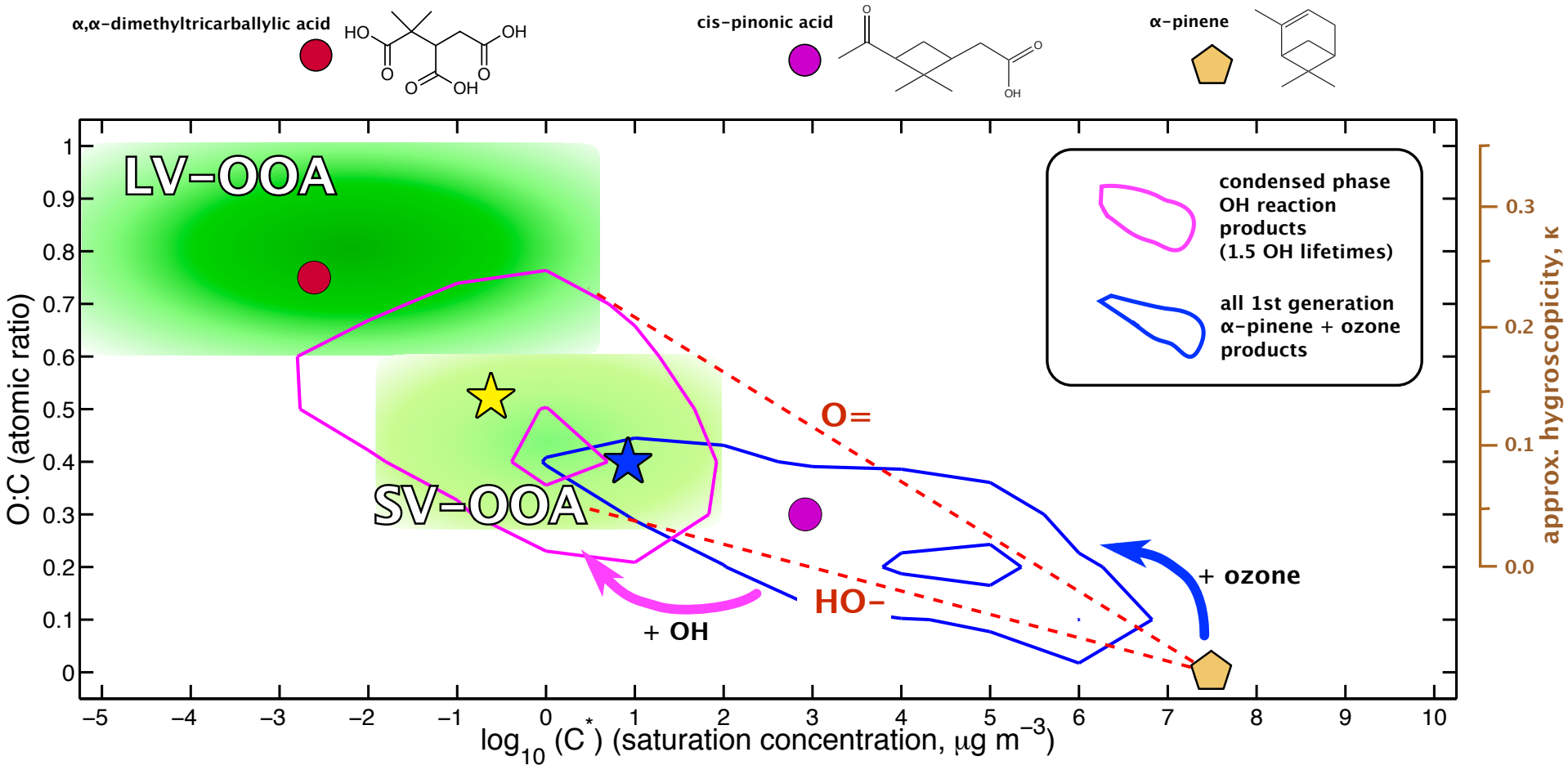


Mass and Molecules Interpreted in 2-Dimensional Space

- Molecules shown (mostly) can be measured via MS (PTRMS or API-MS).

[Donahue, *et al.*, in prep]

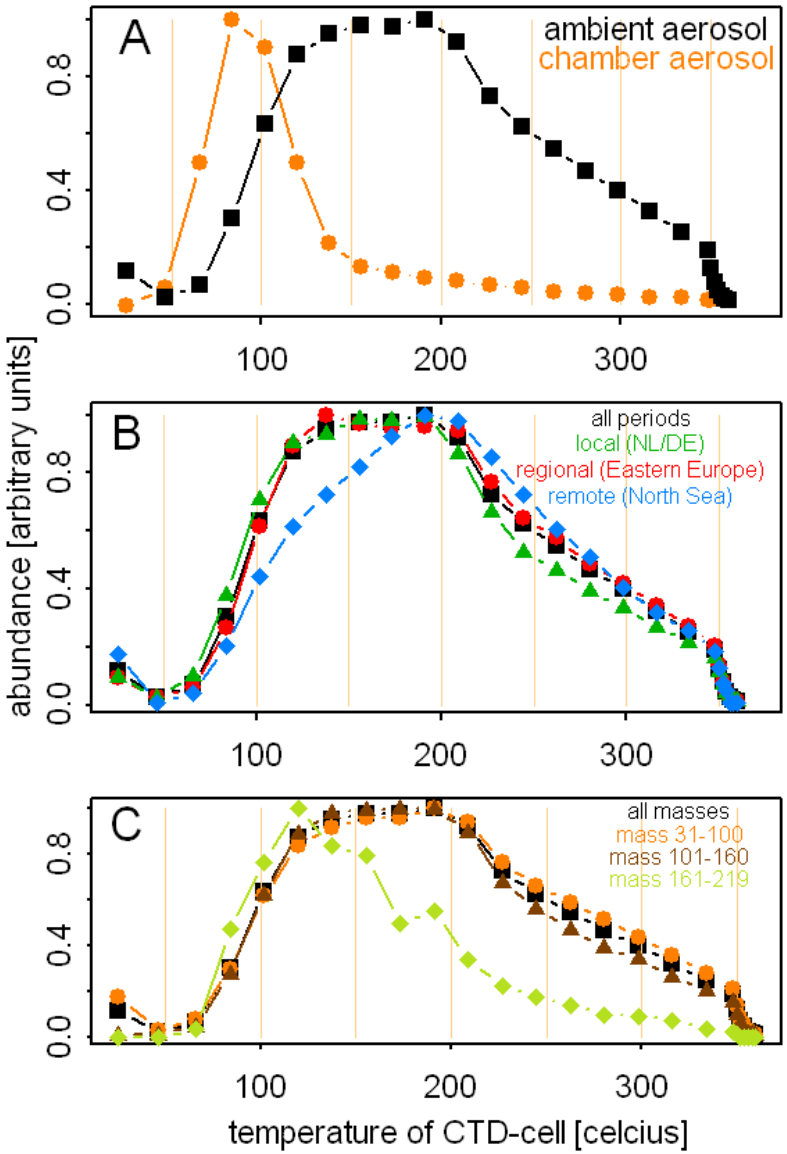
Ambient OOA Interpretation



- Chamber SOA insufficiently oxidized and too volatile for ambient observations.
- Aging moves SOA toward OOA.

[Jimenez *et al., Science*, 2009]

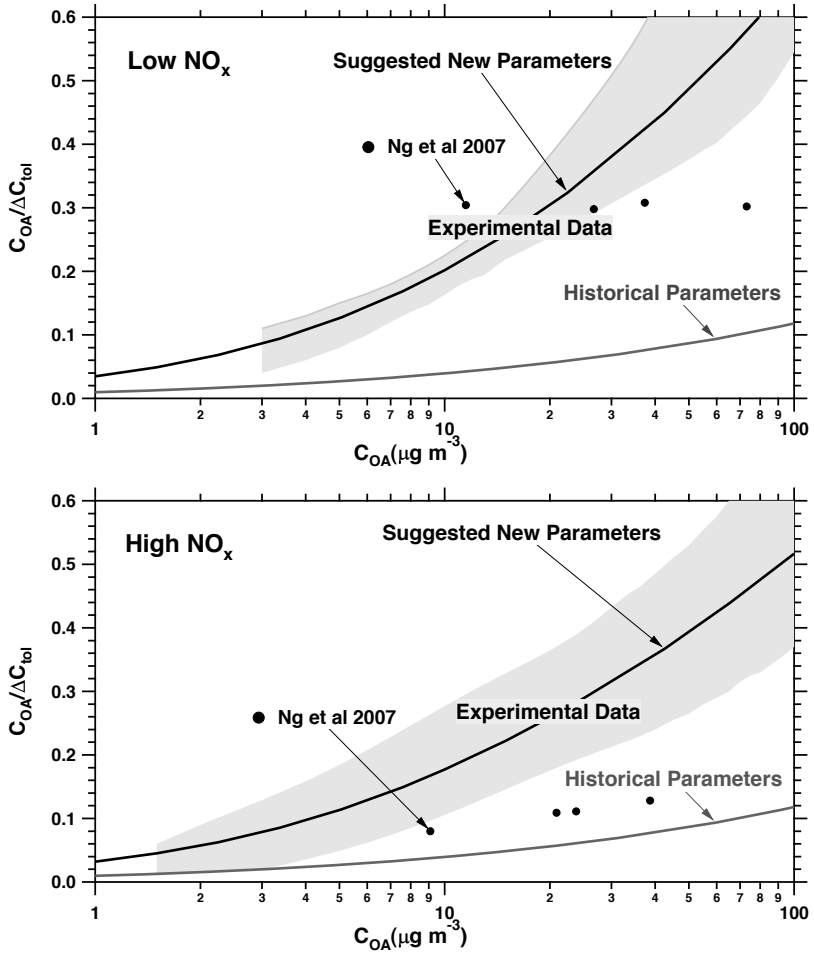
Chamber OA is *NOT* Ambient OA



- Not *just* an AMS thing!
- Thermal desorption PTRMS very different (Cabauw vs Max Planck SOA).

[Holtzinger *et al., ACP* **2010]**

Anthropogenic (Toluene) SOA



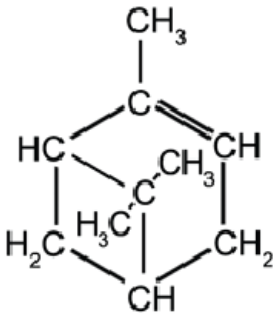
The era of rising yields (JHS):

- Higher SOA from toluene under both high and low NO_x.

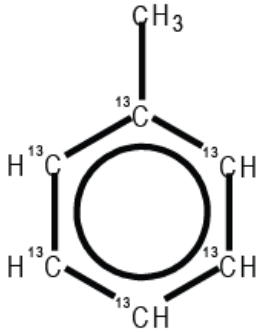
[Hildebrandt, ***et al., ACP*****, 2009]**

Do Biogenic and Anthropogenic SOA Mix?

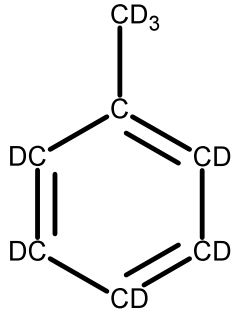
α-pinene

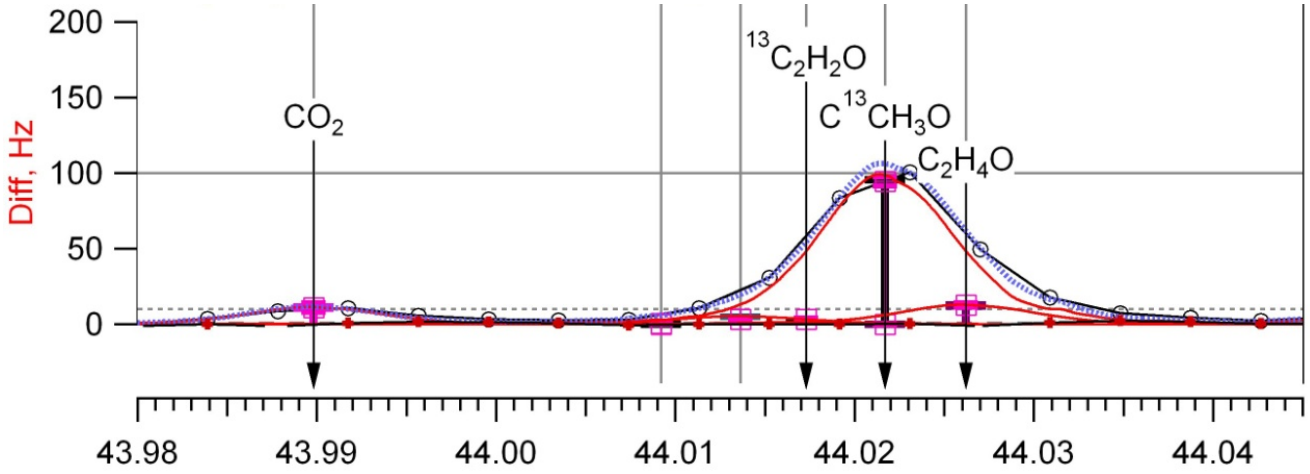


^{13}C-toluene



D-toluene

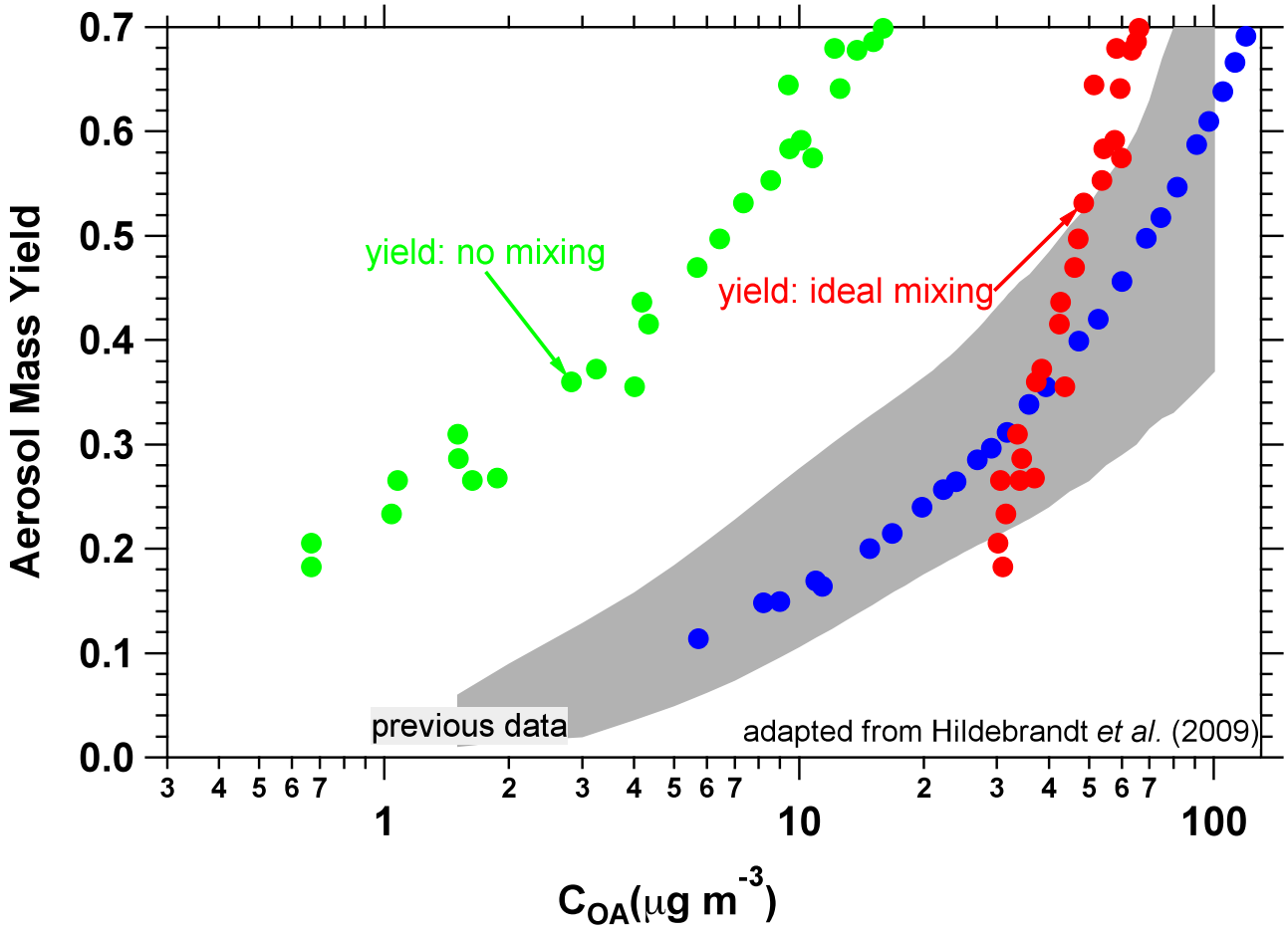




Is the C_{OA} in $\xi_i = \frac{1}{1+\frac{C_i^*}{C_{OA}}}$ the sum of all OA? All SOA??

[Hildebrandt, *et al.*, in prep]

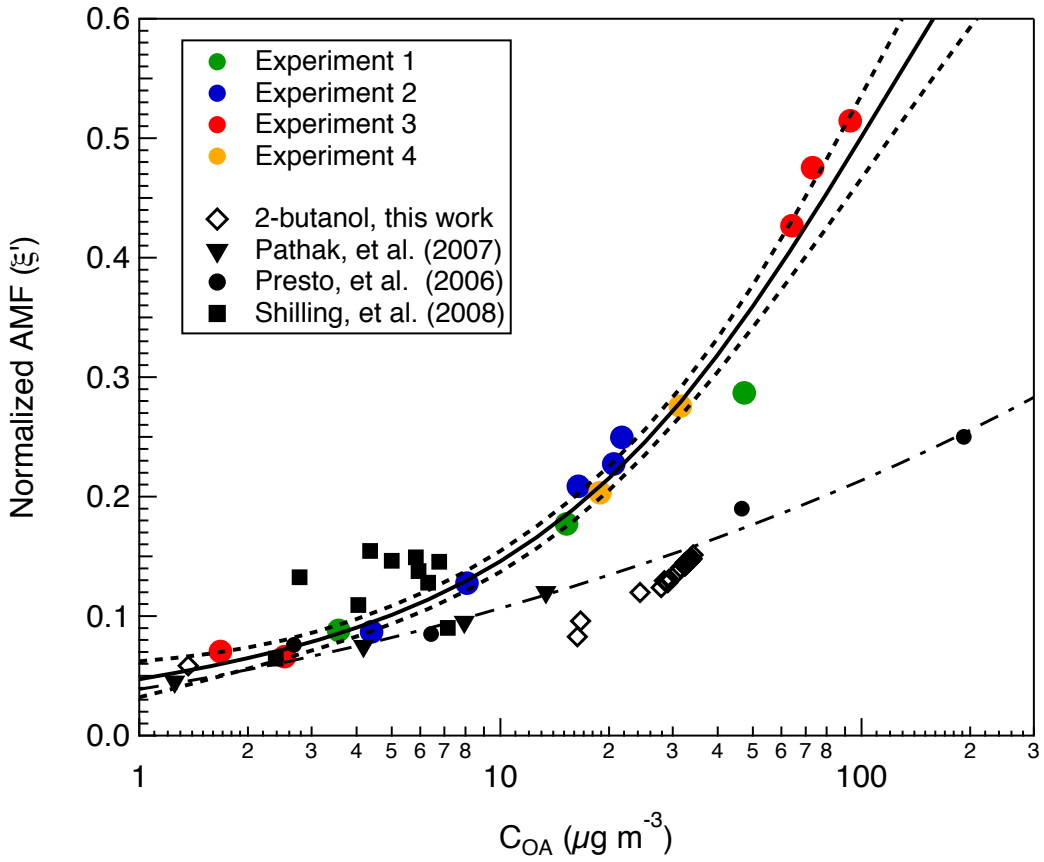
Toluene SOA in α-pinene SOA



- Toluene SOA *does* mix with α-pinene SOA.
- Approximately ideal, within uncertainty in wall-loss corrections.

[Hildebrandt, *et al.*, in prep]

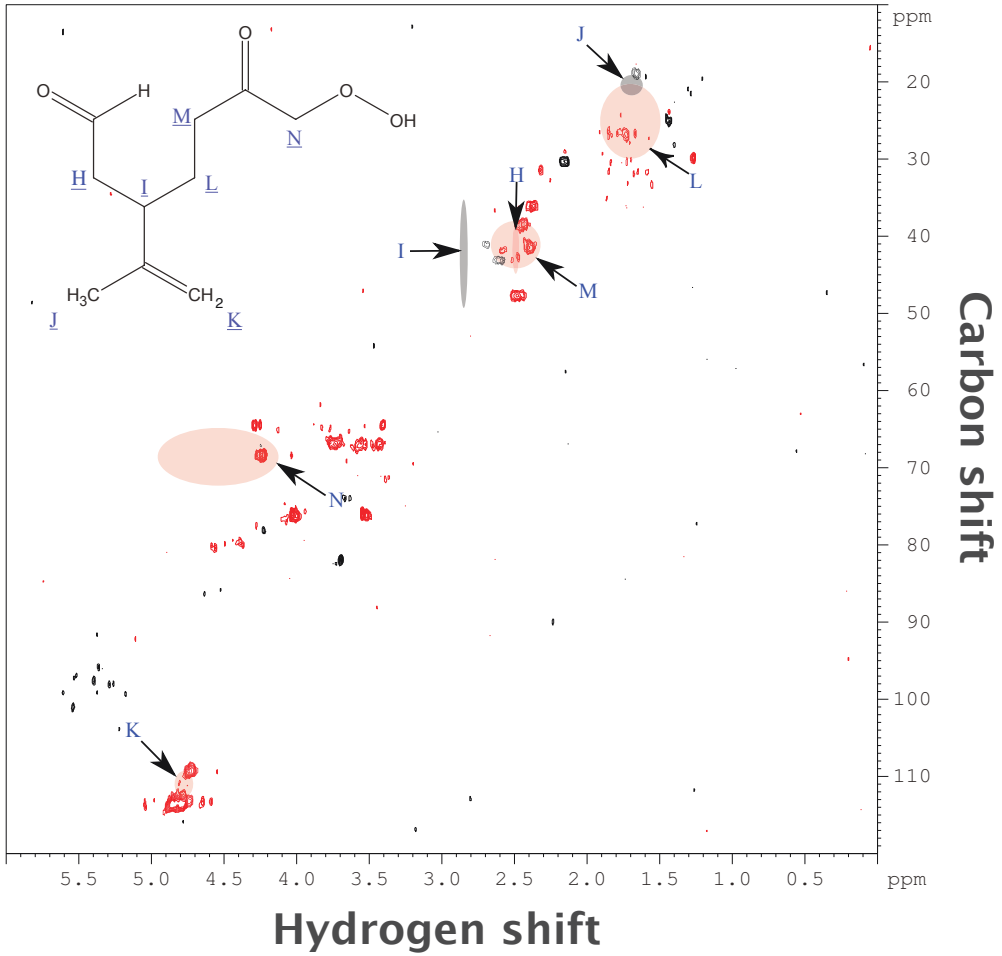
HOOH as OH Scavenger: α-pinene SOA



- HOOH + OH $\rightarrow$ H_2O + HO_2.
- More SOA at 100-1000 $\mu g\ m^{-3}$.
- Consistent with peroxides (ROOH).

[Henry, *et al.,AS&T* submitted]

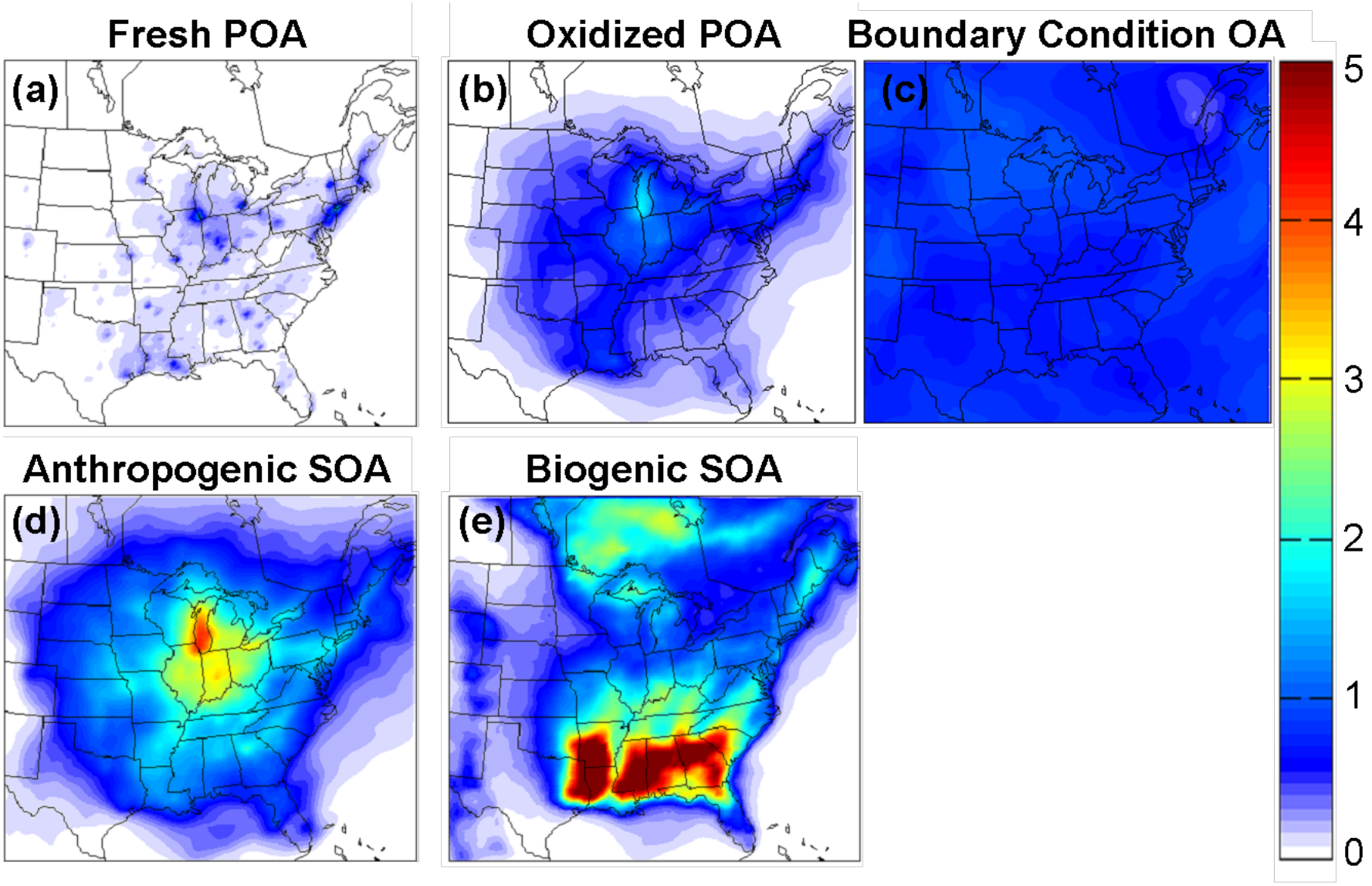
Limonene + Ozone SOA (excess Limonene)



- 2D NMR shows expected product functionality.

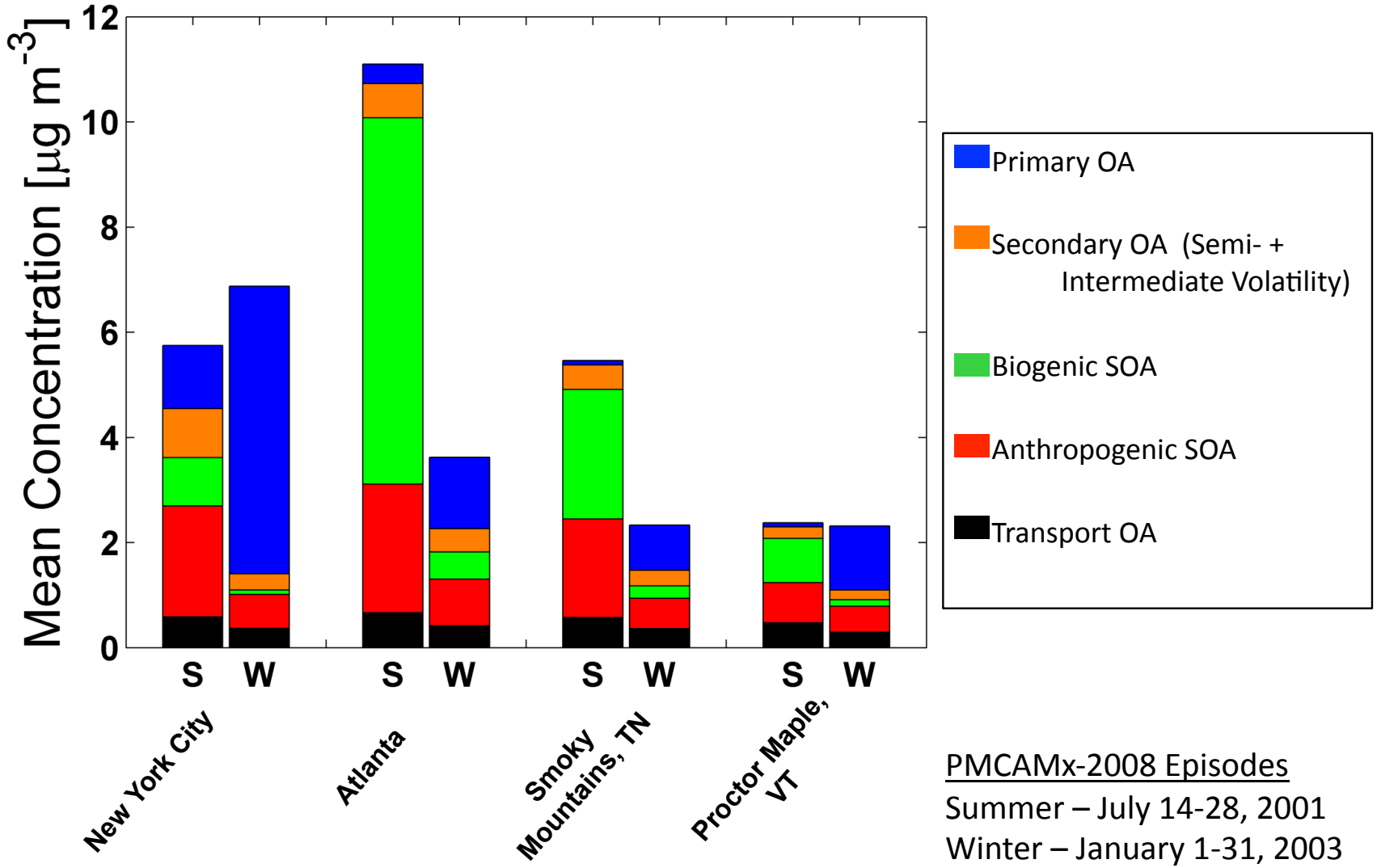
[Maksymiuk, *et al., PCCP*, 2009]

Modeling Rev 1: (PMCAMX 2007)



[Murphy and Pandis, ES&T, 2009]

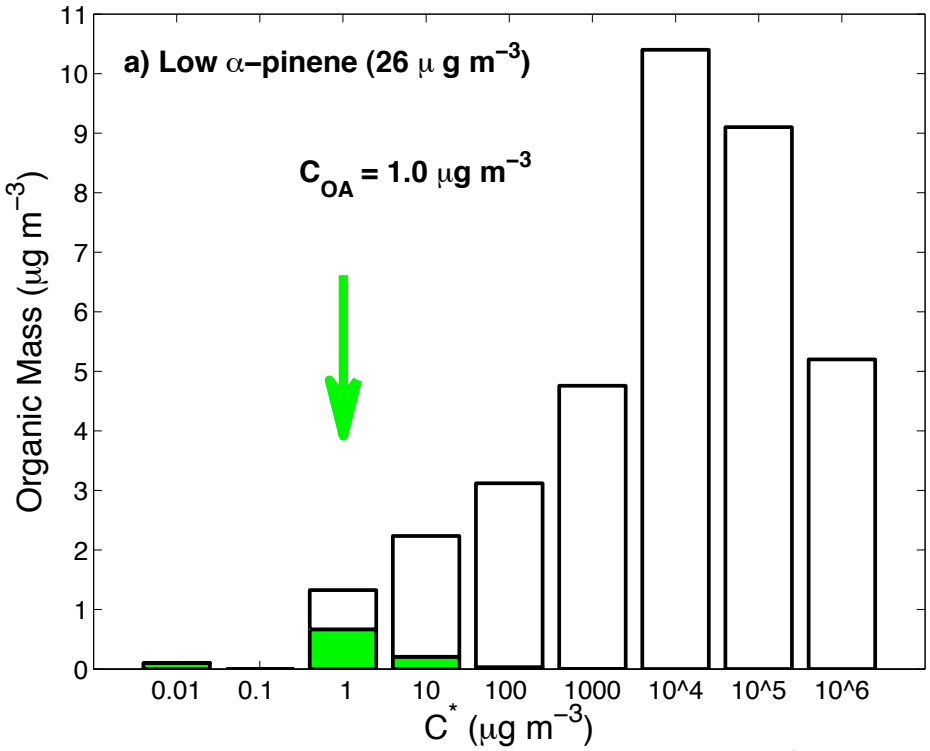
Seasonal Variation: (PMCAMX 2007)

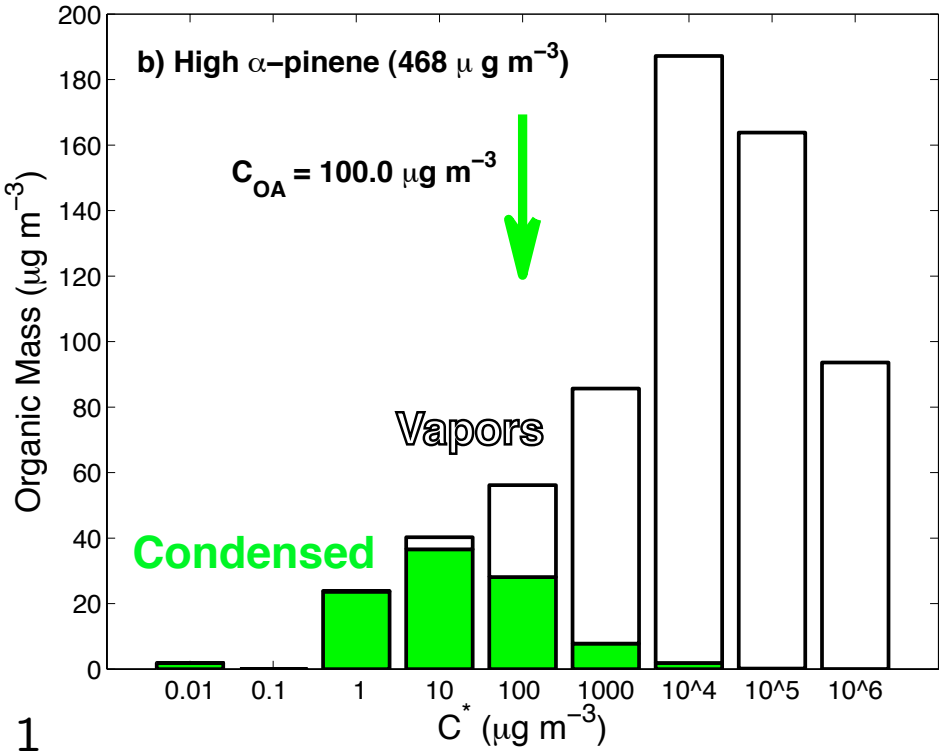


PMCAMx-2008 Episodes
Summer – July 14-28, 2001
Winter – January 1-31, 2003

[Murphy and Pandis, JGRA, submitted]

Aging Motivation



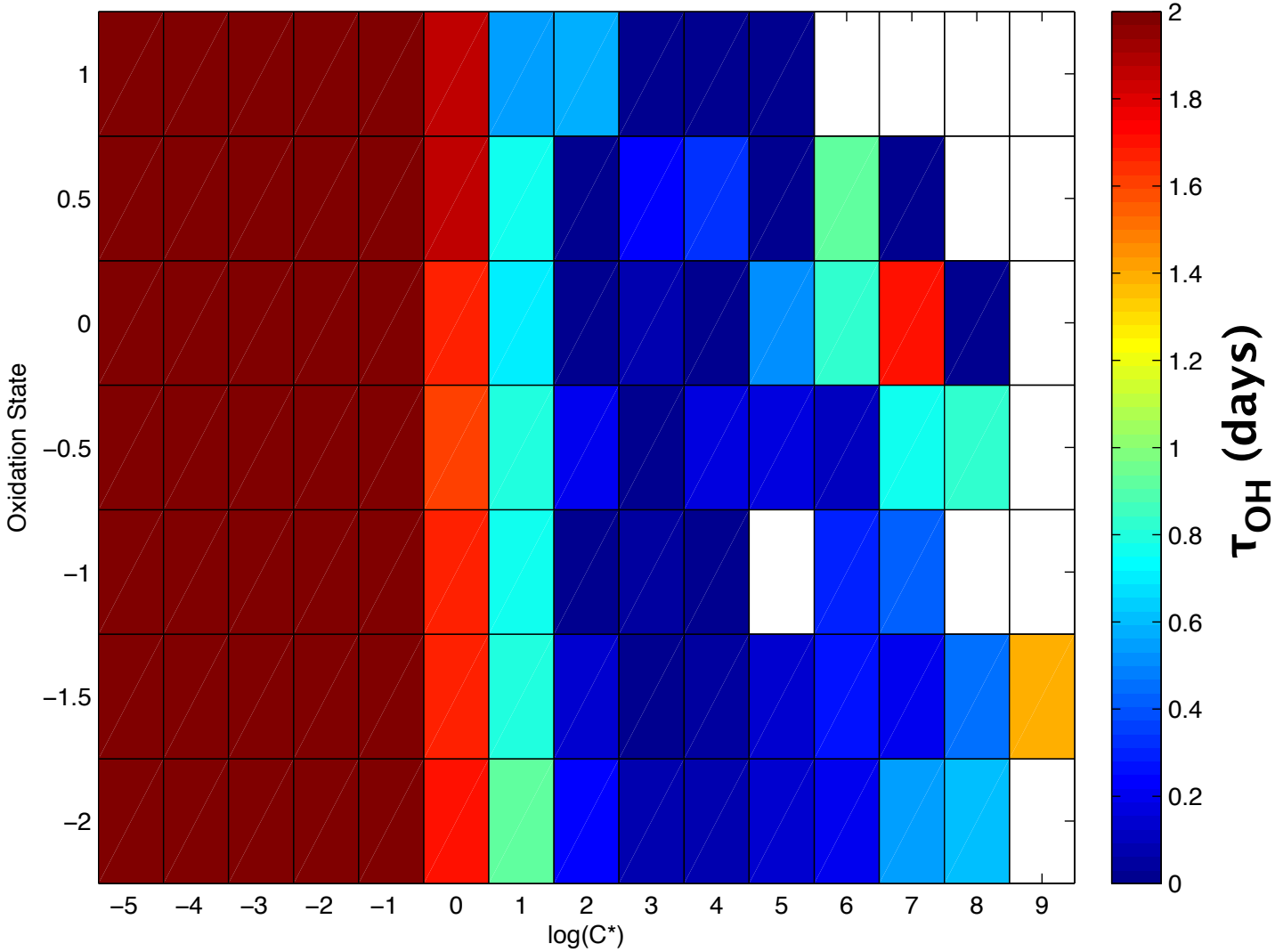


$$\xi_i = \frac{1}{1 + \frac{C_i^*}{C_{OA}}}$$

- The **large** majority of SOA products from α-pinene + O_3 are vapors.
- Many have very low vapor pressure.
- What happens to these vapors when ·**OH** comes calling?

[Donahue, *et al., Atm. Env.* **2009]**

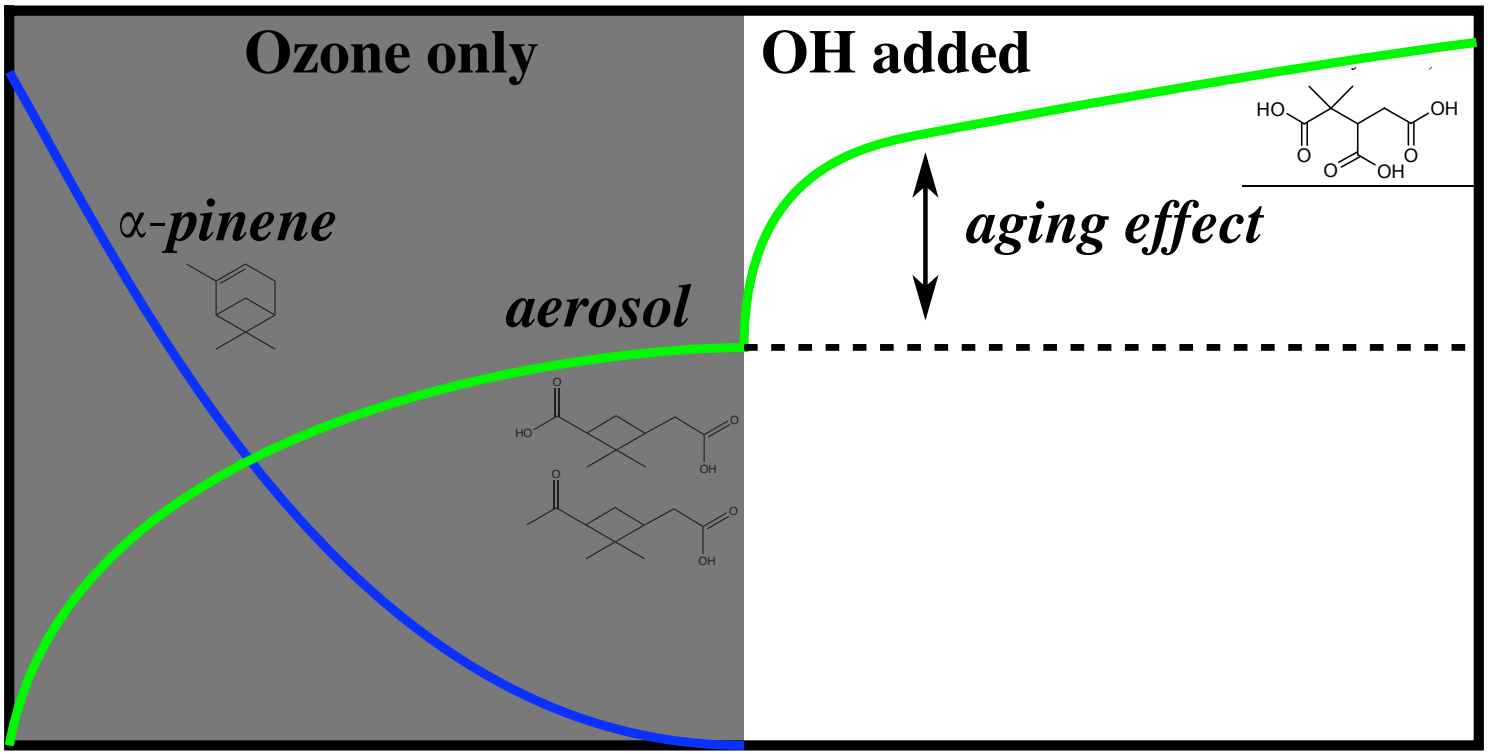
Semivolatile OH Lifetimes



- Generate structures averaging dO/dH = -1, use Atkinson k SAR.
- Gas-phase OH lifetime of SV vapors is very short.
- Semi-volatile vapors are not long for this world.

[Donahue *et al.*, in prep]

Aging Design

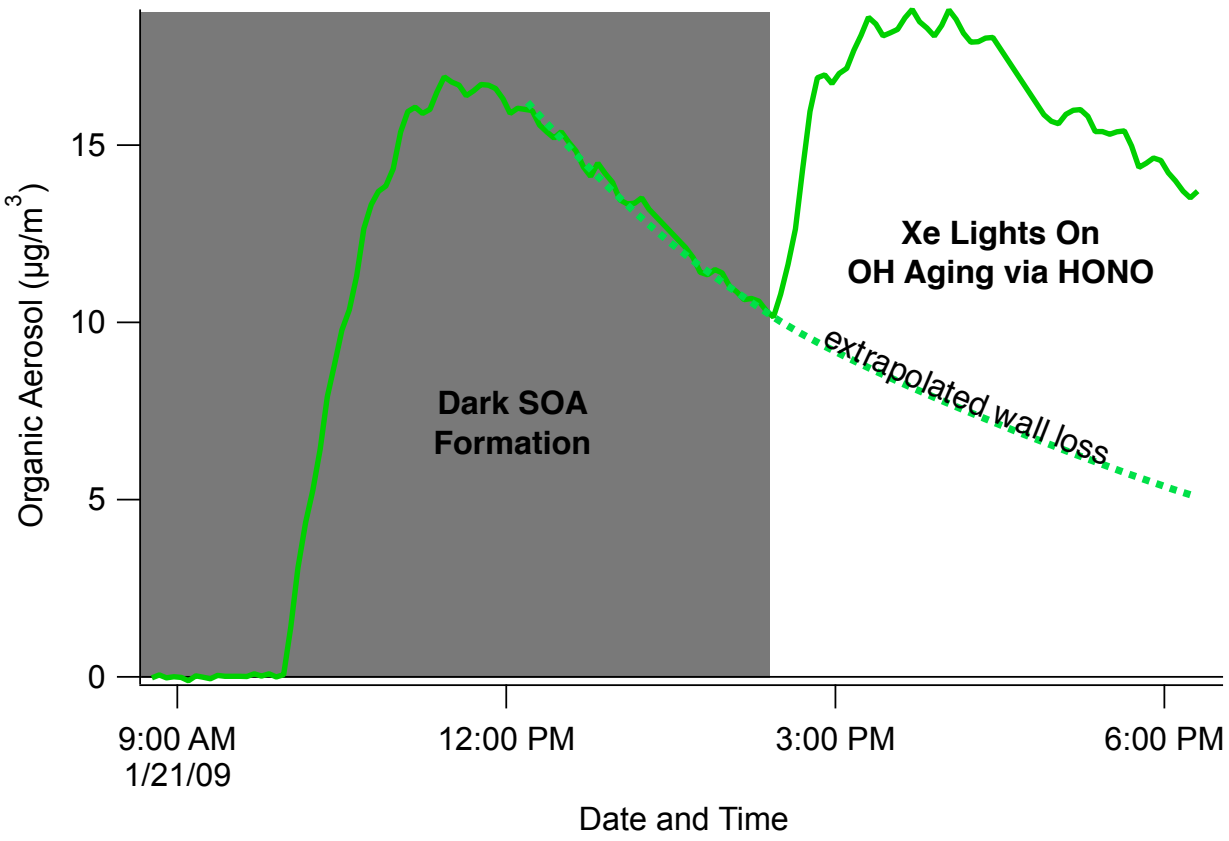


Very simple experimental design:

- Form α-pinene + O_3 SOA (*usually* no scavenger).
- Initiate OH source after all α-pinene gone.
- Watch for (sudden) changes.

[Donahue, *et al.*, in prep]

Unadulterated Results (PSI)

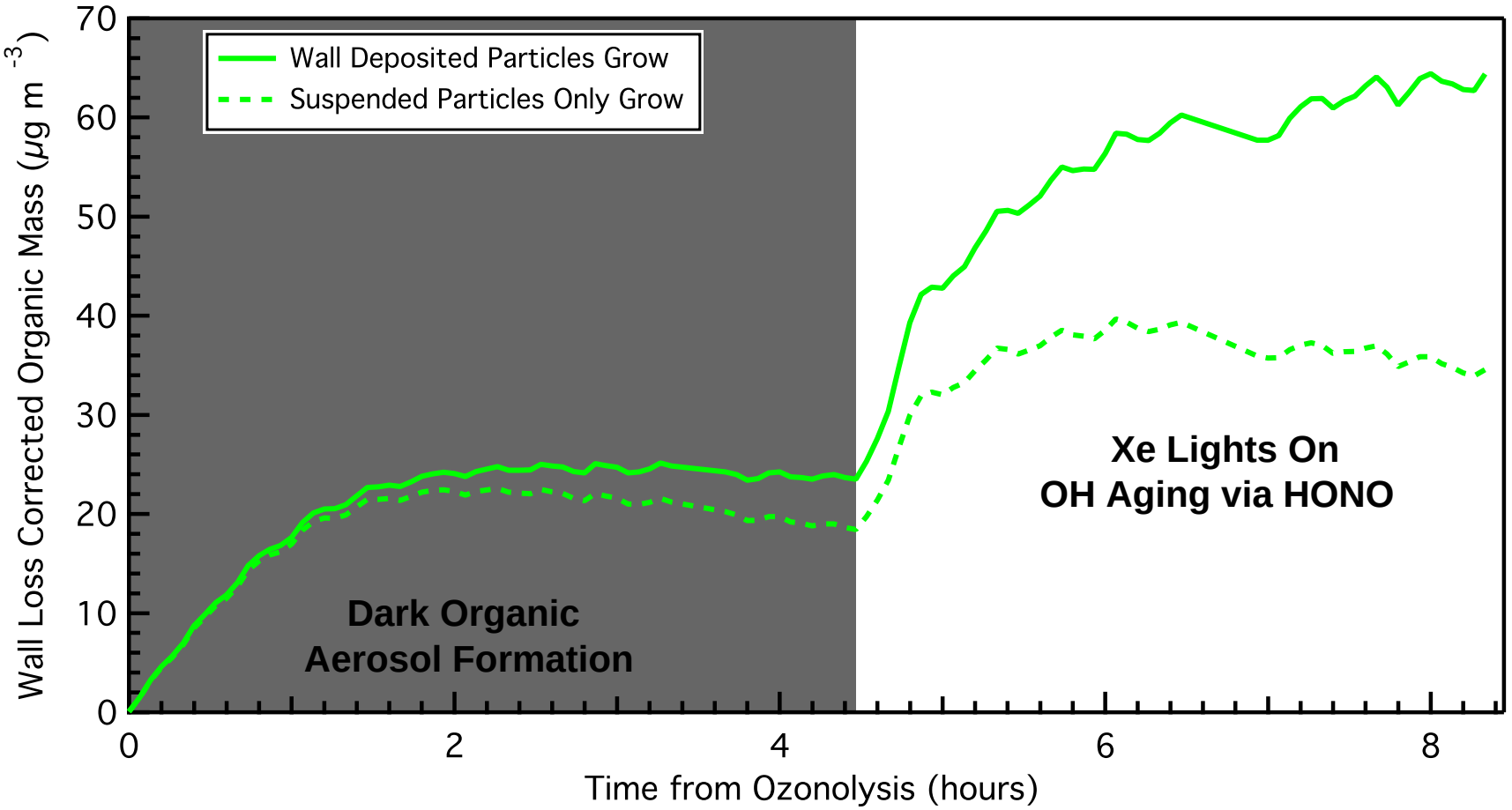


Uncorrected AMS organics with HONO photolysis:

- Sharp increase in SOA after OH turned on.
- Is it 10 μg m^{-3} or a doubling?
- What goes on with the walls?
- (Note – undulation is real, due to T control, more proof this is semi-volatile!)

[DeCarlo, *et al.*, in prep]

PSI HONO + hν

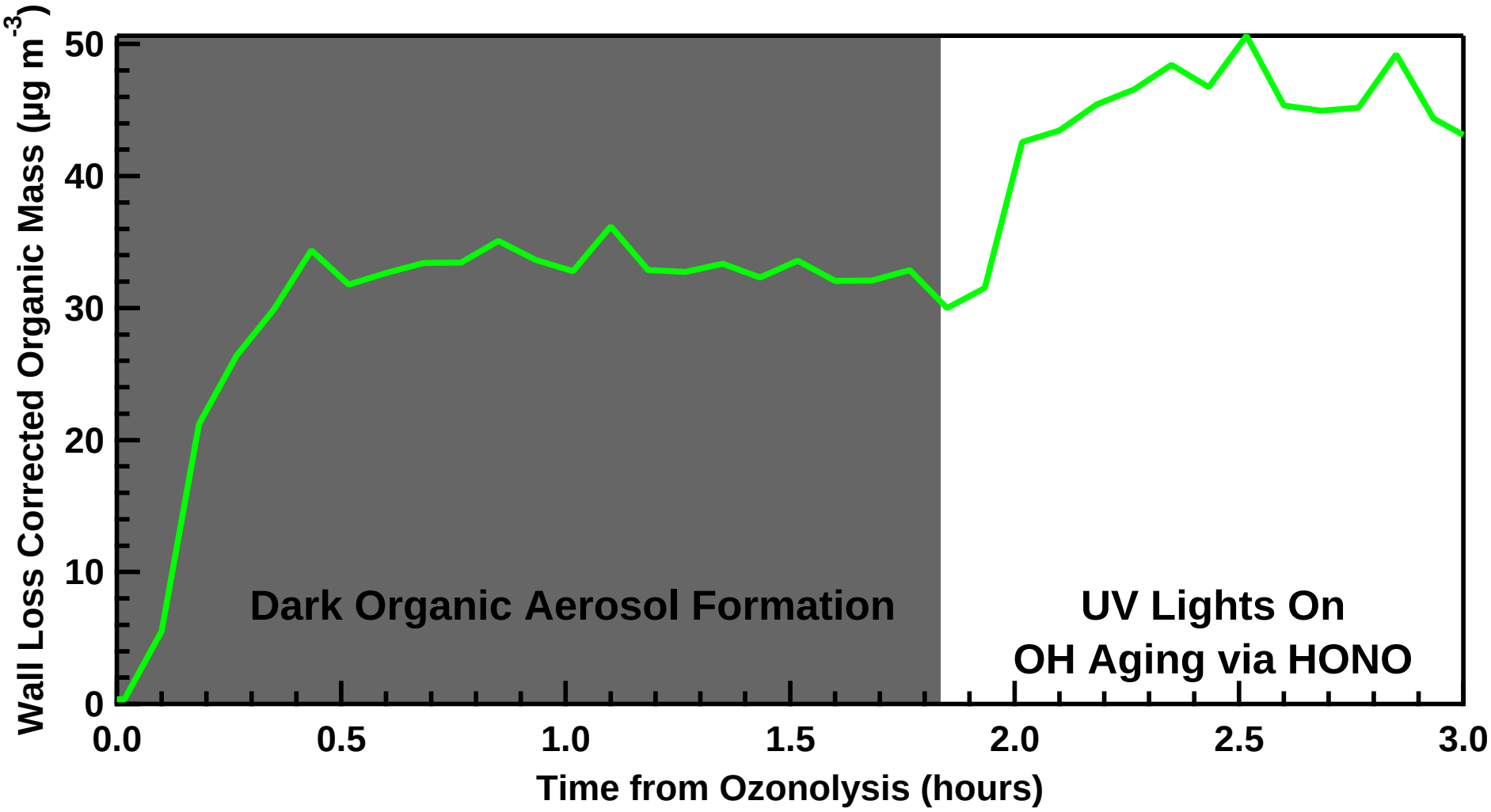


Corrected for wall loss:

- No matter how you slice it, a *big* change in SOA.
- Different lines based on whether wall-deposited particles grow.

[DeCarlo, *et al.*, in prep]

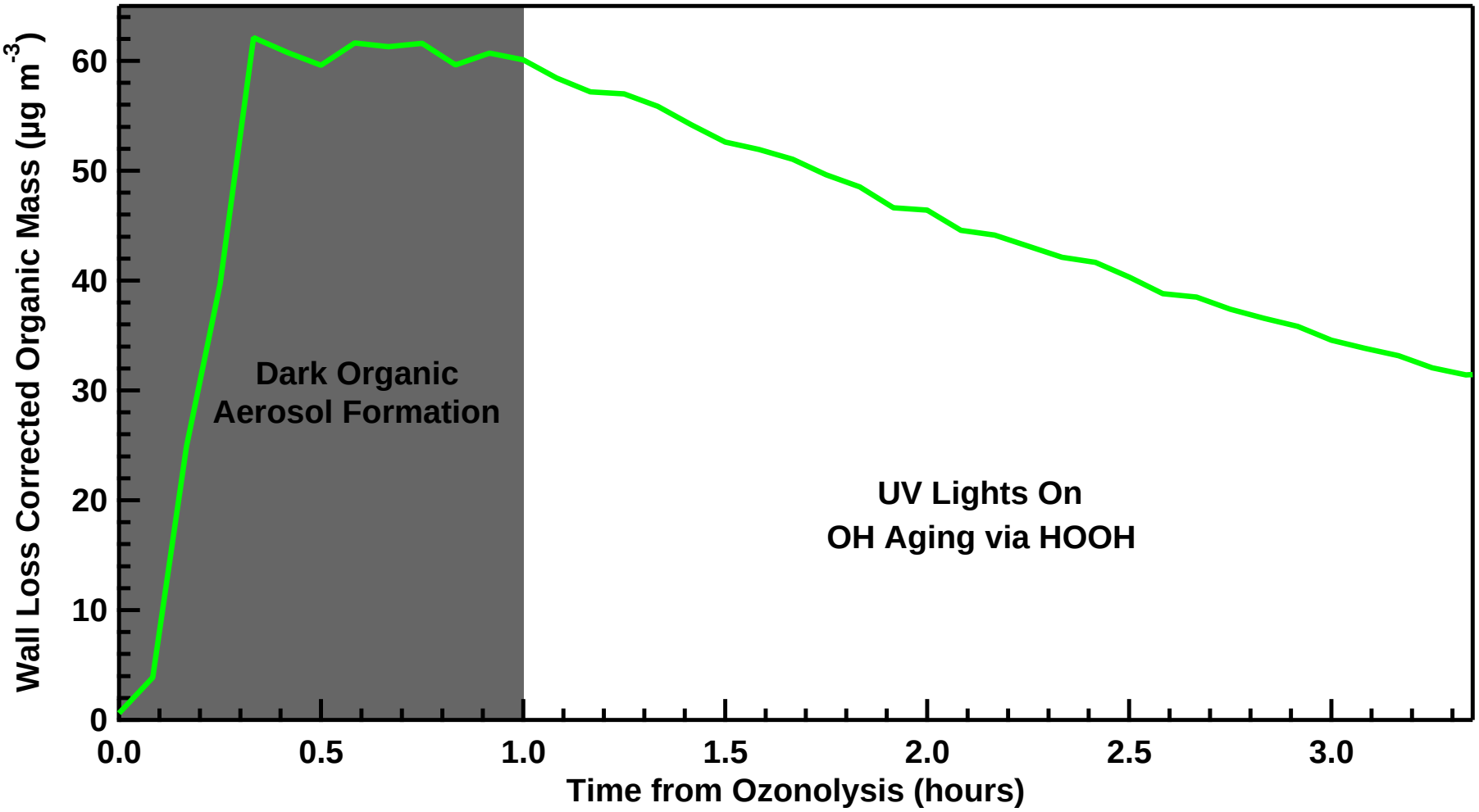
CMU HONO + hν



- Very similar result in CMU chamber.

[Henry, *et al.*, in prep]

CMU HOOH + hν (360 nm)



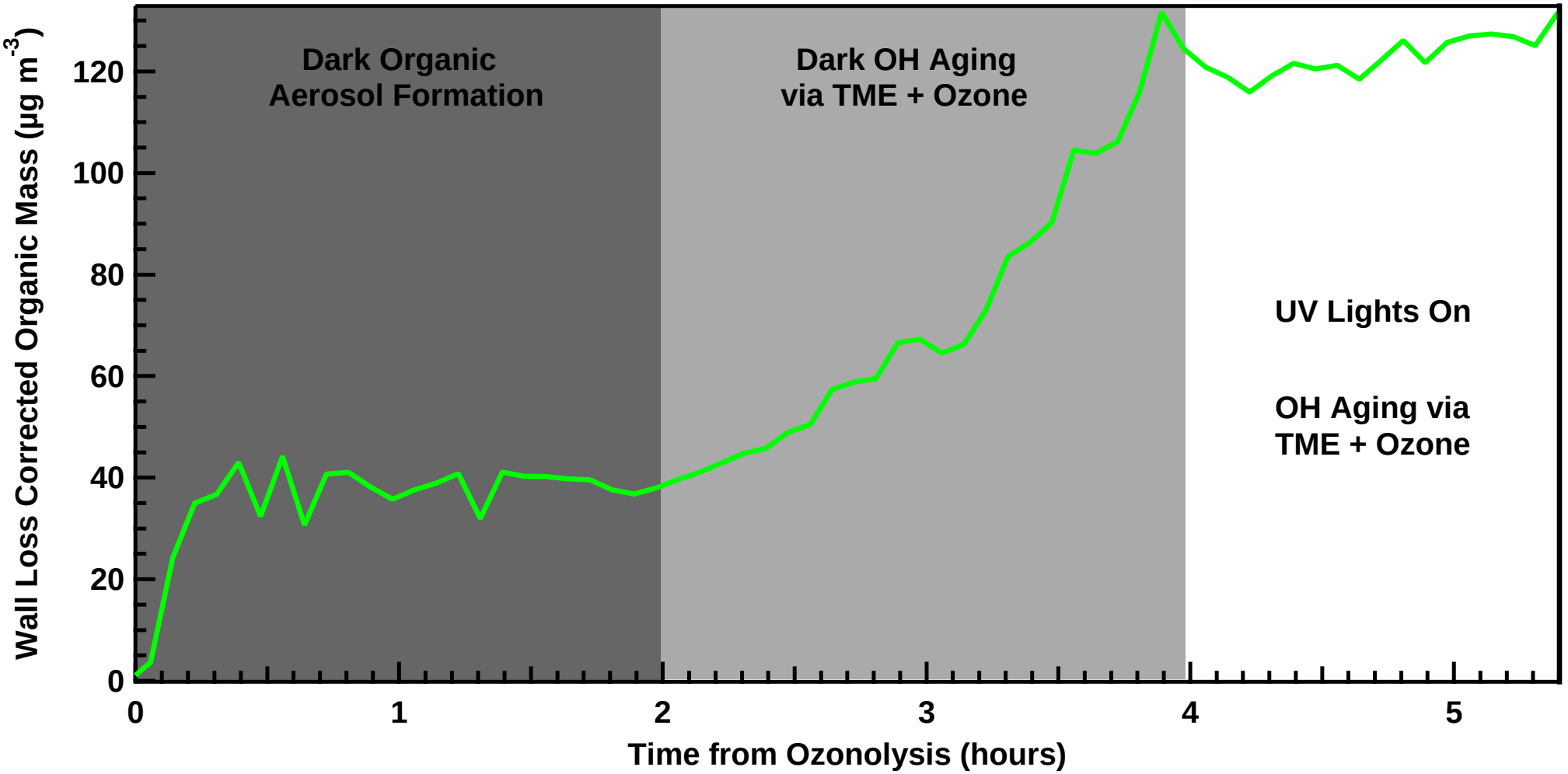
Holy Crap?!

- Shrink using HOOH + UV as OH source.

(Note – all CMU results based on AMS Org:Sulfate.)

[Henry, *et al.*, in prep]

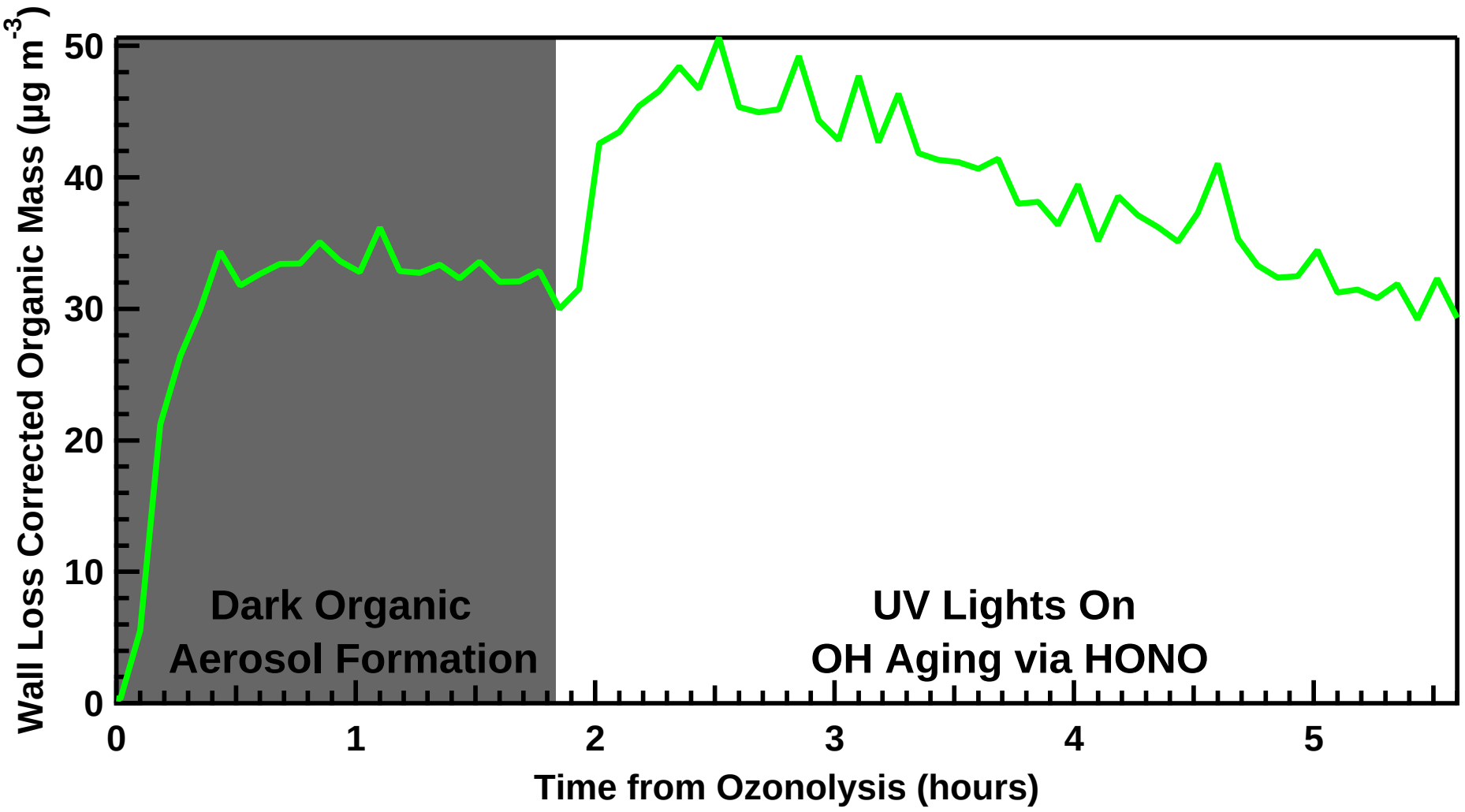
CMU TME + O_3 + hν (360 nm)



- UV halts growth using TME + O_3.

[Henry, *et al.*, in prep]

CMU HONO + hν (360 nm)

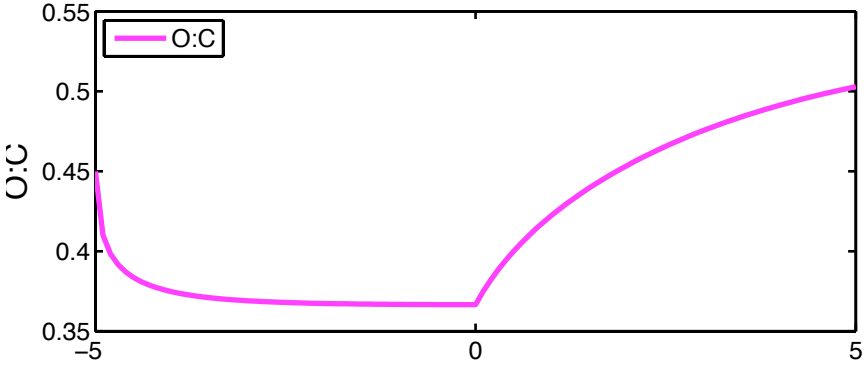


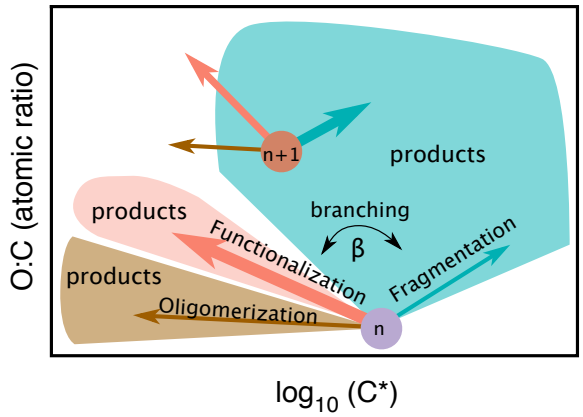
I lied.

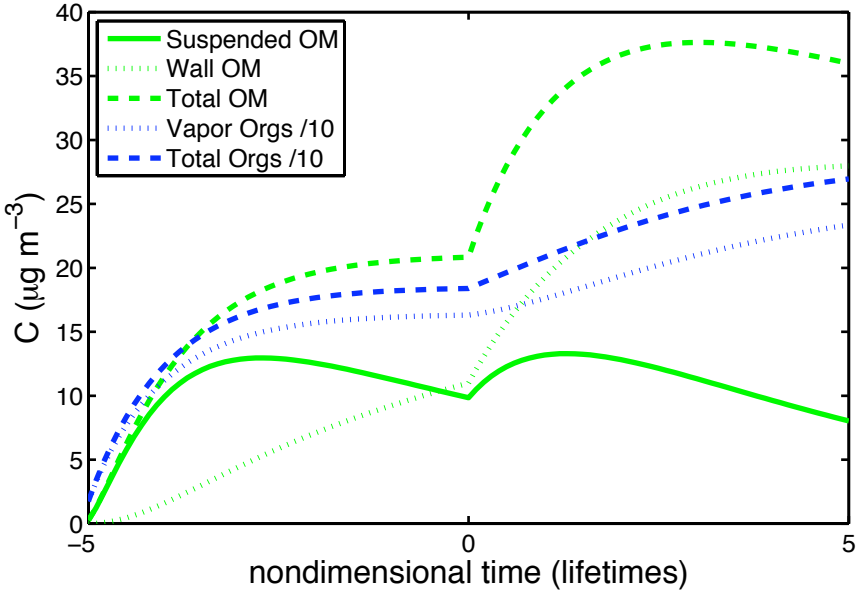
- HONO at CMU is *not* identical to PSI.
- SOA shrinks again after long exposure (less OH after 1st hr).

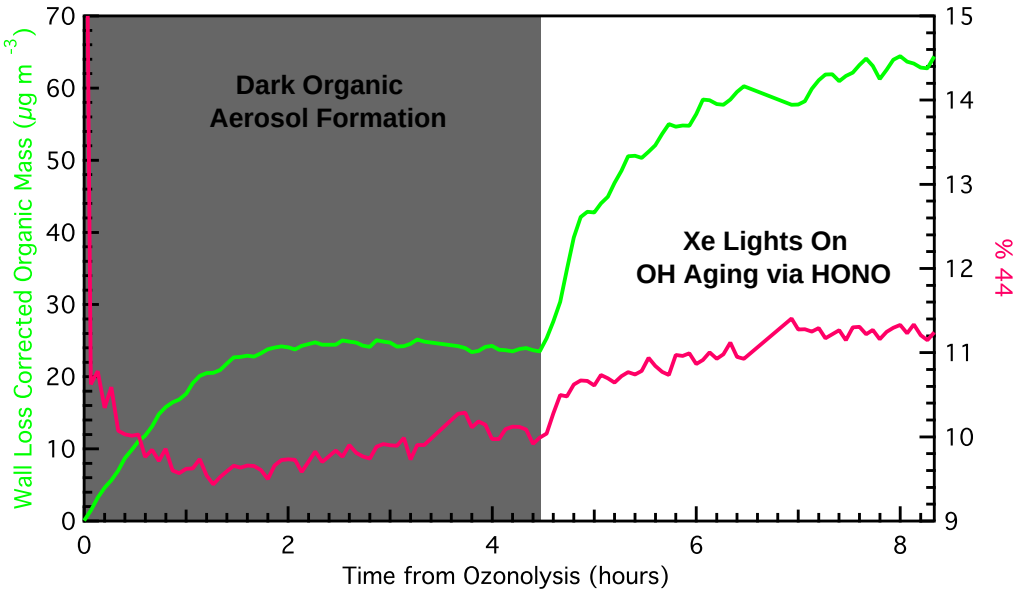
[Henry, *et al.*, in prep]

2-D Model





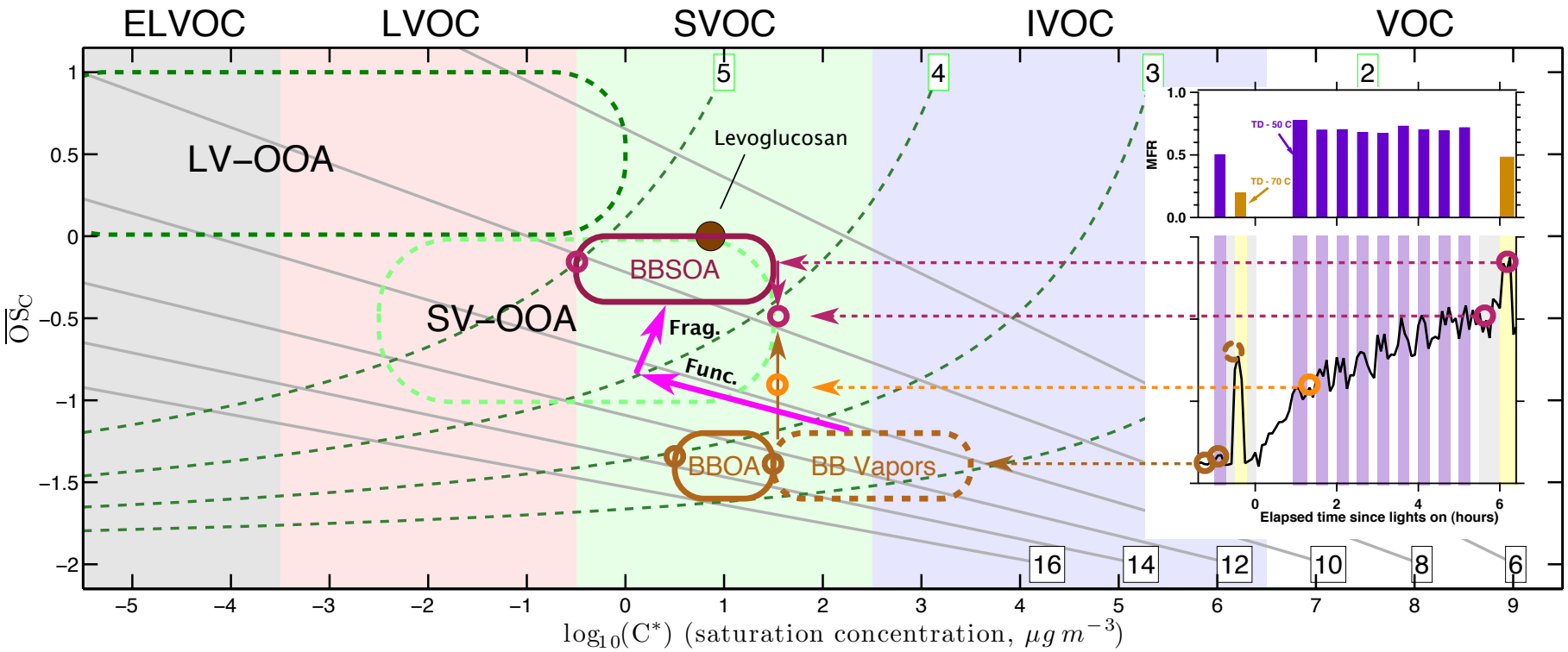




- Model reproduces broad features of data.
- Most products fragment ($O:C^{(1/6)}$).

[Donahue, *et al.*, in prep]

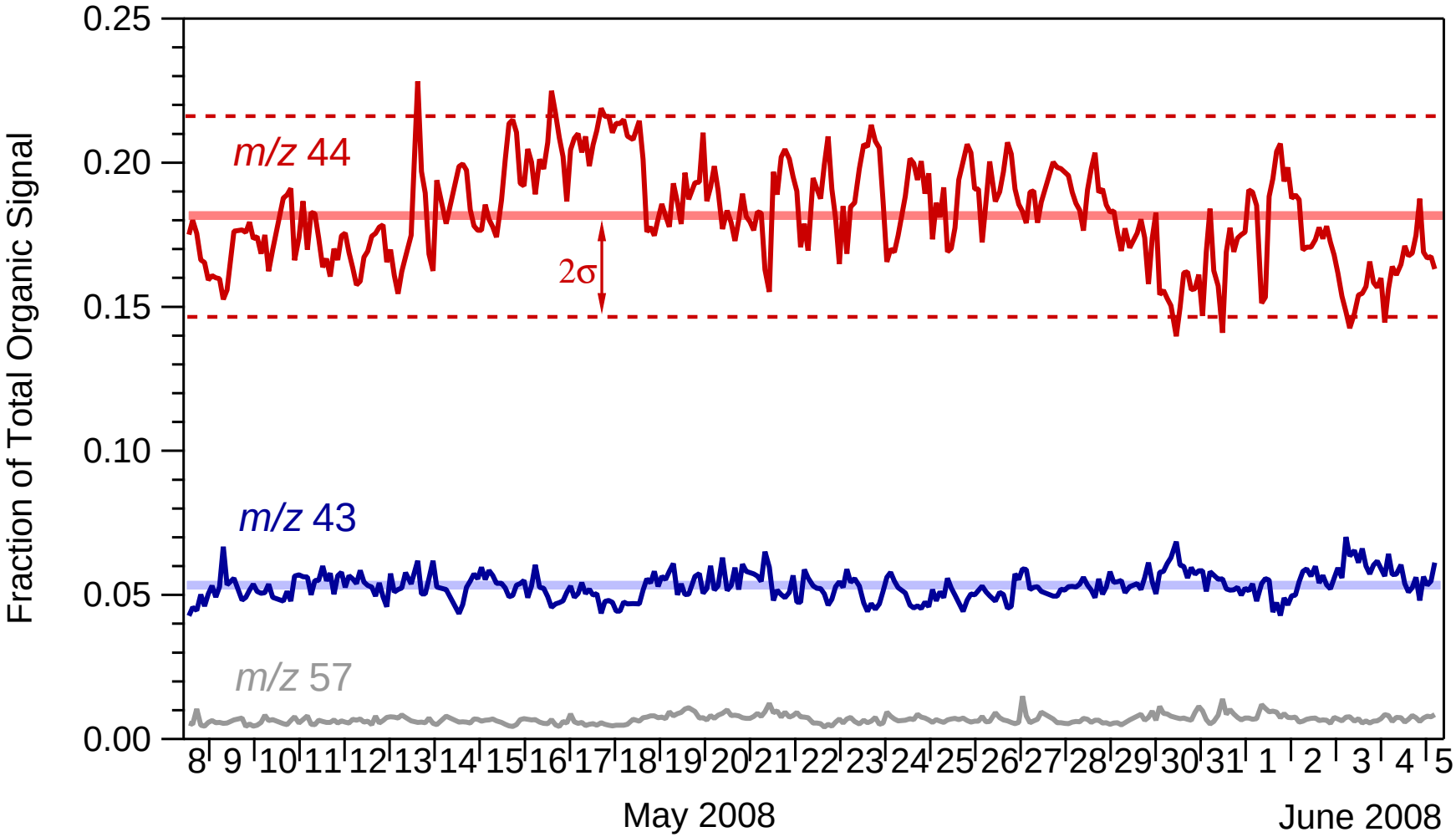
2D-VBS as Diagnostic



- A "skew-T" diagram for OA lab and field data.
  (BBSOA involves substantial fragmentation).

[Kroll *et al.,Nature Chem.*, submitted; Donahue *et al.*, x3, in prep]

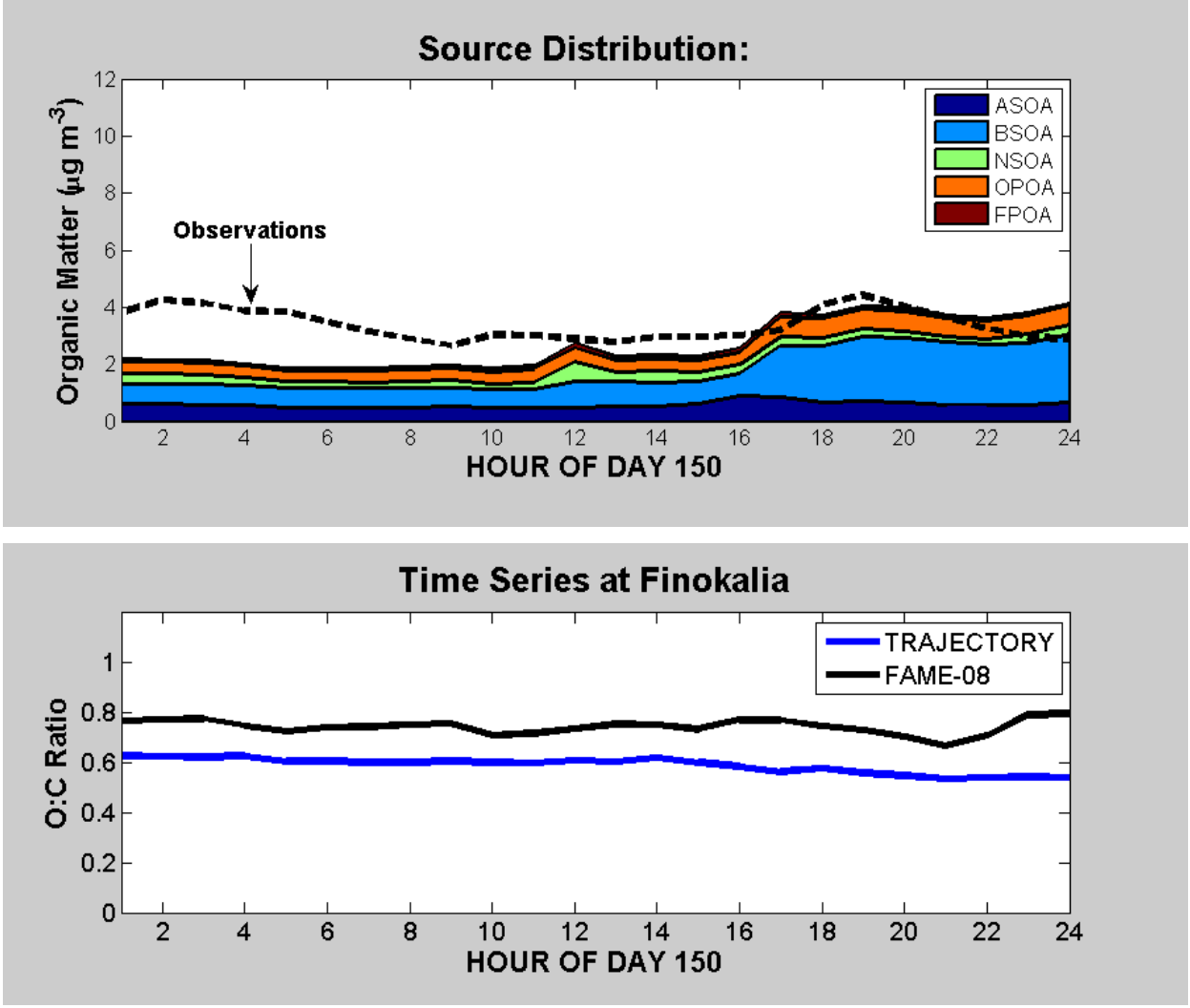
What Happens in the Remote Atmosphere?



- FAME-08 OA composition.
- By May-June OH levels in eastern Mediterranean very high.
- **All** OA in FAME 08 highly oxidized (LV-OOA), no matter what source.
  - Mean fraction f_{44} = 0.18, so $\overline{OS}_c \simeq +0.3$.

[Hildebrandt *et al., ACPD* **2010]**

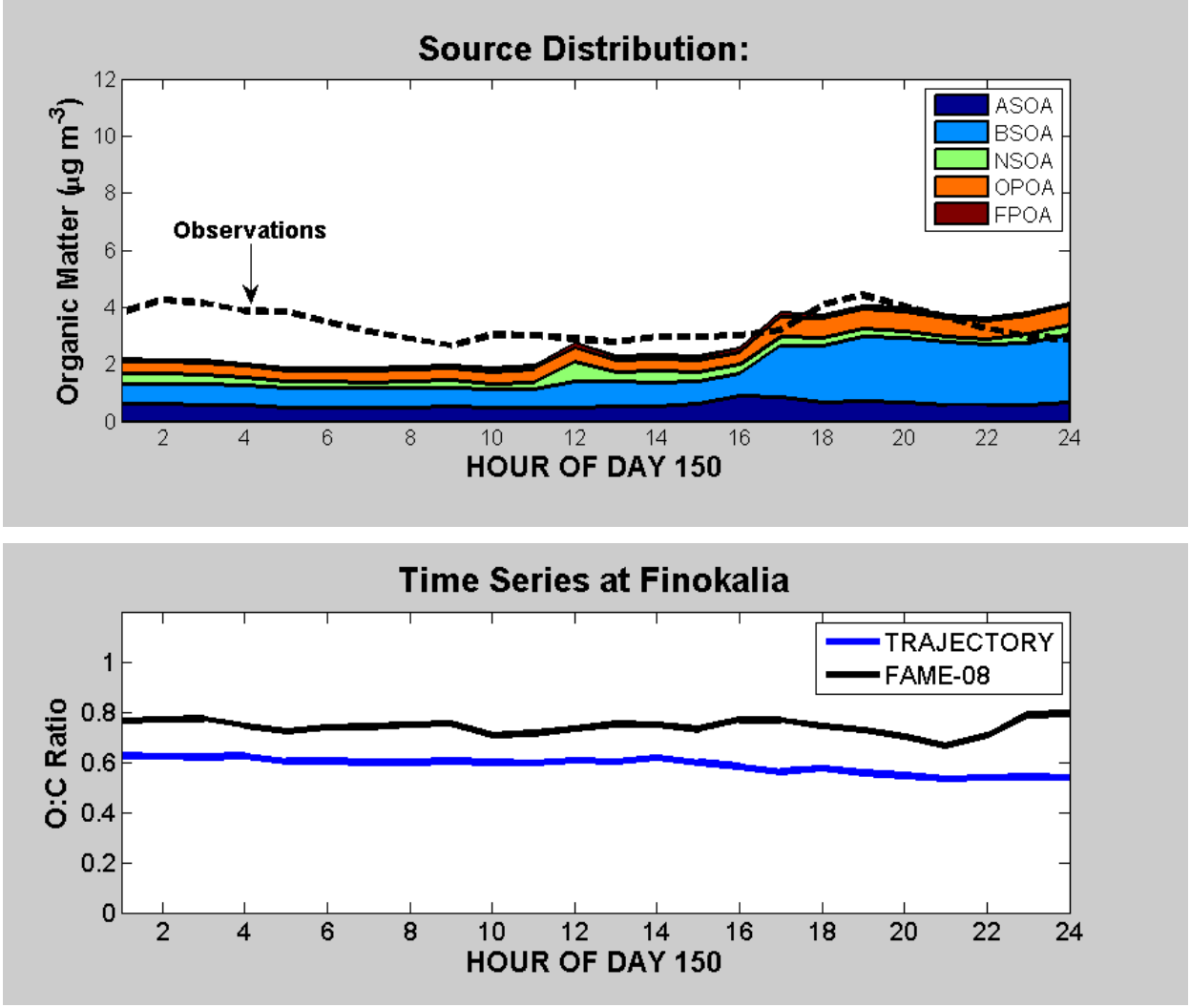
Lagrangian Model with 2D Basis Set



- FAME-08 OA composition.

[Murphy *et al.*, in preparation]

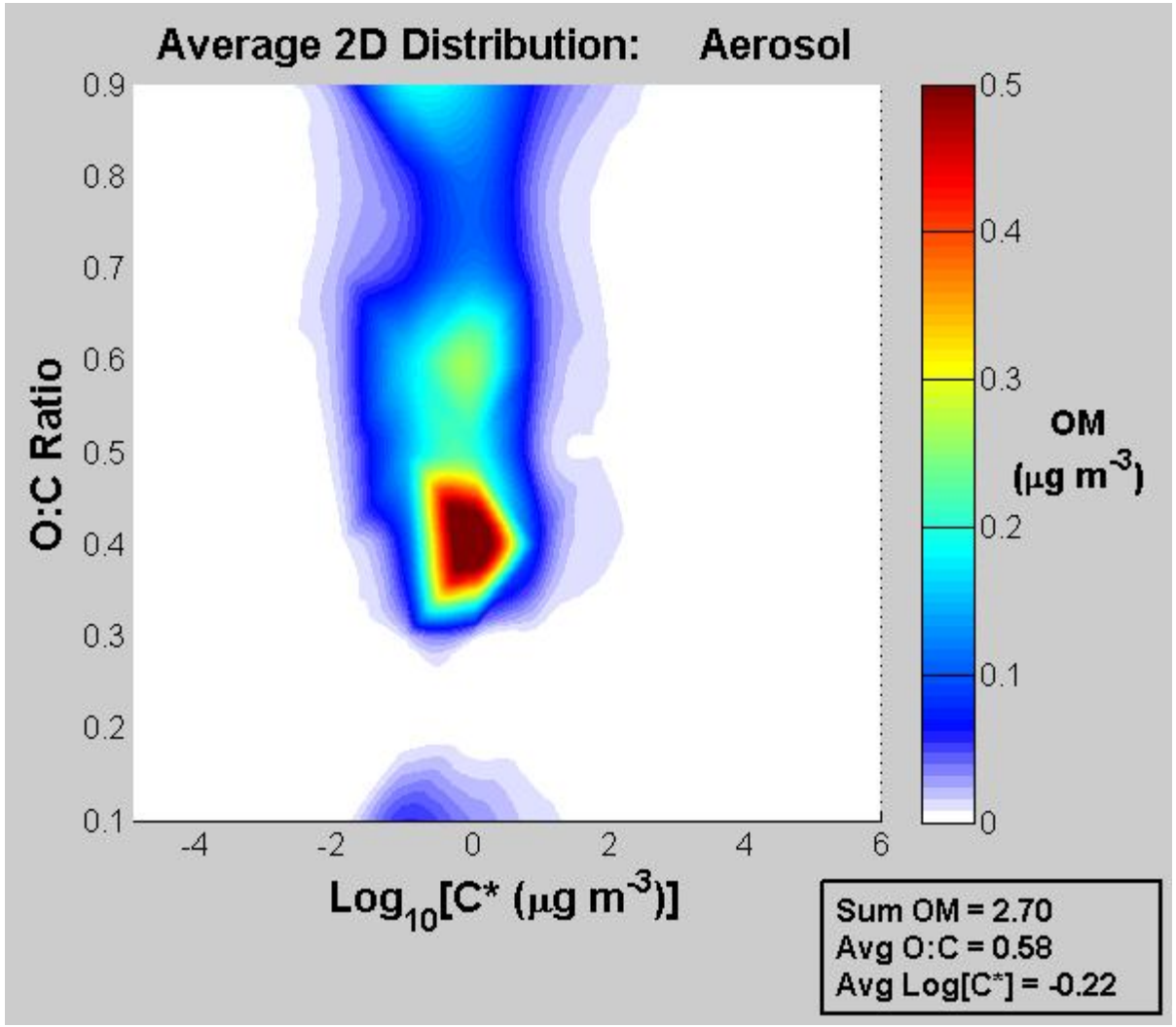
Lagrangian Model with 2D Basis Set



- Comes close on OA levels and oxidation state.

[Murphy *et al.*, in preparation]

Lagrangian Model with 2D Basis Set



- Distribution still a little low in O:C.
- Still - 1 bin mechanism, so OA too volatile.
- Kernel constrained by above experiments in progress.

[Murphy *et al.*, in preparation]

Conclusions

- OA incredibly dynamic, photochemically active in gas phase,
- Photochemical sources and sinks of OA will be needed (OA is an intermediate),
- OA aging is a vital (dominant) part of OA behavior,
- Eastern US has large anthropogenic and biogenic SOA contributors, they mix.
- We have a framework to describe all of this – some of the pieces are in place.
- 30 papers: 10 published, 5 submitted, 15 in preparation...