Recent Aerosol Field and Lab Results, and Implications for Modeling

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University of Colorado-Boulder

Showing data from many collaborators

8th International GEOS-Chem Meeting
Harvard University, 2-May-2017

Pikes Peak from BEACHON-RoMBAS site, D. Day

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NSF NASA UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

CIRES

Outline

- Acidity in remote areas
- Organic Aerosols (OA)
  - Intro
  - Isoprene SOA
  - SOA from Pollution
  - SOA from Biomass Burning
  - Global OA in remote troposphere

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- **Acidity in remote areas**
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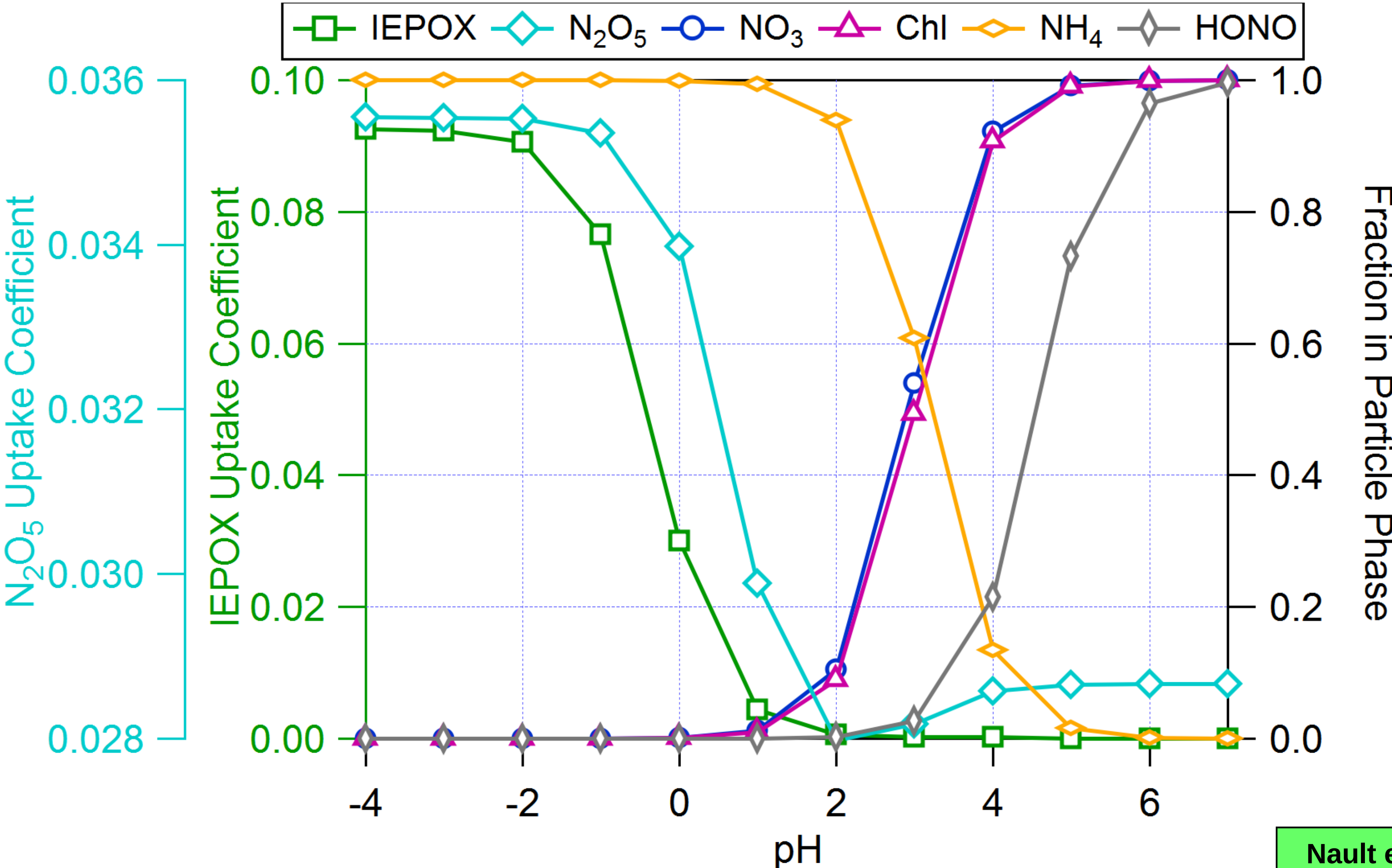
Many Important Atmospheric Chemistry Processes Depend Strongly on pH



Nault et al. in prep.

Calculations done with Aerosol Liquid Water = 2.5 μg m^{-3} and T = 280 K. NO_3, Chl, and NH_4 Partitioning calculated using eq. from Guo et al., ACPD, 2017; N_2O_5 uptake adapted from Bertram and Thornton, 2009; IEPOX uptake calculated using eq. from Gaston et al., EST, 2014; HONO calculated adapting eq. from Guo et al., ACPD, 2017;

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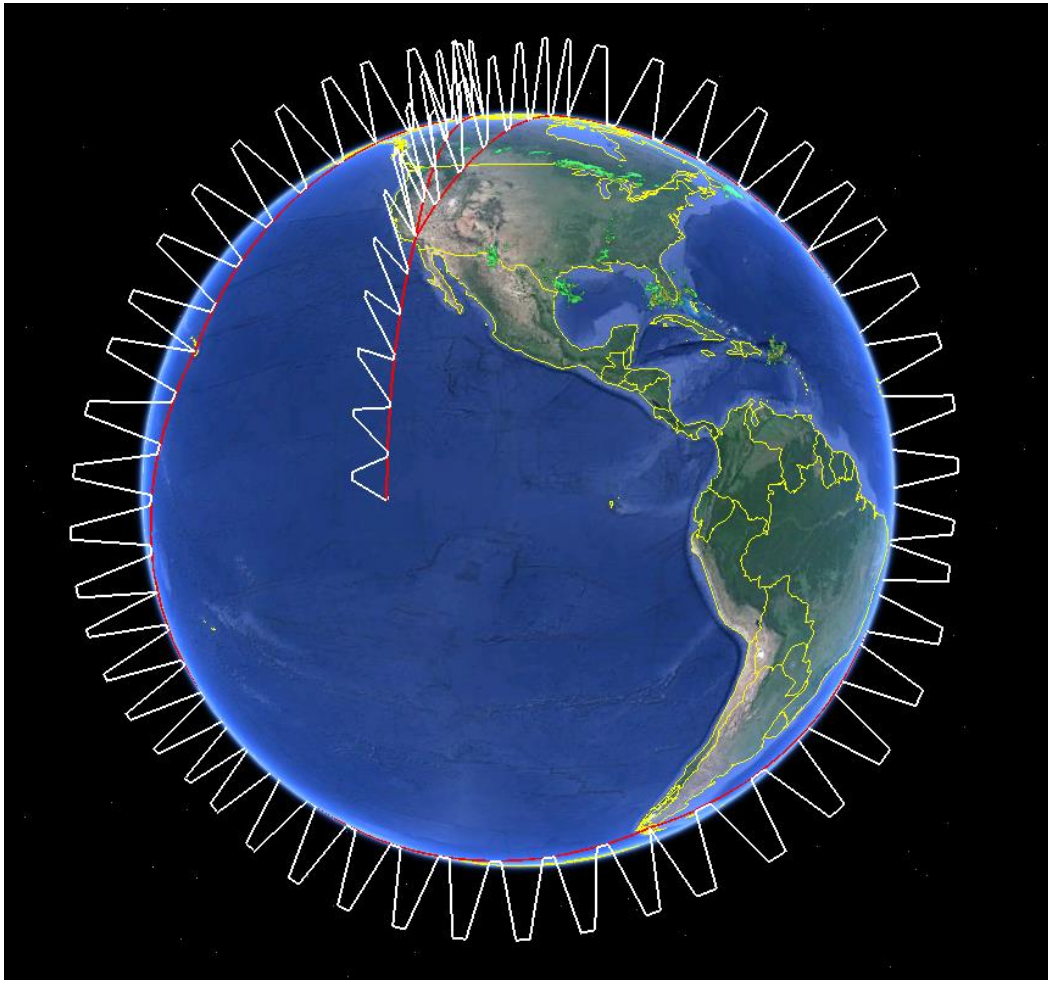
NASA ATom Project 2016-2018

- Extensive systematic sampling of the global atmosphere
- Far from the sources of funding! ☺ ☺ ☺
- 4 circuits in 4 seasons
  - 2 completed very successfully
  - 2 to go
- PI: S. Wofsy (Harvard)



Data shown here: http://tinyurl.com/atom-jg

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NASA ATom Project

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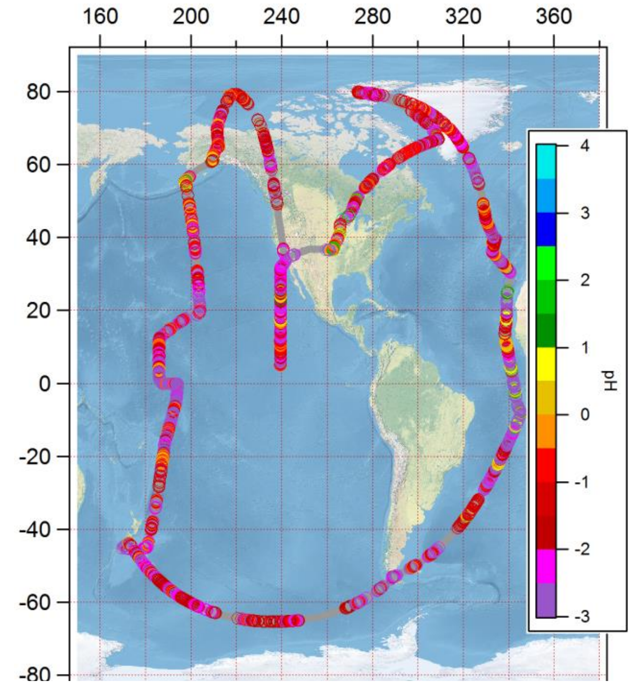
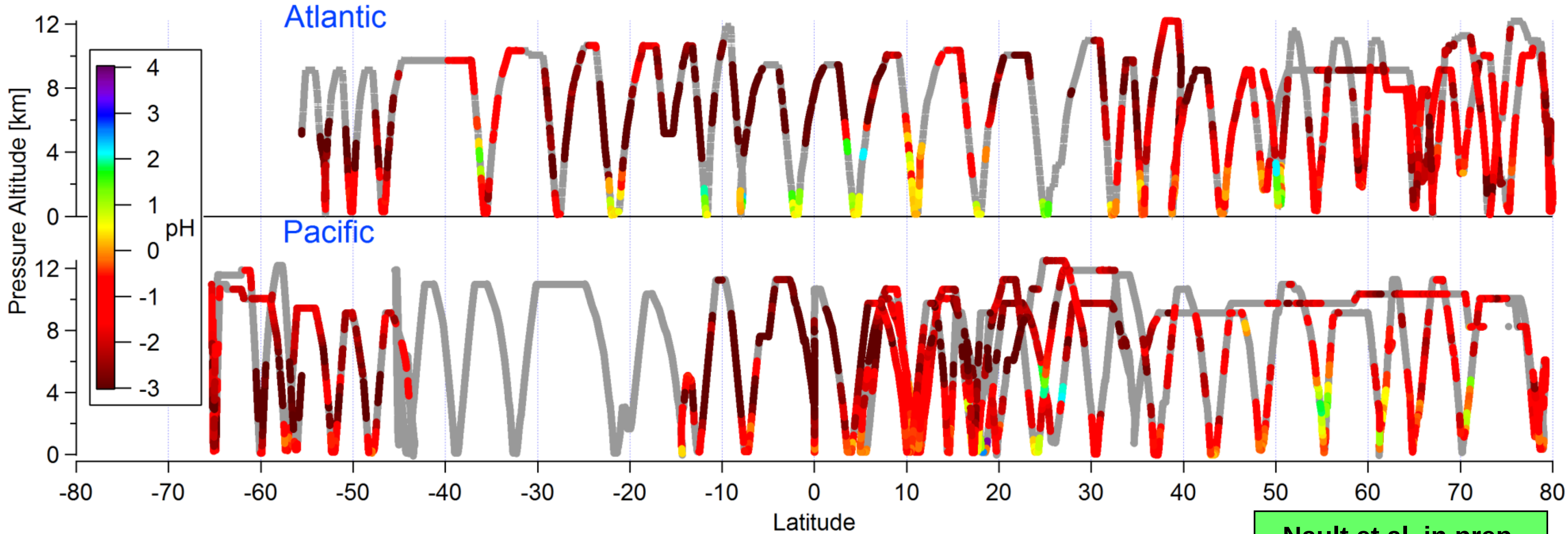
Remote Submicron Aerosol is very Acidic

- pH from E-AIM model with measurements as inputs
- In both ATom-1 and 2





Nault et al. in prep.

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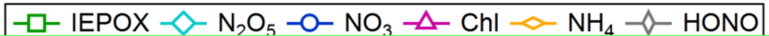
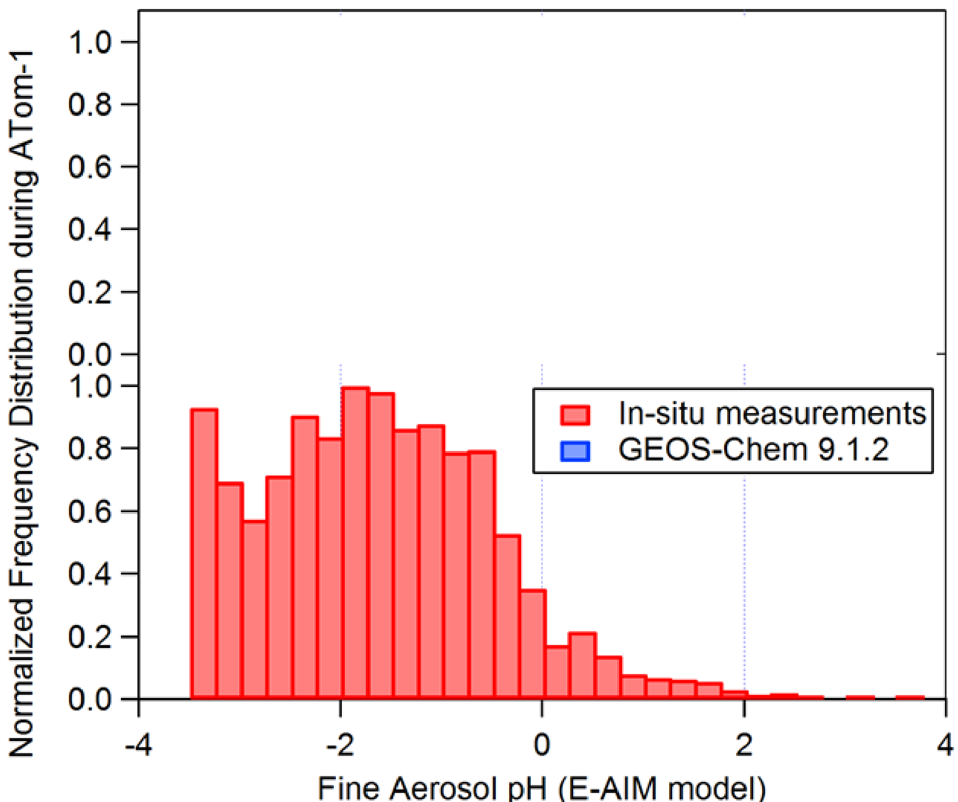
Aerosol Acidity in the remote troposphere

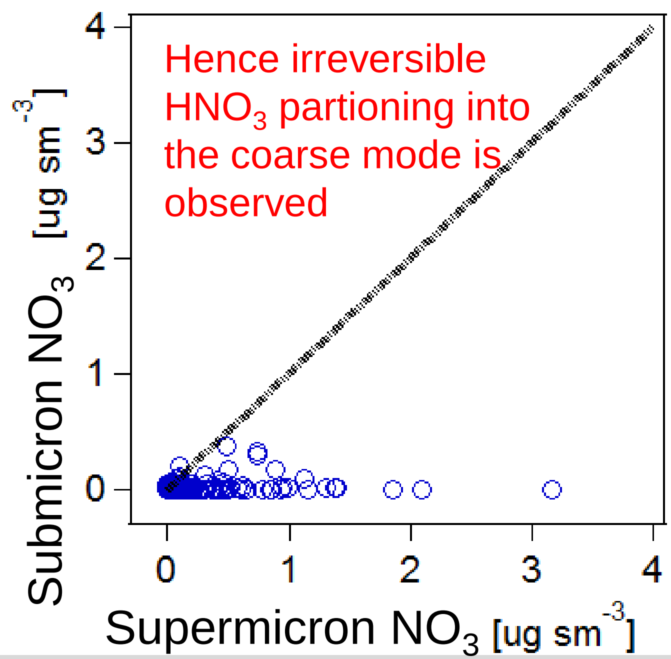


- Take home points
  - Remote aerosol is very acidic (mostly pH < 0)
  - GEOS-Chem 9.1.2
    - Remote pH may be too high by + 1 unit
    - NH_3(g) might be too high – Very preliminary

Nault et al. in prep.



- *Preliminary*
- Standard GEOS-Chem results in pH about 1 unit higher



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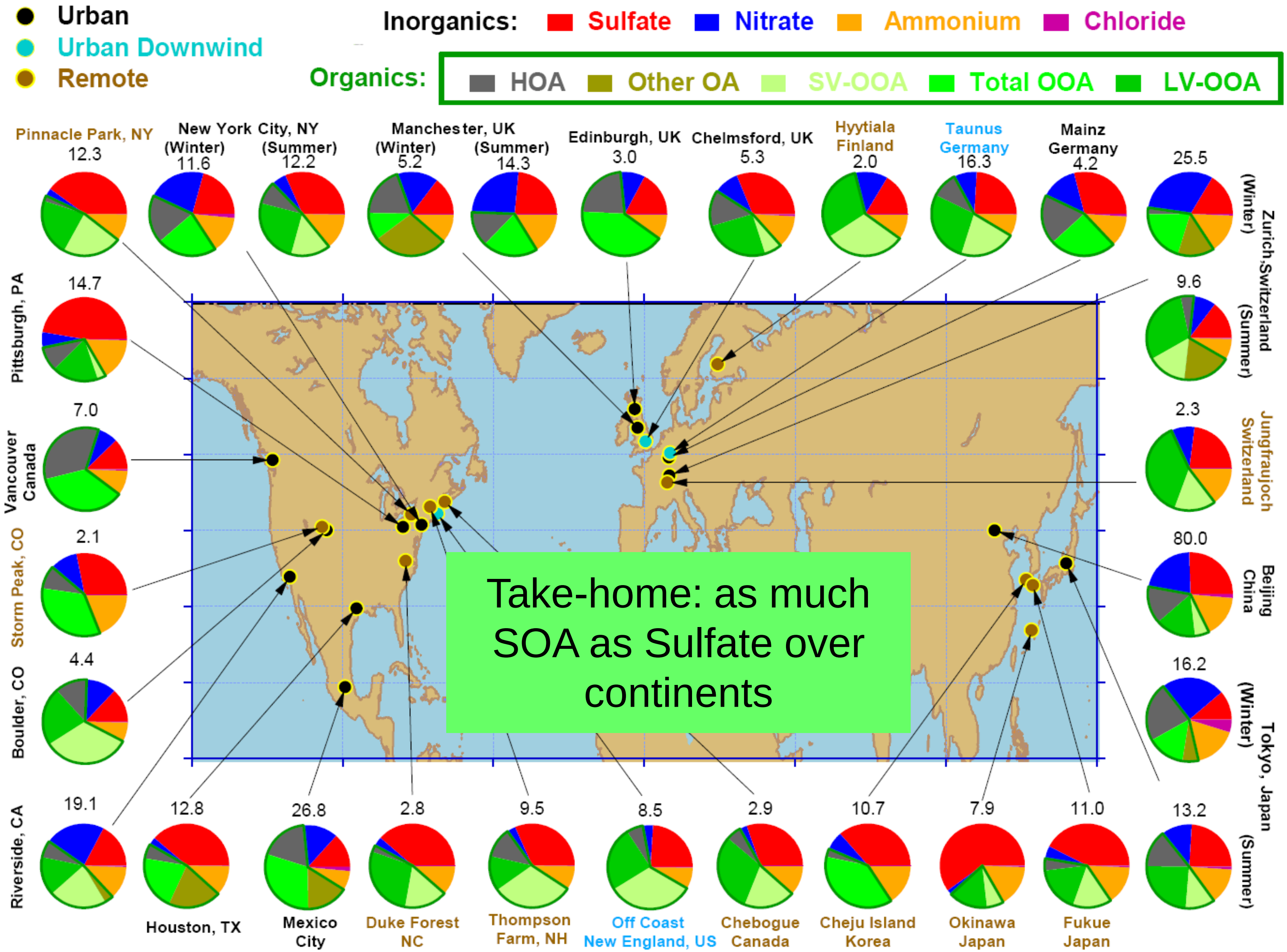
"Worldwide" Submicron Aerosols



Jimenez et al. Science 2009

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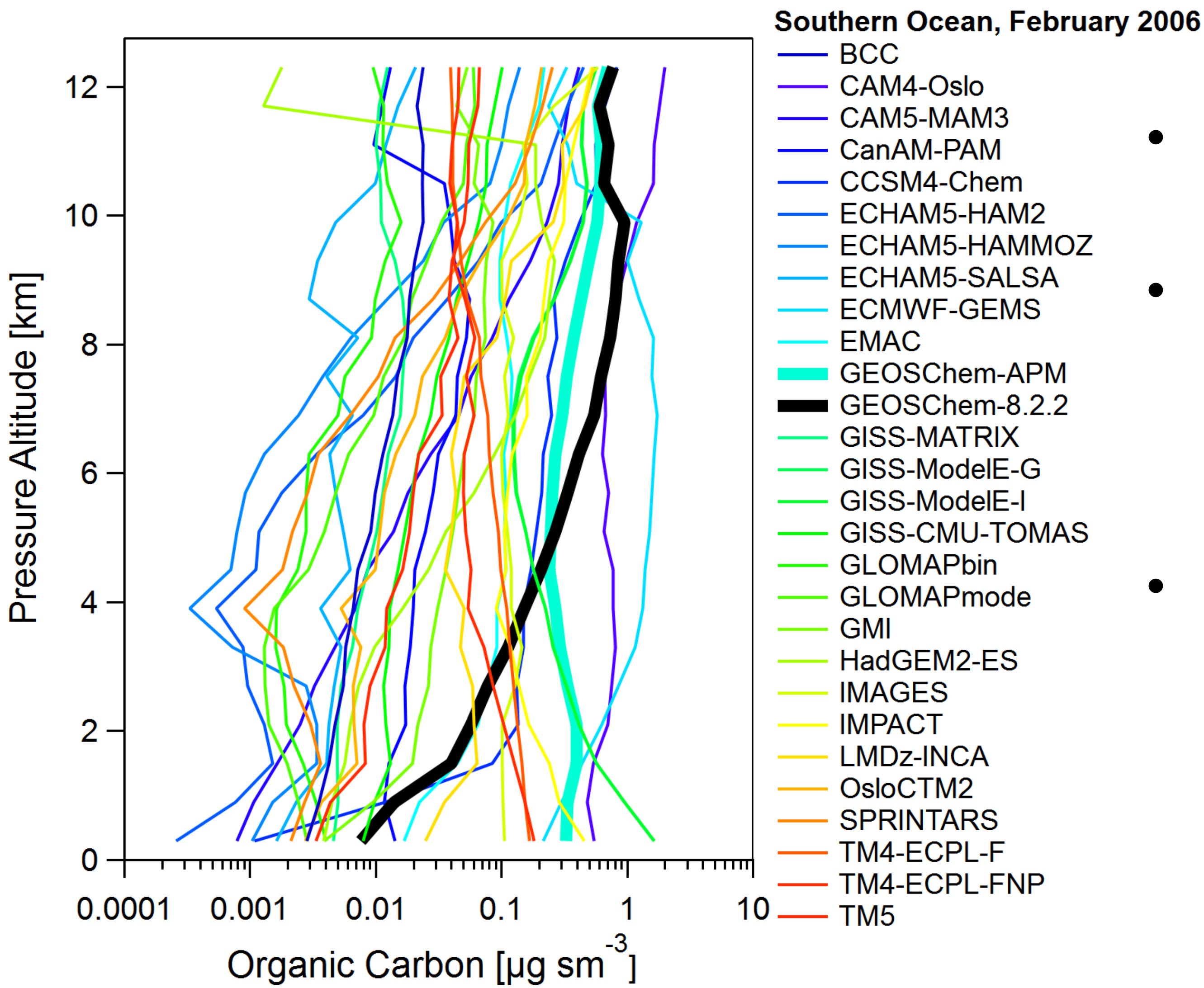
2014 AEROCOM Model Intercomp

AEROCOM-2 (Tsigaridis et al. 2014)



- Global models differ by x1000
- No indication that more complex models are doing better
- GEOS-Chem v.8.2 and APM on the higher side

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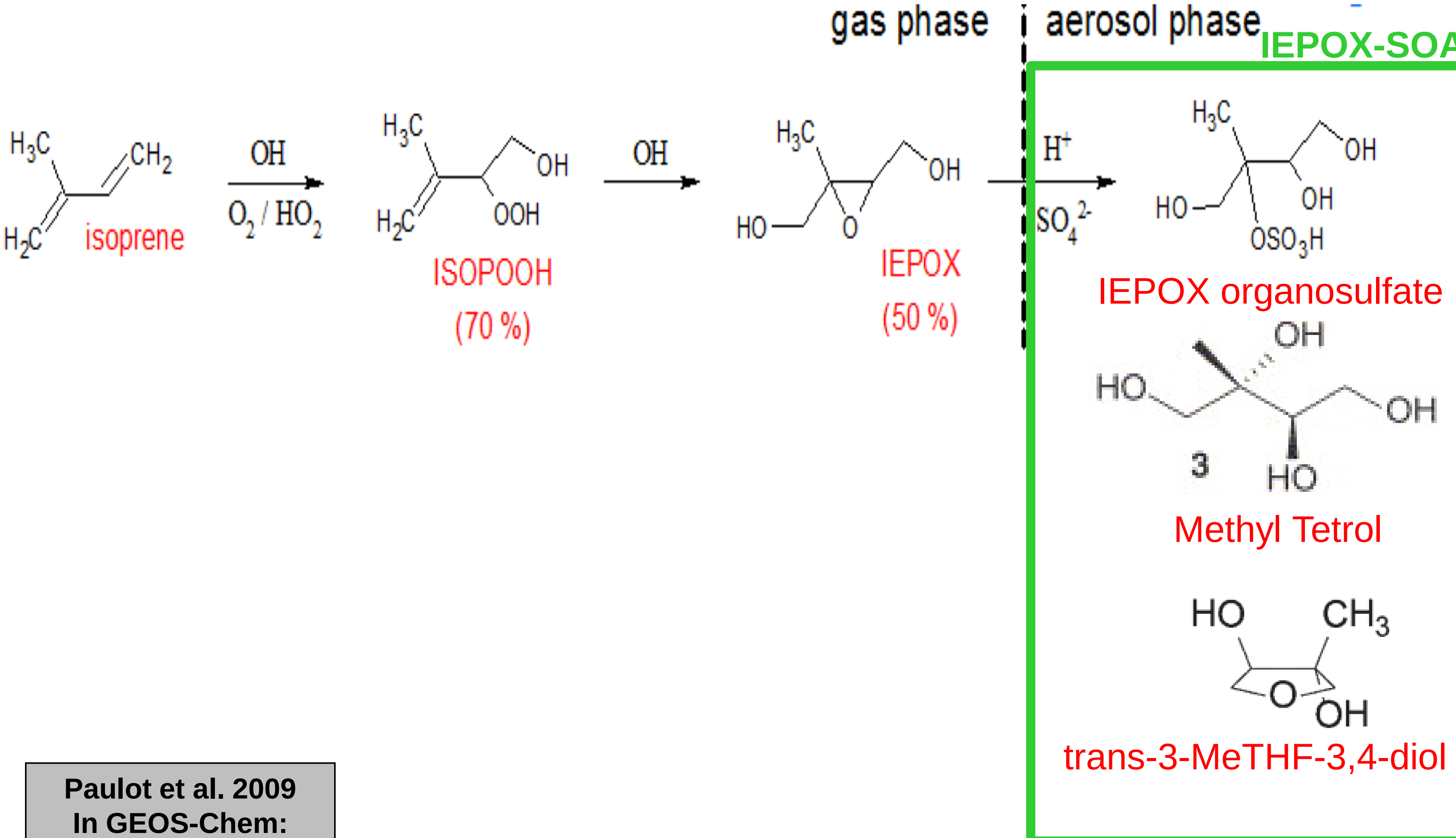
SOA from Isoprene IEPOX



(Really mostly oligomers)

Paulot et al. 2009
In GEOS-Chem:
Marais et al., 2016
Bates et al.

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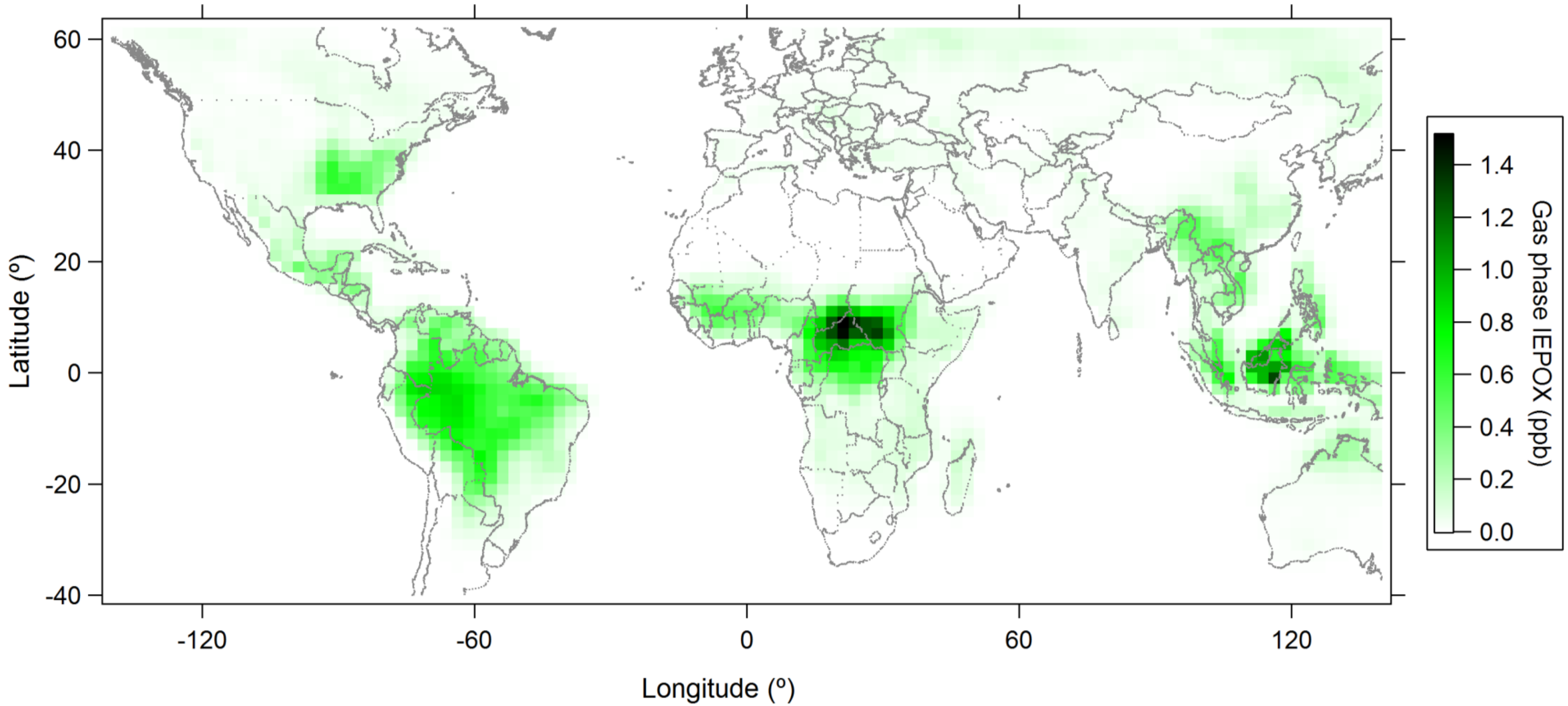
Measured IEPOX-SOA Globally

IEPOX-SOA Other OA

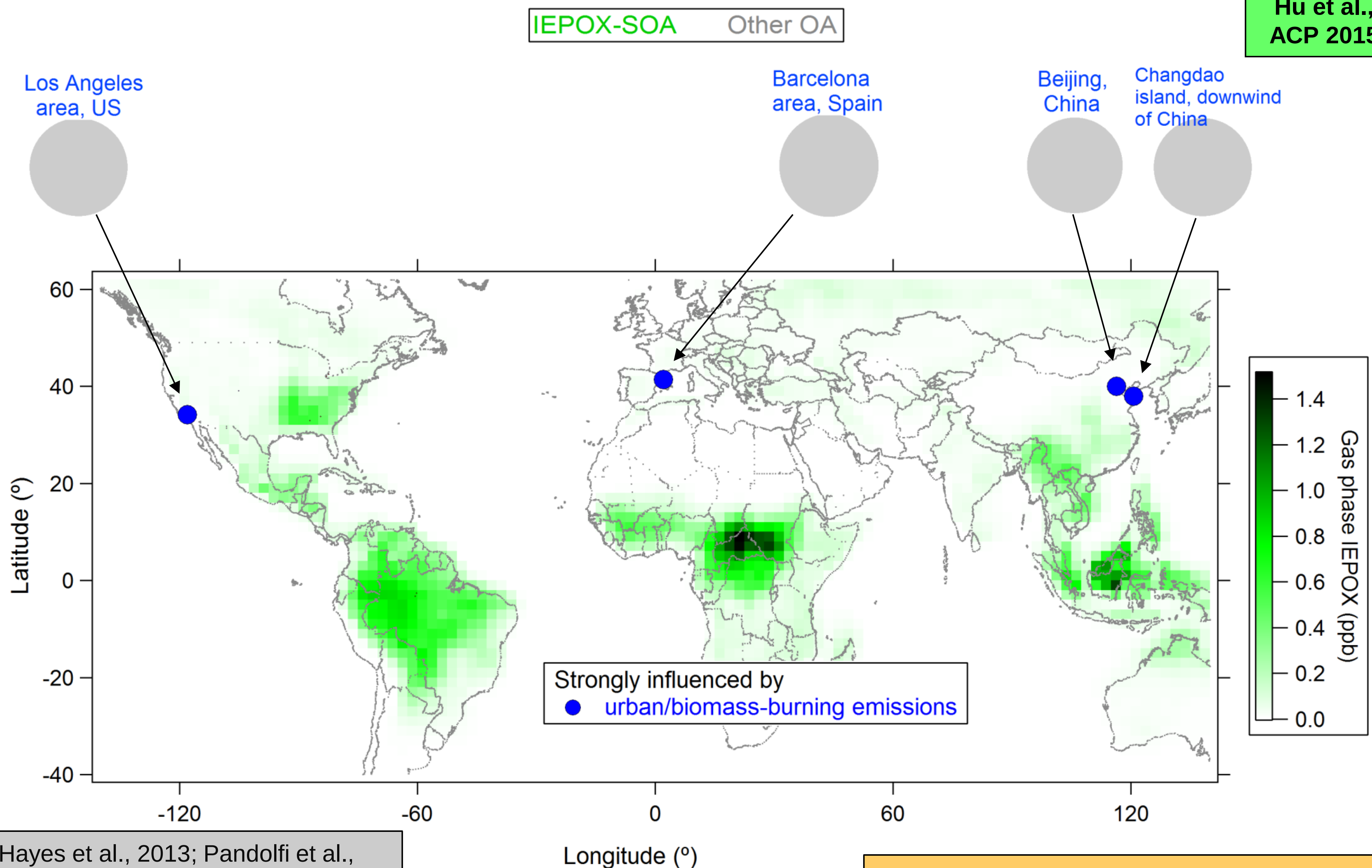
Hu et al., ACP 2015

GEOS-Chem gas phase IEPOX for July 2013 by Fabien Paulot



Measured IEPOX-SOA Globally

Hu et al., ACP 2015



Hayes et al., 2013; Pandolfi et al., 2014; Hu et al., 2013

GEOS-Chem gas phase IEPOX by Fabien Paulot

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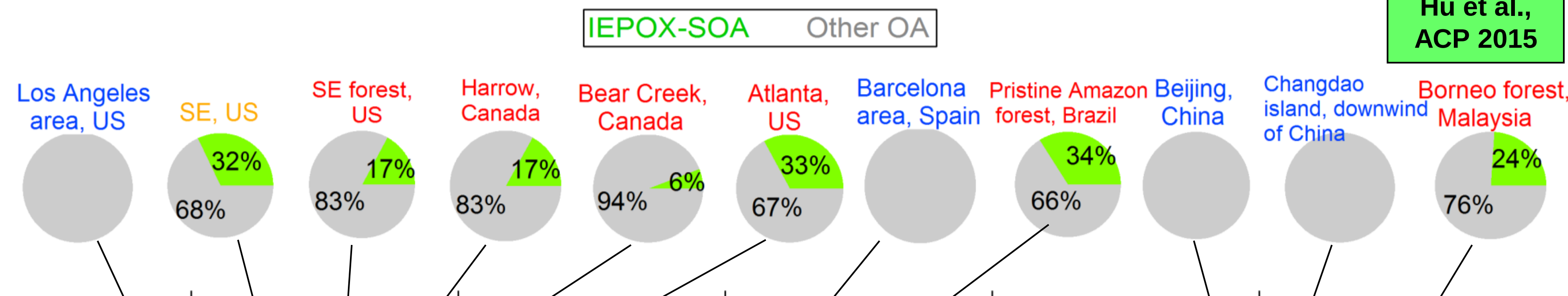
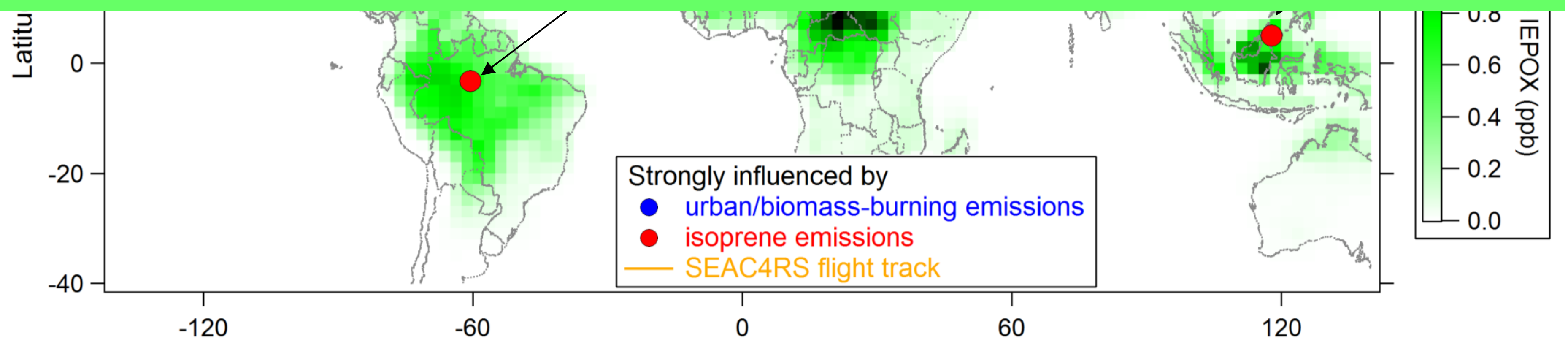
Measured IEPOX-SOA Globally

Hu et al., ACP 2015



- Take home points
  - IEPOX-SOA important when high isoprene and limited NOx
  - It ages slowly (Hu et al., ACP 2016)
  - It is not the whole OA even there
  - There are several other important OA sources



Hayes et al., 2013; Pandolfi et al., 2014; Hu et al., 2013; Robinson et al., 2011; Chen et al., 2014; Budisulistiorini et al., 2013; Slowik et al., 2011

GEOS-Chem gas phase IEPOX by Fabien Paulot

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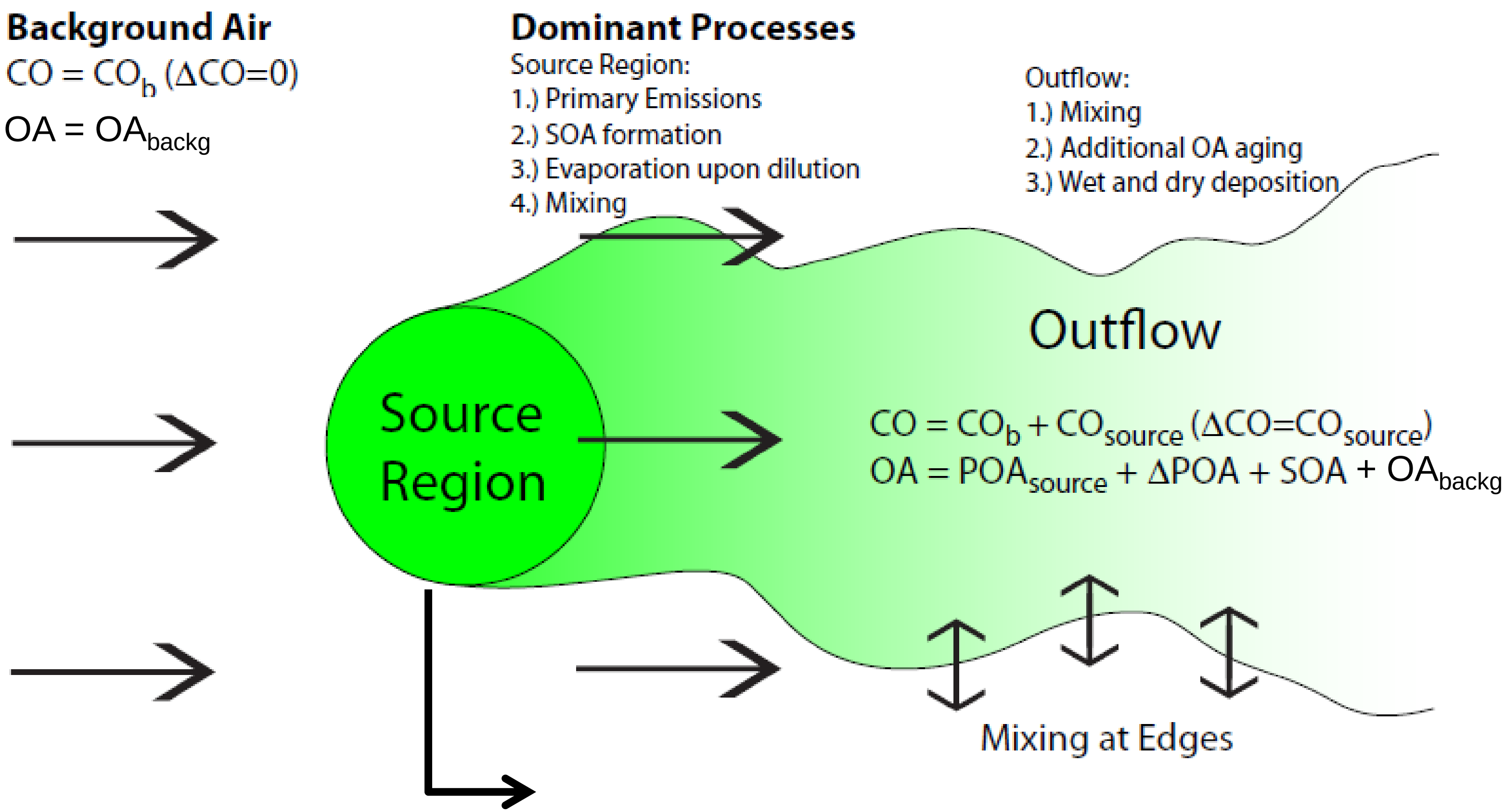
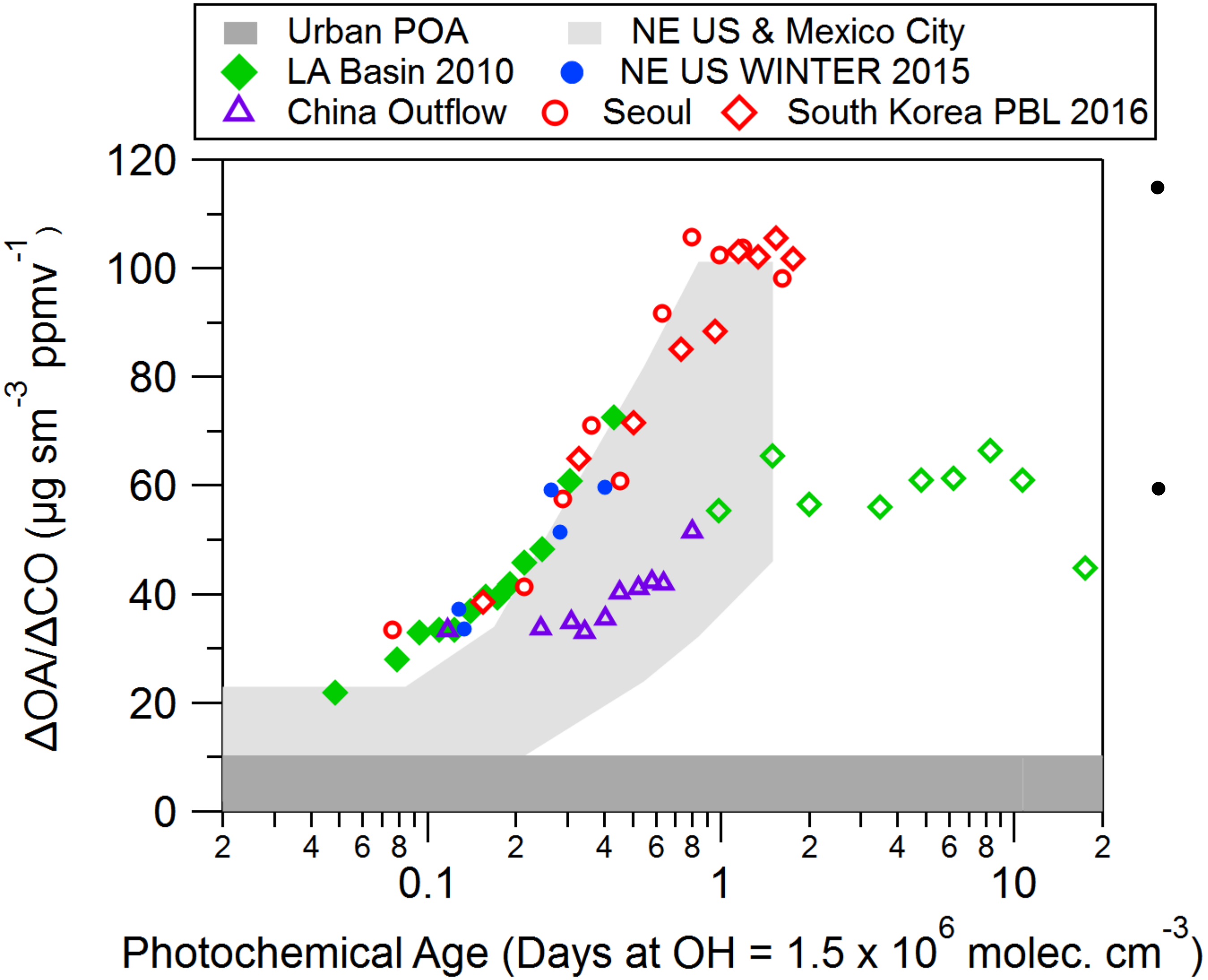
Quantifying SOA from large sources in a regional background



- ΔCO used as surrogate of SOA precursors
- It also allows to correct for dilution
- Use species ratios to estimate photochemical age

DeCarlo et al., ACP 2010

Pollution OA vs. Age



- Different locations similar when normalized in this way
- Aircraft and flow reactor data indicate SOA formation mostly done after 1 day

DeCarlo et al ACP 2010
Hayes et al JGR 2013
Hu et al. ACP 2013
Ortega et al. ACP 2016
Schroder et al. in prep.
Nault et al. in prep.

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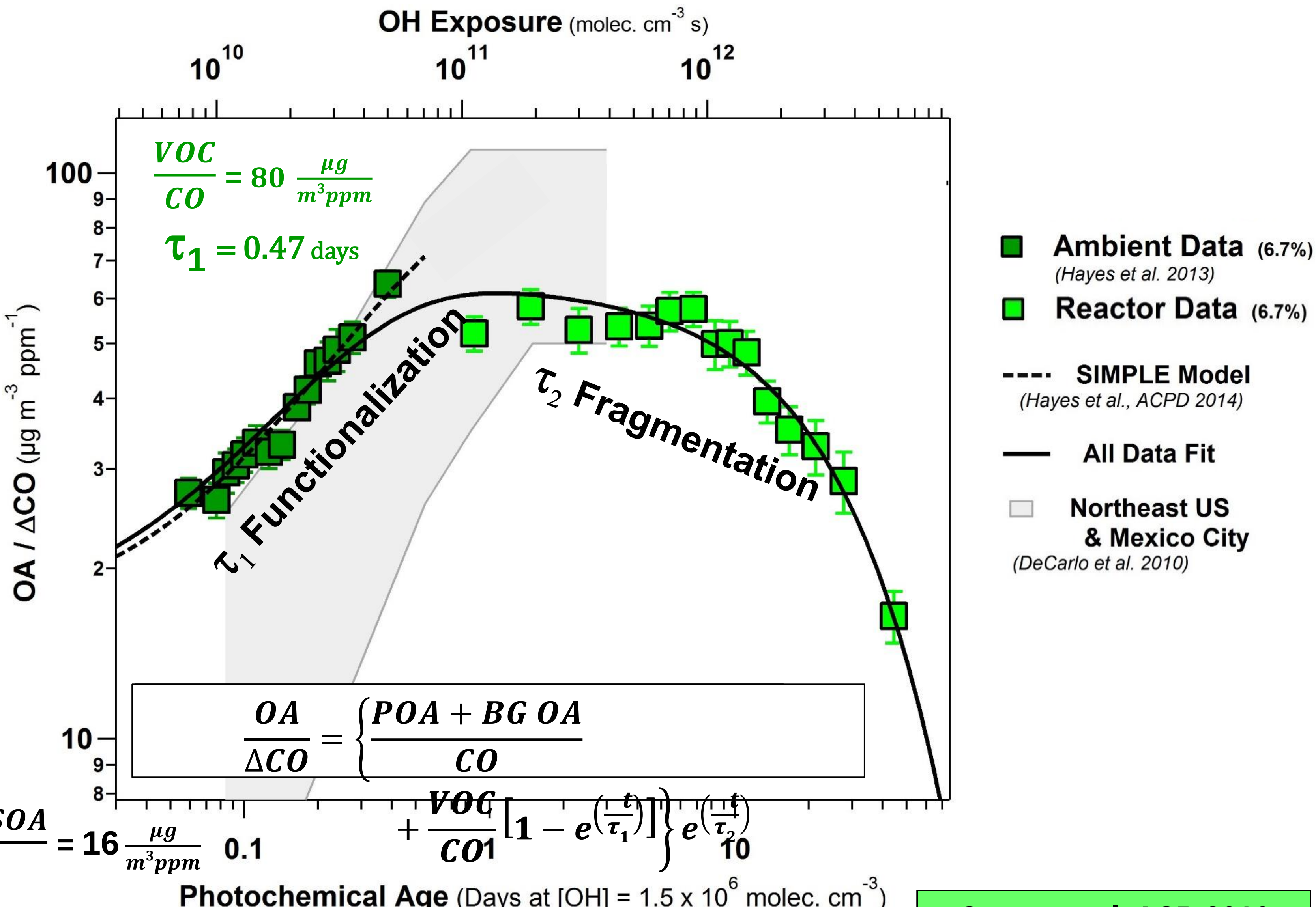
Evolution of OA with Age

CalNex LOS ANGELES



$$\frac{OA}{\Delta CO} = \left\{\frac{POA + BG\ OA}{CO} + \frac{VOC}{CO}\left[1 - e^{\left(-\frac{t}{\tau_1}\right)}\right]\right\} e^{\left(-\frac{t}{\tau_2}\right)}$$

$$\frac{POA+BG\ SOA}{CO} = 16 \frac{\mu g}{m^3 ppm}$$

Ortega et al. ACP 2016

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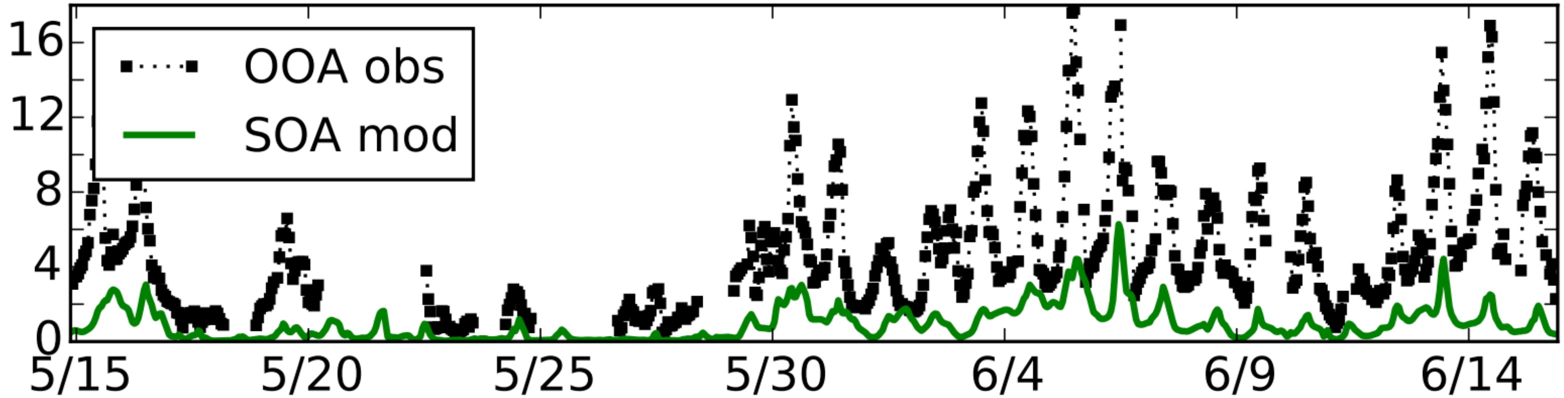
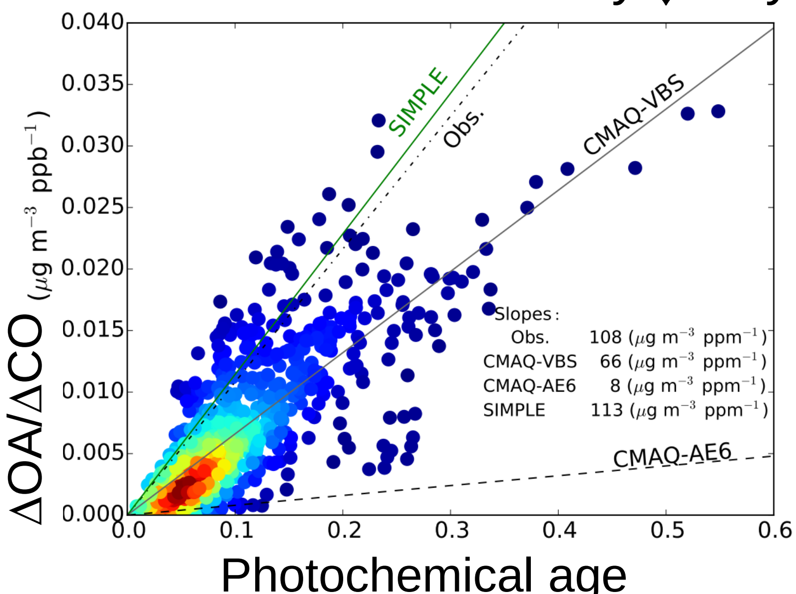
Use tracer ratios whenever possible!

- Initial result: CMAQ urban SOA low by x5.2



- Real: emissions ↓ or dispersion ↑ x2 ; phot. age ↓ x1.5 ; real urban SOA formation efficiency ↓ only x1.8!



- Take home point:
  - Compare tracer ratios when possible
  - Very useful to isolate different types of errors

Woody et al. ACP 2016

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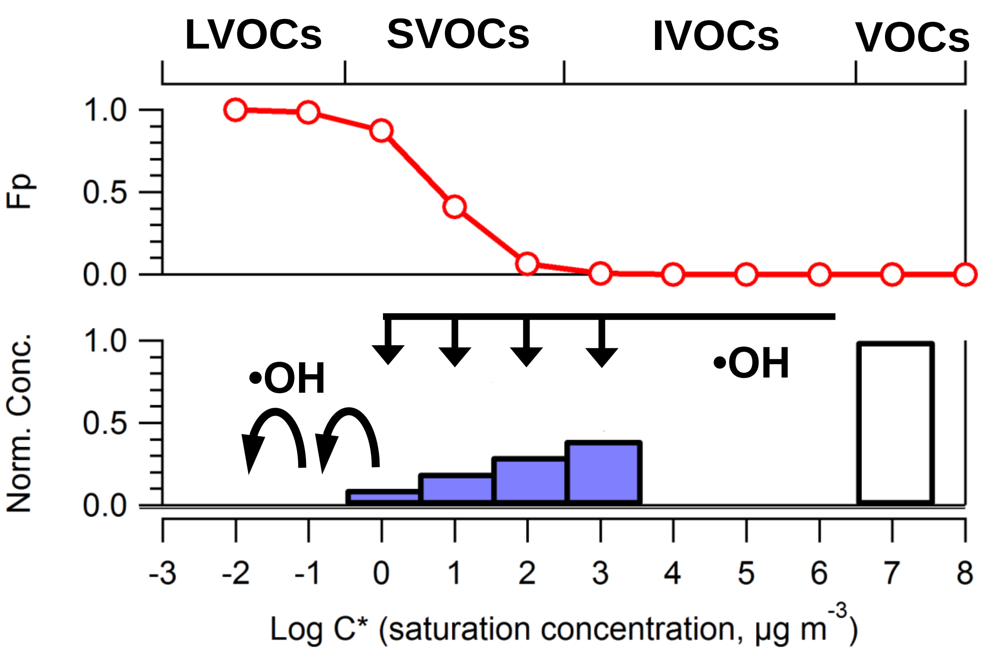
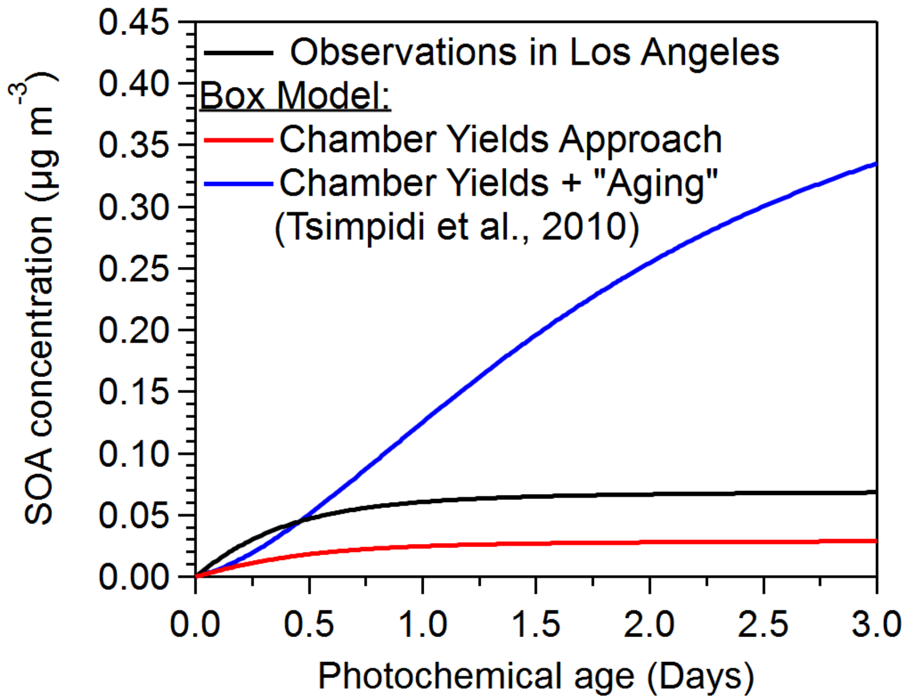
Careful w/ "VOC Aging" Parameterizations





- Added artificial "aging" to compensate for low SOA at low ages
- Empirical at the time. Likely compensating for later-discovered losses to Teflon chamber walls
- "Wild" unconstrained increases at high ages
- Excessive OA over larger scales

Tsimpidi et al., ACP 2010
Hayes et al., ACP 2015
Ma et al., ACPD 2016

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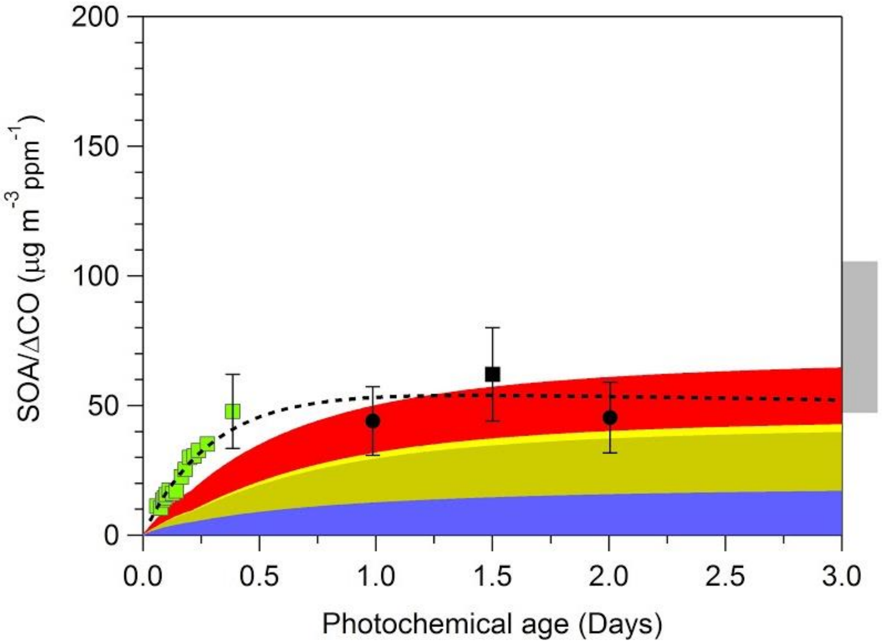
How to represent pollution SOA now

If you care about the details:
Use updated parameterizations
(e.g. Ma et al. ACPD 2017)



If you don't care about the details,
But want the right amount of
pollution SOA in your model runs

SIMPLE SOA Model

- "SIMPLifiEd parameterization of SOA from combustion emissions"
- Hodzic & Jimenez, 2011; Cubison et al., 2011; Hayes et al., 2015

- VOC* proportional to CO emissions as:
  E_{VOC*} / E_{CO} (g/g) = 0.069
- VOC* + OH → SOA_{nv}
- k = 1.25 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}
- where SOA_{nv} is non-volatile SOA

- More and more chemically-specific mechanisms will become available over the next decade

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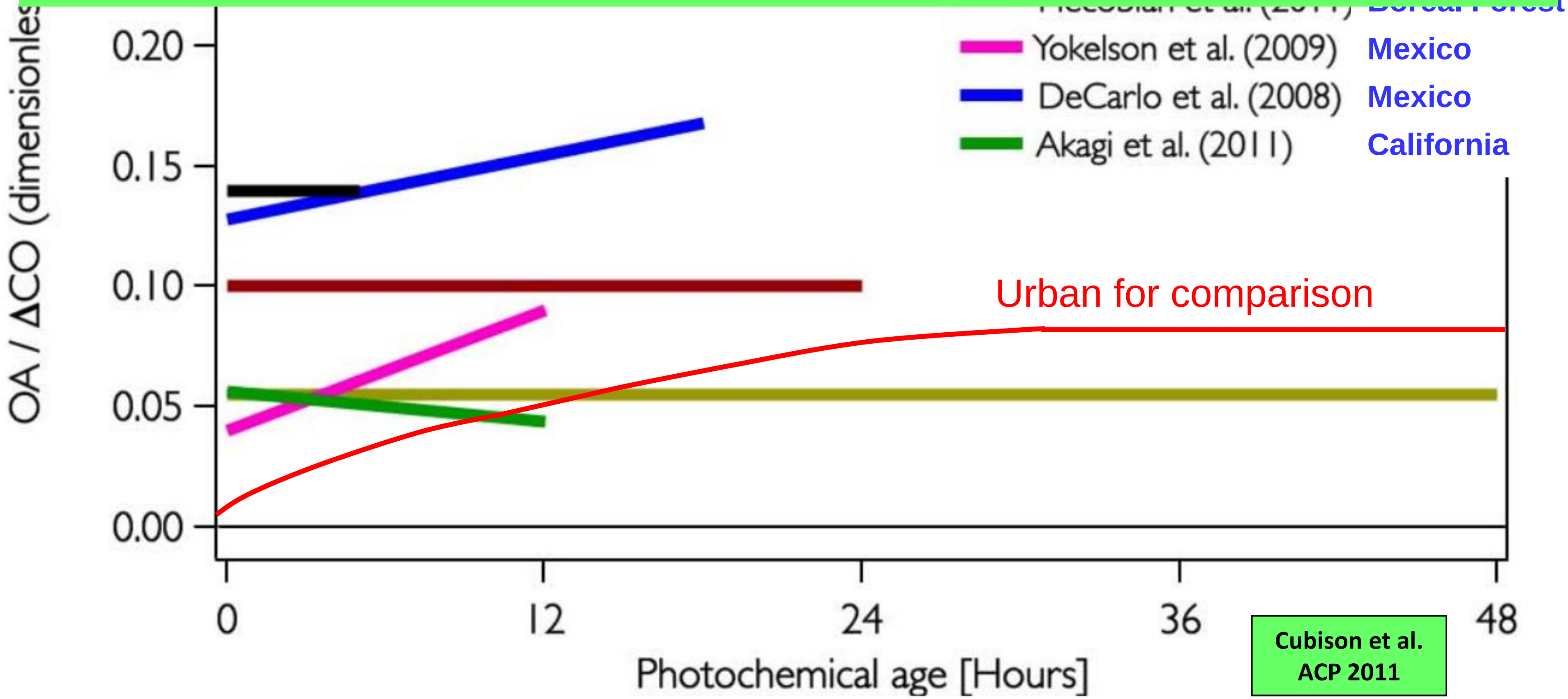
Net SOA Formation in Wildfire Plumes

Update (Rev. Geophysics, soon to be in press):
- 17 published aircraft studies on aging of BB emissions
  - 10: no change in OA with aging
  - 4: increase
  - 3: decrease



Cubison et al. ACP 2011

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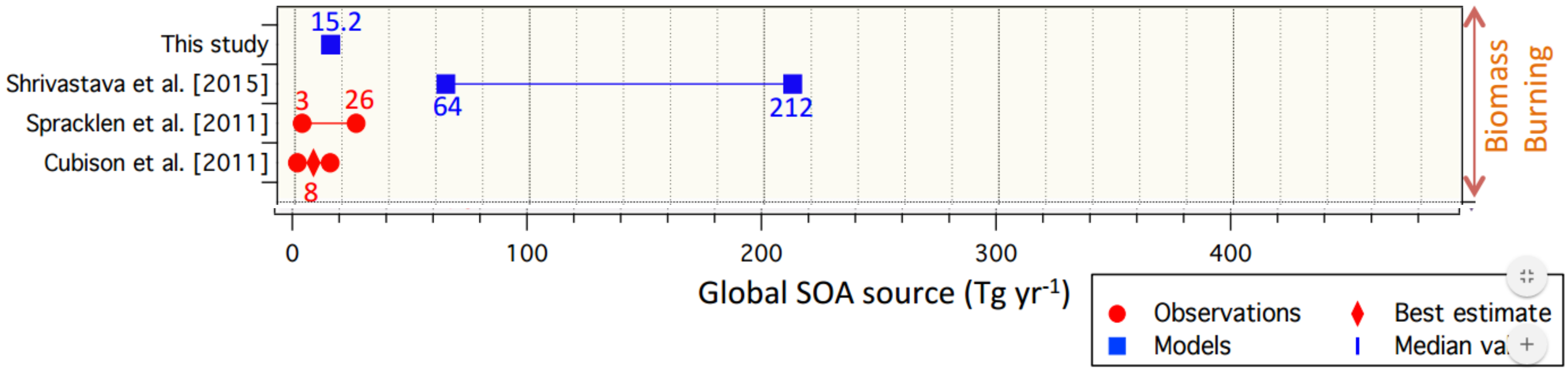
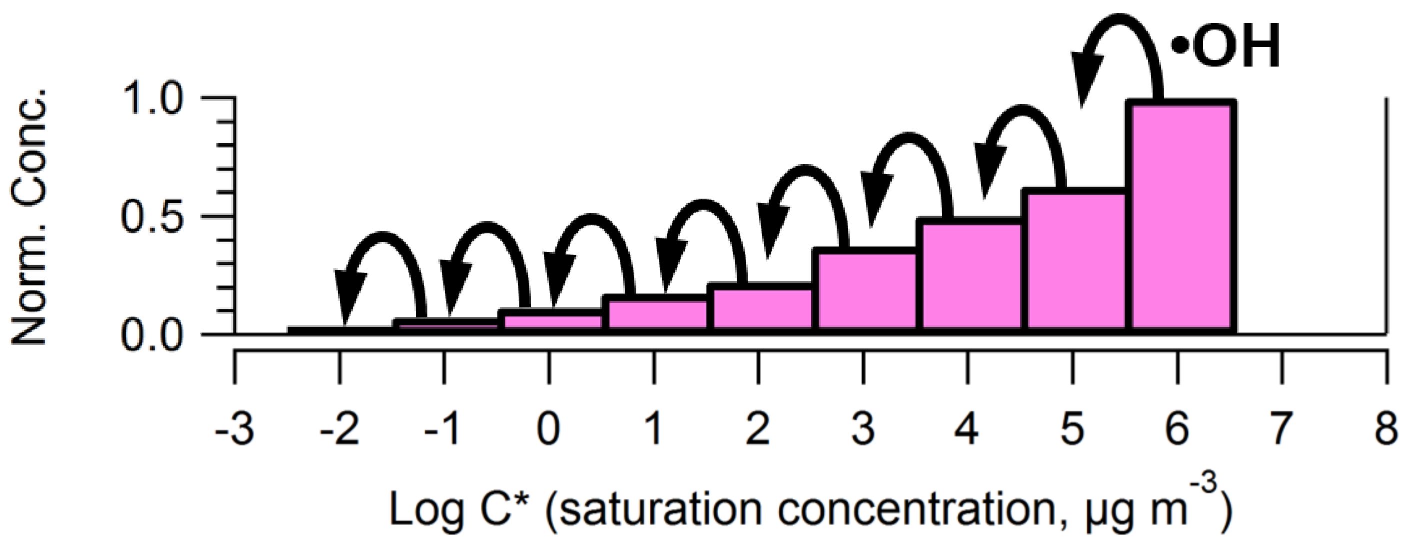
Global Budget of BB SOA



- Net SOA formation potential of BB is low
- Be careful about what we include in models



Hodzic et al. ACP 2016

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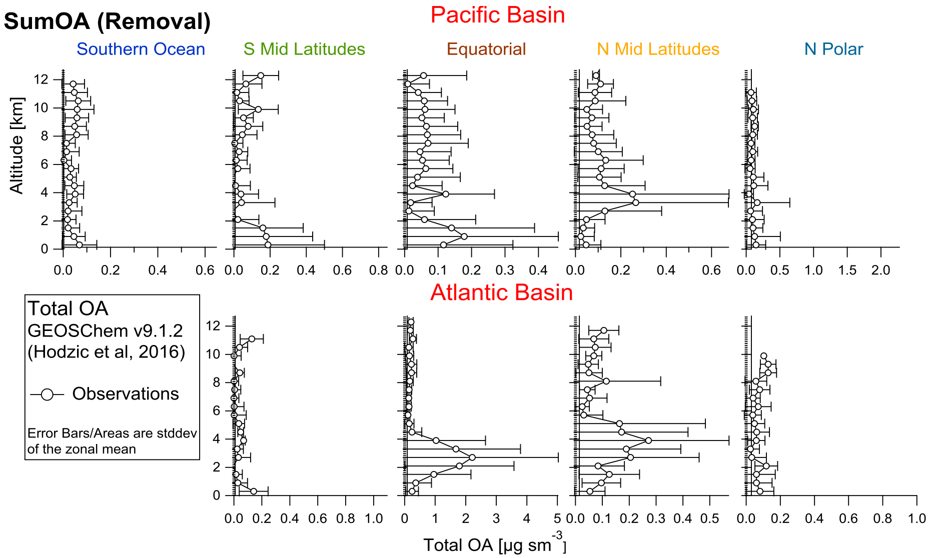
ATom-2 OA vs GEOS-Chem v9.1



Model: Hodzic et al. ACP 2016

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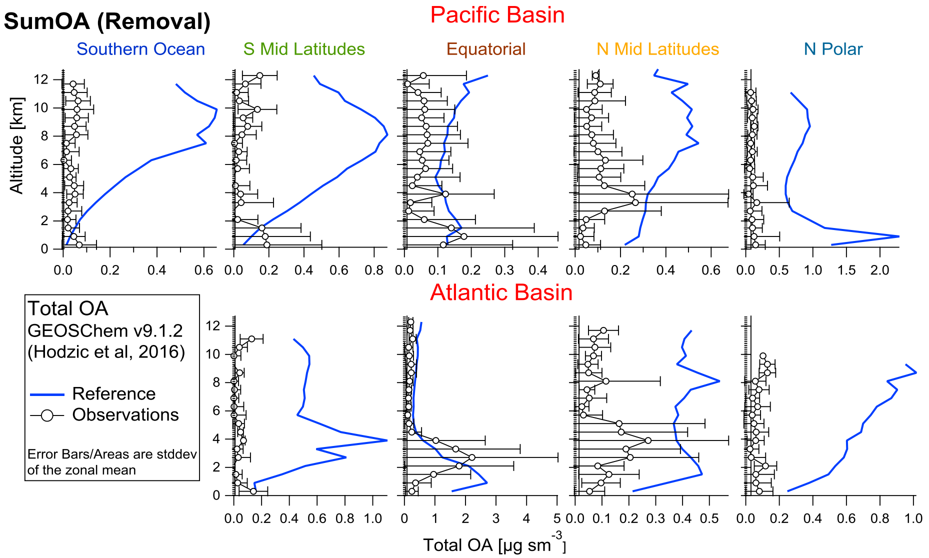
ATom-2 OA vs GEOS-Chem v9.1

Default GEOS-Chem often very high, esp. higher up



Model: Hodzic et al. ACP 2016

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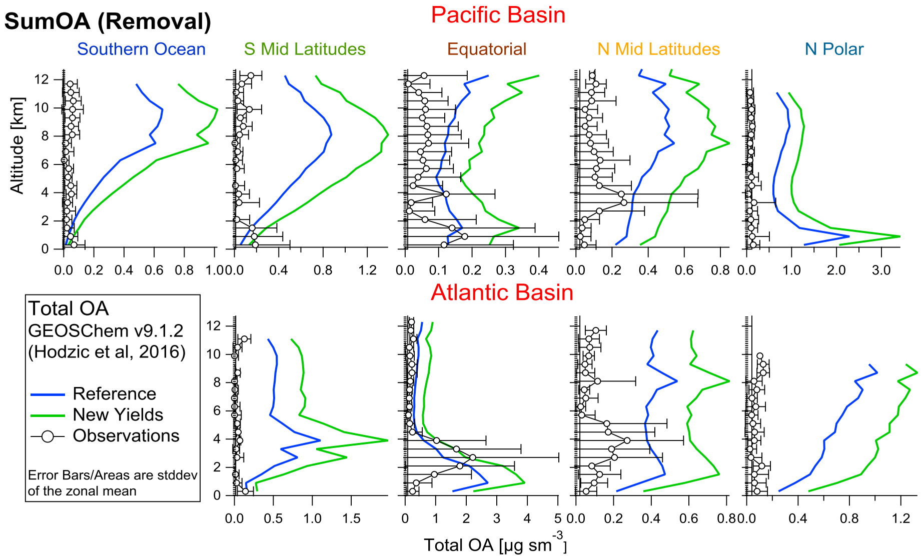
ATom-2 OA vs GEOS-Chem v9.1

Adding updated yields makes things worse

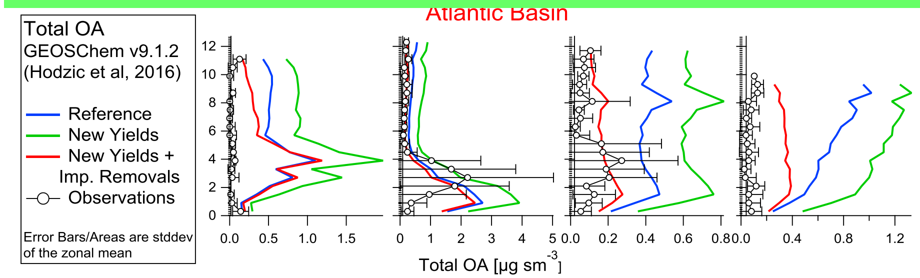


Model: Hodzic et al. ACP 2016

ATom-2 OA vs GEOS-Chem v9.1

Shortening lifetime (photolysis or het. Chem.) helps

- GEOS-Chem 9.1.2 high against remove observations
- Adding sources to match missing SOA in near-field makes it worse
- Reducing chemical lifetime (OH het. ox., photolysis…) improves it
- *Preliminary, there could be other explanations*



Model: Hodzic et al. ACP 2016

Summary

- Acidity in remote areas
  - Very low pH, ~1 unit lower than GC
- Organic Aerosols (OA)
  - Isoprene SOA
    - Important, but not all the OA even in high regions
  - SOA from Pollution
    - $\tau \sim 1$ day, similar & can be parameterized
  - SOA from Biomass Burning
    - Net: small compared to POA
  - Global OA in remote troposphere
    - Lower than GC, may need to speed up removals

BACKUP SLIDES

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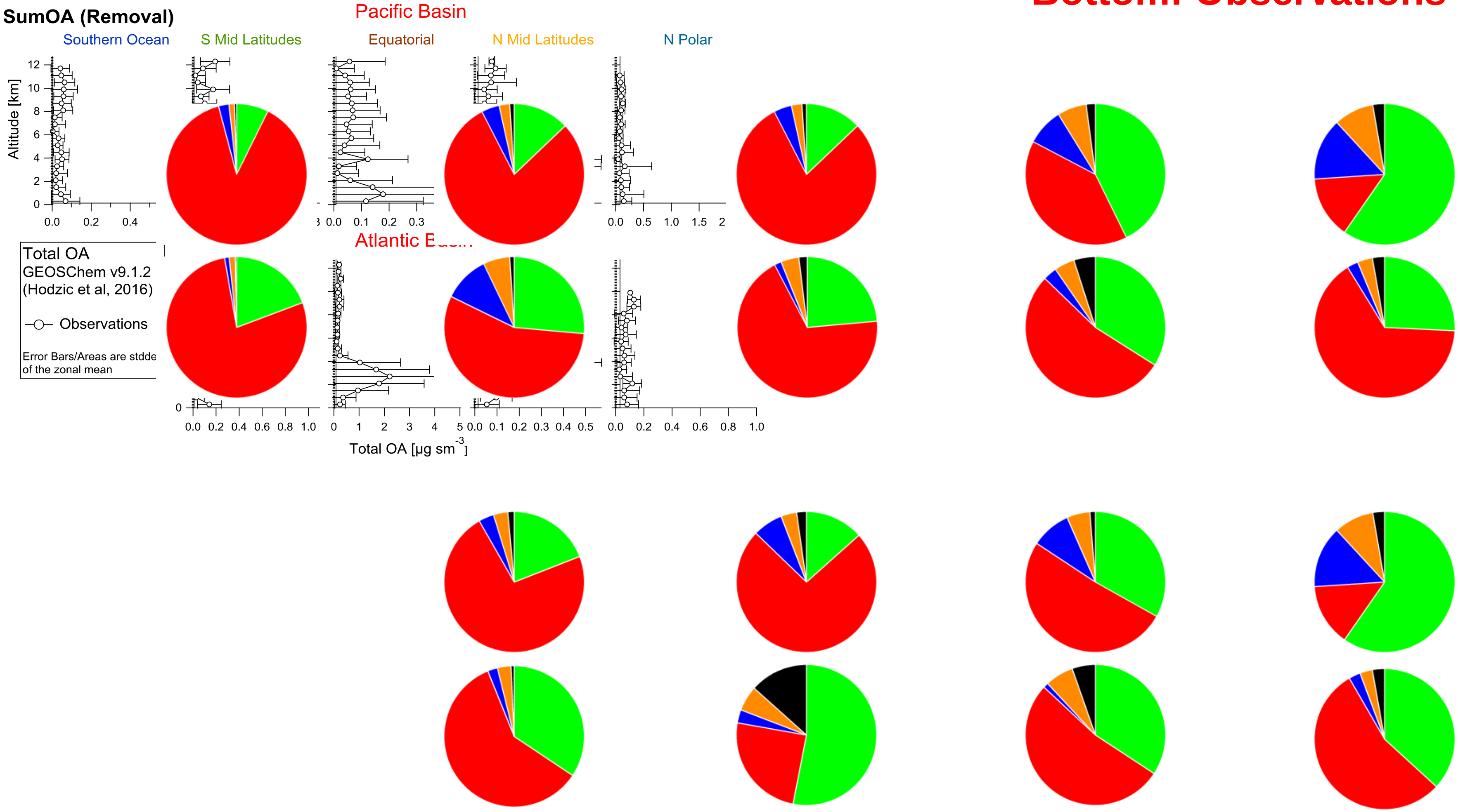
ATom-2 OA vs GEOS-Chem

TOP: Geos Chem
Bottom: Observations



Model: Hodzic et al. ACP 2016

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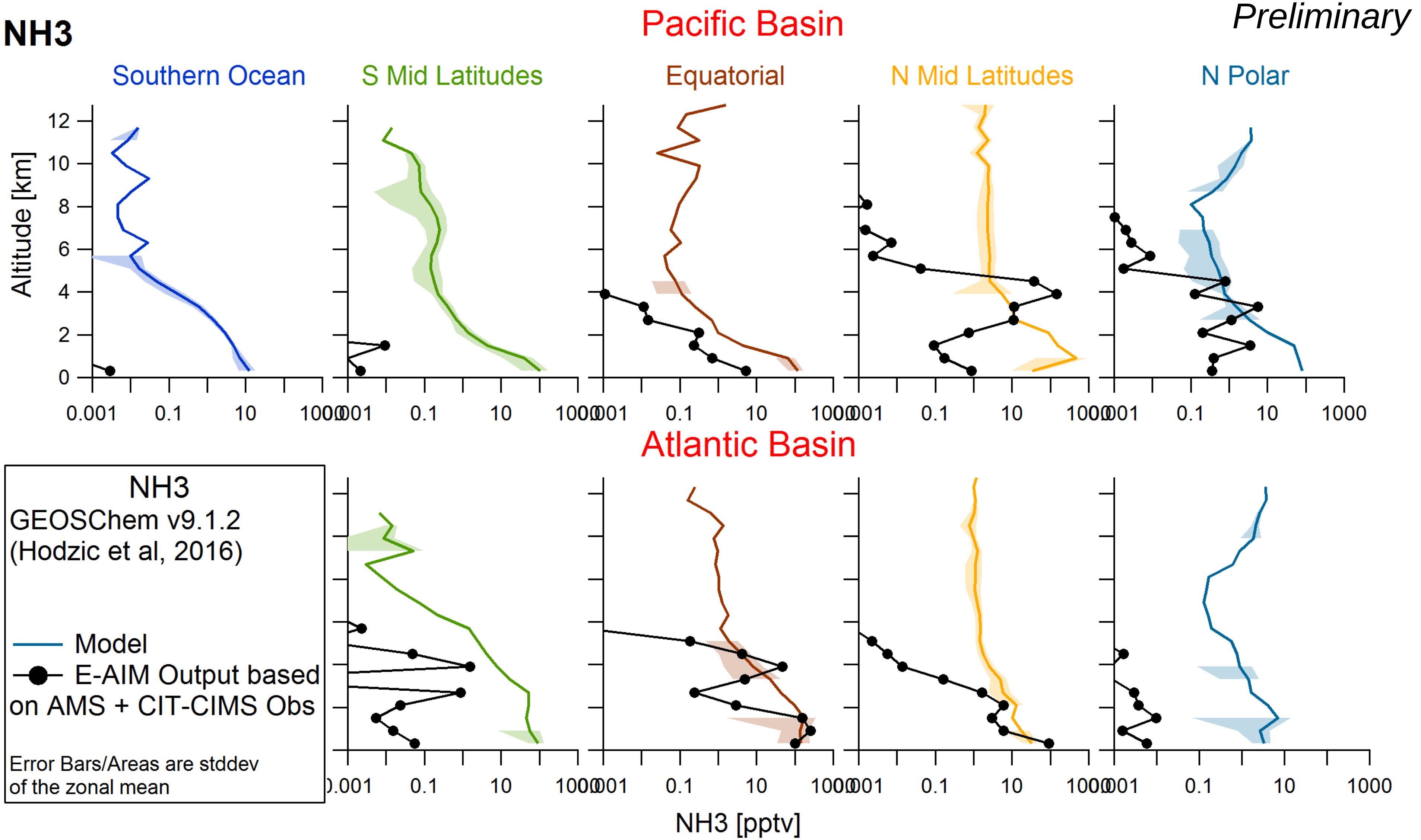
NH_3(g) from meas. + E-AIM vs. GEOS-Chem v.9.1

Preliminary



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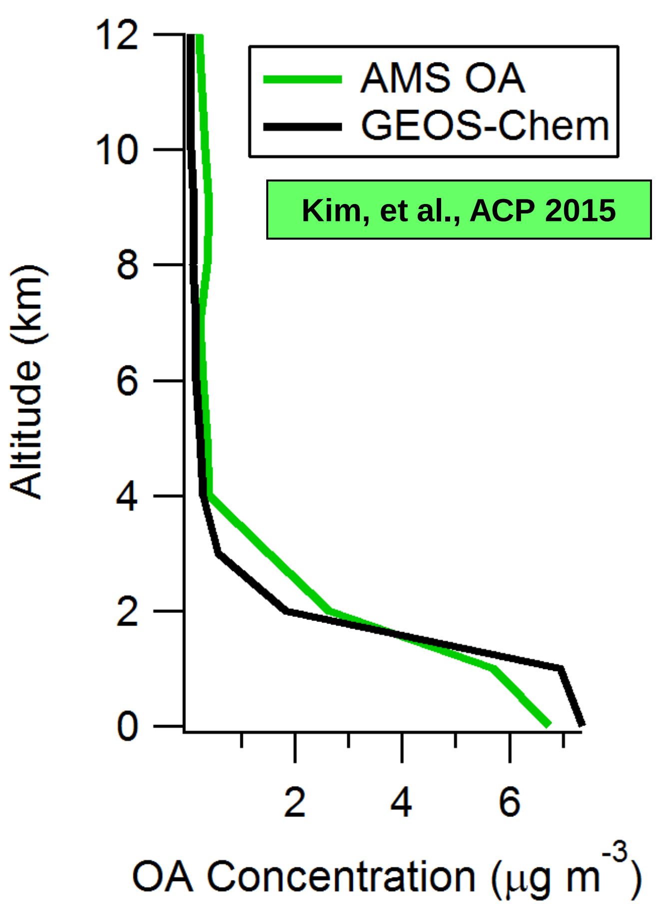
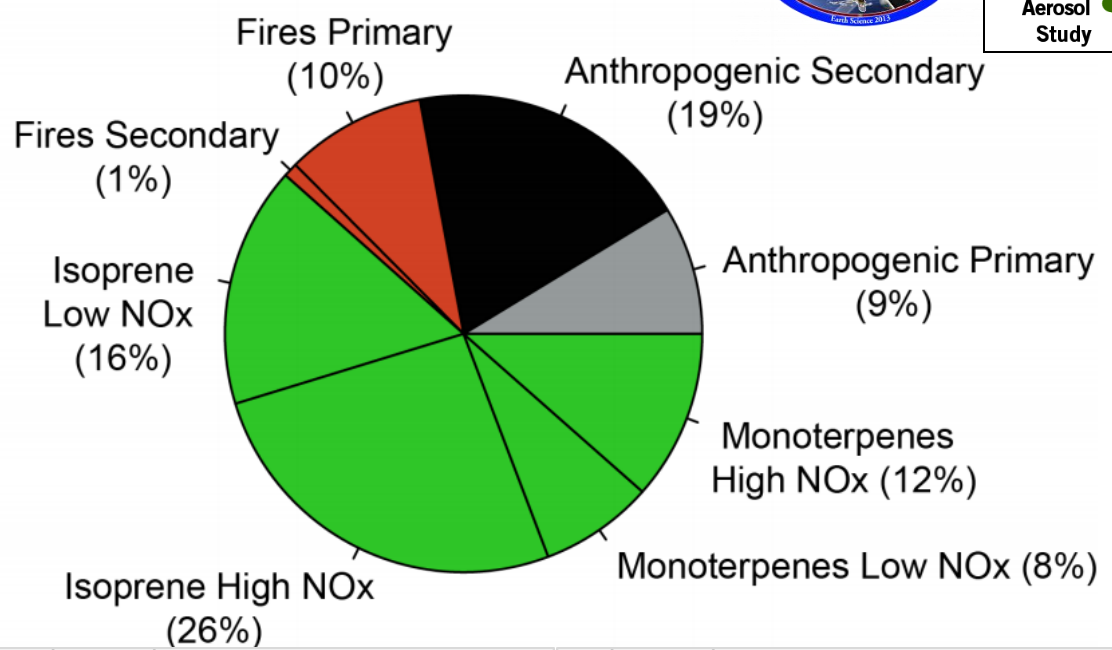
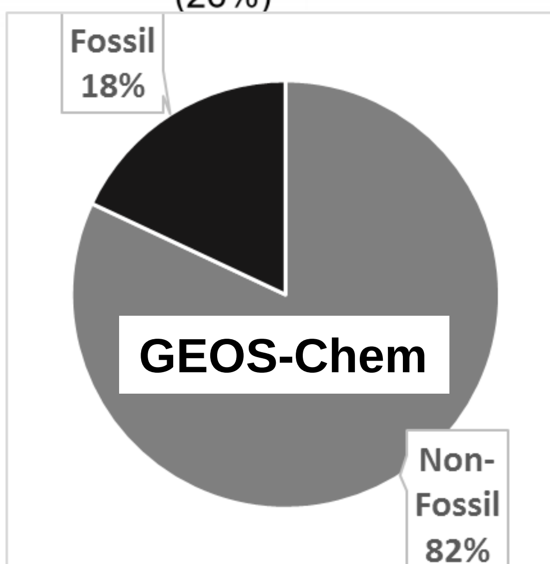
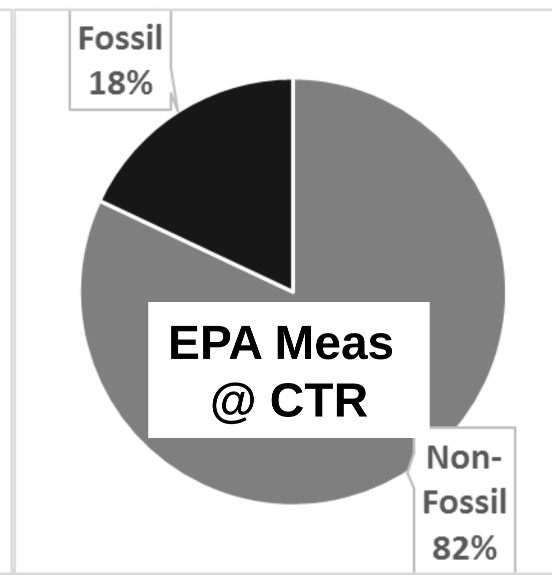
Modeled Sources in SE US

SOAS Southern Oxidant & Aerosol Study









- Consistent anthro fraction
  - Modern C (cooking)

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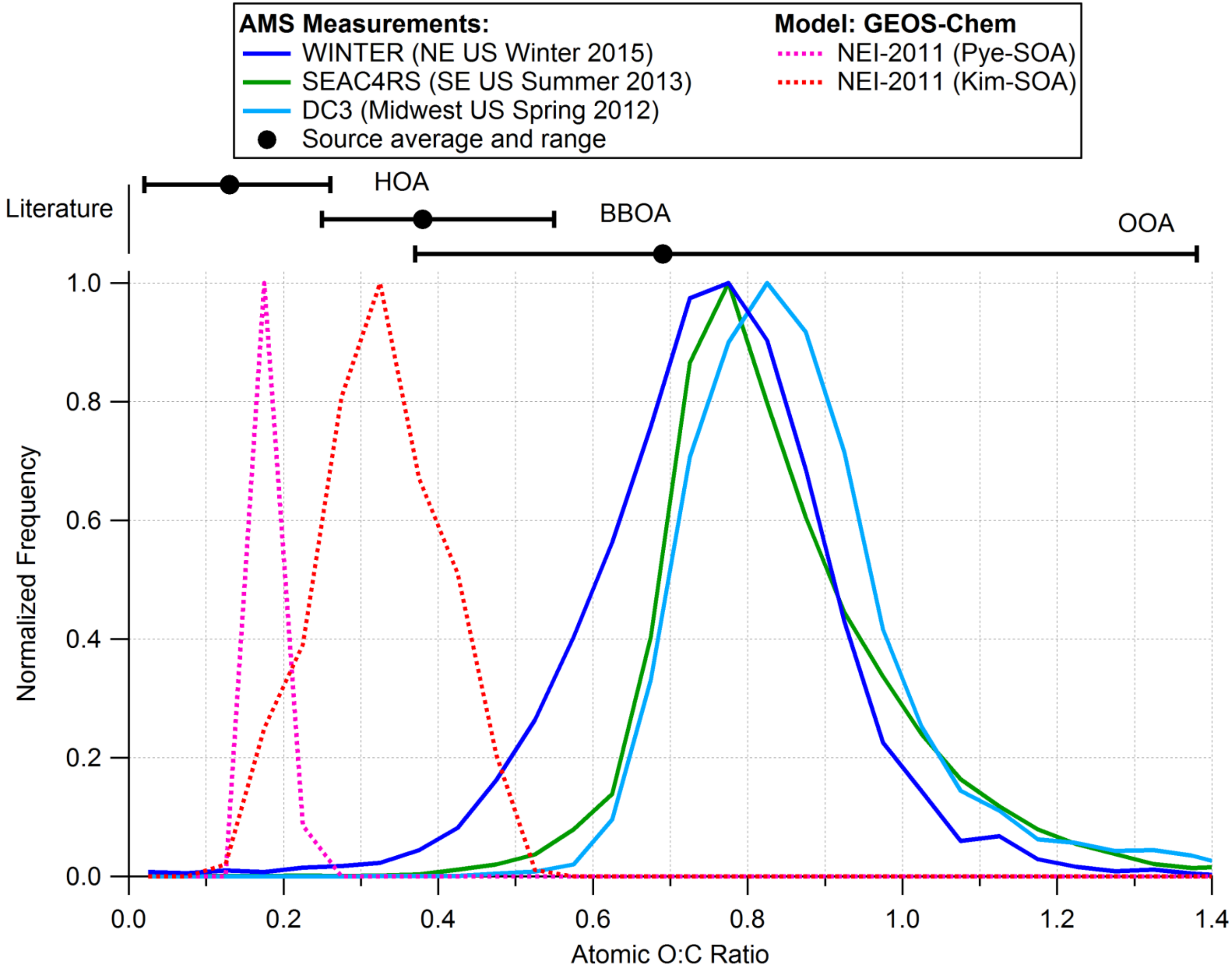
O:C Measurements vs GC v10.1



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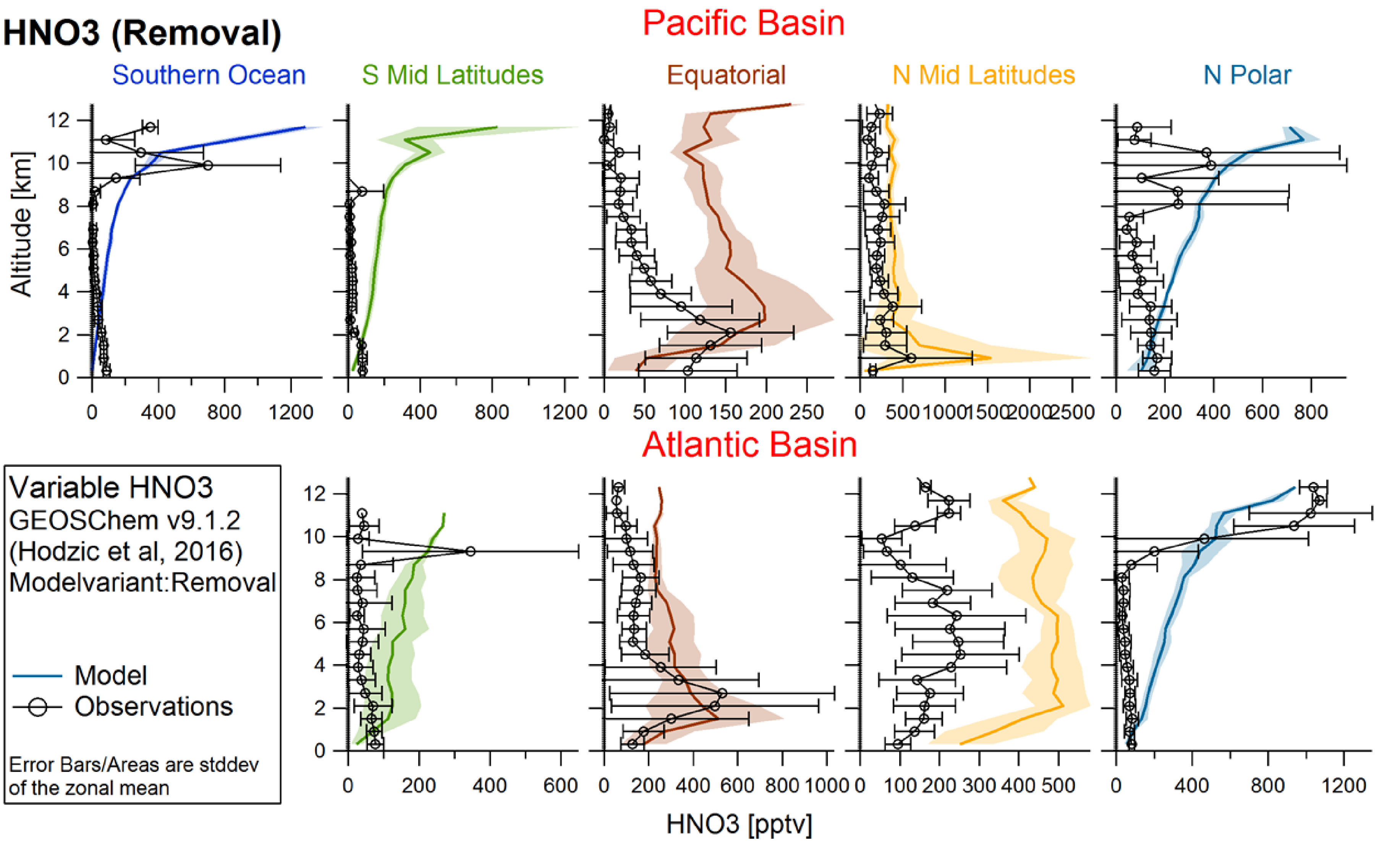
HNO3 (Removal)



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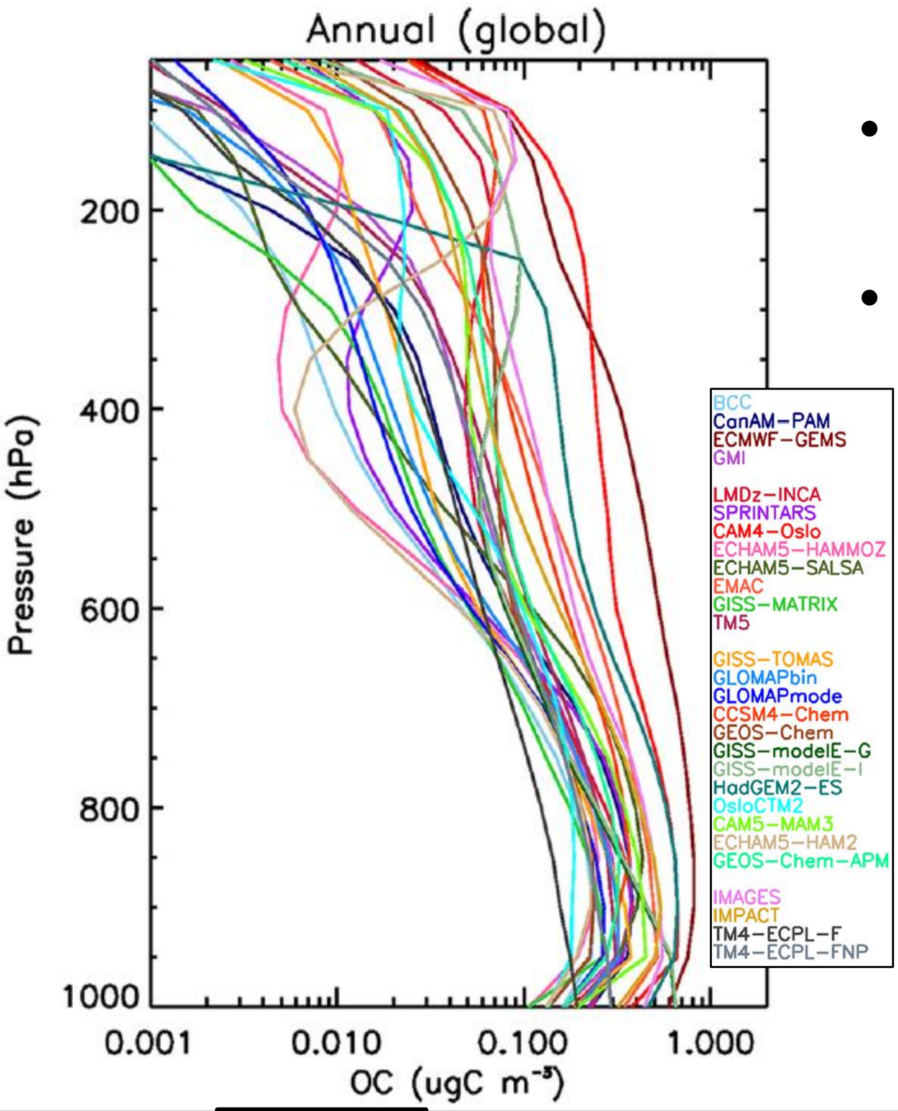
2014 AEROCOM Model Intercomp

AEROCOM-2 (Tsigaridis et al. 2014)



- Global models differ by x5 at surface, x100 aloft…
- No indication that more complex models are doing better
- *We are not there yet…*

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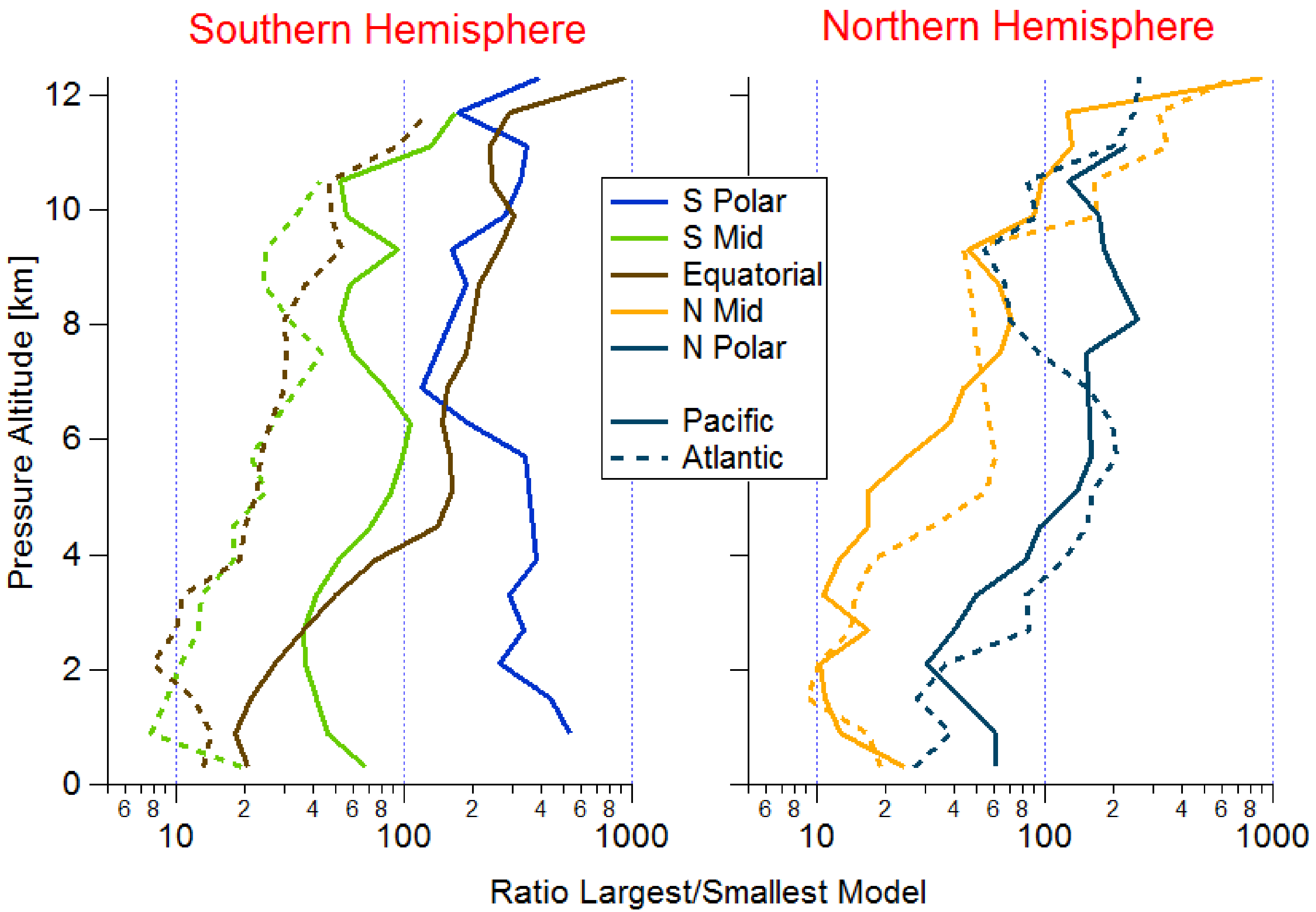
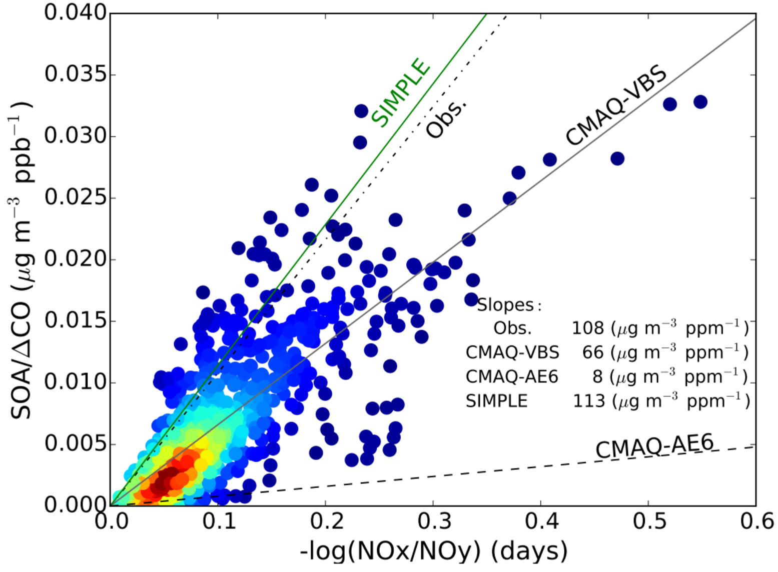
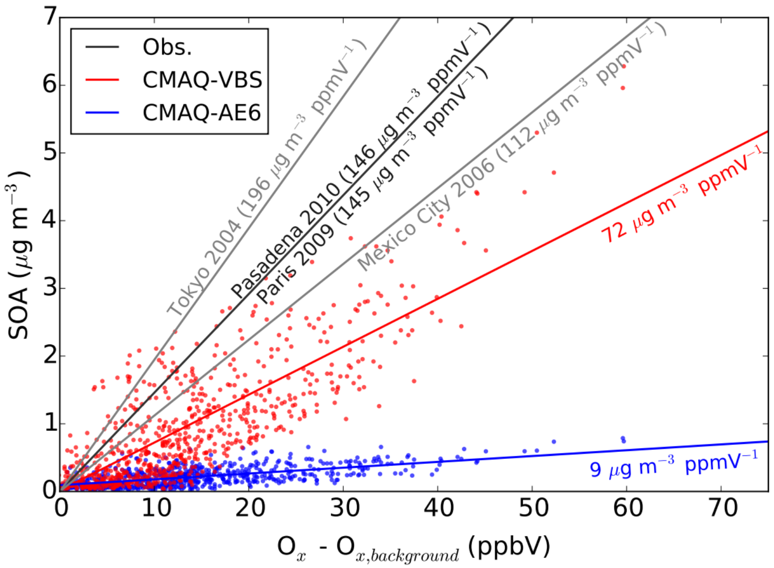
OA: AeroCom Model Comparison



Plotted w/ results in Tsigaridis et al, 2014

Monthly averages, Aug 2005


SIMPLE
Obs.
CMAQ-VBS
CMAQ-AE6
Slopes:
Obs. 108 (μg m⁻³ ppm⁻¹)
CMAQ-VBS 66 (μg m⁻³ ppm⁻¹)
CMAQ-AE6 8 (μg m⁻³ ppm⁻¹)
SIMPLE 113 (μg m⁻³ ppm⁻¹)
SOA/ΔCO (μg m⁻³ ppb⁻¹)
-log(NOx/NOy) (days)


Obs.
CMAQ-VBS
CMAQ-AE6
Tokyo 2004 (196 μg m⁻³ ppmV⁻¹)
Pasadena 2010 (146 μg m⁻³ ppmV⁻¹)
Paris 2009 (145 μg m⁻³ ppmV⁻¹)
Mexico City 2006 (112 μg m⁻³ ppmV⁻¹)
72 μg m⁻³ ppmV⁻¹
9 μg m⁻³ ppmV⁻¹
SOA (μg m⁻³)
Oₓ - Oₓ,background (ppbV)

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Net BB-SOA in the Global OA Budget

- Global OA budget ~ 180 Tg OA yr^{-1}
  - Hallquist et al. 2009; Heald et al., 2010; Spracklen et al., 2011

$\Delta OA_{global}^{aging} = \left(\frac{\Delta OA_{aging}}{POA}\right) x\, POA_{global}$	$\Delta OA_{global}^{aging} = \left(\frac{\Delta OA_{aging}}{\Delta CO}\right) x\, CO_{global}$
= **8 ± 7** (field)	= **7 ± 6 Tg OA yr^{-1}** (field)

- **Potentially Important global source, 5% of global OA**
  - **But certainly not the major source**

Cubison et al. ACP 2011

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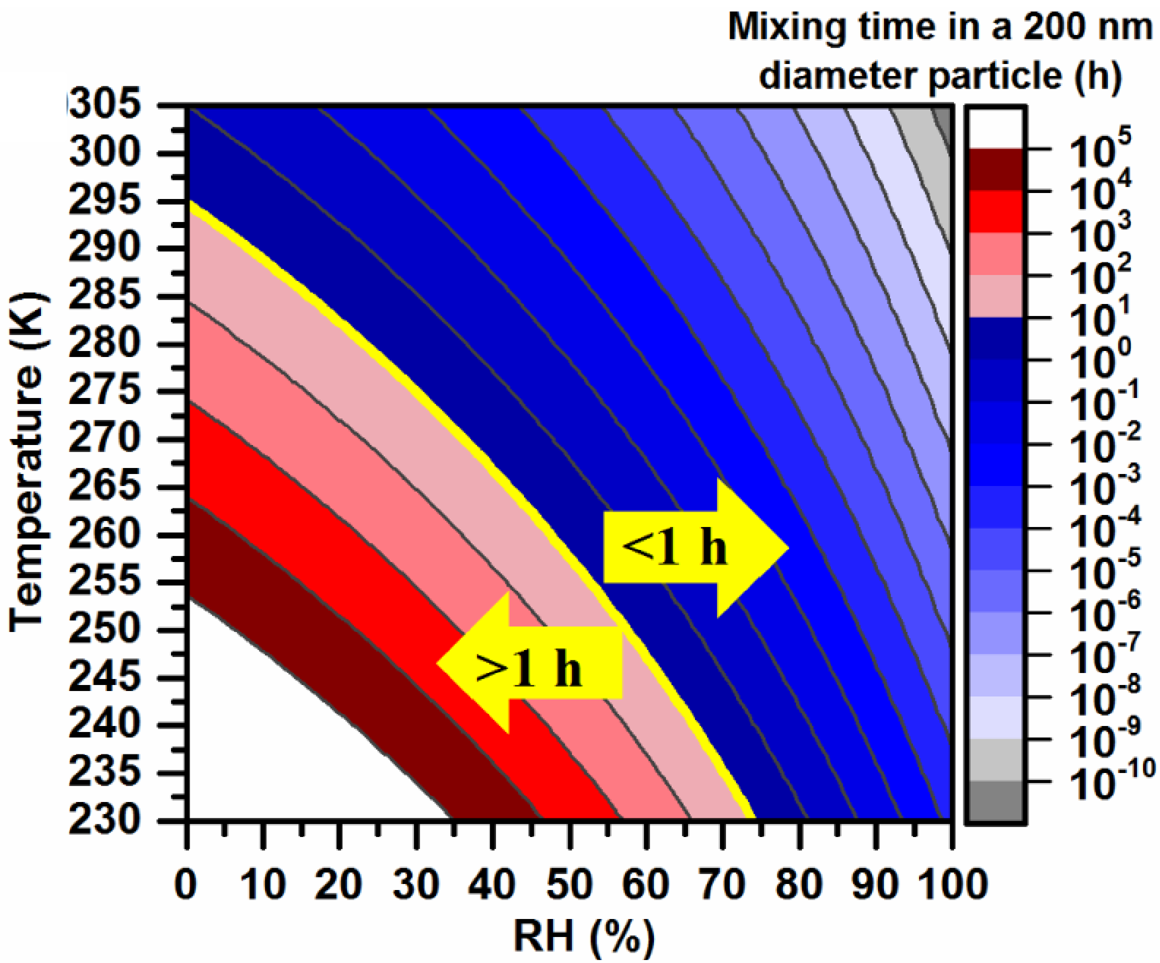
Slow Diffusion in SOA?: PBL

- Slow diffusion prevalent at low RH, low T



Derive parameterization for α-pinene SOA, constrained from ambient & cold measurements vs RH

Maclean et al., ACPD 2017

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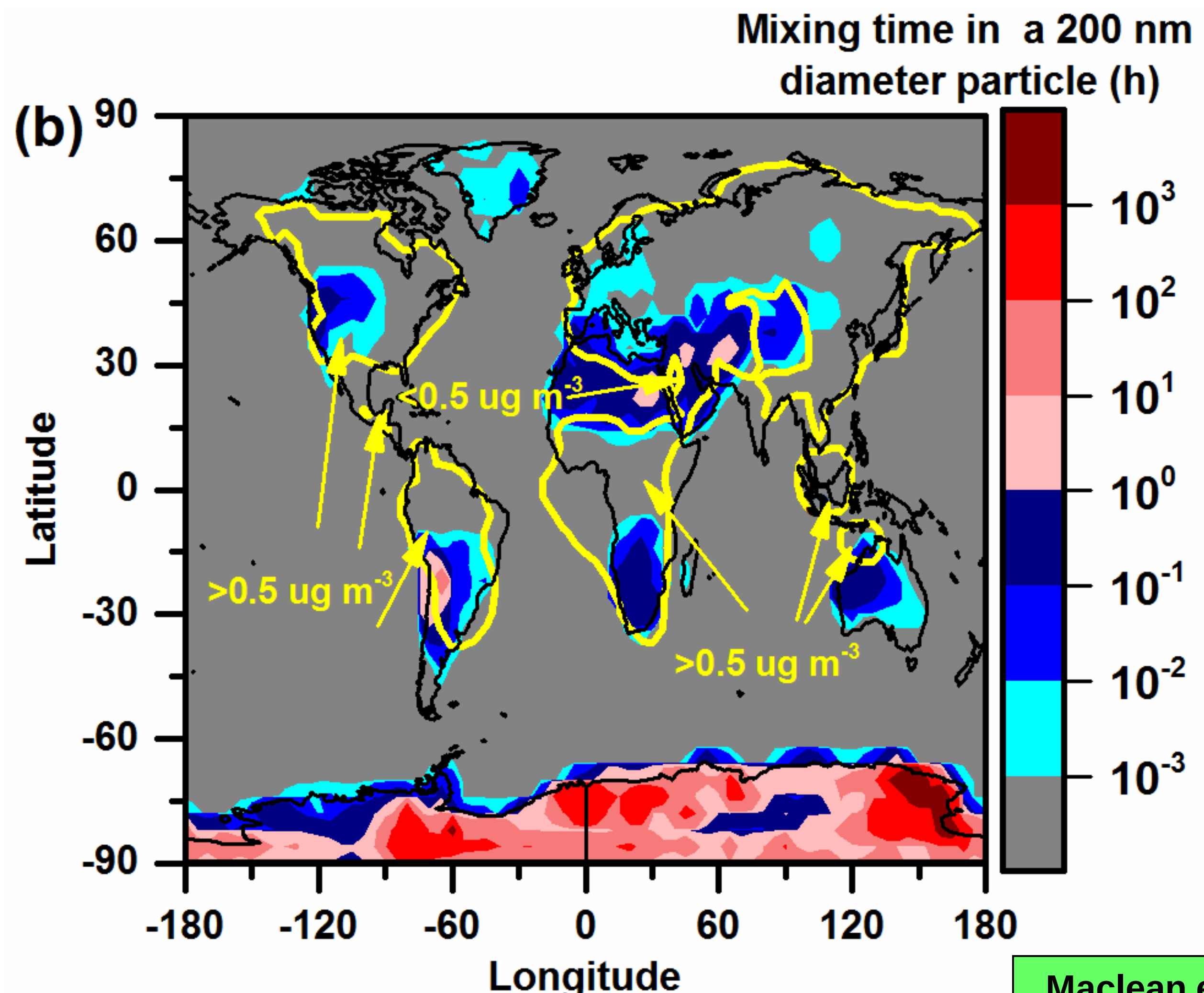
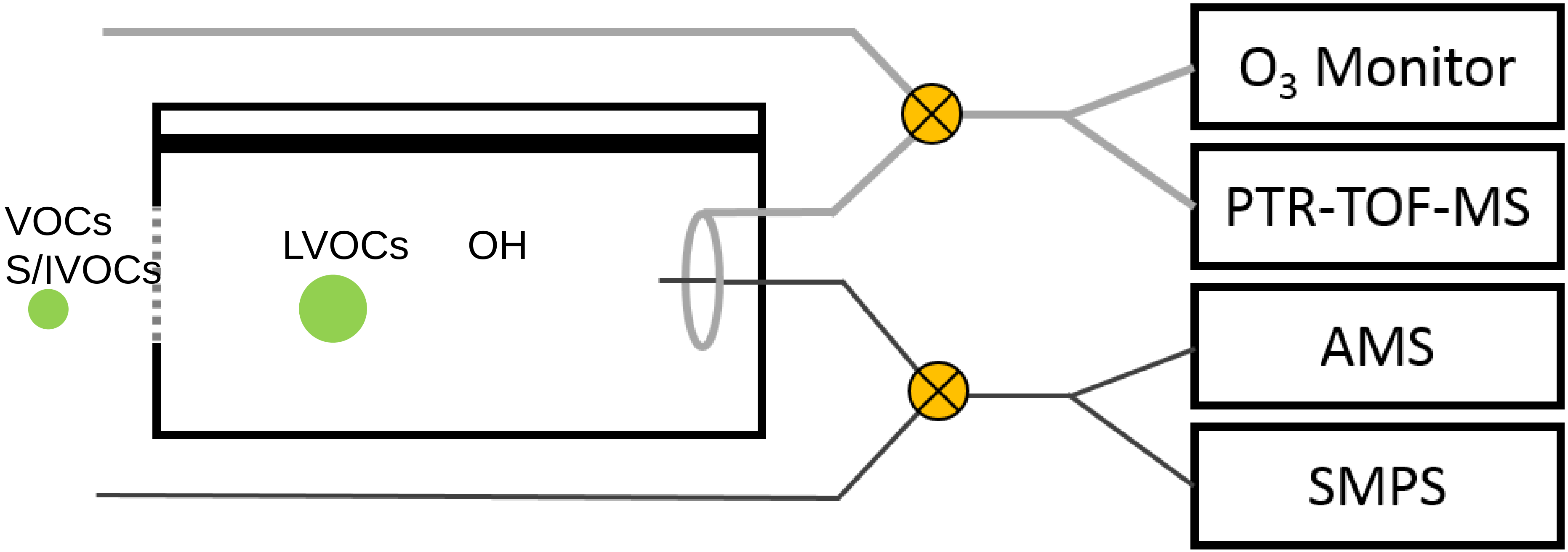
Rapid mixing for biogenic SOA in PBL almost everywhere



Maclean et al., ACPD 2017

Measuring Potential SOA Mass in the Field

Extract more information for model testing from ambient measurements



→ Alternative to large chambers: **~ few min. residence time, portable**

→ Can also sample from OFR with, e.g., CCN counter, CIMS, etc.

PAM reactor: Designed by Prof. Brune at Penn State
Early OFR Studies: **Kang et al., ACP 2007, 2011; Lambe et al., AMT 2011…**
Our experimental work: **Ortega et al. ACP 2013; Li et al. ES&T 2013; Ortega et al. ACP 2016; Palm et al. ACP 2016; Hu et al., ACP 2016; Palm et al., ACPD 2017; Palm et al. in prep.; Hu et al. in prep.**
Our modeling work: **Li et al. JPCA 2015; Peng et al. AMT 2015; Peng et al. ACP 2016; Peng et al., in prep.**