QUANTIFYING ORGANIC AEROSOL REMOVAL IN THE REMOTE TROPOSPHERE: CONSTRAINTS ON PHYSICAL & CHEMICAL REMOVAL OF OA PROVIDED BY THE ATOM MISSION

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Chat Wed, 06 May, 16:15–18:00 CEST

THE NASA ATOM MISSION: PROFILING THE REMOTE ATMOSPHERE FROM 0-13 KM

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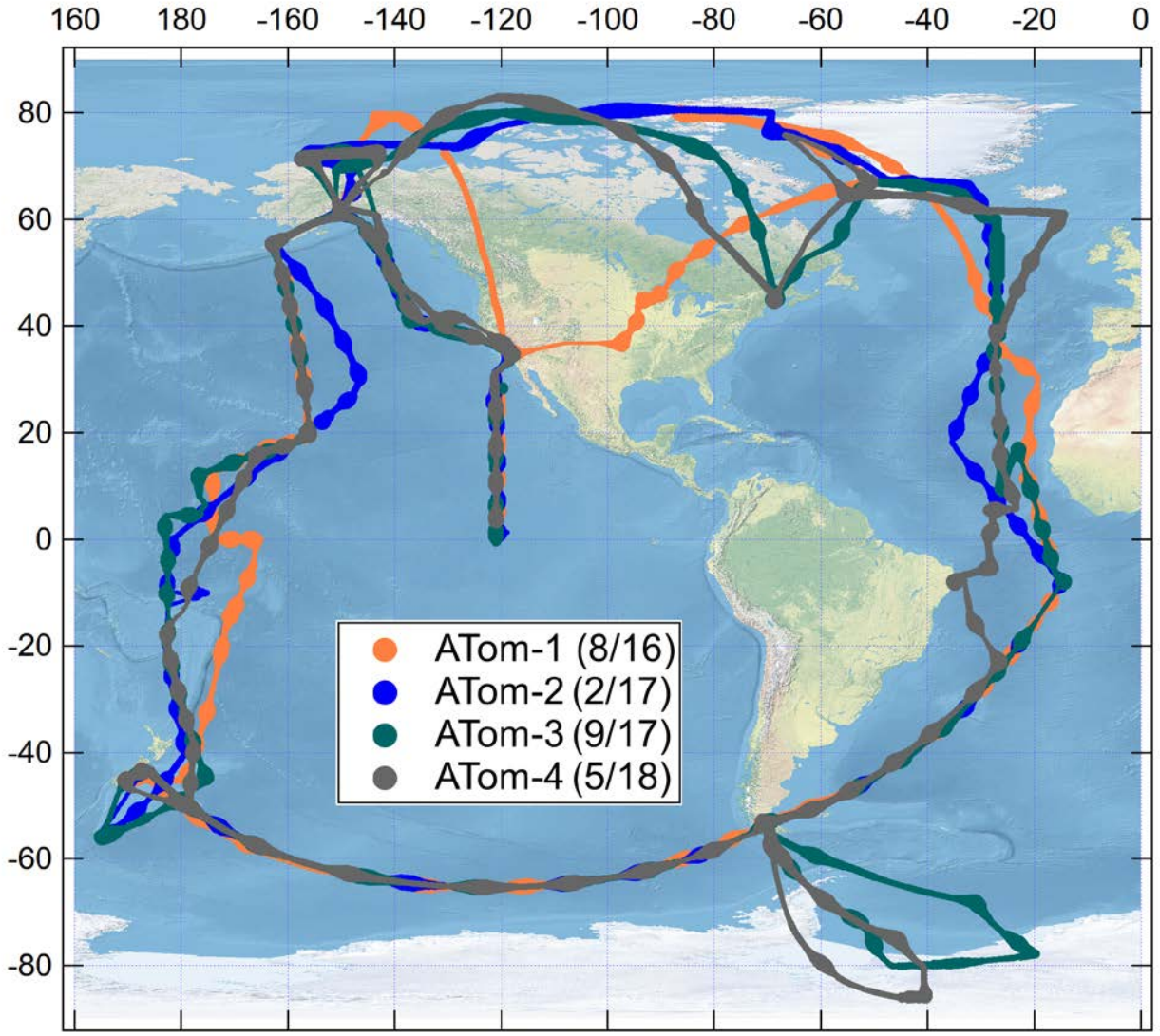


Aircraft Mission, NASA DC-8

Objective: Characterize the composition and chemistry of the global background

Four deployments:

- ATom-1: Aug 2016 (NH Summer)
- ATom-2: Feb 2017 (NH Winter)
- ATom-3: Oct 2017 (NH Fall)
- ATom-4: May 2018 (NH Spring)

Continuous, non-targeted profiling of the troposphere from 0 to 12.6 km (about 140 profiles per deployment)

Highly instrumented payload, with a comprehensive aerosol package:

- Aerosol sizers in the range 3-10^4 nm and aerosol volatility measurements (NOAA)
- Below-the-wing cloud probes (U Vienna)
- Chemical composition from filters and mist chamber IC (UNH SAGA), single particle MS (NOAA PALMS) and CU Aircraft HR-AMS (CU Boulder, this work)

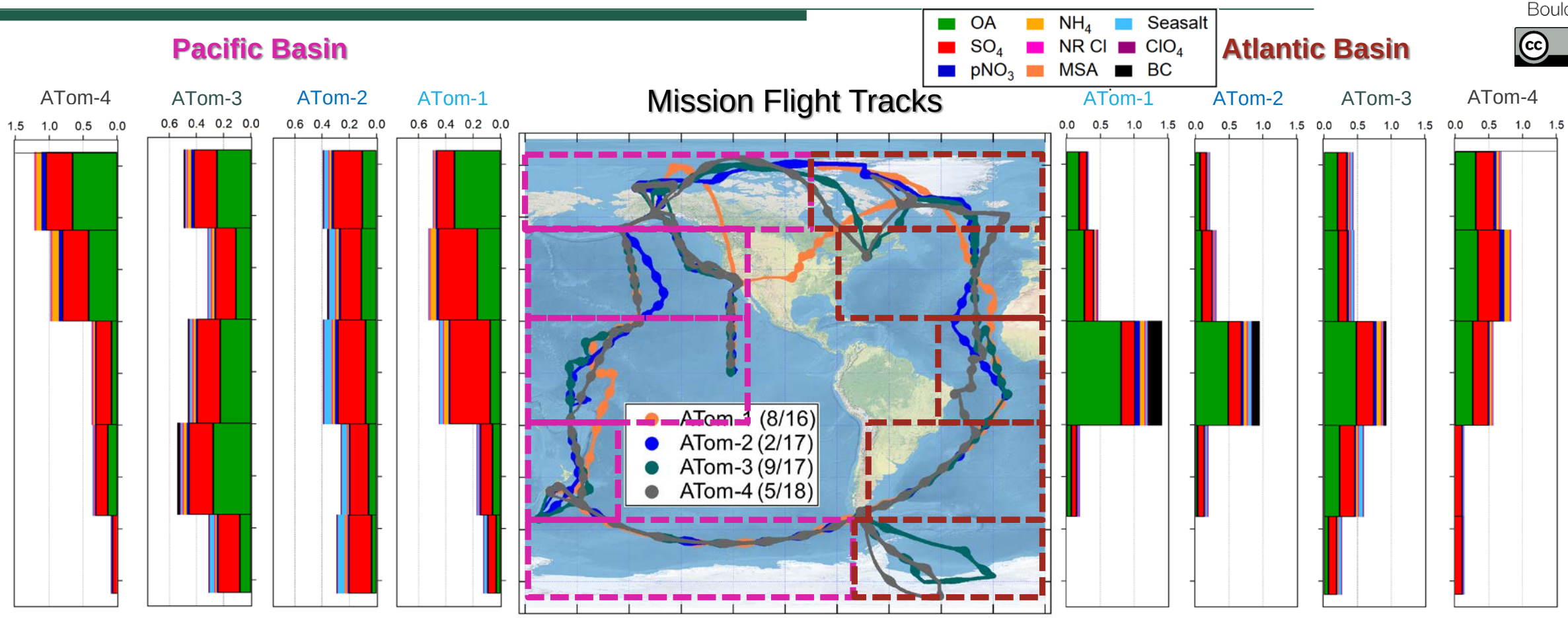
A highly redundant set of VOC and reactive gas analyzers complements the payload

All data is publicly available at NASA DAAC (https://daac.ornl.gov/ATOM)

Brock et al, 2019; Froyd et al, 2019; Hodzic et al, 2020; Thompson et al, in prep

EGU2020-12202 (this session) provides an overview of the ATom mission

ZONAL COMPOSITION OF PM1 AEROSOL FOR ALL 4 ATOM MISSIONS



- Chemical PM1 measurements are consistent with the collocated physical (aerosol volume) and chemical (sulfate, seasalt, OA) measurements (Talk EGU2020-11863)
- Outside of the MBL, concentrations were fairly comparable on average, slightly higher in NH (particularly ATom-1 and 4) and in the Atlantic Basin.
- Both the equatorial Atlantic (African and Amazonian outflow, depending on the season) and the Northern Pacific (East Asian outflow) stand out with higher mass concentrations (2x-4x larger than typical background). Predominantly BB (especially African outflow), but some urban/anthropogenic sources as well
- Sulfate, OA and seasalt (in the MBL) are the main components observed. NH_4 is negligible outside the MBL, aerosols were highly acidic (Talk EGU2020-11366)

ATOM: OA MAJOR COMPONENT OF IN THE REMOTE ATMOSPHERE

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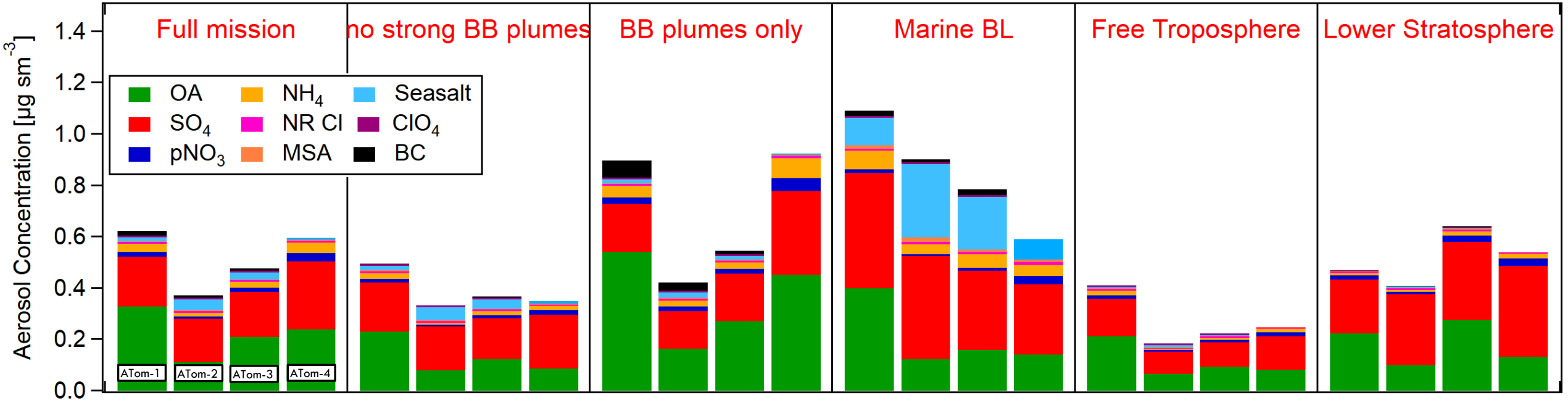

- Strong influence of fire emissions for ATom-1 (NH) and 3 (SH), ATom-2 cleanest and windiest (MBL), hence high PM1 seasalt.
- ~0.3 µg sm^{-3} PM1 outside of BB plumes in the FT (about 1-2 Mm^{-1})
- 30-50% OA contribution, mostly sulfate otherwise
- Outside BB plumes, nitrate is organic, regardless of altitude.
- Very small organosulfate fraction (~1%) Appreciable MSA in the MBL (up to 0.4 µg sm-3) and the FT.
- Episodic large OA plumes in the lower stratosphere, often associated with old BB plumes.

AMS Data available at
https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1716

Hodzic et al, 2020, Campuzano-Jost et al, in prep

REVISITING AEROCOM-II: BOTH OA SOURCES AND REMOVAL ARE TOO LOW!

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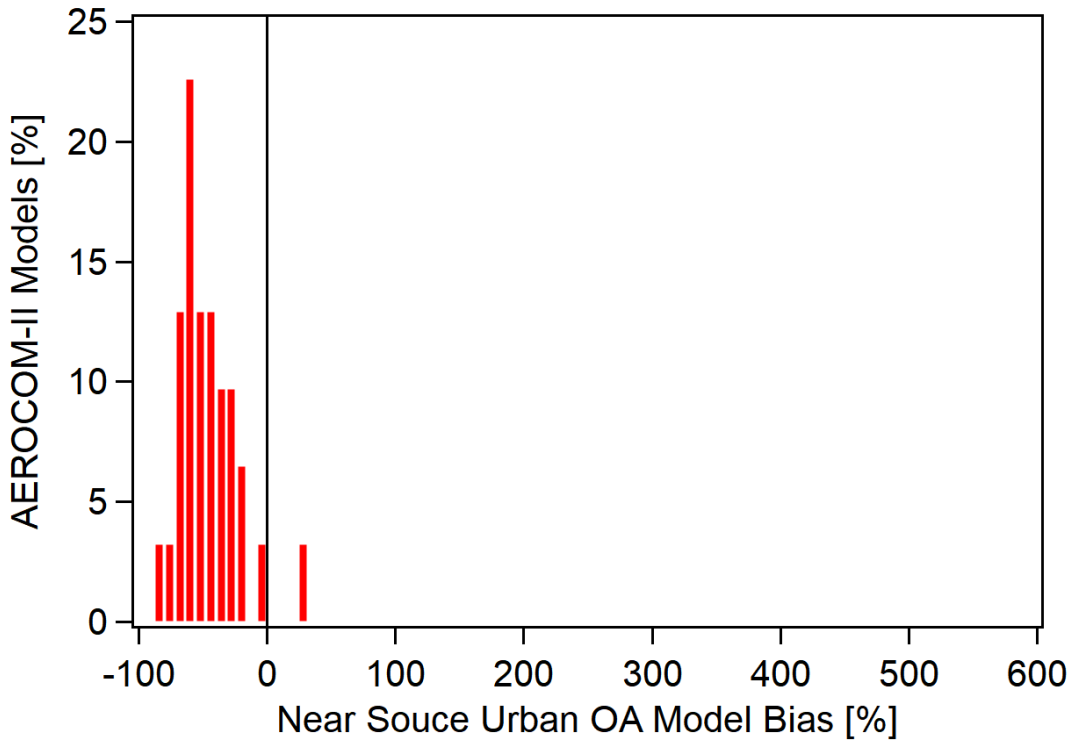
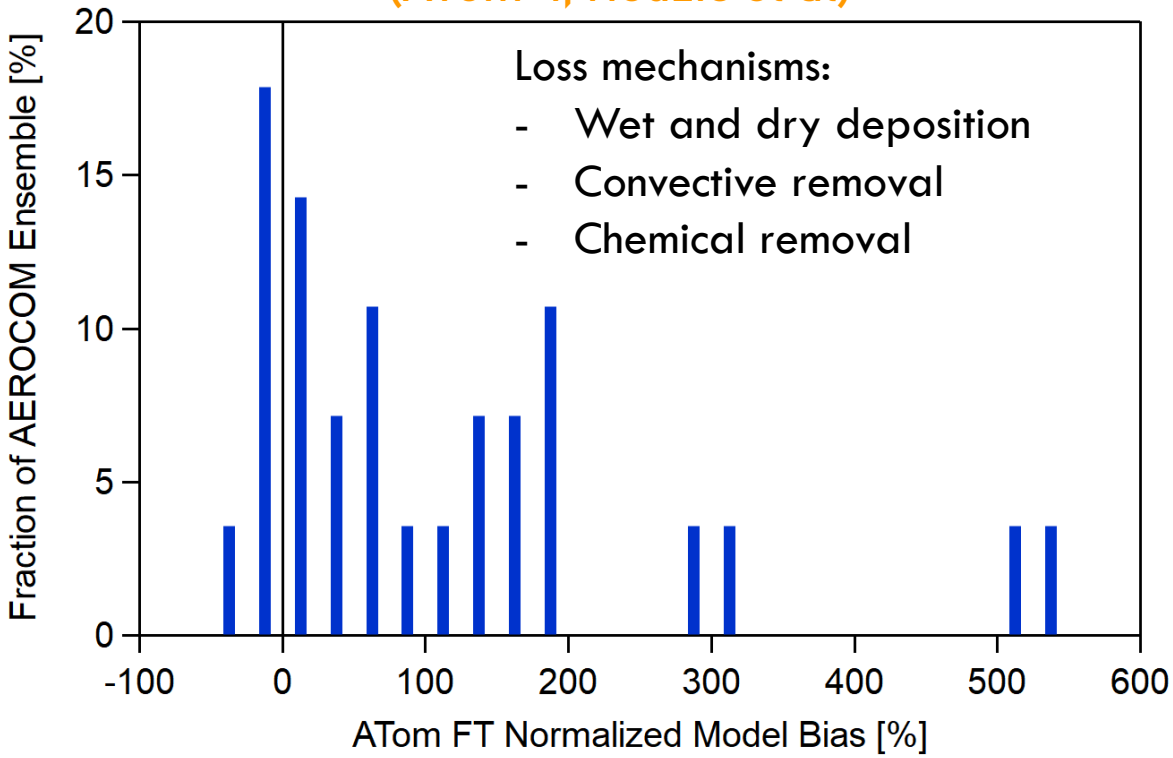
Model performance close to sources



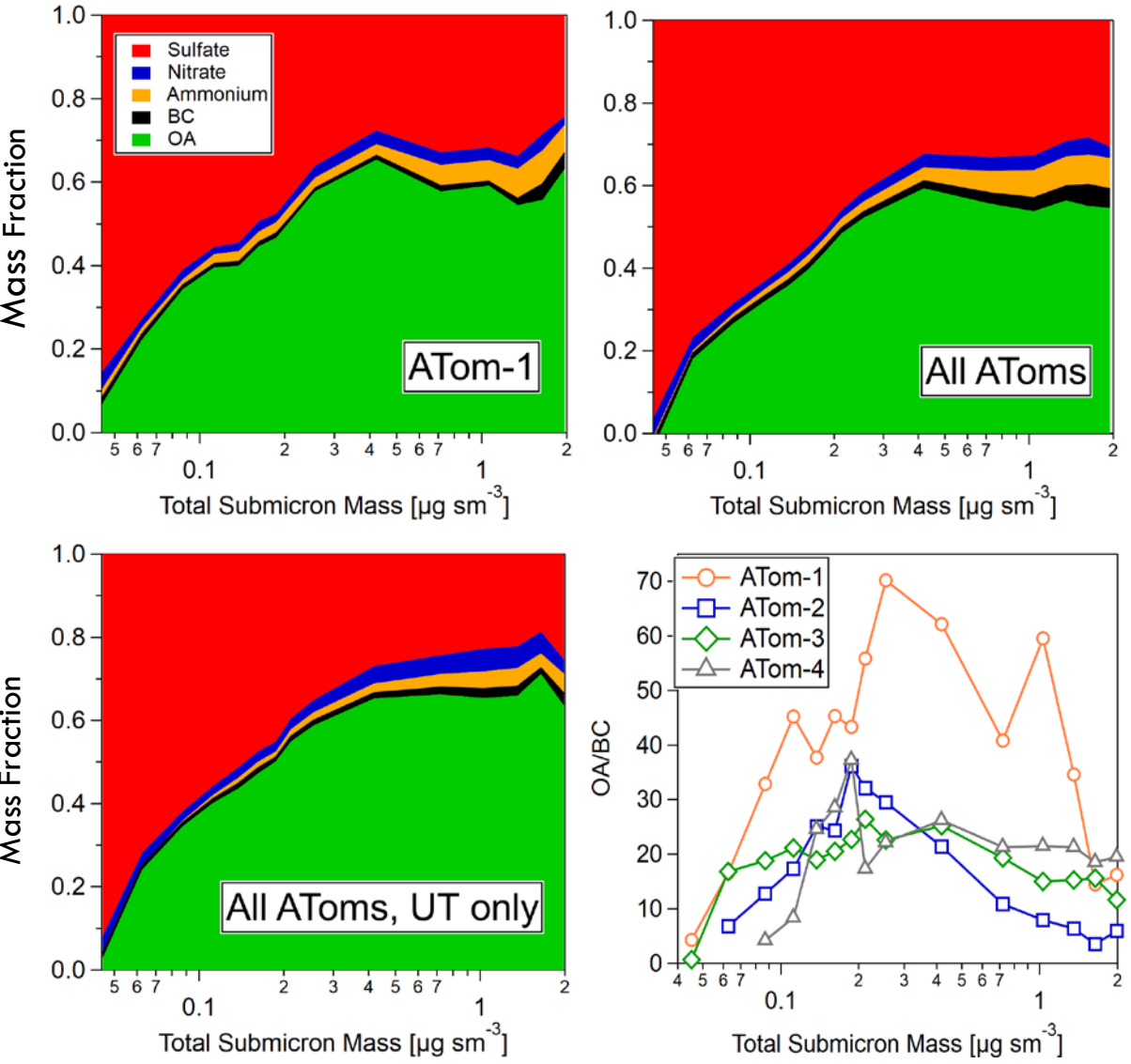
Model performance away from sources (ATom-1, Hodzic et al)



- Performance near sources has improved since due to updated yields and mechanisms
- Stronger loss mechanisms in the remote atmosphere are needed to compensate
- Newer, post AEROCOM-II models exhibit a lower bias in the remote atmosphere, but neither capture the source mix (POA vs SOA) nor the extent of aerosol aging properly (Hodzic et al, ACP 2020)

Tsigaridis et al, 2014, Hodzic et al, 2020

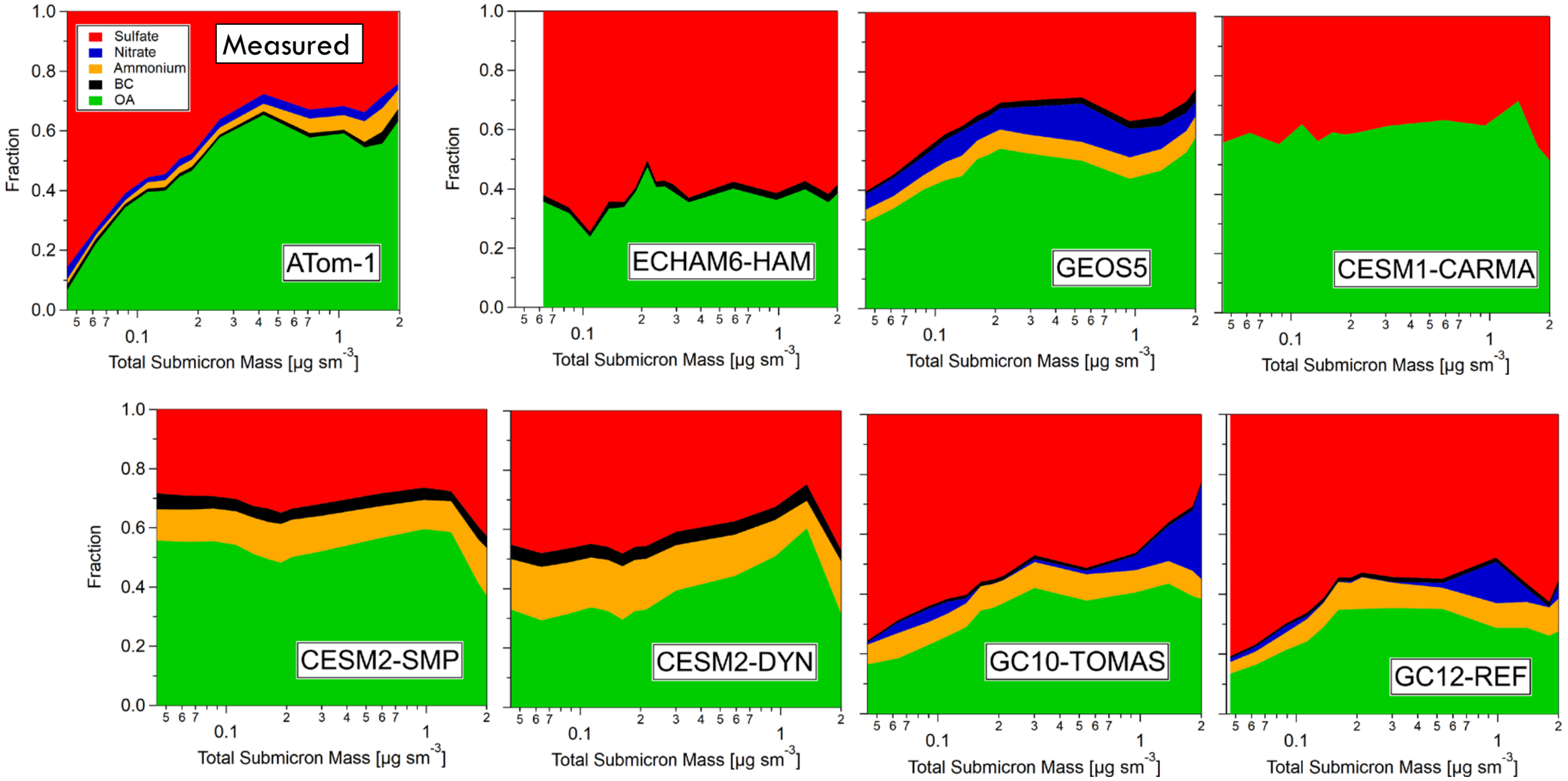
OA FRACTION DECREASES WITH TOTAL PM1



- All major aerosol sources are outside the free troposphere (FT) (except of some small fraction of sulfate and possibly OA from nucleation (Williamson et al, 2019)
- Assume differences in source inputs are small once sampling occurs far enough from sources
- Aerosol is removed in the FT by wet deposition (1-2 weeks lifetime) + other processes.
- Therefore, total PM1 aerosol mass is a good proxy for time since emission
- Robust dependency of the OA/SO_4 on total PM1 concentration in the measurements, especially in the UT (<500 mbar)
- Partially driven by slow formation of SO_4 in the FT. But suggests efficient OA removal vs both SO_4 and black carbon (BC)

Pruppacher & Jaenicke, 1994; Tsigaridis et al, 2014

THIS IS NOT REFLECTED IN MODELS: ATOM-1



* Fractions calculated for the species commonly reported. Some models do not include nitrate, others (CESM2) scale ammonium with sulfate assuming neutralized aerosol

IMPORTANCE OF CONVECTIVE REMOVAL SCHEME FOR FT AEROSOL

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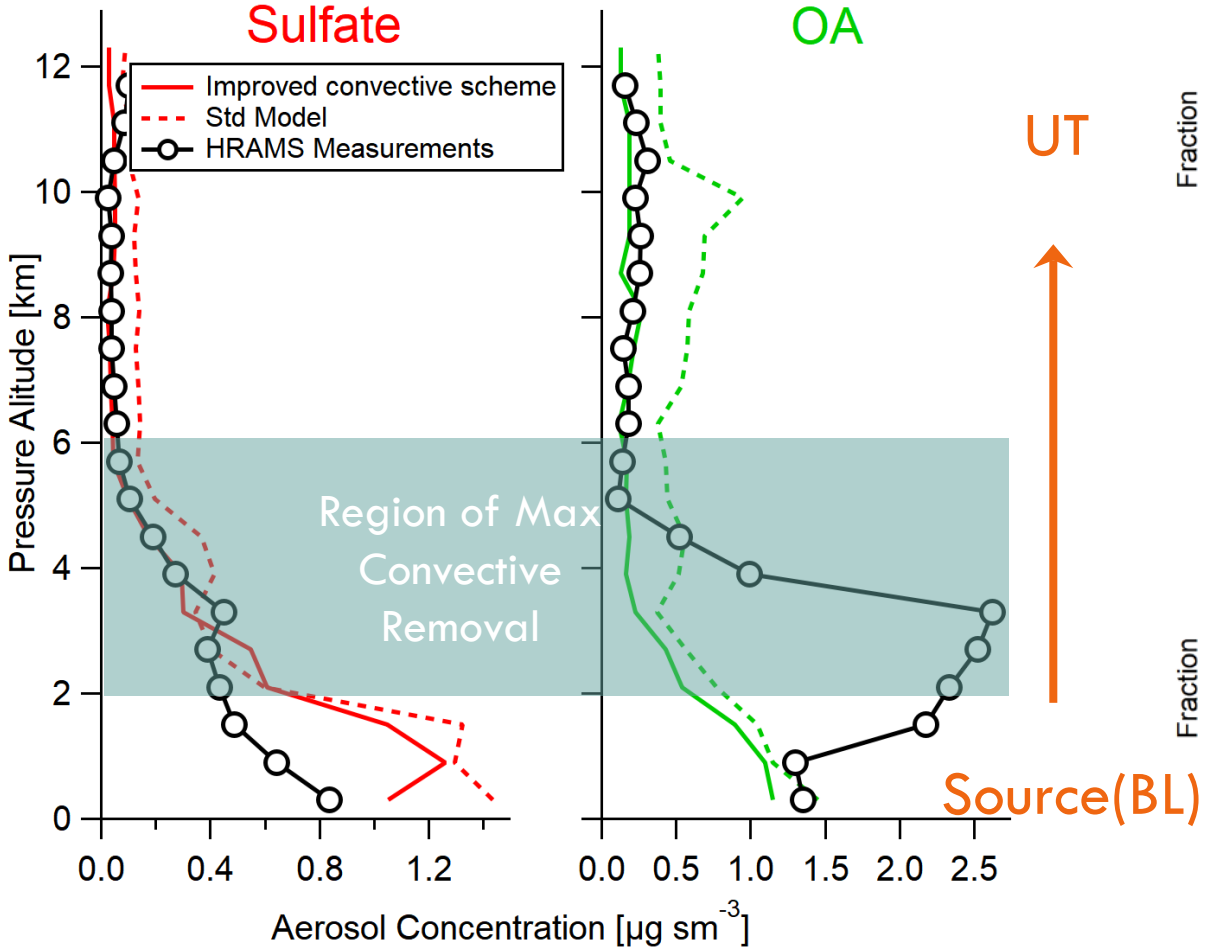
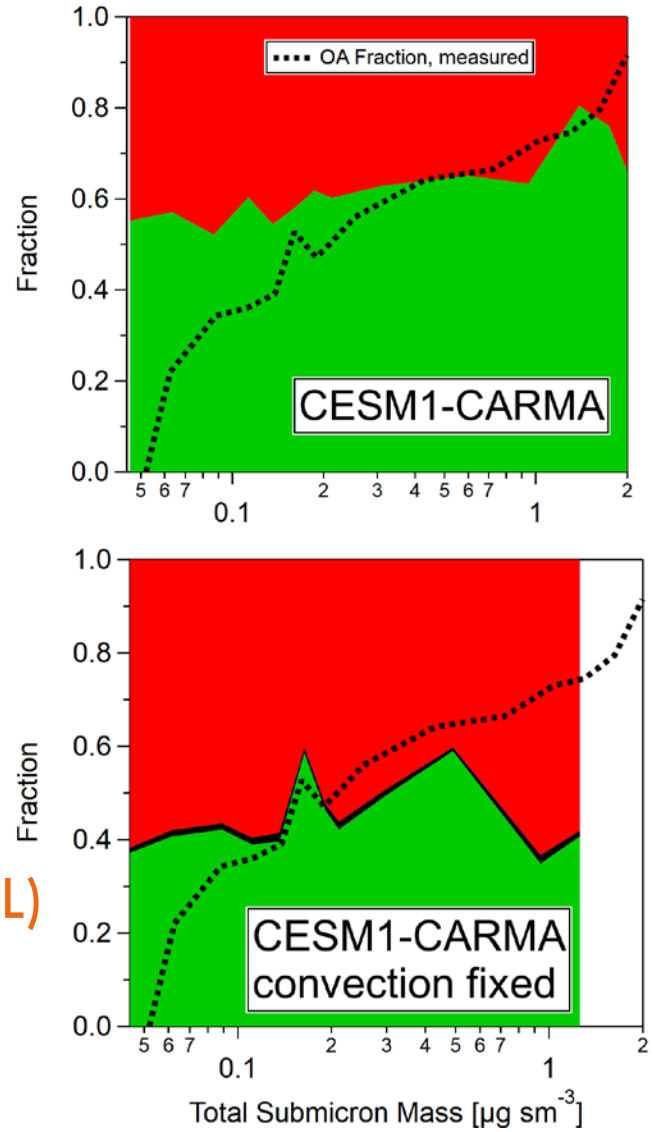
Equatorial Pacific, ATom-1: CESM1-CARMA without/with convective fix





- A time integration bug (Yu et al, 2018) has CESM & CESM2 severely underestimating convective removal
- This leads to overestimation of aerosol transport into the UT (<500 mbar)
- Large impact for primary species (BC and seasalt), but also for secondary species (SO_4 and OA)
- Model with improved convective losses reproduces BL/FT gradient much better
- For CESM-CARMA physical removal cannot explain the preferential OA removal observed in ATom data

Murphy et al, 2018; Yu et al, 2019, Hodzic et al, 2020

PHOTOCHEMICAL OA LOSS MECHANISMS

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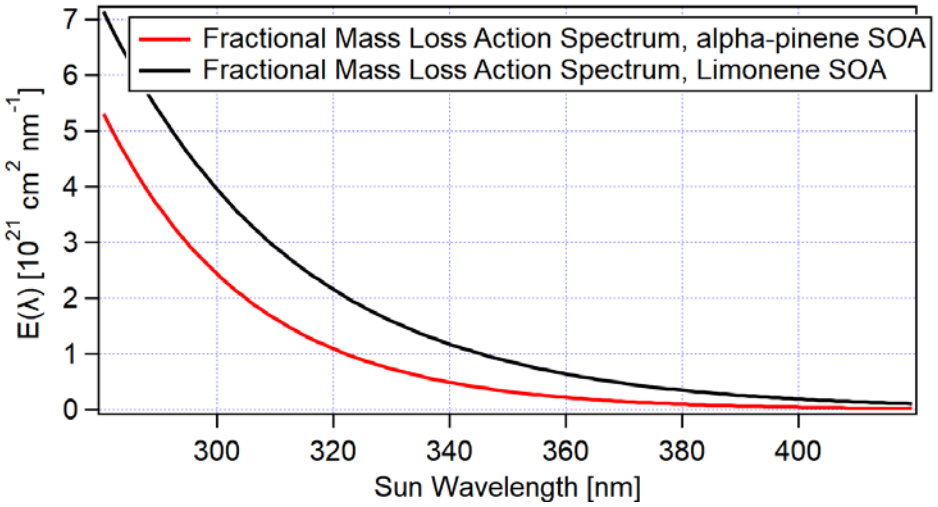
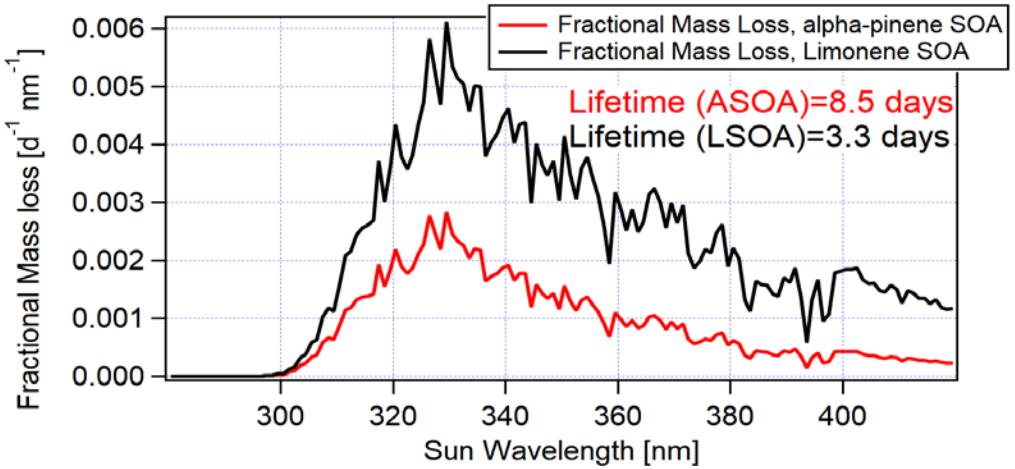
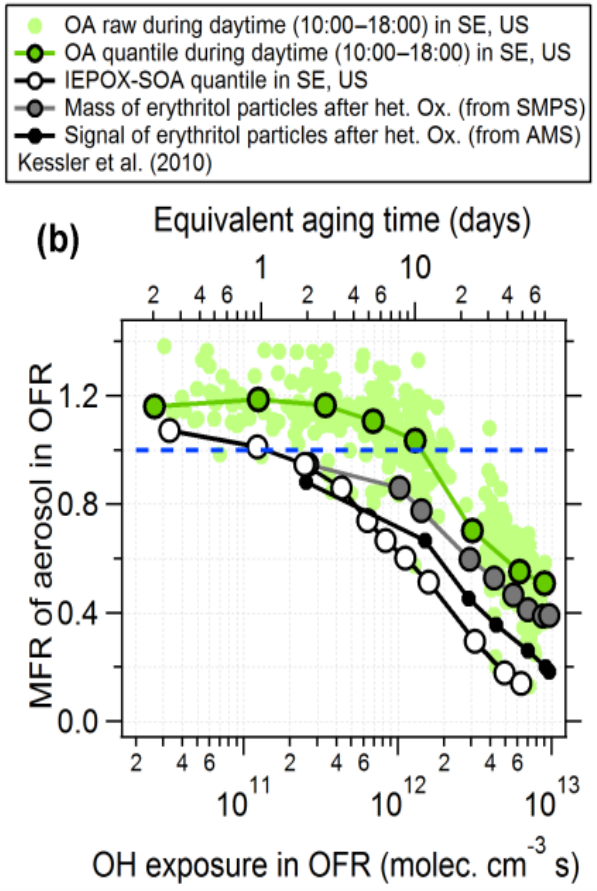
Photolysis of OA





Heterogeneous oxidation by OH (O_3)



- Fast photolysis of some types of SOA has been demonstrated
- Bleaching might slow down or stop this process and leave a photoresistant core.

- Heterogeneous uptake of OH on OA with γ~0.1-1 has been measured in the field.
- Diffusion limitations unlikely for liquid, acidic particles
- Could explain removal of a pyroCB plume in the stratosphere

In both cases a first order loss with a lifetime of ~ 10 days in the FT is expected

Hodzic et al, 2016, Hu et al, 2016, Malecha et al, 2018, Yu et al, 2019, O'Brien & Kroll, 2019

DERIVING AIRMASS AGE FOR THE ATOM TRACK

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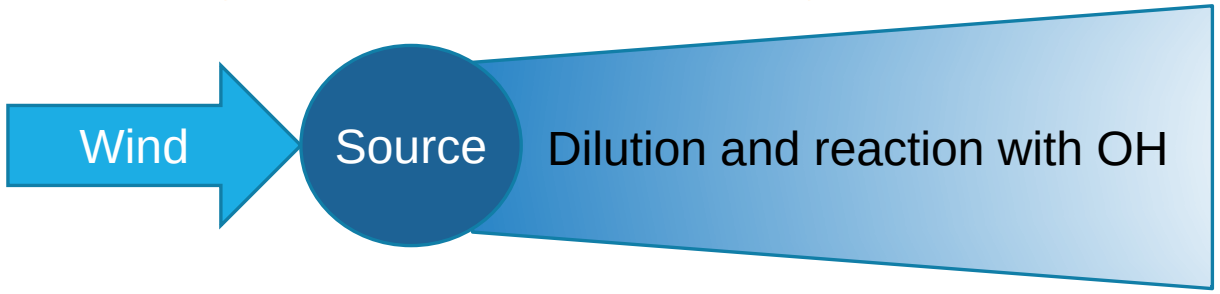
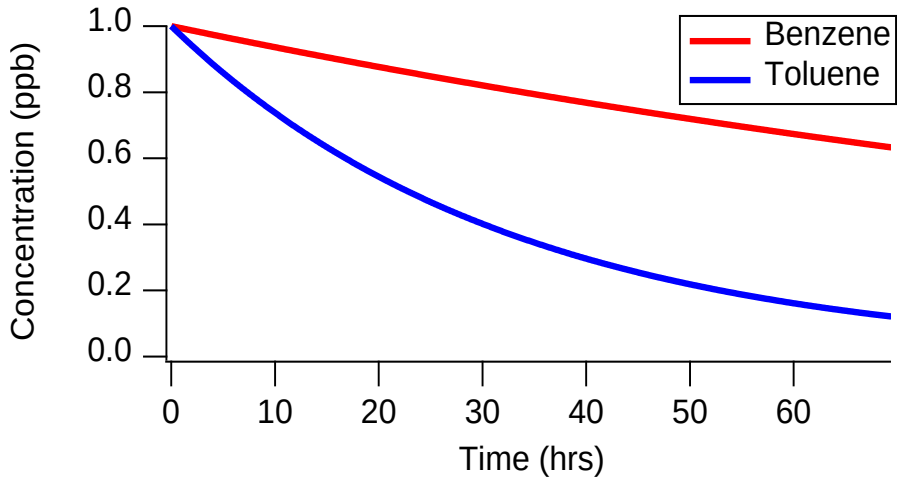
Estimating age from a photochemical clock (typical emission study scenario)

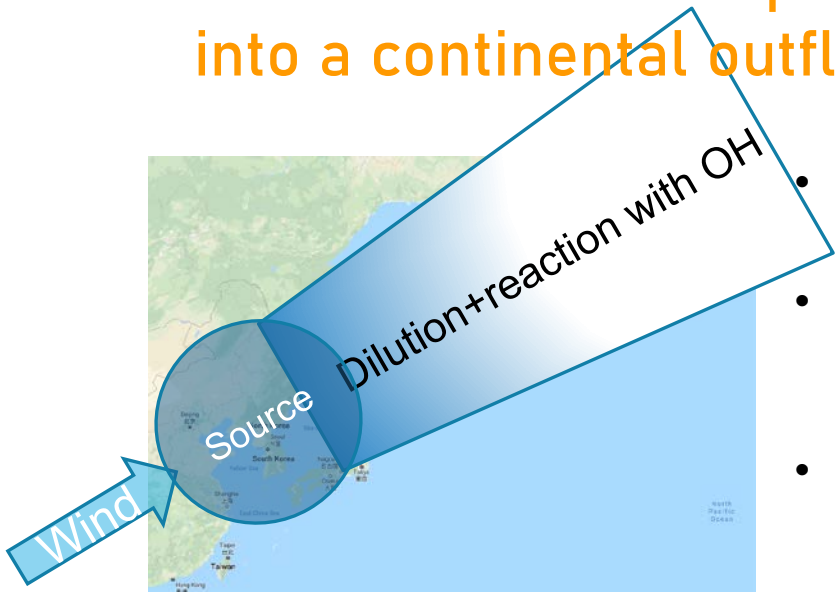


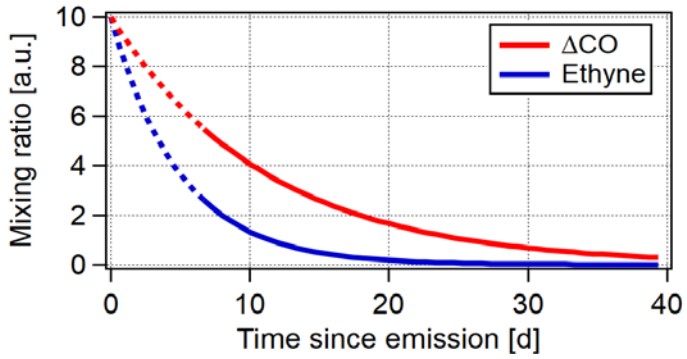


$$\tau([OH]) = -\frac{1}{k_a - k_b}\left\{ln\frac{[A]}{[B]} - ln\frac{[A]_{t=0}}{[B]_{t=0}}\right\}$$

Parrish et al 2007, Borbon et al, 2013, Nault et al, 2020

Now combine multiple sources into a continental outflow "soup"





- Mixing scales on the order of days
- For urban sources, VOC emission/ΔCO ratios well known
- Within factor of 2-3x, urban OA/ΔCO are well known as well
- Larger variability of BC/ΔCO
- BB contributions introduce large uncertainty on all these inputs

- Dilution will not affect the ratios observed, but bias the clock fast
- Polar and hemispheric circulation complicate these further

ESTIMATING AIRMASS AGE FOR A SUBSET OF THE ATOM (1-3) DATA

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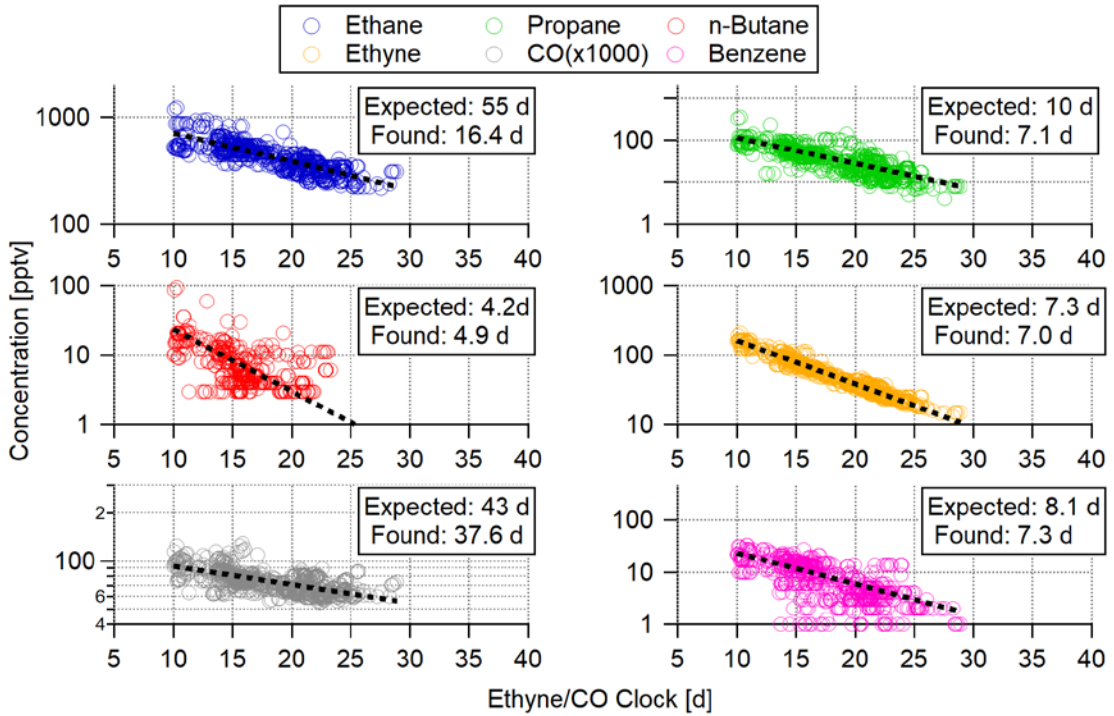
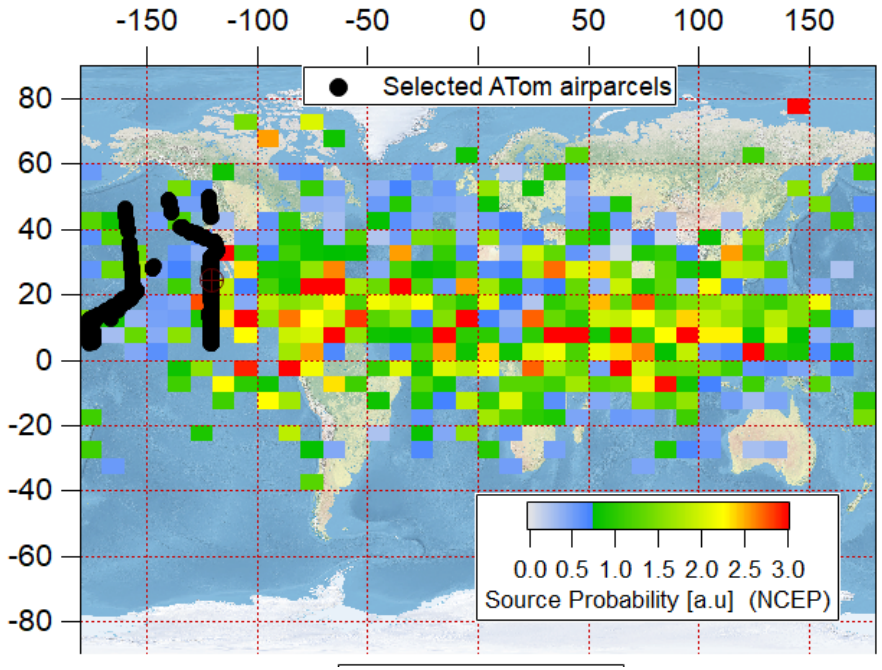
Criteria for a useful chemical clock dataset:

1. Upper FT only (<500 mbar), no stratospheric influence
2. No sources with unknown hydrocarbon ratios
   - Exclude any fresh or aged BB (PALMS BB marker)
   - Exclude the SH and the poles
3. Not too close to sources (well mixed, age>acetylene lifetime, >10 d)
4. Filter for high alkane plumes

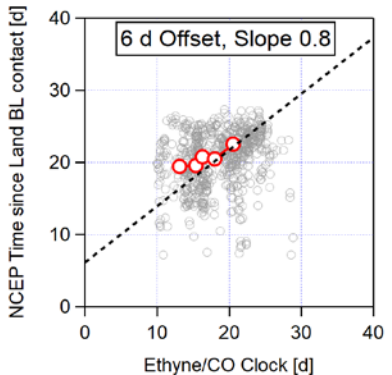
Gas phase tracer removal vs clock for subset



Selected data and source regions (Backtraj)



Backtrajectories vs chemical age



- Gas phase data suggest well-mixed airmasses and a consistent clock
- General agreement with (fairly uncertain) 30-day NCEP backtrajectories suggest possibly some, but not large dilution bias (=> chem clock running too fast)

ATOM 1-3: OA LIFETIMES IN THE UT

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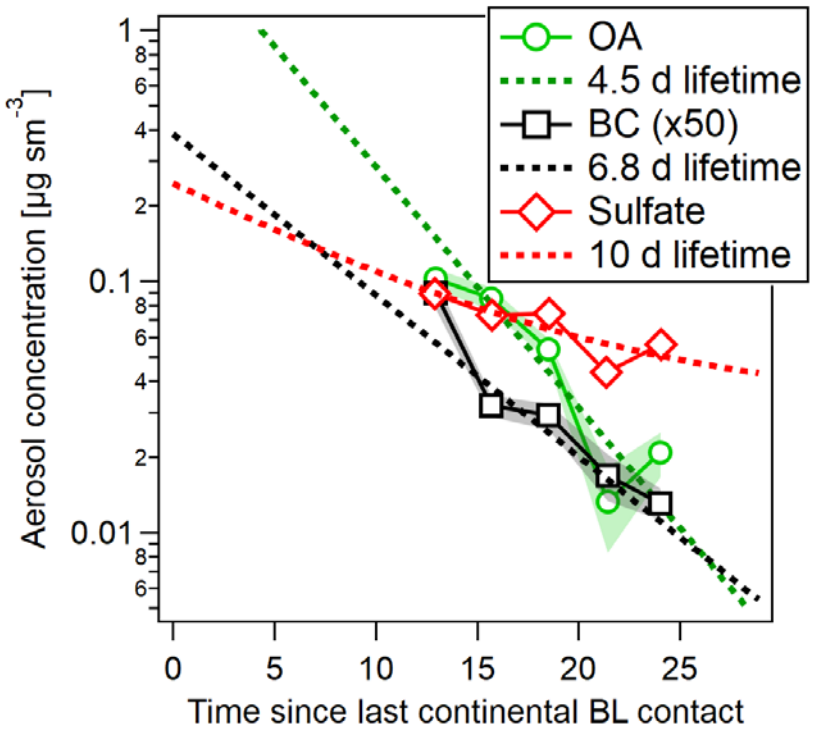
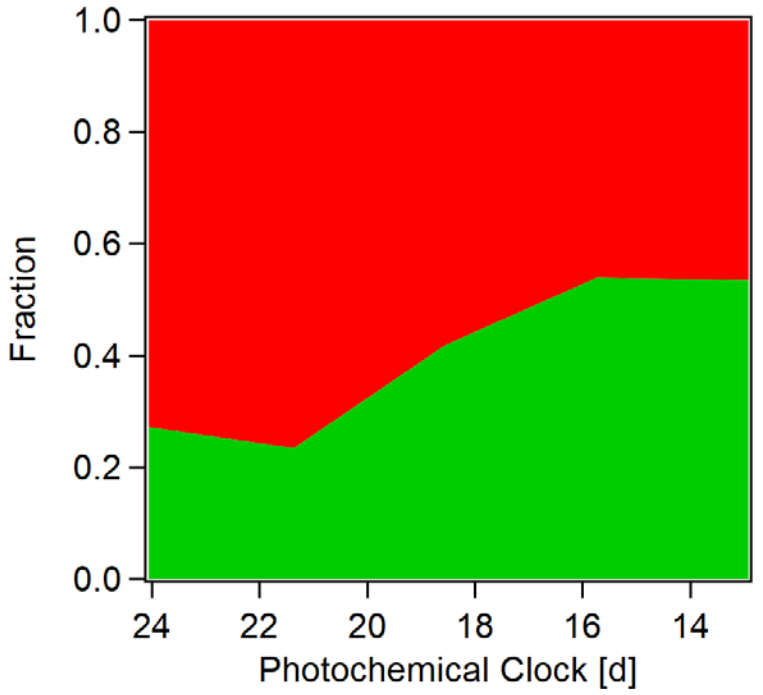
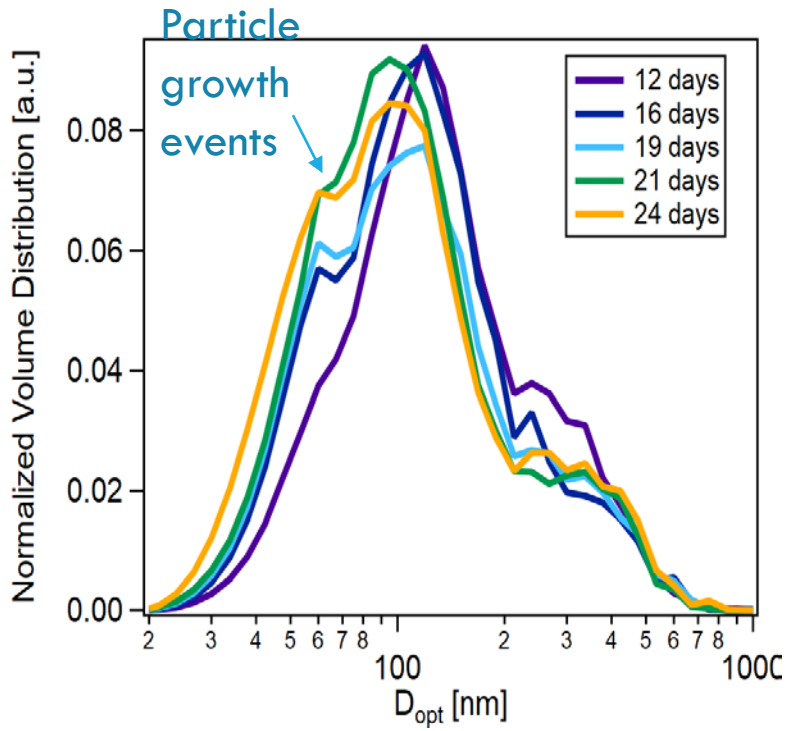
Aerosol species vs chemical age



Fractional composition (reversed clock)



Normalized Aerosol Volume vs chemical age



- Lifetime for chemical OA removal (relative to BC physical loss): 13 d
- Size distributions suggest slow shrinking of the accumulation mode, but also contribution of nucleation/particle growth at longer ages, hence removal estimate is an upper limit
- In-situ formation likely explains the difference between BC and sulfate removal

COMPARISON WITH CESM2 OUTPUT, SAME CLOCK & FILTERING

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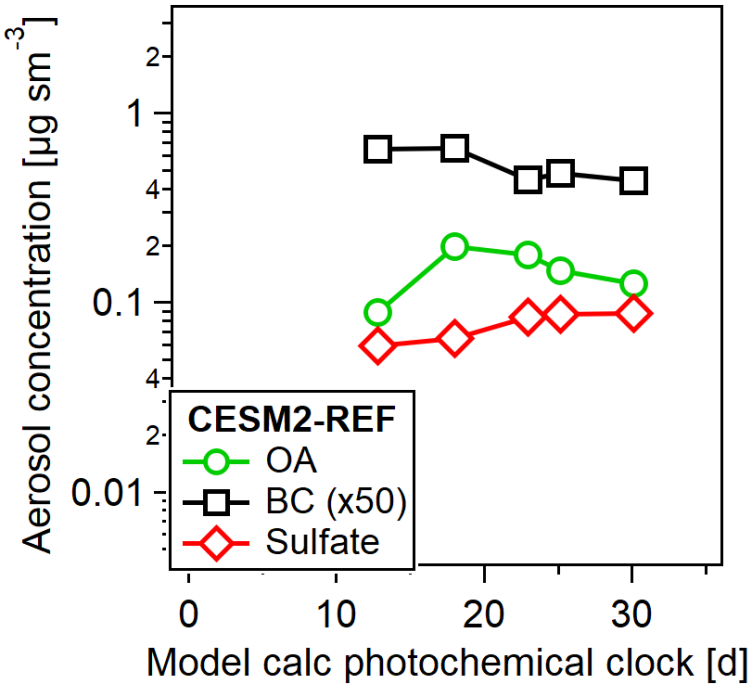
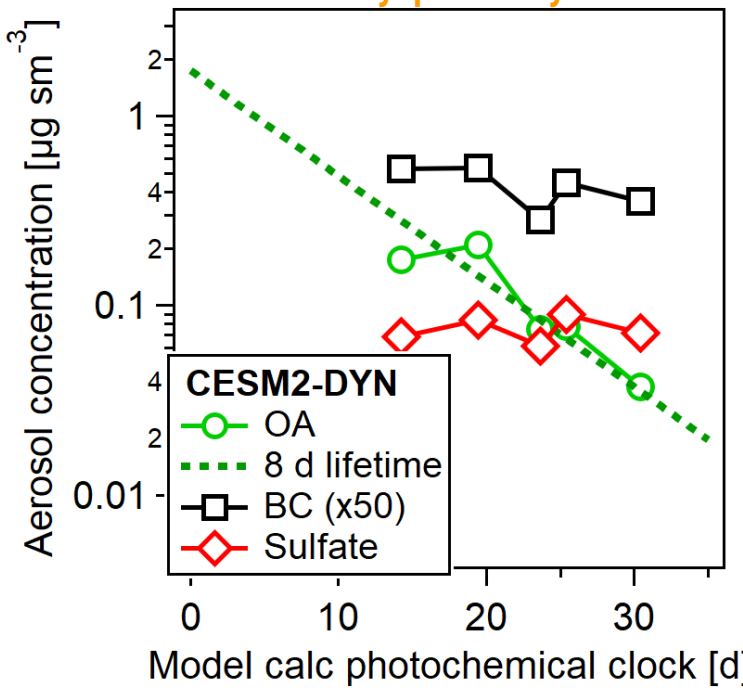
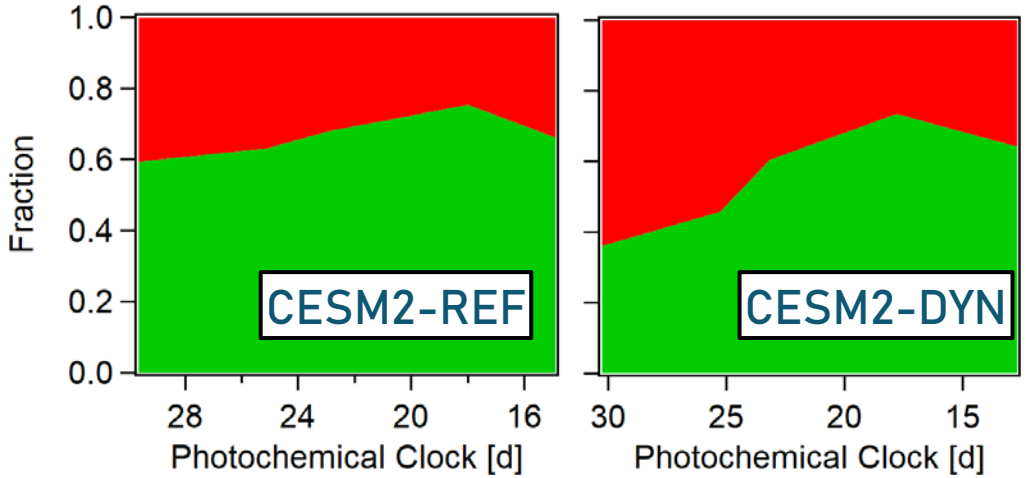
Std Model



Improved Model,
Stronger Sources, VBS
9 day photolysis



Fractional composition
(reversed clock)



- Using the same analysis as for the field data, we are able to retrieve a removal rate from the model very close to the prescribed photolysis rate that was inputed into it, giving us confidence in our method
- No significant BC removal in the model, since this version of CESM2 does not have the convective fix
- Improved Model (DYN) version of the model shows more realistic trend in OA/SO_4 ratios in the remote FT vs age, POA/OA fractions still unrealistically high (partly b/c of convection bug)

Hodzic et al, 2016, Tilmes et al, 2019

CONCLUSIONS

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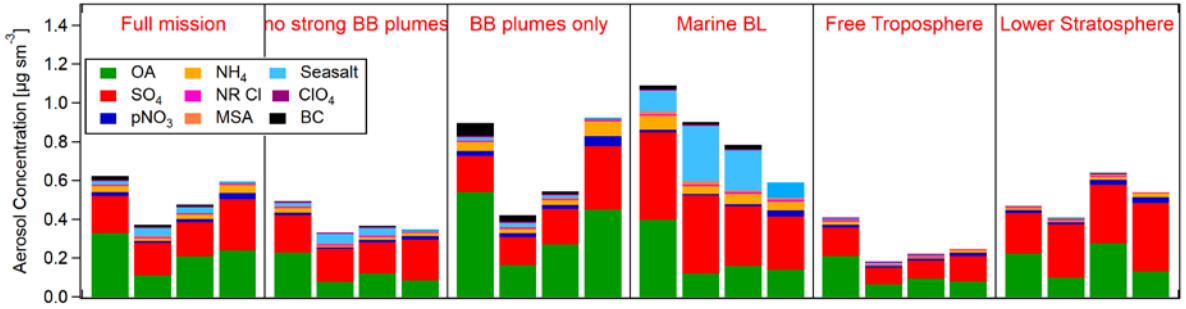
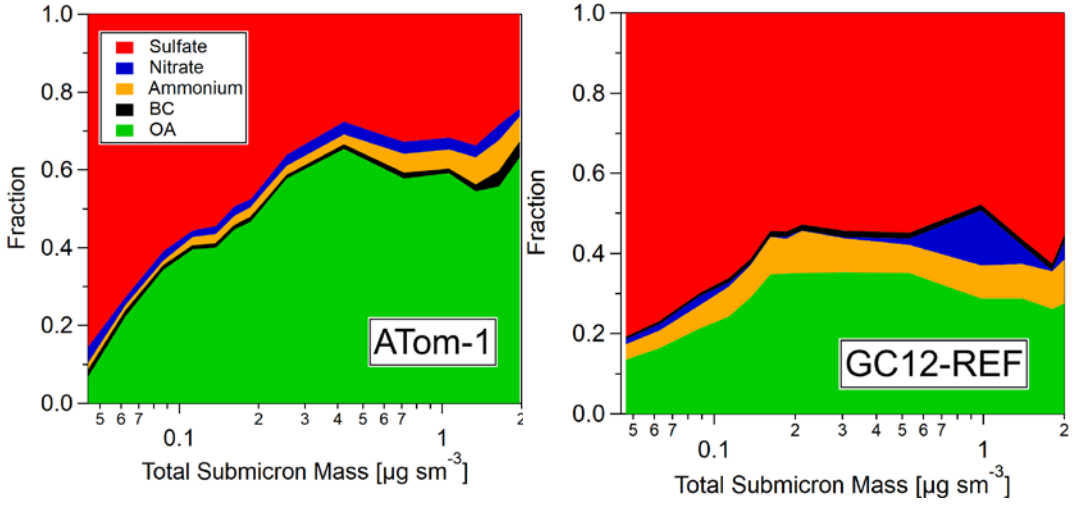
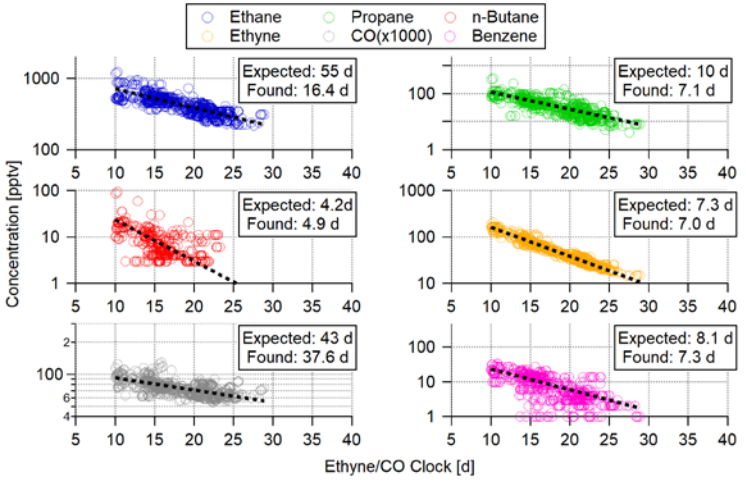
1. ATom PM1 FT average concentrations similar across deployments



2. Less OA in cleaner air, not really reflected in models



3. NH subpolar FT VOC ratios fairly constant, suitable for a campaign wide photochemical clock



4. ~13 d chemical removal rate for ATom 1-3 OA