

High Concentration Aerosol Event Mask

Objective

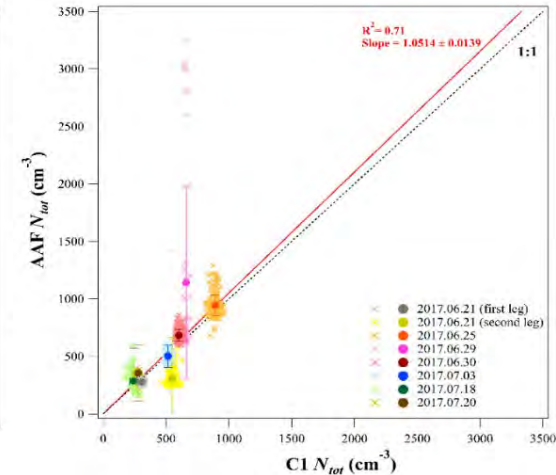
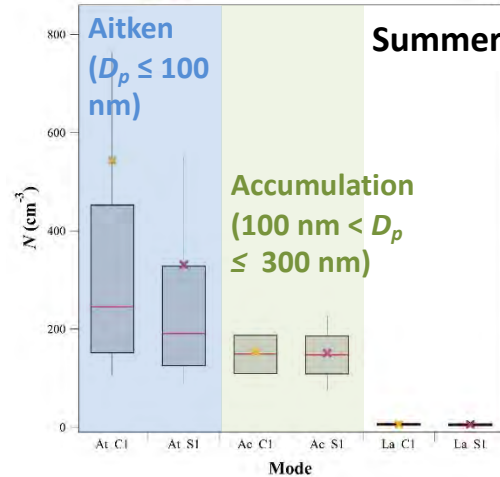
- Identify high concentration submicron aerosol events associated with local sources at the Eastern North Atlantic (ENA) ARM Central Facility (C1) Aerosol Observing System (AOS)

Approach

- Develop an algorithm to mask periods that do not represent regional aerosol
- Validate the mask with a temporary Supplementary site (S1), collocated measurements and observations

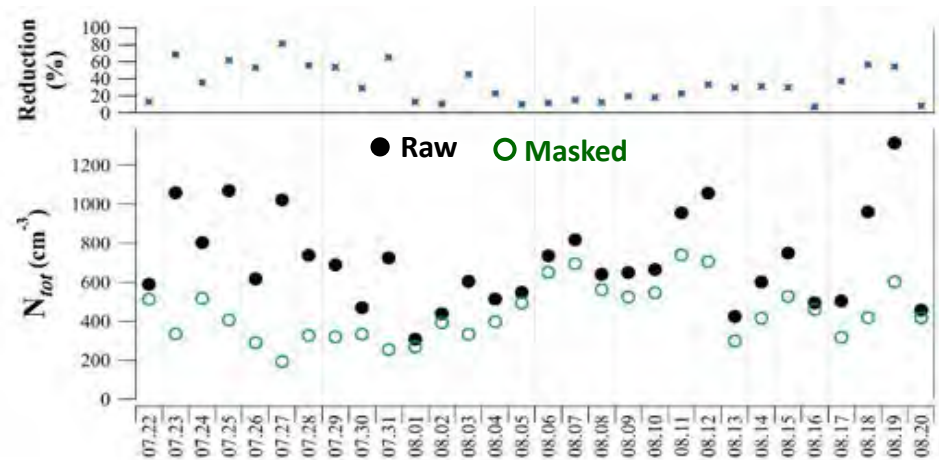
Impact

- Aerosol processes involving Total submicron or Aitken mode particles should be masked
→ Monthly means reduced by factors of 1.65 (Summer), 1.55 (Winter)
- Accumulation mode less impacted – reduced by factors of 1.07 (S), 1.33 (W)
- Can be applied to other Facilities



Box and whisker plot with mean (x) and median (-) # conc.

Masked AOS vs AAF total submicron number conc.



Daily mean submicron aerosol number concentrations and percent reduction after applying the mathematical mask

F. Gallo, J. Uin, S. Springston, J. Wang, G. Zheng, C. Kuang, R. Wood, E. B. Azevedo, A. McComiskey, F. Mei, A. Theisen, J. Kyrouac, and A. C. Aiken.

“Identifying a regional aerosol baseline in the Eastern North Atlantic using collocated measurements and a mathematical algorithm to mask high submicron number concentration aerosol events.” *Atmospheric Chemistry and Physics*, in press. (2020) [DOI: <https://doi.org/10.5194/acp-2020-49>]

Aerosol Vertical Transport at the Southern Great Plains

Objective

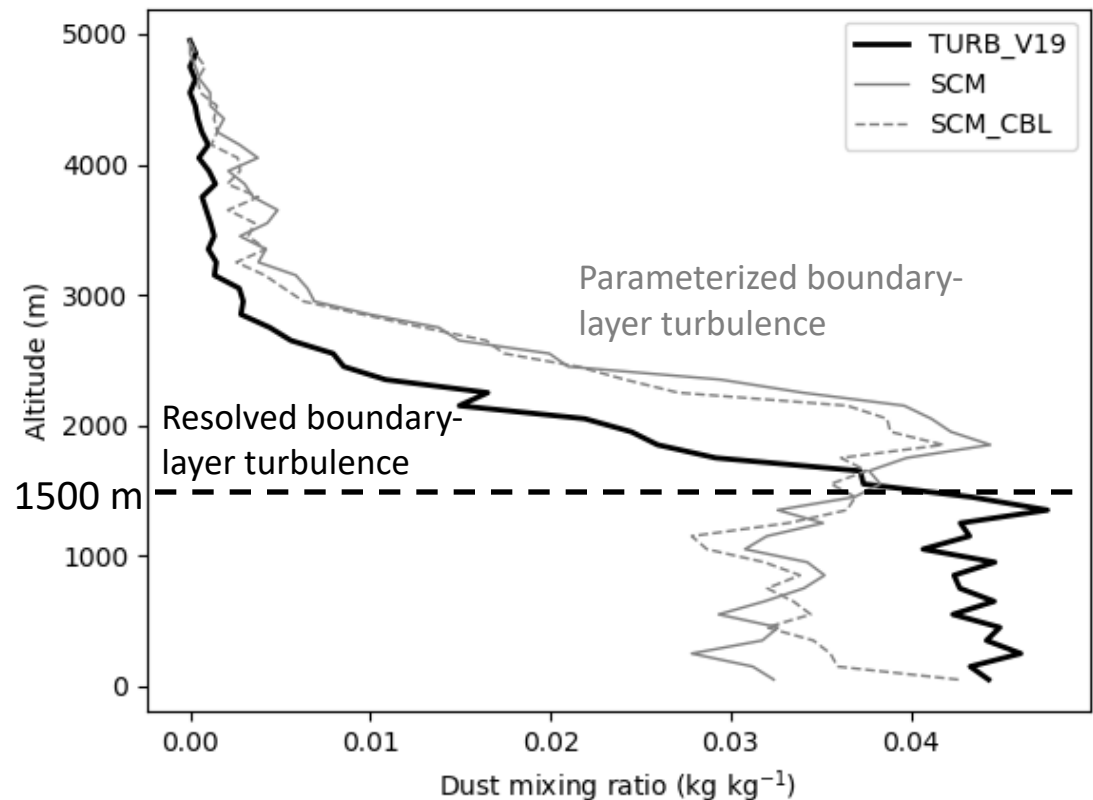
- Better understand the impact of resolved versus parameterized turbulence on the vertical export of aerosol from the boundary layer

Approach

- Perform Lagrangian simulations of aerosol vertical transport, using meteorological fields from boundary-layer turbulence simulations (LASSO LES ensemble)
- Collapse the LASSO domain to a quasi-single column, and repeat the simulation with and without turbulence parameterizations

Impact

- In the quasi-single-column model, turbulent export above 1500 m is increased by 58% when using a turbulence parameterization, and 72% without the parameterization.

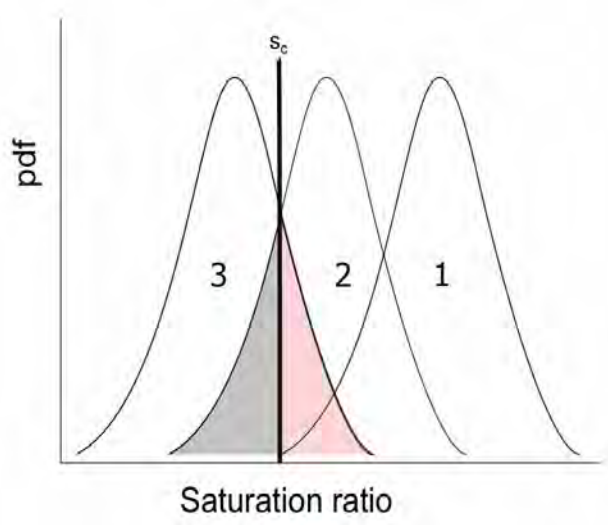


Vertical distribution of dust aerosol, 12 hours after a simulated emission at the surface.

FLEXPART-WRF simulations to assess dust transport in the convective boundary layer at the Southern Great Plains site, Gavin Cornwell and Susannah Burrows, *in prep.*

The Role of Turbulent Fluctuations in Aerosol Activation and Cloud Formation

P. Prabhakaran, A.S.M. Shawon, G. Kinney, S. Thomas, W. Cantrell, R. Shaw
Michigan Technological University

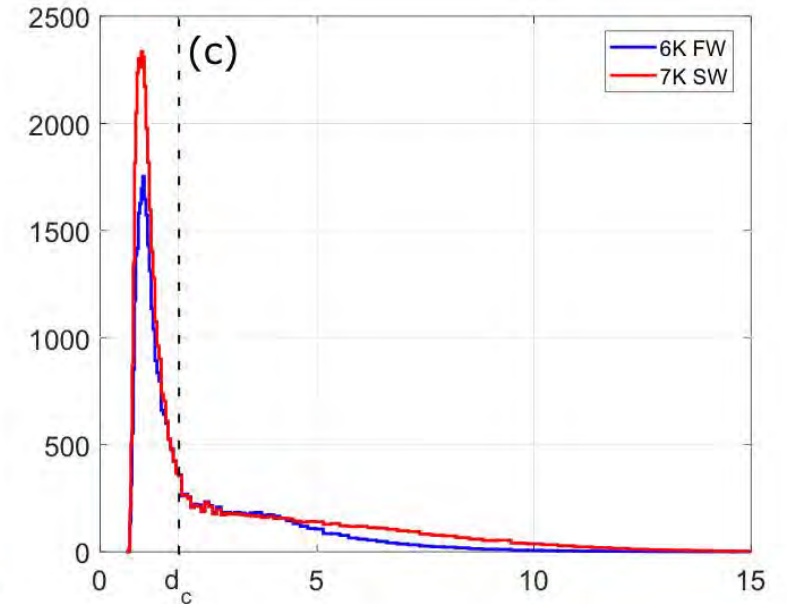
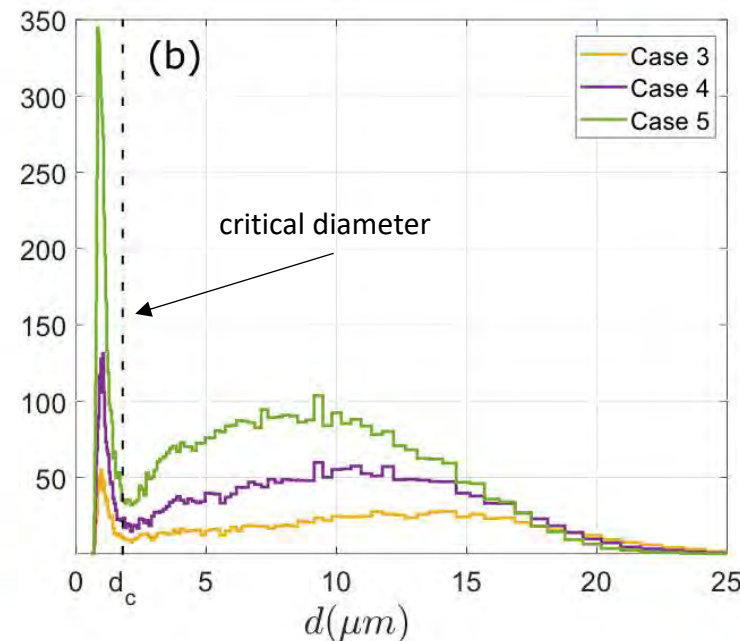
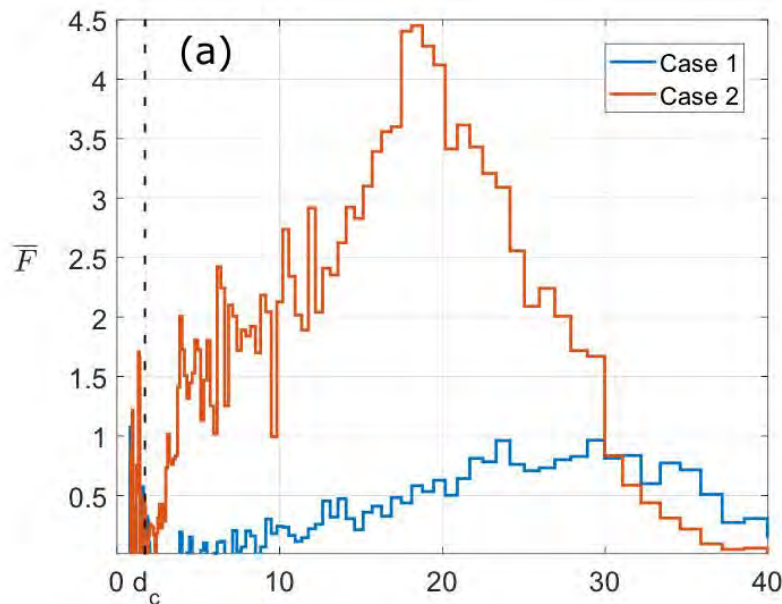


1(a): $\overline{S}_{\text{environ}} \gg S_{c,\text{aerosol}}$; fluctuations play a minimal role in activation

2(b): $\overline{S}_{\text{environ}} > S_{c,\text{aerosol}}$; fluctuations play an intermediate role

3(c): $\overline{S}_{\text{environ}} < S_{c,\text{aerosol}}$; activation is only through fluctuations

For all experimental data shown below, aerosol was 130 nm NaCl.



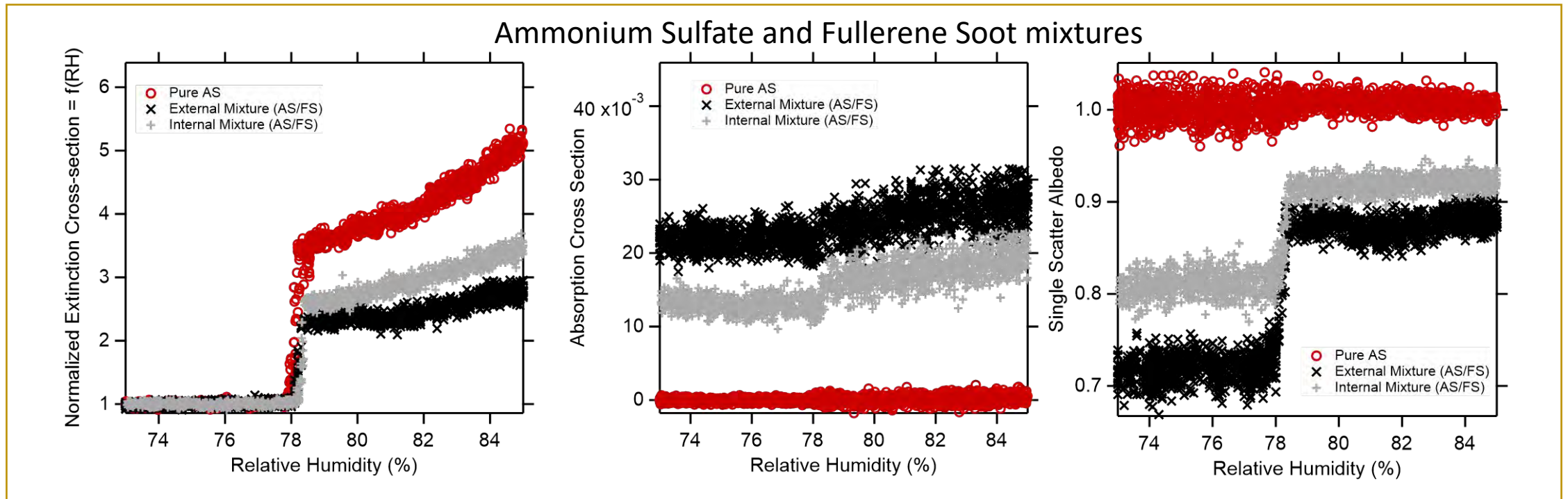
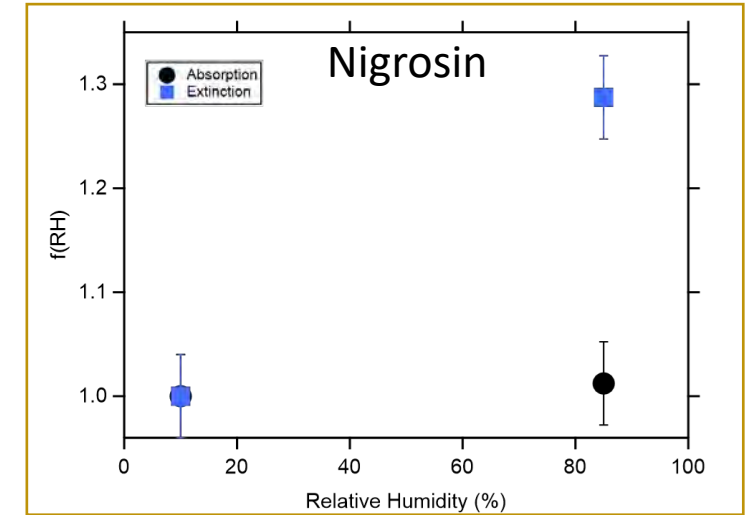
Variability in light absorption by aerosols and the influence of water uptake

Chris Cappa & Qi Zhang

UCDAVIS

Goal: Understand how water uptake affects aerosol light absorption

- Consider various pure absorbing particle types (BrC and BC)
- Assess influence of mixing with non-absorbing components
- Consider influence of photochemical aging



Optical-Chemical Properties of Aged Woodbury Fire Smoke

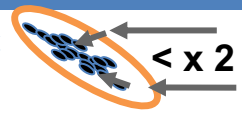
Lee, Dubey, Aiken, Chylek & Carrico, LANL, JGR- Atm 2020

BC...

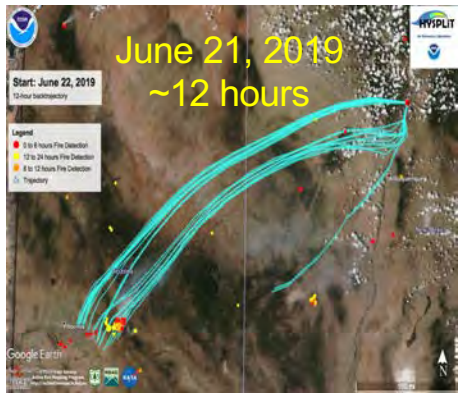


450 nm: $9 \text{ m}^2/\text{g}$
870 nm: $5 \text{ m}^2/\text{g}$

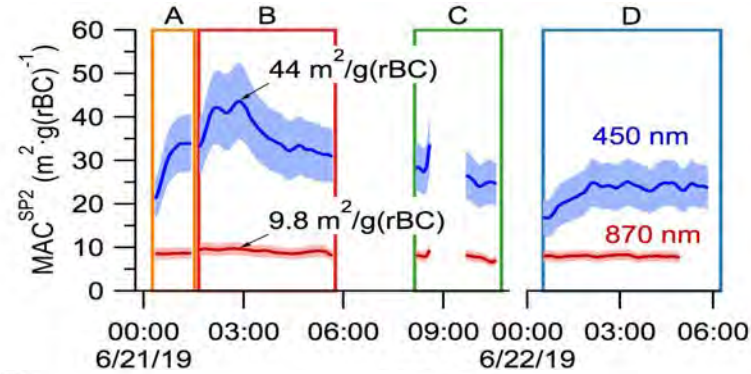
Coated BC



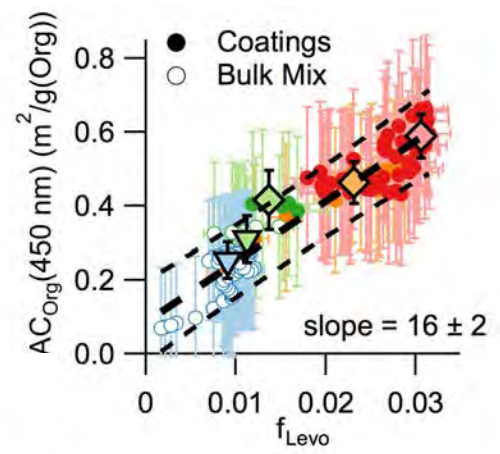
BrC ??



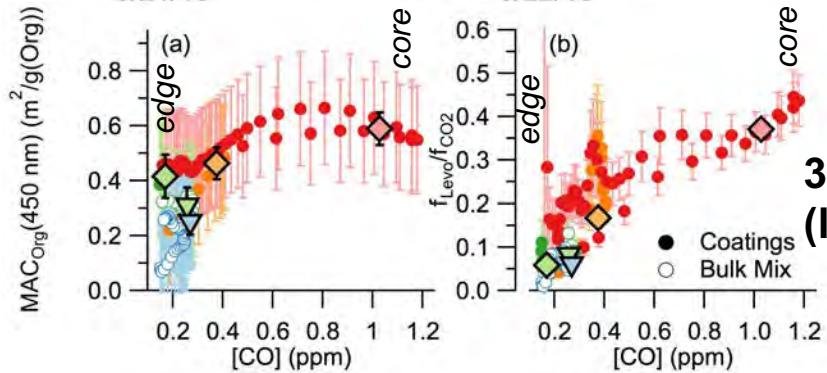
1. $\text{MAC}_{\text{BC+BrC}}$



2. MAC_{BrC} vs. f_{Levo}



3a. Lower MAC_{BrC} at plume edge (lower CO)



3b. More oxidation/mixing (lower $f_{\text{Levo}}/f_{\text{CO}_2}$) at plume edge

The Portable Ice Nucleation Experiment chamber (PINE): first deployment at SGP-GIF

Objective

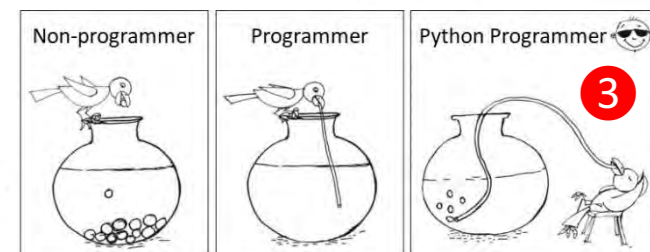
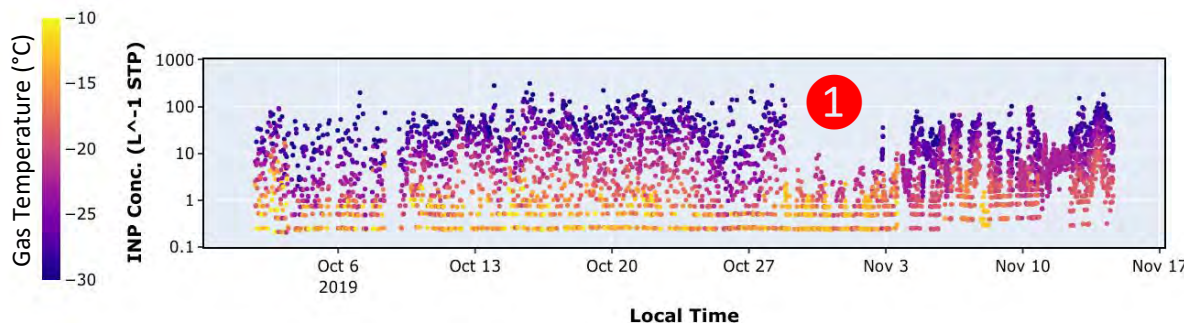
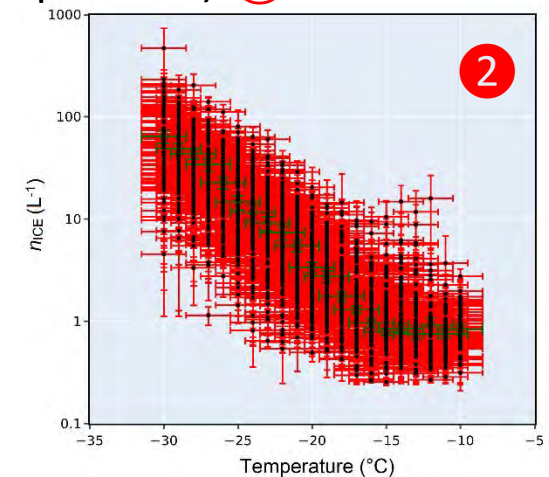
- **45 days** ground-based ice-nucleating particles (INP) measurement using PINE at SGP
- Remote & semi-autonomous operation of PINE via network on a **24/7 basis**

Outcome

- INP $> 0.2 \text{ L}^{-1}$ with ~ 8 min measurement time resolution for Oct. 1 – Nov. 14, 2019 **①**
- IN spectra in the T range of -10 to $-30 \text{ }^\circ\text{C}$ (~ 45 min to obtain a spectrum) **②**

Outlook

- Various IN parameterizations - n_s isoline, ABIFM etc.
- Immersion vs. deposition - droplets required for IN?
- Dynamics, thermodynamics & microphysics link?
- Looking into CCN-INP relationship & supermicron INP
- Research-Education Integration 😊 Webex-based **Python** hands-on for INP research (\$ free) - please contact me **③**



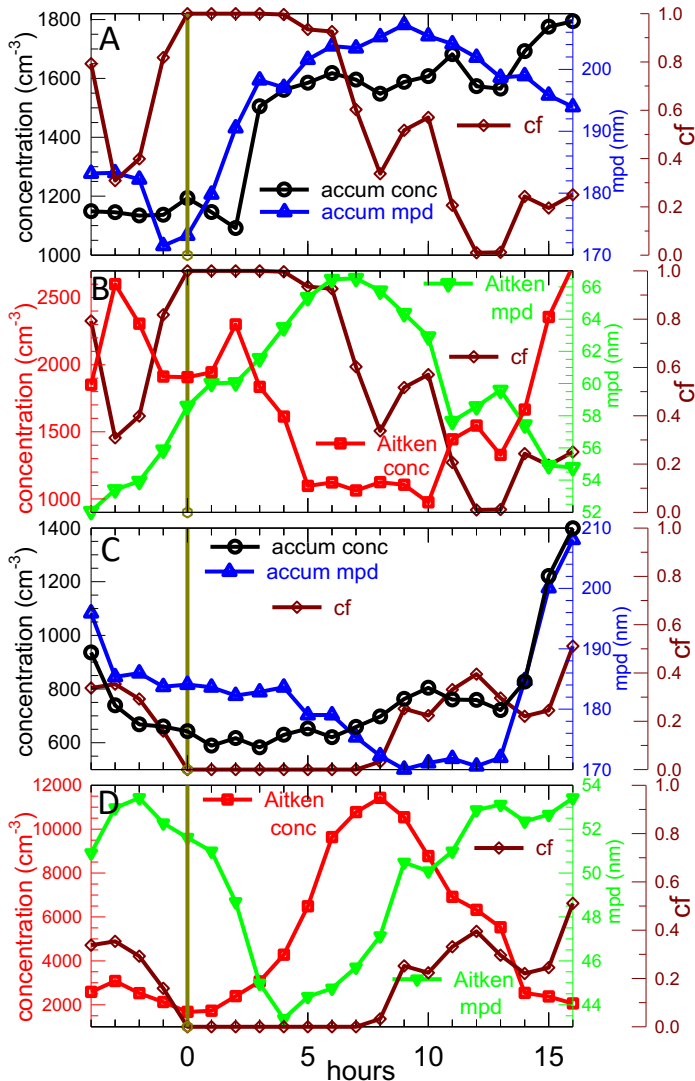


Fig. 1. Mean concentration and mean particle diameter (mpd) for consecutive cloud hours. **A & B** for 5 days of 7+ hours of cloud fraction (cf) > 0.75 & mixing height (MH) > cloud base altitude (cba). **C & D** for 4 days of 7+ hours of cf0. **A & C** for accumulation mode (diameter 100-825nm). **B & D** for Aitken mode (25-100nm diameter).

Noble & Hudson, 2019: Effects of continental clouds on surface Aitken and accumulation modes. JGRA, 124, 5479-5502.

Conclusions:

At SGP in May 2003 clouds exclusively produced the accumulation mode and inhibited production of the Aitken mode. Production of both modes occurred only during daylight when oxidants for cloud chemical reactions promoted accumulation particles and photochemistry produced Aitken particles.

Need to test at other times/seasons and other locations with cf, cba, MH and aerosol size spectra.

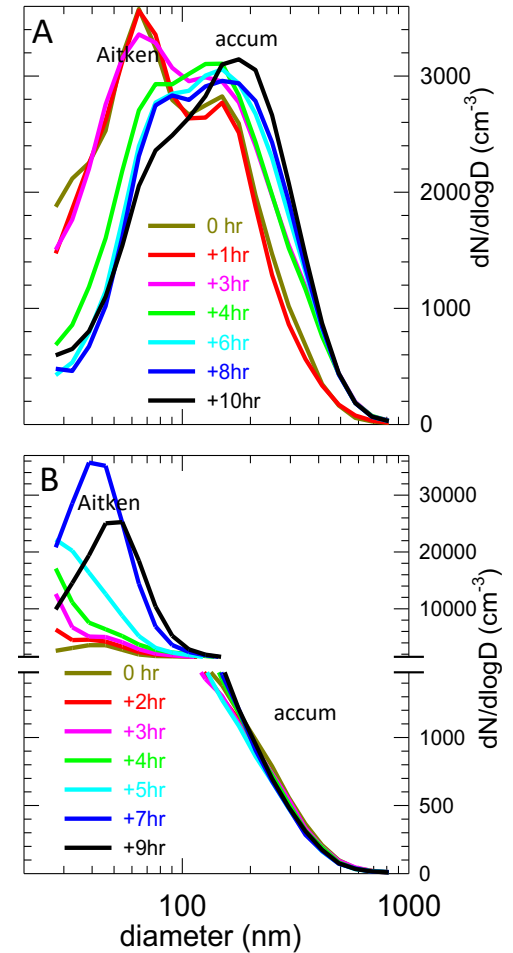
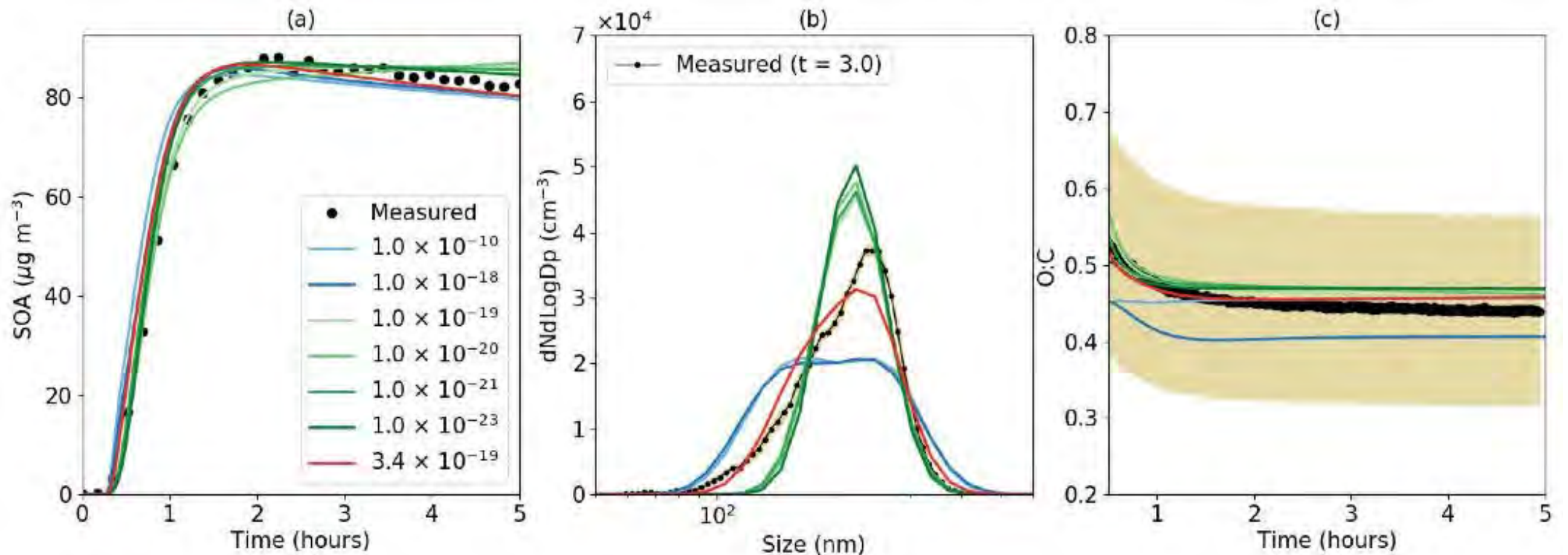


Fig. 2. Mean particle size distributions after the initial onset of 7+ consecutive hours of **A)** cf > 0.75 when MH > cba and majority of hours are daylight; & **B)** daylight cf0. Hours following onset are also shown as denoted by legend.

Particle Size Distribution Dynamics Can Help Constrain the Phase State of Secondary Organic Aerosol (DE-SC0017975)

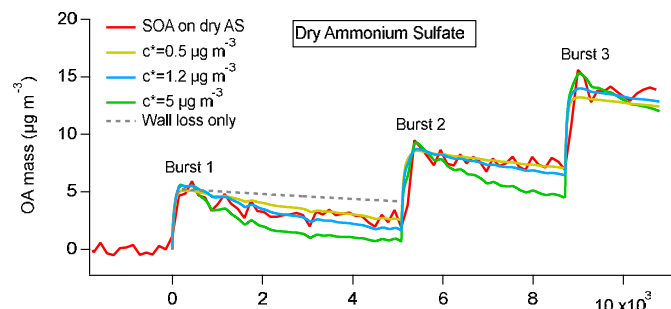
Yicong He, Theodora Nah, Nga L. Ng, Lauren A. Garofalo, Delphine K. Farmer, Rahul Zaveri, Christopher D. Cappa, Jeffrey R. Pierce, and **Shantanu H. Jathar**

Chamber experiment for α -pinene+O₃ with no seed and RH<5%

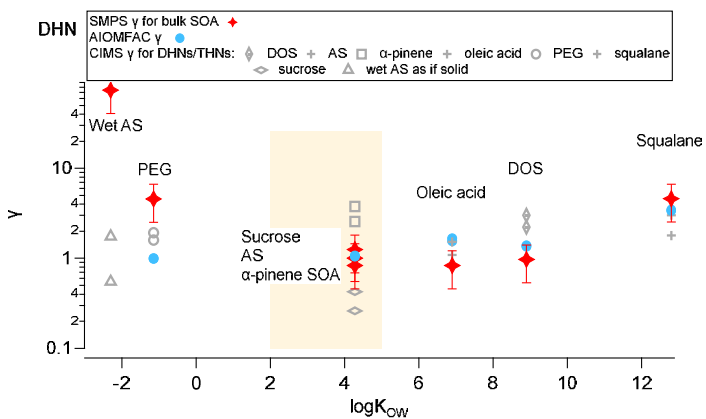


- Takeaway: application of a detailed chemistry-microphysics model suggests **SOA has a D_b of $1-4 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$** when constrained to mass, O:C, and number size distribution data

Chamber burst of SOA, followed by evap.

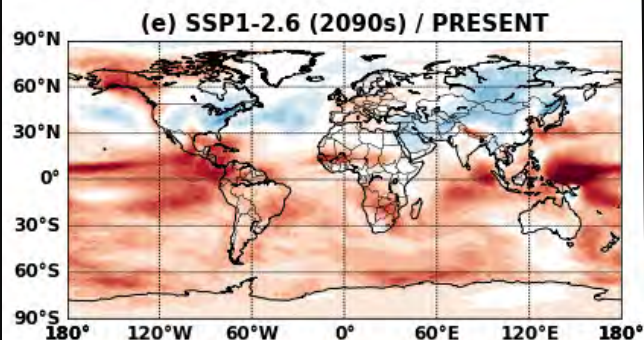


Use to estimate activity coefficients of SOA

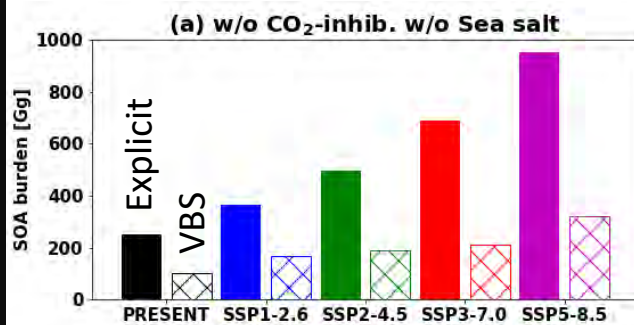


Liu et al., in revision, ES&T Letters

IEPOX-SOA under future climate

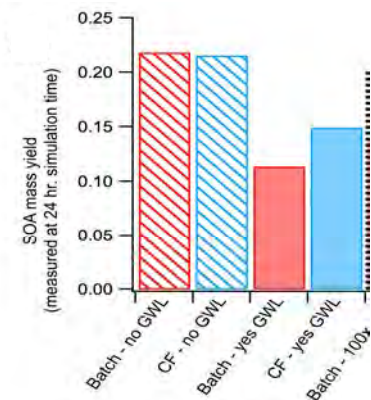


f(scenario), very different than VBS

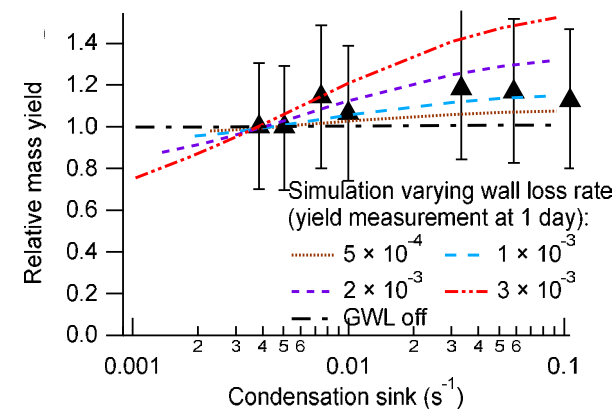


Jo et al., submitted, ACP

Wall losses do impact CF Chambers



Yield vs. CS ~ constant compatible w/ this



Krechmer et al., submitted, ES&T

Exploring natural aerosol formation from DMS oxidation and implications for aerosol forcing

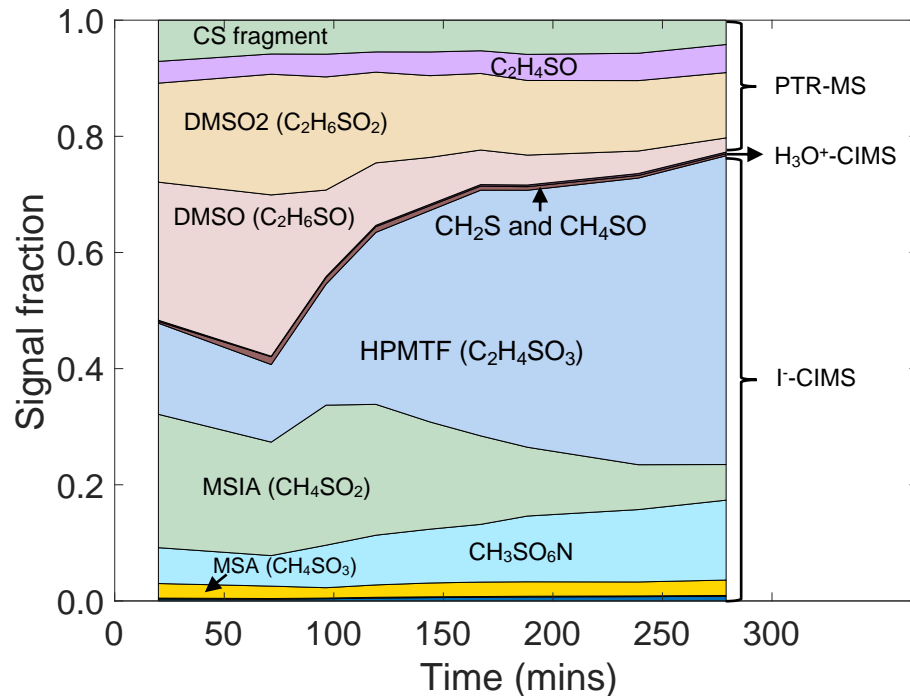


Jesse Kroll, Colette Heald,
Qing Ye, Matthew Goss, Ka Ming Fung

Dimethylsulfide (DMS): the dominant precursor to natural sulfate aerosol

Mechanism is complex and uncertain; but mechanistic details control amount, distribution of aerosol

(1) Laboratory studies



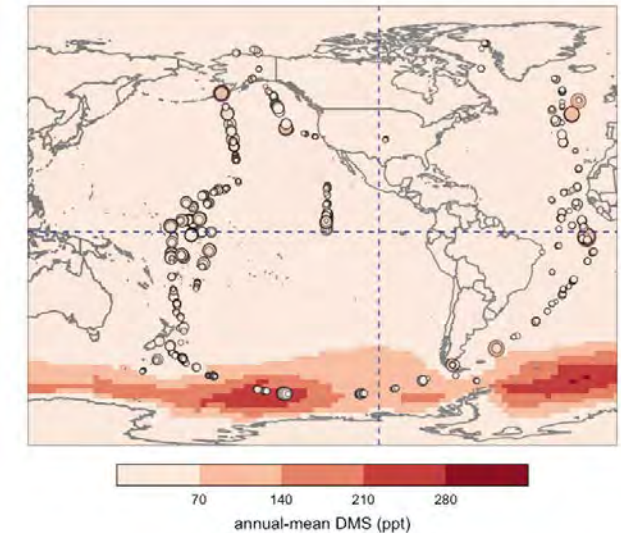
Chamber experiments:
DMS+OH+NO_x

Products measured with multiple
mass spectrometers

← Results from one experiment:
fractional concentrations of
gas-phase S-containing products

Will provide mechanistic, kinetic info
for use in models

(2) Global modeling



Expanding DMS gas-phase and aqueous-phase
chemistry in CAM-Chem based on the literature.
Starting to evaluate with observations (here ATom).

"Fungal shrapnel" found in the air during HI-SCALE

Observations:

- During the 2016 HI-SCALE campaign at the SGP ground site, we identified sporadic events of **fungal fragments many times smaller and more numerous** than we knew existed.
- These fragments were most likely bits of **fungal spores** that burst after swelling with water.

Approach:

- In situ size-resolved nanoparticle composition by Thermal Desorption Chemical Ionization Mass Spectrometry (TDCIMS).
- We identified the fungal fragments by the detection of **chitin**, the main component of fungal cell walls, and **sugar alcohols** such as mannitol, which is a major energy storage molecule in fungal cells.

Impacts:

- Possible source of **fungal allergens** at higher numbers and deeper lung deposition than intact cells.
- Possible source of efficient **ice nuclei** as has been observed for some particles of biological (e.g. bacterial, fungal, viral) origin.

Fig. 1. Ambient aerosol size distributions over an "event" and a "non-event" period close in time.

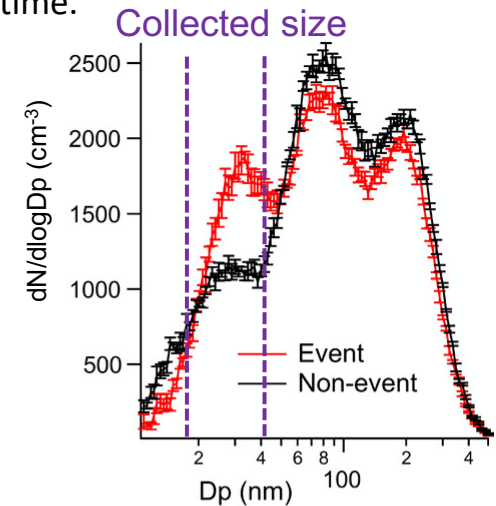
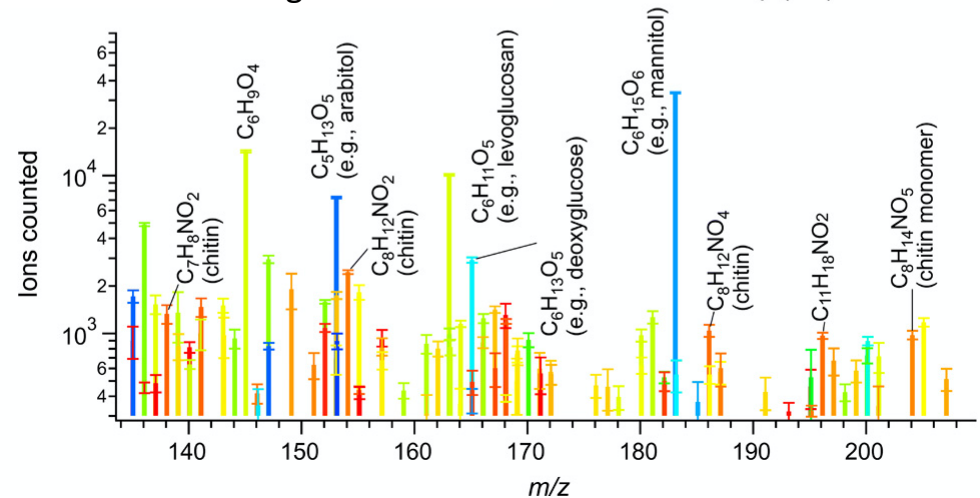


Fig. 2. TDCIMS positive ions detected during the event period. Warm colors are mostly pyrolysis products of chitin. Cool colors include desorbed sugar alcohols.

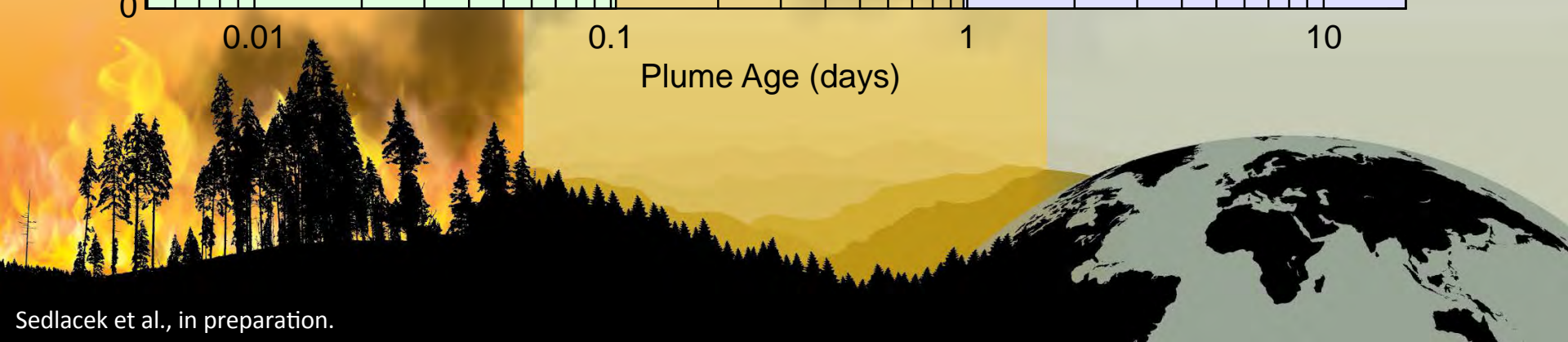
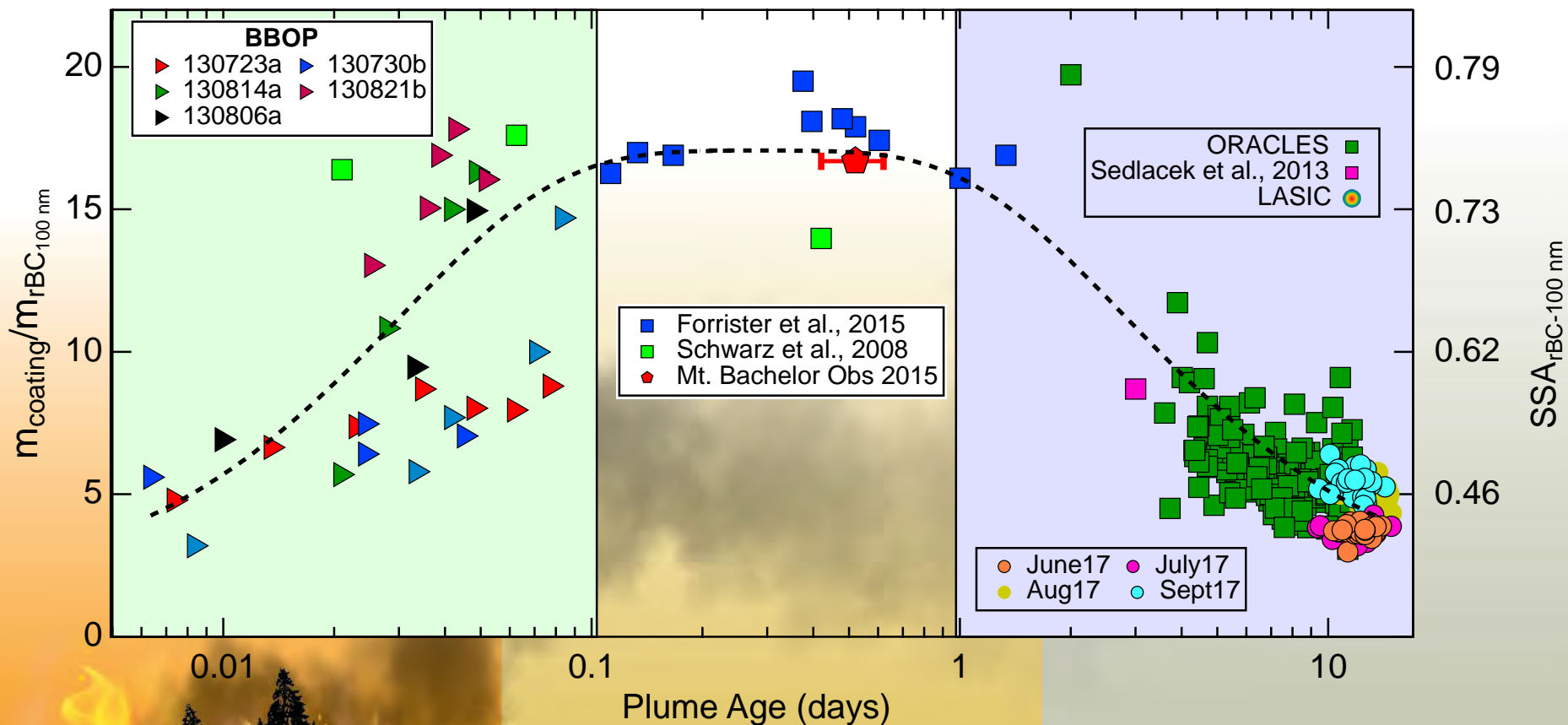


Lawler, M. J.; Draper, D. C.; Smith, J. N. Atmospheric Fungal Nanoparticle Bursts. *Sci. Adv.* **2020**, *6* (3), eaax9051. <https://doi.org/10.1126/sciadv.aax9051>.

Biomass Burning Black Carbon Mixing State Lifecycle

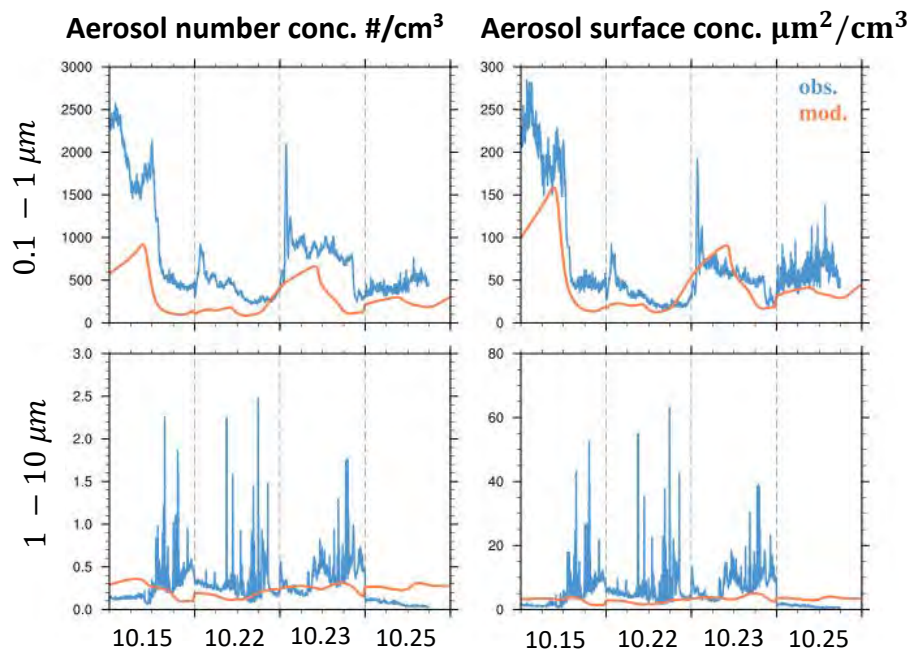
Ernie R. Lewis and Arthur J. Sedlacek III, BNL

BBOP, ORACLES, and LASIC provide an unprecedented opportunity to examine BB aerosol lifecycle.

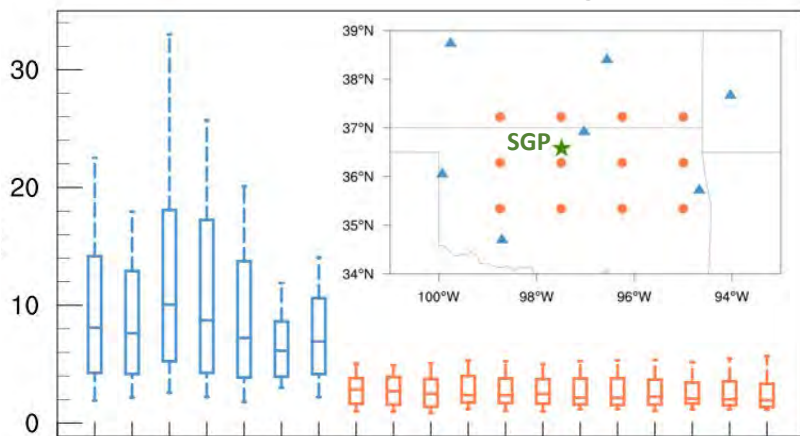


Evaluating aerosol and INP representations in CESM2 with observations from SGP Aerosol-Ice Formation Closure Study

Xiaohong Liu, Yang Shi, Nicole Riemer, Naruki Hiranuma, Paul DeMott, Daniel Knopf



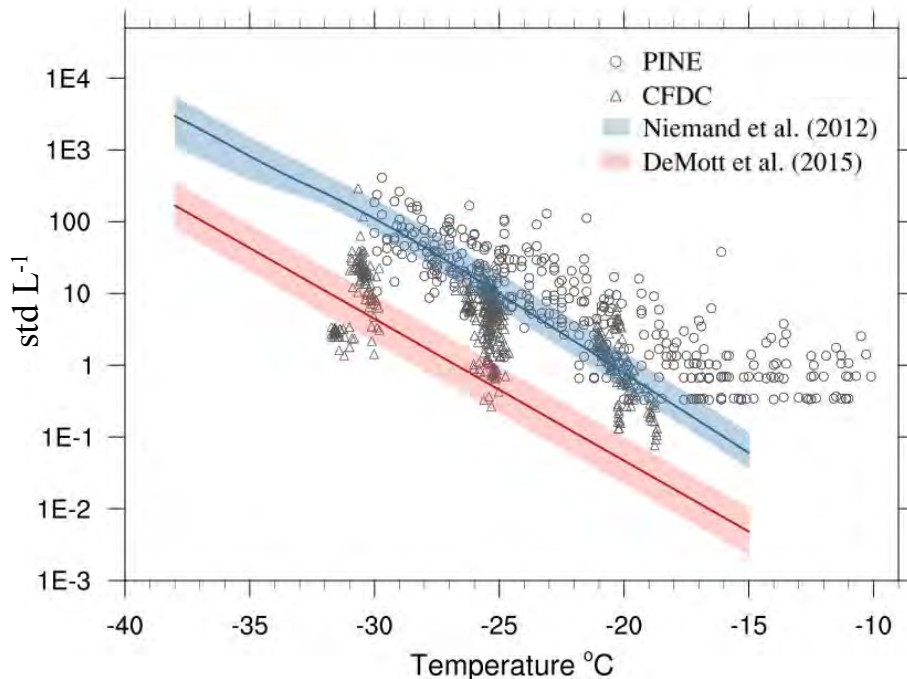
Dust mass concentration, $\mu\text{g}/\text{m}^3$



IMPROVE sites

Model

INP # concentration comparison (Oct. 15, 22, 23, 25)



- CESM2 underpredicts total aerosol number and surface area, especially for coarse mode aerosols. Modeled coarse mode aerosols less variable.
- Simulated INP concentrations from Niemand et al. (2012) are 1 order of magnitude higher than those from DeMott et al. (2015). Niemand et al. agrees better with observations. However, it is likely due to a high bias in this scheme, since simulated large particle number and dust mass are both underestimated.

Exploring sources of ultrafine and nucleation mode particles

Normalized $dN/d\ln D$ (-)

0 0.5 1

Objective

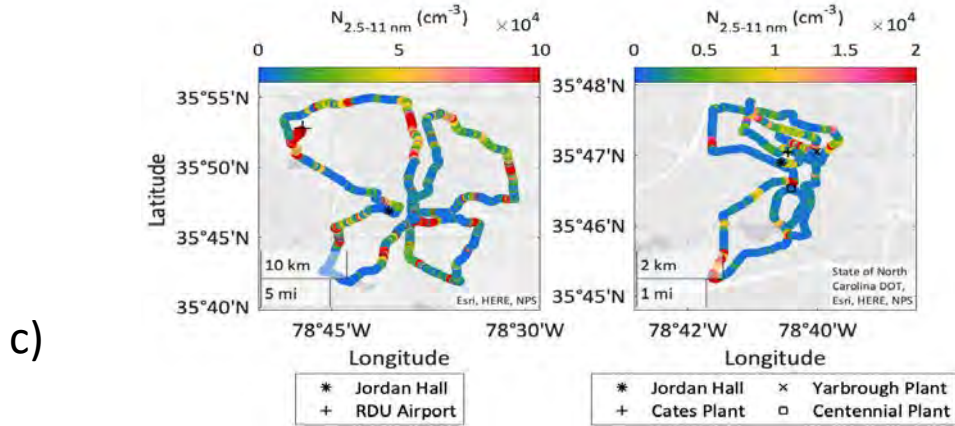
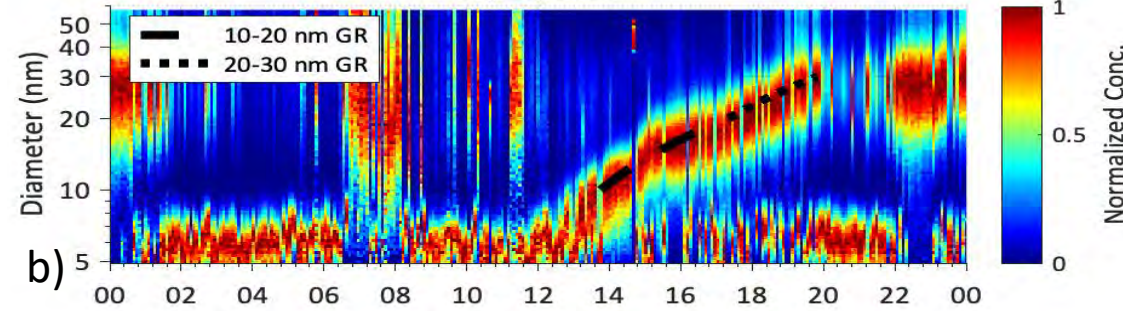
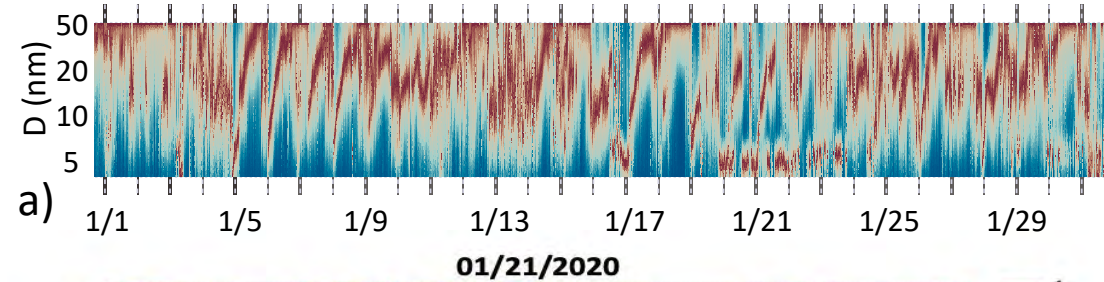
- Improved understanding of ultrafine particle sources in Raleigh, NC

Approach

- Collection of ambient aerosol size distribution and concentration data from April to June 2019 and November 2019 to May 2020
- Measurements of 2.5 to 11 nm sized particle concentration at 10 Hz
- Deployment of a mobile measurement system between March and May 2020.

Impact

- In urban environments in the SE US frequent new particle formation events occur at near-surface and aloft
- Numerous point sources of sub-10 nm sized particles contribute to complex aerosol size distribution dynamics
- Primary sub-10 nm sized particles could grow and contribute to CCN



a) and b) normalized spectral number density from the SMPS system and c) Spatial distribution of 2.5–11 nm size particles

• Zimmerman, A. M. D. Petters, N. Meskhidze, Exploring sources of ultrafine and nucleation mode particles in Raleigh, NC, in preparation.

• Meskhidze, N., J. C. Jaimes-Correa, M. D. Petters, T. M. Royalty, B. N. Phillips, A. Zimmerman, R. Reed (2019), Possible Wintertime Sources of Fine Particles in an Urban Environment, *J. Geophys. Res. Atmospheres*, 124. <https://doi.org/10.1029/2019JD031367>

Temporal Variability and Relationships between Aerosol Size Distribution, Hygroscopicity, and Cloud Condensation Nuclei Spectra in the Southern Great Plains

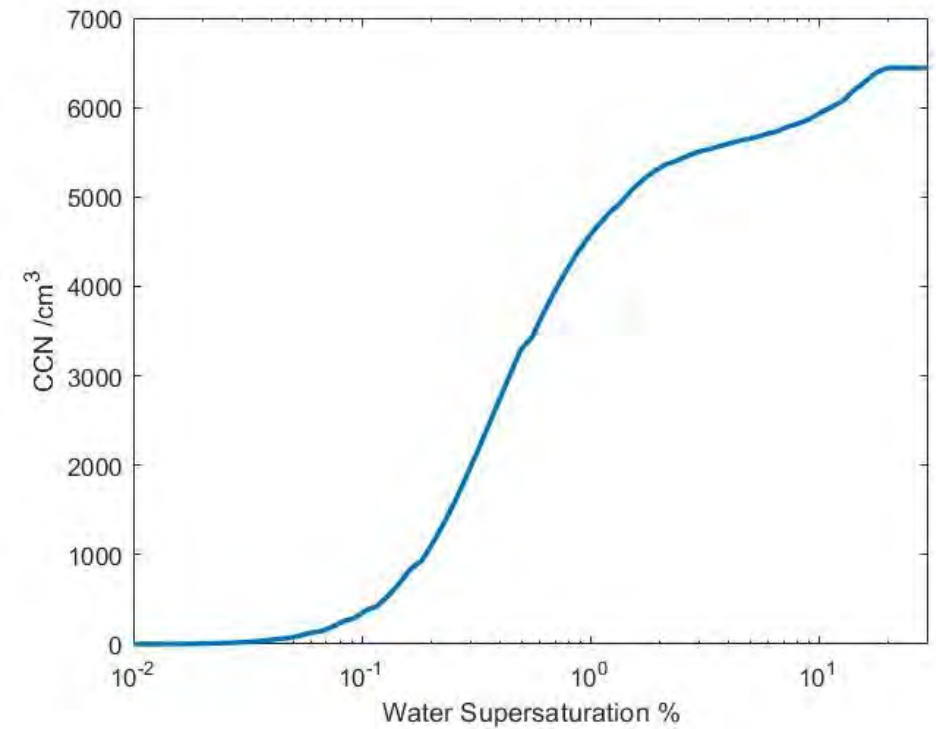
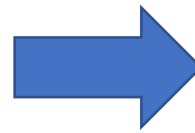
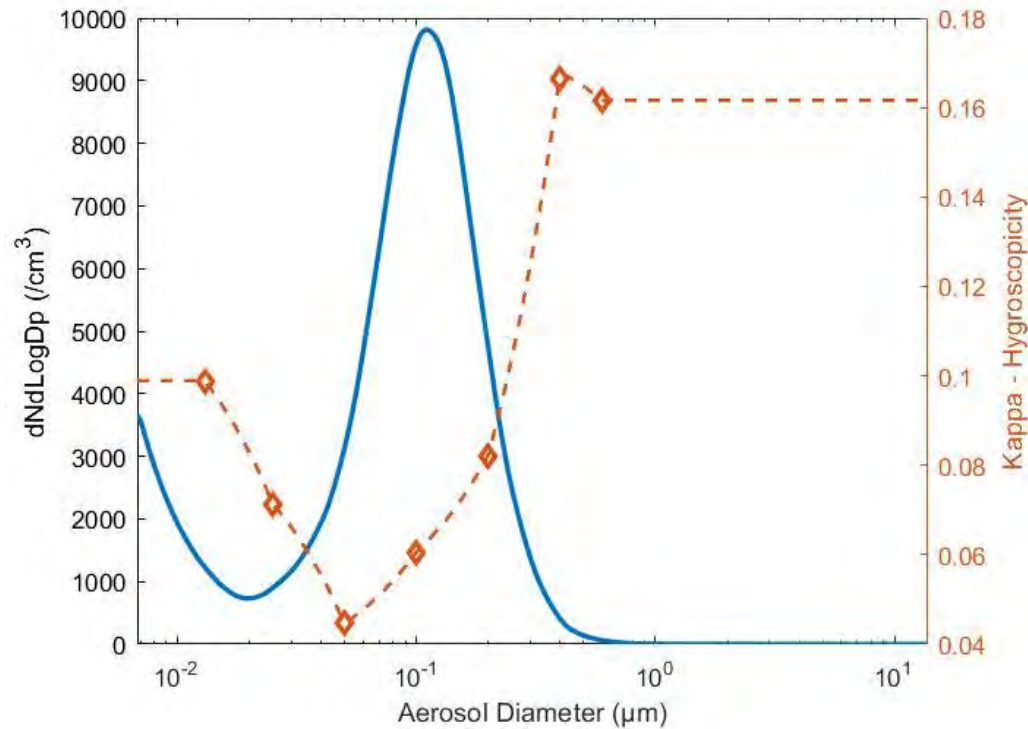
R. J. Perkins, P. J. Marinescu, E. J. T. Levin, D. R. Collins, and S. M. Kreidenweis

Used a 5 year continuous dataset from the ARM SGP site:

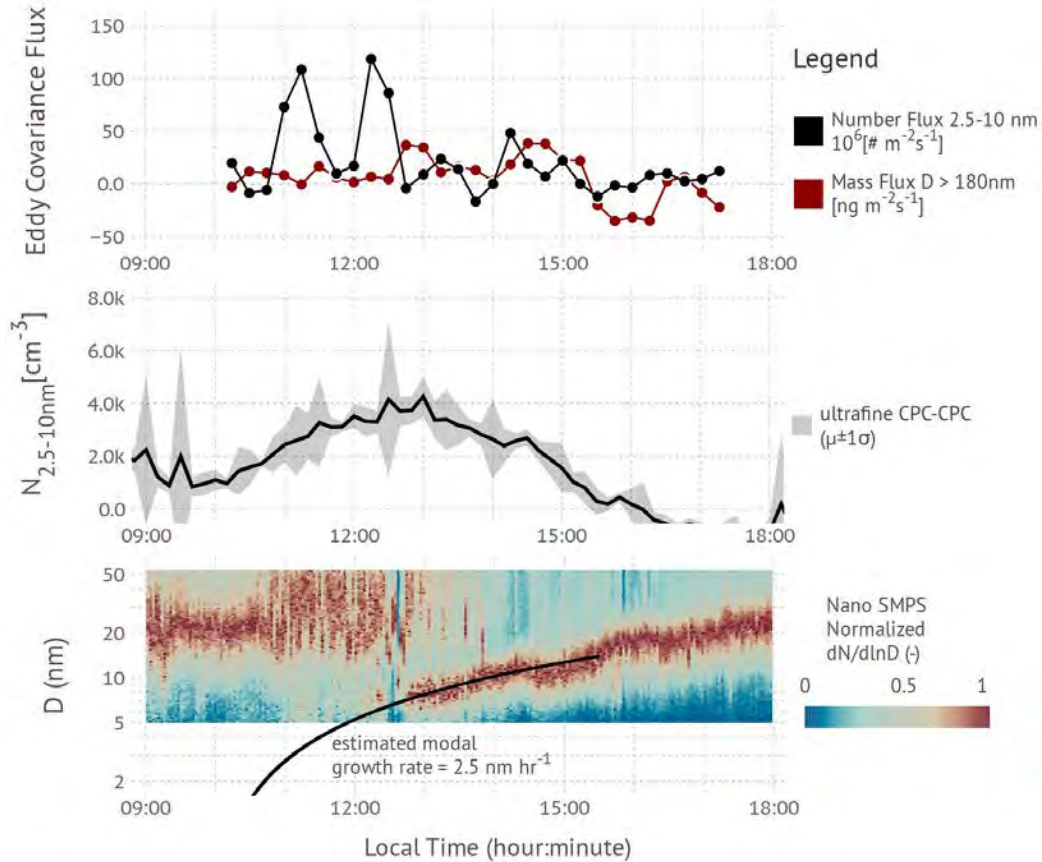
- ~40k concurrent size (Marinescu et al. 2019) and hygroscopicity (Mahish and Collins 2017) measurements.
- ~22k concurrently measured CCN spectra for comparison.
- ACSM and Nephelometer data for quality assurance.

Resulting CCN spectrum over expanded supersaturation range

- 0.01% to ~20% supersaturation, compared to ~0.1-1% from DMT CCN counter.
- Resulting spectra to be added to ARM archive this summer.
- Analysis underway to understand causes of variability across timescales.



Size-resolved flux measurements of *sub-10* nm particles



Co-located size distribution and EC number flux-measurement

Upcoming Deployments

- SGP: September 2020
- TRACER-campaign, Houston: June-September 2021

Motivation

- New particle formation (NPF) followed by modal growth contributes to CCN production.
- New particle formation may be initiated at the surface or aloft.
- Need to identify the origin of nucleation events.

Approach

- Eddy-covariance flux measurements using condensation particle counters (CPCs) with different size cuts.
- Use concentration difference to identify size-resolved 2.5-10 nm vertical turbulent flux.
- Collocate flux with size distribution measurement and NPF events.

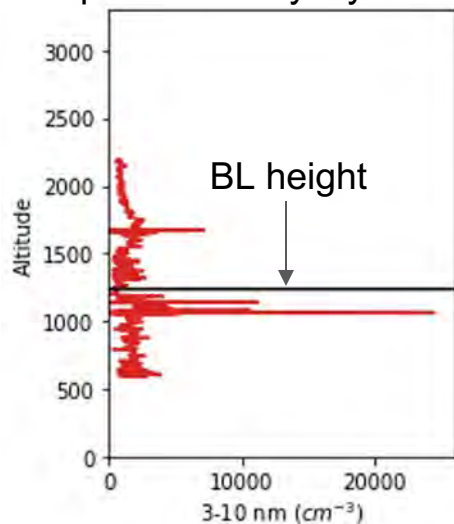
Impact

- Provide insights into the dynamics of ultrafine particle concentration.

Aerosol nucleation and growth during HISCALE

Sam O'Donnell, Jeff Pierce (CSU), Jim Smith (UCI), many others

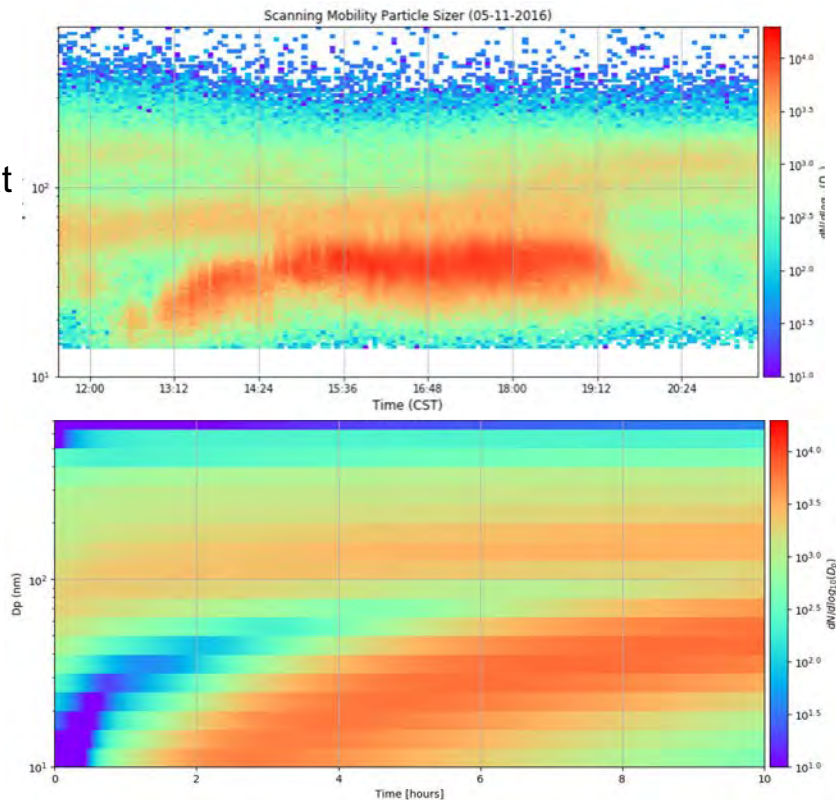
Aircraft-observed nucleation
at top of boundary layer



Nucleation and
growth observed at
surface

Mechanistic
modelling of
nucleation and
growth

GOAL: Use column modelling to connect the vertical
profile of nucleation to the surface measurements.

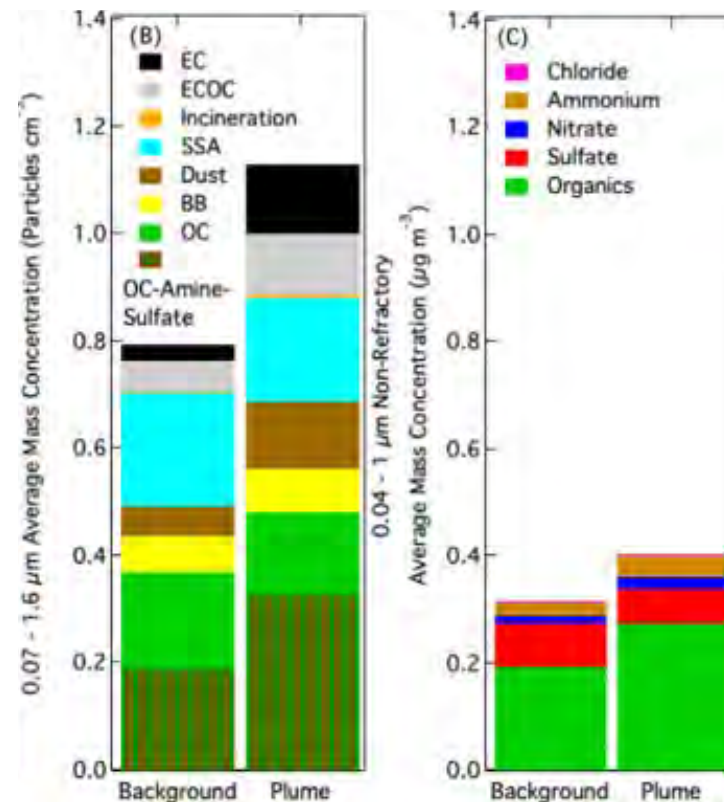


Kerri Pratt, Univ. of Michigan

Highlight of results from Aug. – Sep. 2016 ARM Field Campaign at Oliktok Point, Alaska

Objective: Single-particle mass spectrometry measurements for individual particle chemical composition, source identification, and mixing state determination (32,880 particles analyzed)

- Oliktok Point is a coastal Arctic field site in an oil field.
- 8 single particle types:
 - **OC-amine-sulfate** (increased contribution during growth events); **OC**
 - **Sea salt aerosol (SSA)**
 - **EC-sulfate**; **ECOC-sulfate** (diesel combustion)
 - Dust; Biomass burning (BB); Incineration (metals)
- ACSM measured **OA, sulfate, nitrate, and ammonium - internally mixed with OC-amine-sulfate, OC, ECOC, and BB particles.** Aged SSA was also present.
- ATOFMS non-refractory particle mass in agreement (within uncertainty) with ACSM.
- ~37% (on average) of the aerosol mass was refractory (SSA, EC, dust, and incineration particles).



M.J. Gansch[#], J. Liu[#], C.E. Moffett, R.J. Sheesley, N. Wang, Q. Zhang, T.B. Watson, K.A. Pratt, "Diesel soot and amine-containing organic sulfate aerosols in an Arctic oil field." *Environmental Science & Technology*. 54 (1), 92-101. (2019) <https://doi.org/10.1021/acs.est.9b04825>.

Photochemical Aging Alters SOA Partitioning Behavior

Objective

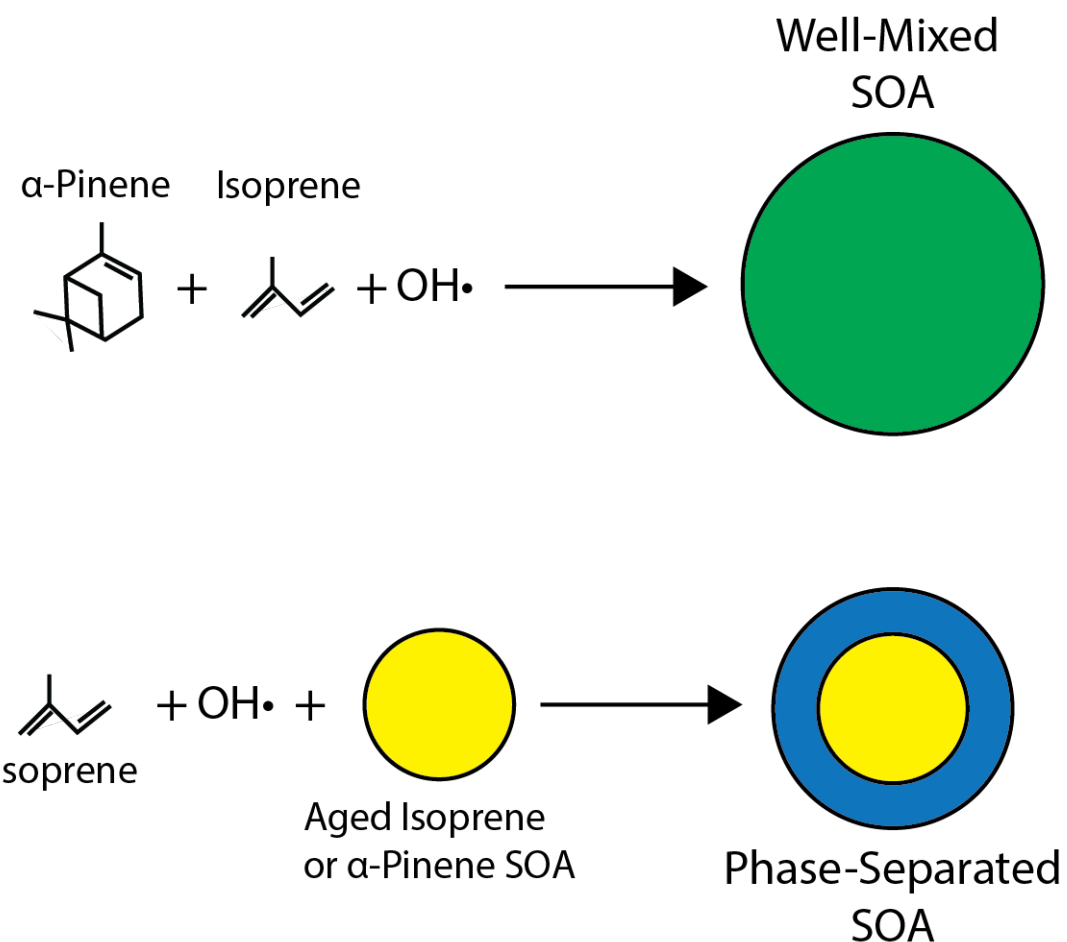
- Evaluate equilibrium partitioning approaches to predicting SOA formation in lab experiments as a function of RH and SOA aging.

Approach

- Conduct chamber experiments in which SOA from two precursors is formed 1) simultaneously and 2) sequentially after 15-18 hours of aging.
- Compare experimental data to model predictions which assume equilibrium either is or is not achieved.

Results

- Equilibrium partitioning was achieved in co-condensation experiments.
- Phase separation was observed in sequential condensation experiments due to aging, even at 85% RH.
- Results help to resolve some seemingly divergent conclusions regarding diffusion limitations that exist in the literature.
- Models can use equilibrium partitioning to describe fresh, but not aged, SOA formation.



SOA generated from isoprene and α -pinene mixtures reached equilibrium when SOA was fresh. However, SOA formed separate phases after particles aged for 15-18 hours, even at 85% RH. These findings inform models that predict aerosol growth and mass.

Predictions of viscosity of organic aerosols from volatility distributions

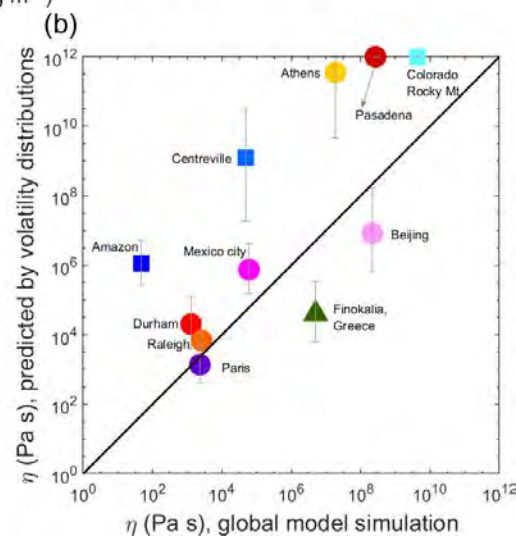
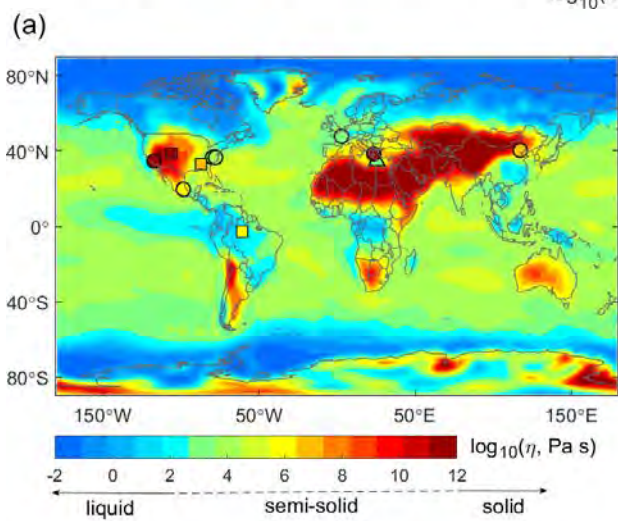
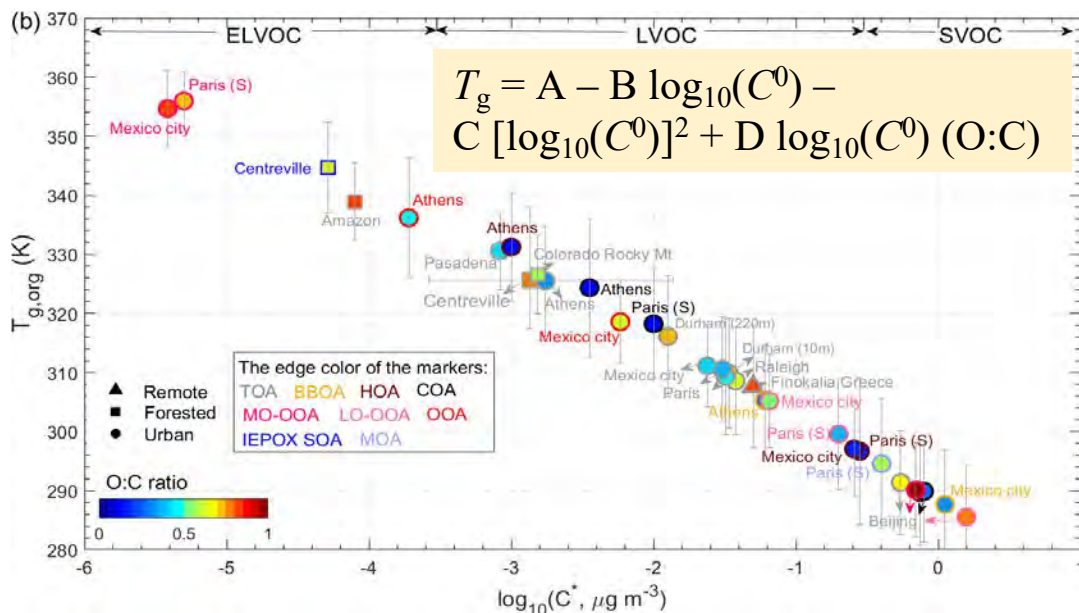
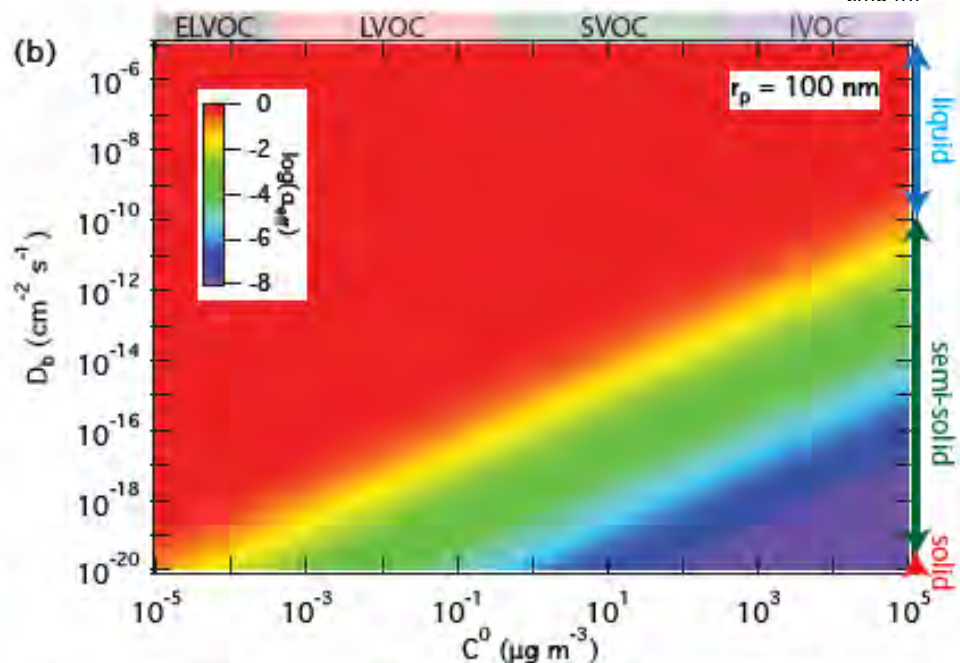
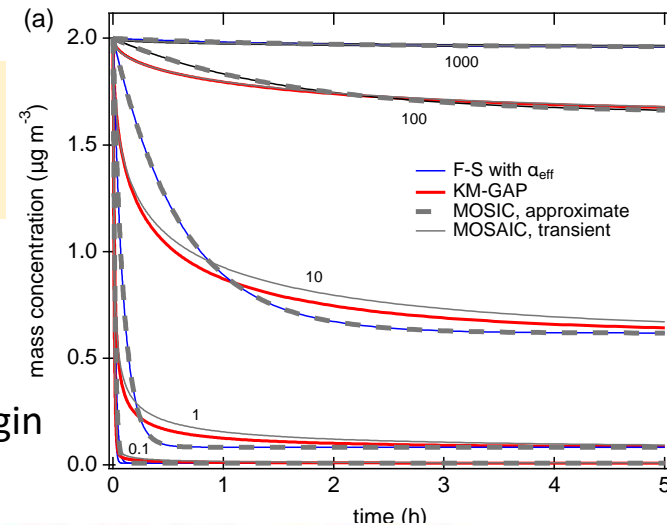
Mass Accommodation in SOA Partitioning

Effective α

$$\alpha(x) = \alpha_s \frac{1}{1 + \frac{\alpha_s \omega C^0}{4 D_b \rho_p} x \cdot 10^{-12}}$$

C_0 : volatility, D_b : diffusivity
 x : penetration depth

Implementation in Fuchs-Sutugin gas diffusion formulations



Insights in IEPOX multiphase chemistry using integrated model-measurement approaches

Mega Octaviani¹, Manish Shrivastava^{1,*}, Alla Zelenyuk¹, Rahul Zaveri¹, Yue Zhang²

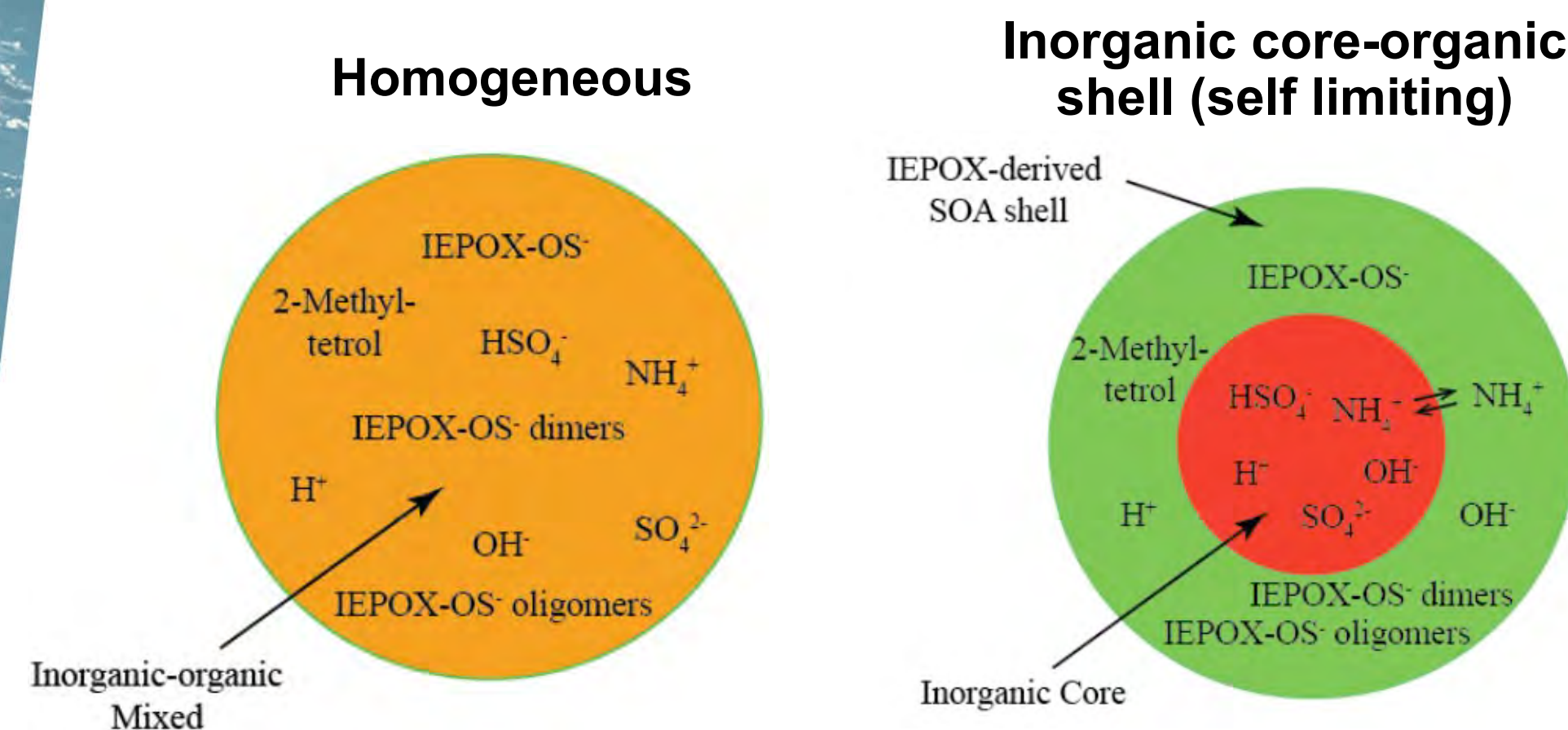
¹Pacific Northwest National Laboratory, Richland, WA, USA

²Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina, Chapel Hill, NC, USA

*Corresponding author: ManishKumar.Shrivastava@pnnl.gov

Introduction

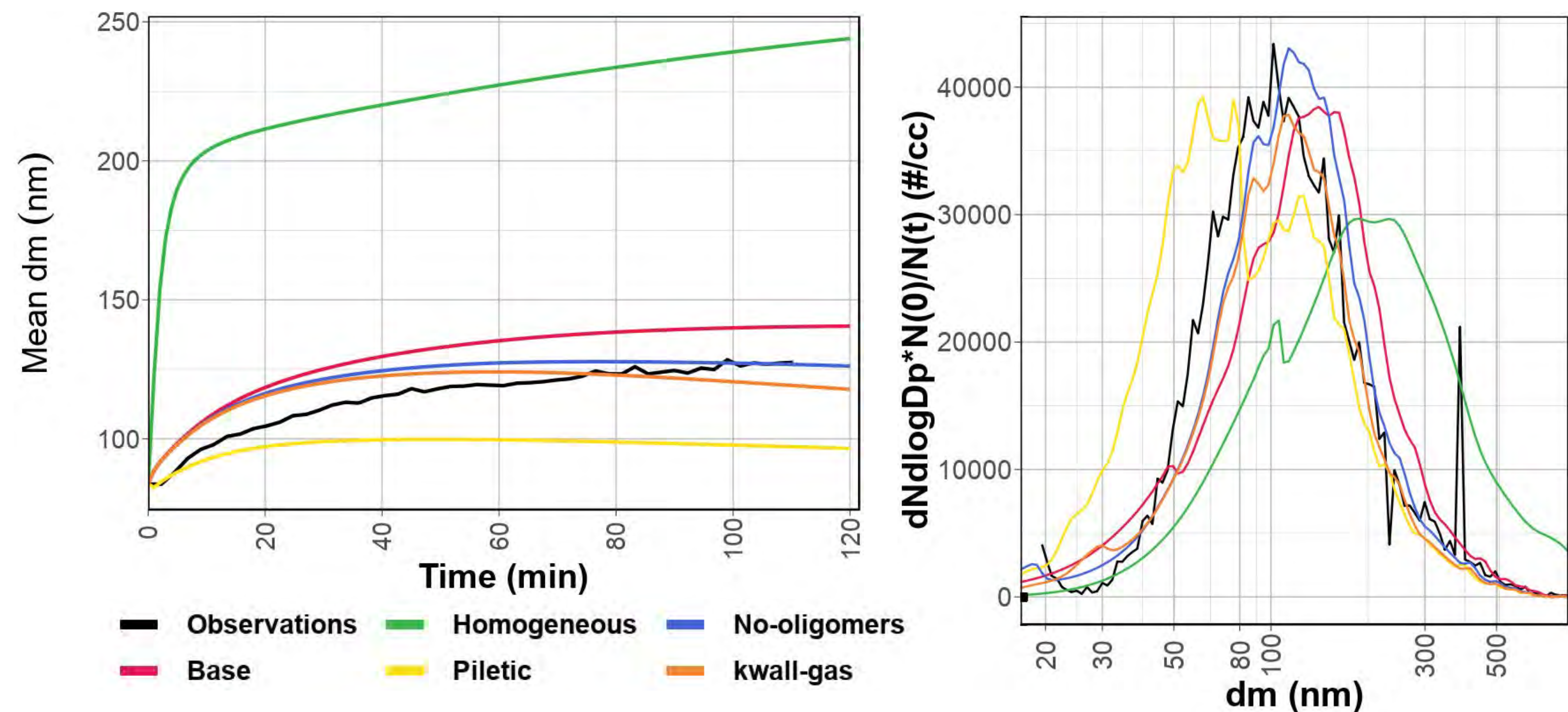
Isoprene epoxydiol (IEPOX) is a key precursor of isoprene-derived secondary organic aerosols (SOA) in the atmosphere. We present a modeling study of the multiphase chemistry of IEPOX using recent understanding of the IEPOX-derived SOA formation pathways and evaluate results with EMSL measurements of IEPOX-SOA (Riva et al., 2016).



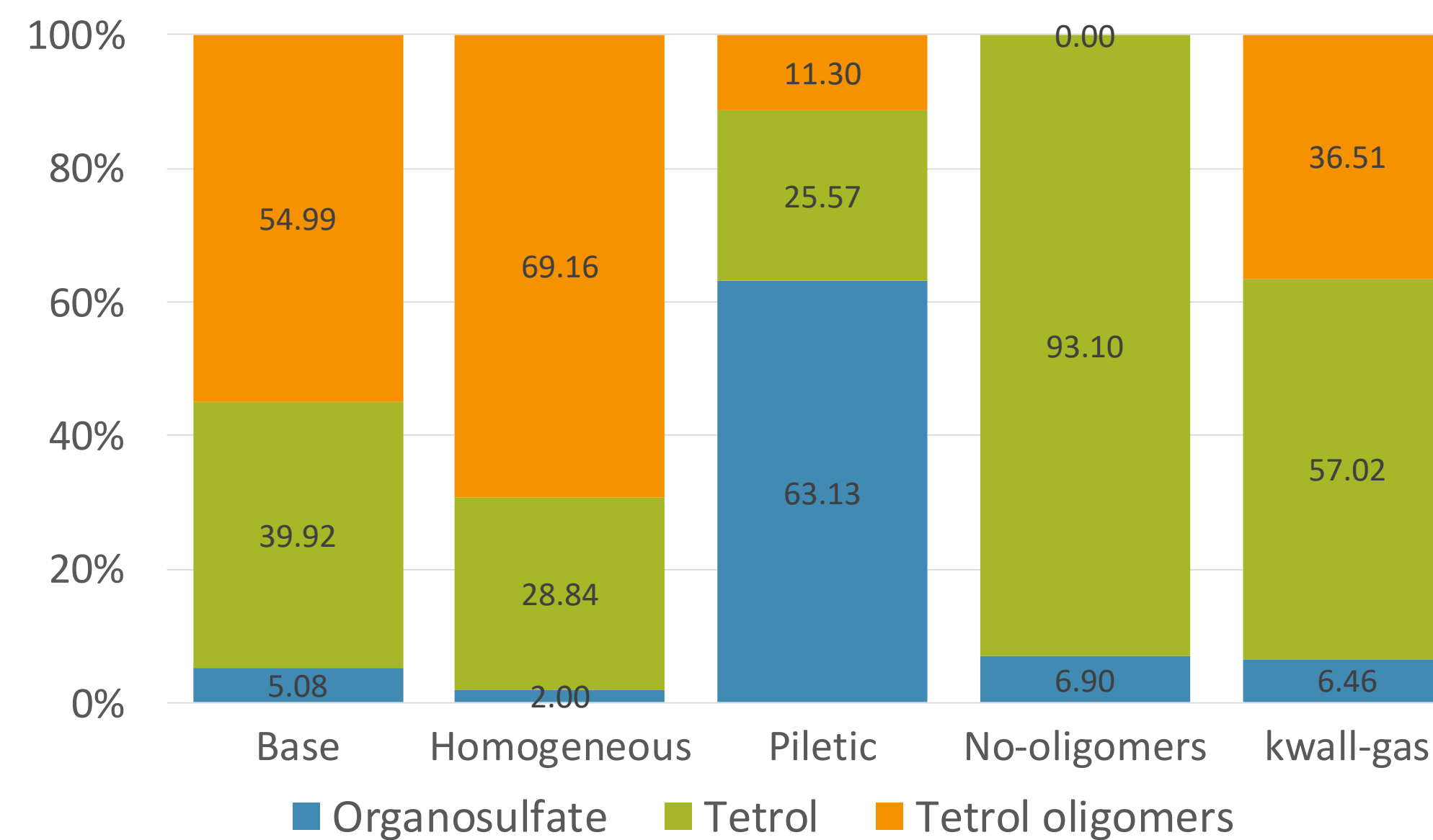
Figures adopted from Zhang et al. (2019)

Scenario	Particle Morphology	Reaction rate constant ¹	Oligomerization	Gas-phase wall loss (1/k _{wall})
Base	Core-shell	Eddingsaas	Included	2 hr
Homogeneous	Homogeneous	Eddingsaas	included	2 hr
Piletic	Core-shell	Piletic	Included	2 hr
No-oligomers	Core-shell	Eddingsaas	None	2 hr
Kwall-gas	Core-shell	Eddingsaas	Included	1 hr

¹The first-order reaction rate constant in the aqueous phase can be calculated following Eddingsaas et al. (2010) and Piletic et al. (2013)



Simulated evolution of aerosol mean diameter and the size distribution of aerosol number concentration



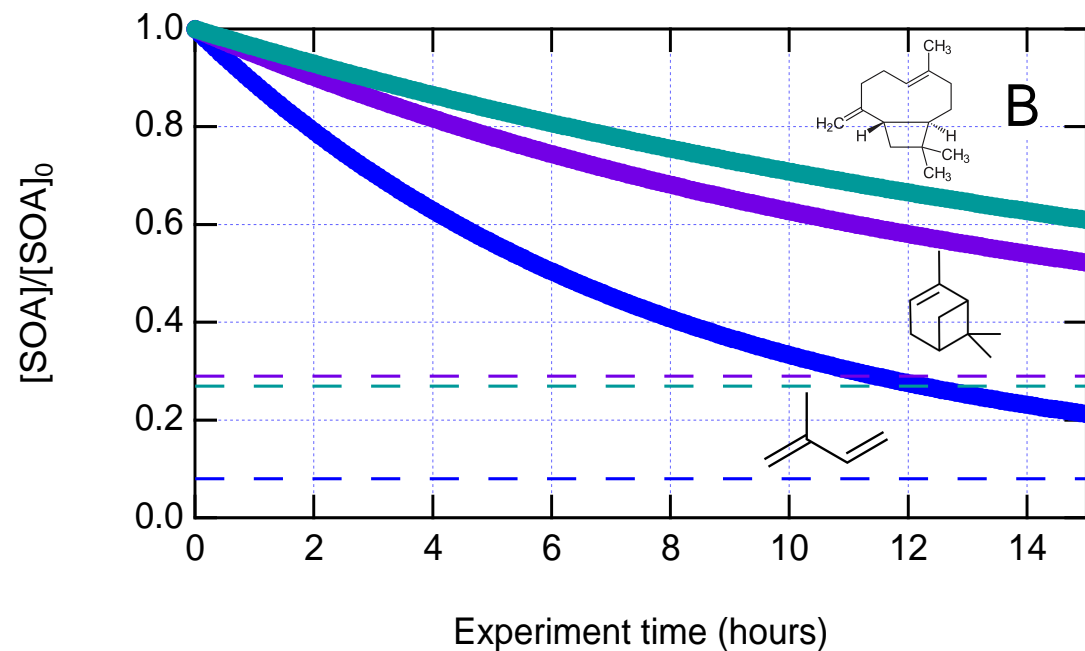
Relative contributions (% of mass) of IEPOX-derived SOA

Conclusions

- Homogeneous mixing causes too much growth while self-limiting effects of IEPOX-SOA (core-shell) explain observations
- Different chemistry treatments and oligomerization timescales change IEPOX-SOA composition (tetrols, organosulfate, oligomers)

Photolysis is a Major Removal Mechanism that Controls the Budget of Organic Aerosol

Maria Zawadowicz, John Shilling, PNNL



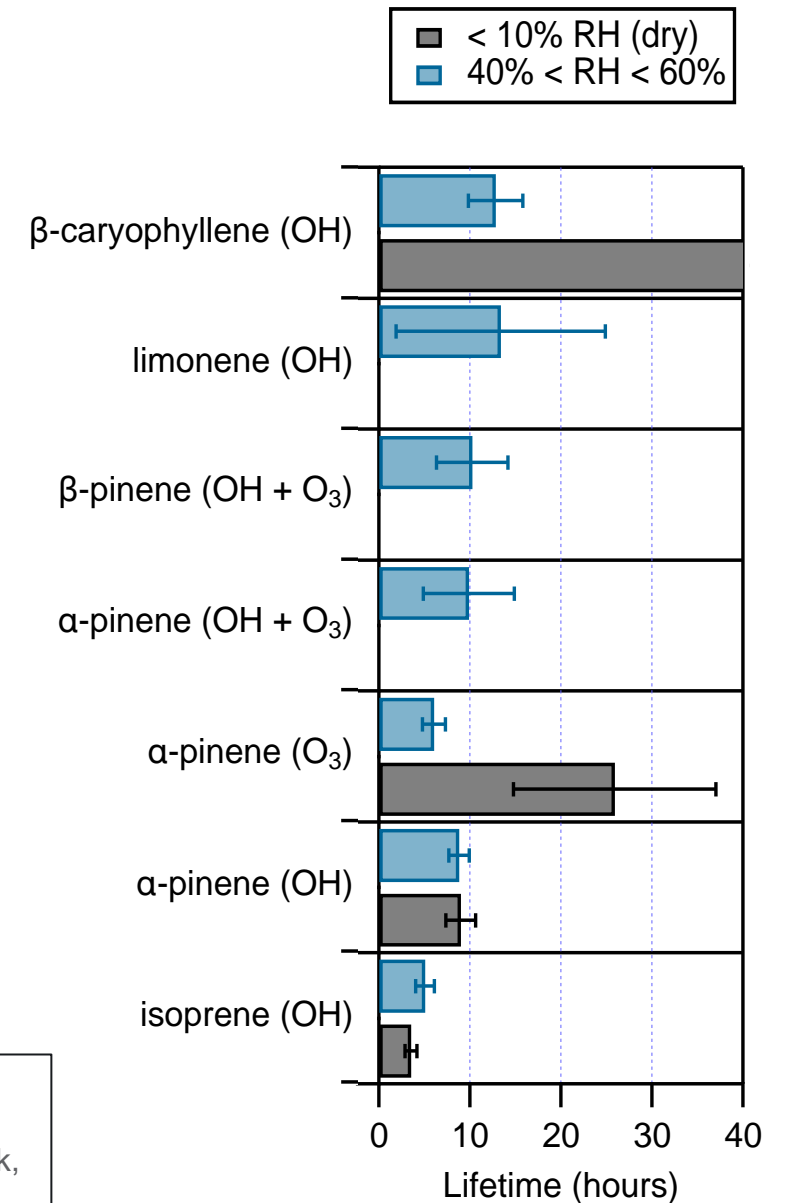
- SOA particles formed from biogenic precursors, such as isoprene (blue line), α -pinene (purple) or β -caryophyllene (green) shrink upon exposure to UV radiation. The rate of photolysis was found to be highly species-dependent.

- When scaled to atmospheric lifetime, most SOA systems showed a lifetime shorter than 10 hours.

- The new set of photolysis constants will enable the modeling community to more accurately understand how aerosols are removed from the atmosphere.

See our paper:

Zawadowicz M A, B H Lee, M Shrivastava, A Zelenyuk, R A Zaveri, C Flynn, J A Thornton, and J E Shilling. 2020. "Photolysis Controls Atmospheric Budgets of Biogenic Secondary Organic Aerosol," *Environmental Science & Technology*, 54(7):3861–3870, DOI:10.1021/acs.est.9b07051.



Applying explicit mechanisms to describe volatility-driven Isoprene SOA formation and evolution

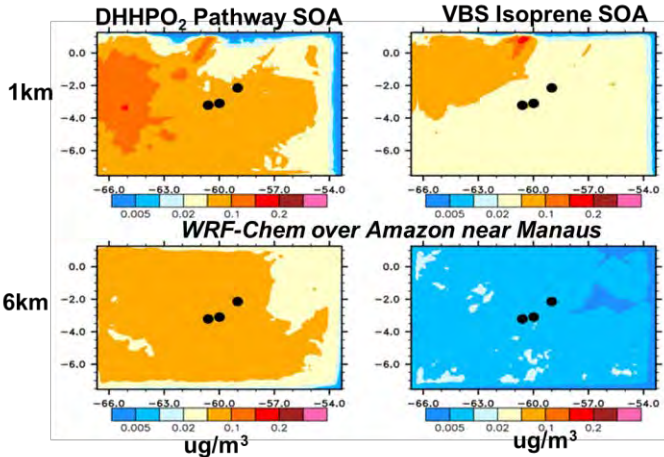
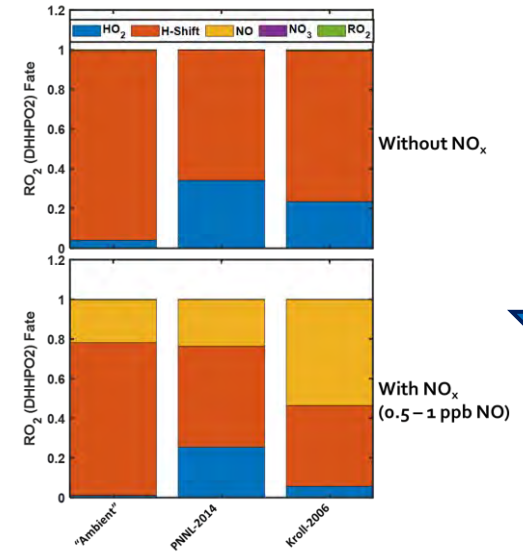
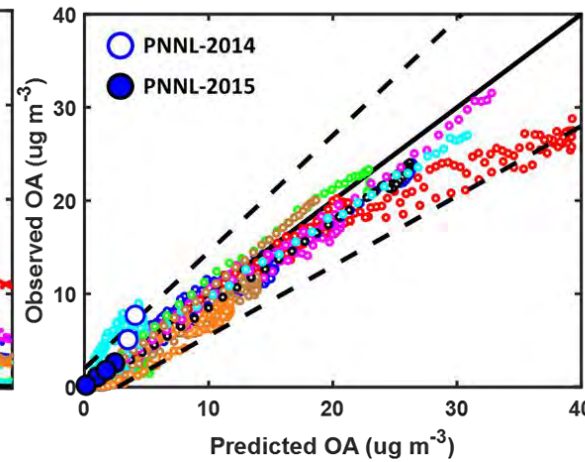
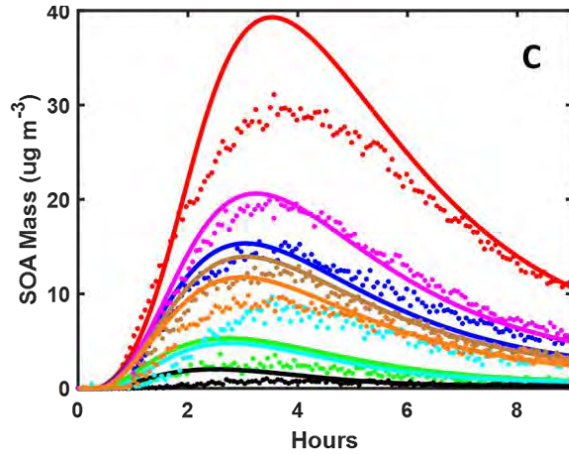
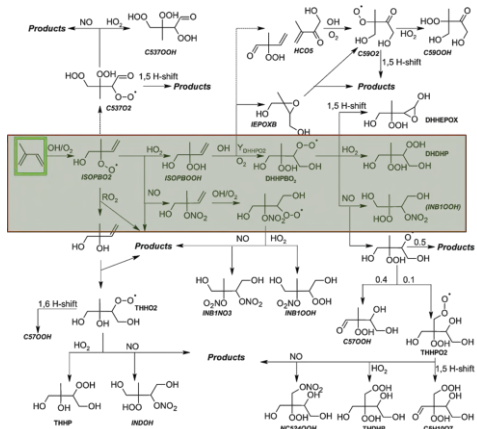
Joel Thornton (UW), John Shilling, Manish Shrivastava, Emma D'Ambro, Maria Zawadowicz, Jiumeng Liu

Explicit gas-phase mechanism >1000 reactions

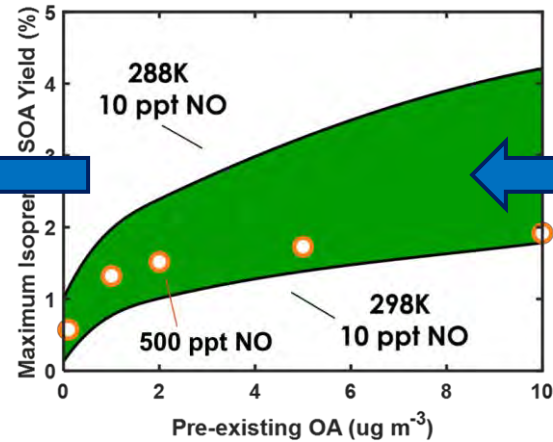
Dynamic Gas-Particle Partitioning

Explicit Multi-phase Chemical Aging

Insights into Chamber Experiment Representativeness

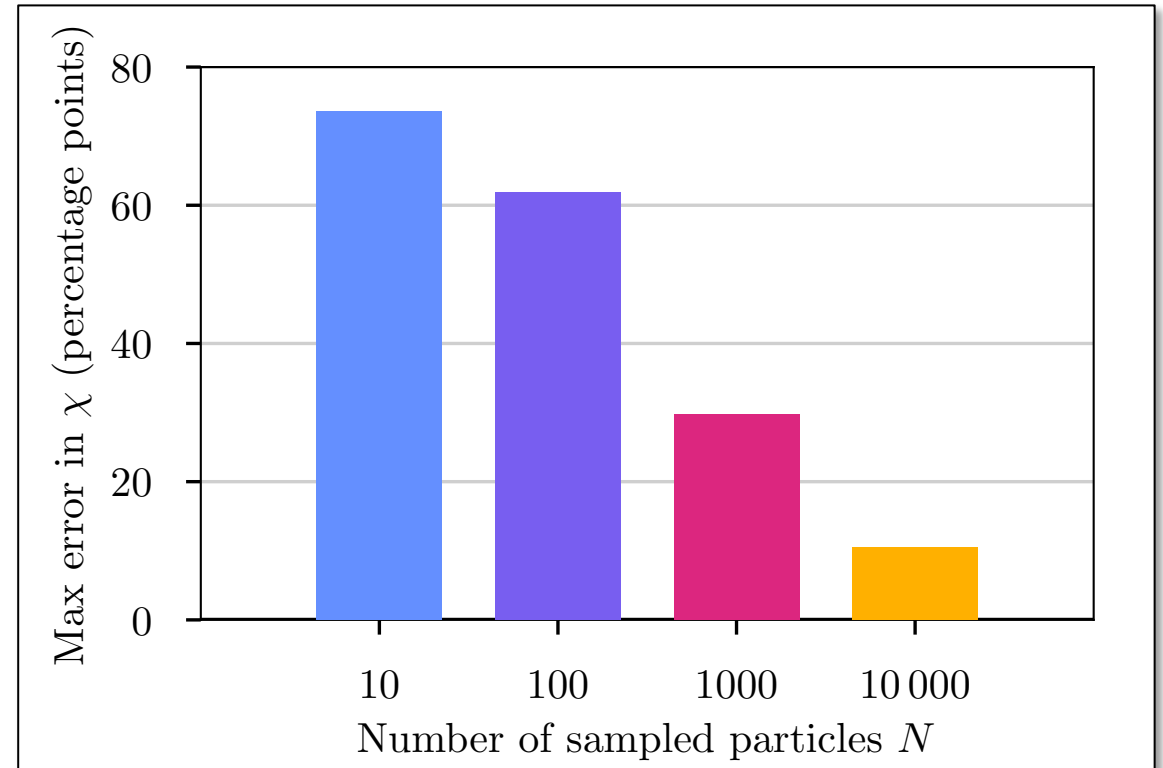
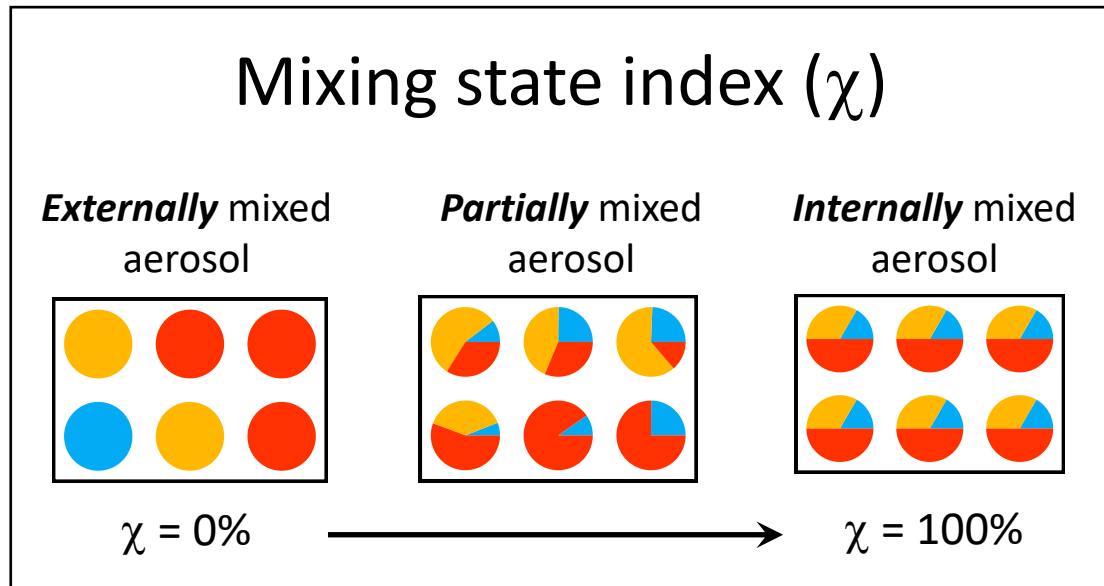


Application to DOE GO-AMAZON campaign



Insights into Important Atmospheric Processes

How many particles should we sample to measure mixing state?

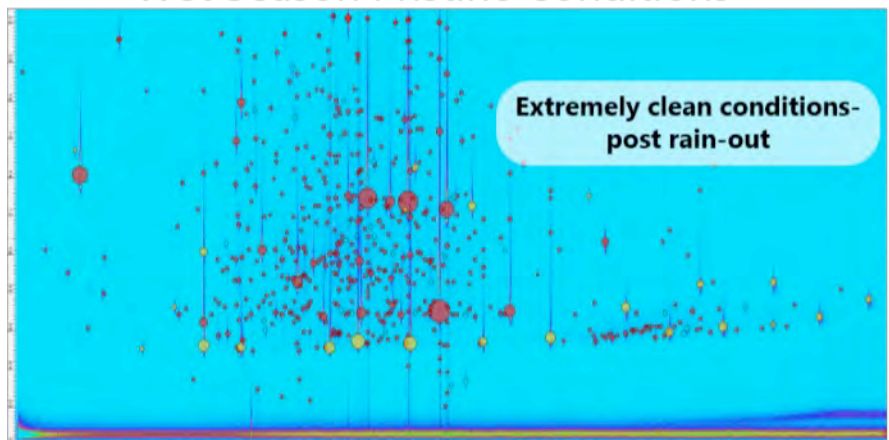


J. T. Gasparik, Q. Ye, J. H. Curtis, A. A. Presto, N. M. Donahue, R. C. Sullivan, M. West, N. Riemer, "Quantifying errors in the aerosol mixing-state index based on limited particle sample size," *Aerosol Sci. Technol.* (in revision, 2020).

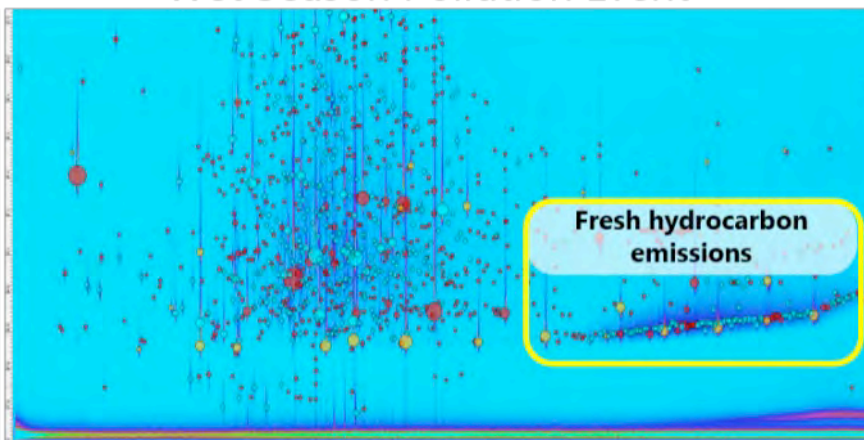
Tracking chemical complexity during GoAmazon 2014/5 and globally

Lindsay Yee, Emily Barnes, and Allen Goldstein at UC Berkeley

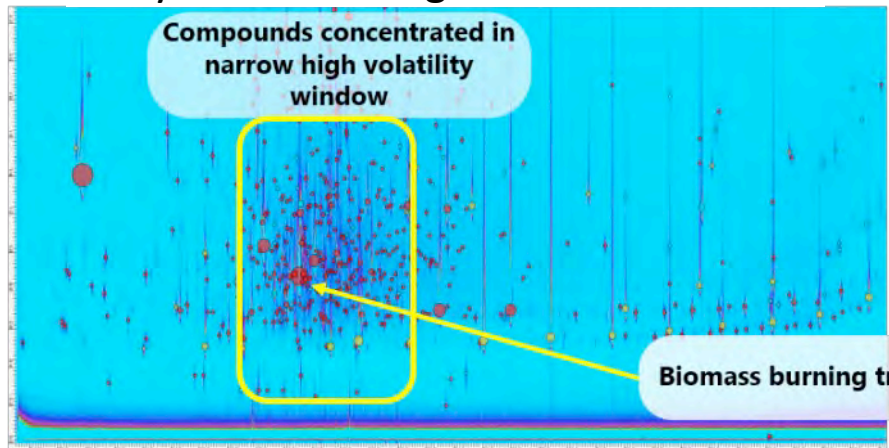
Wet Season Pristine Conditions



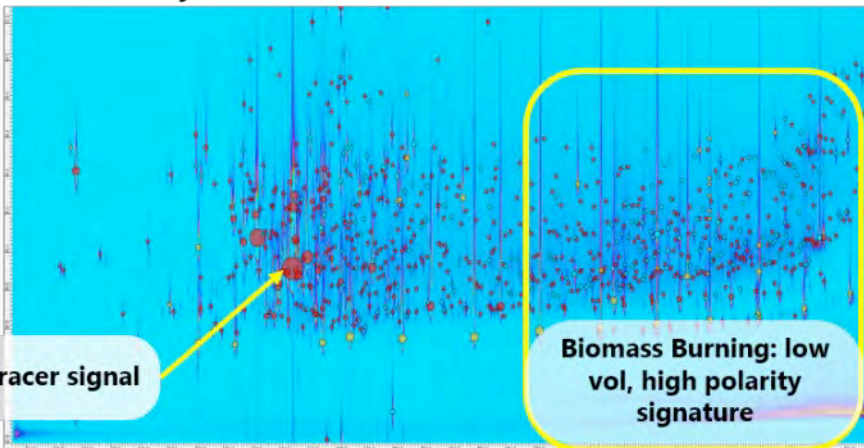
Wet Season Pollution Event



Dry Season Background Conditions



Dry Season Pollution Event



By the numbers:

- 1,484 unique compounds
- 100 compounds make up ~75% of total signal
- 500 compounds make up ~90% of total signal
- **Identification of new tracers with specific chemical signatures via timelines analyses**

UCB GLOBES EI mass spectral library (open-access):

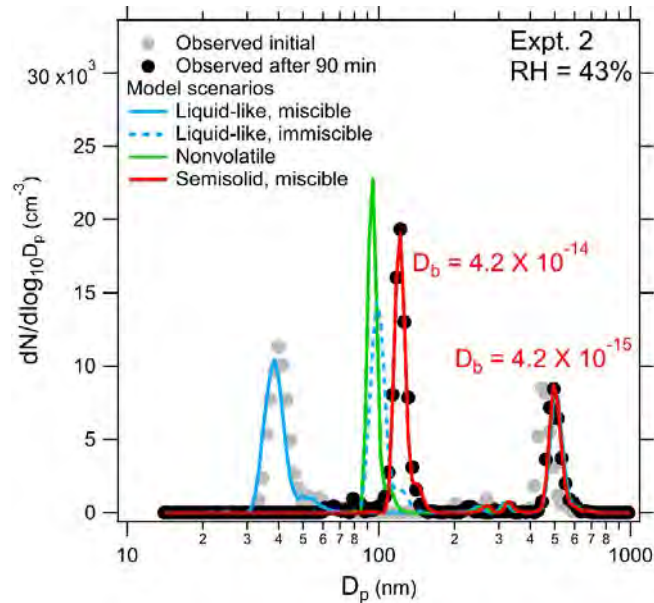
- <https://nature.berkeley.edu/ahg/resources/>
- > 3,500 electron impact MS with source-specific metadata
- **Identification of reoccurring tracers of global atmospheric importance**

Chromatograms of selected filter samples from GoAmazon 2014 field campaign analyzed in GCxGC EI/HR-ToF-MS

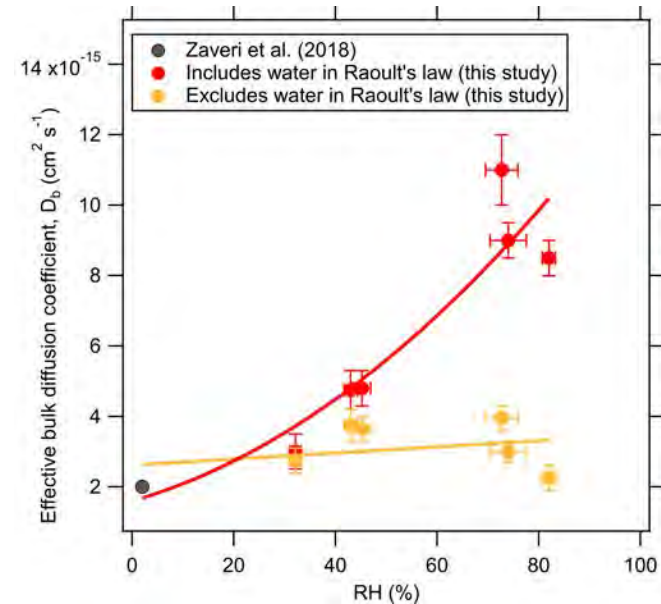
Particle-phase diffusion modulates partitioning of semivolatile organic compounds to aged SOA

R.A. Zaveri, J.E. Shilling, A. Zelenyuk, M.A. Zawadowicz, K. Suski, S. China, D.M. Bell, D. Veghte, and A. Laskin

Objective: Investigate the role of bulk diffusion in partitioning of SVOCs to aged SOA



Comparison of the observed and modeled aerosol size distribution evolution due to isoprene SOA formation in the presence of Aitken mode (potassium sulfate) and accumulation mode (aged a-pinene SOA) aerosol at different RH



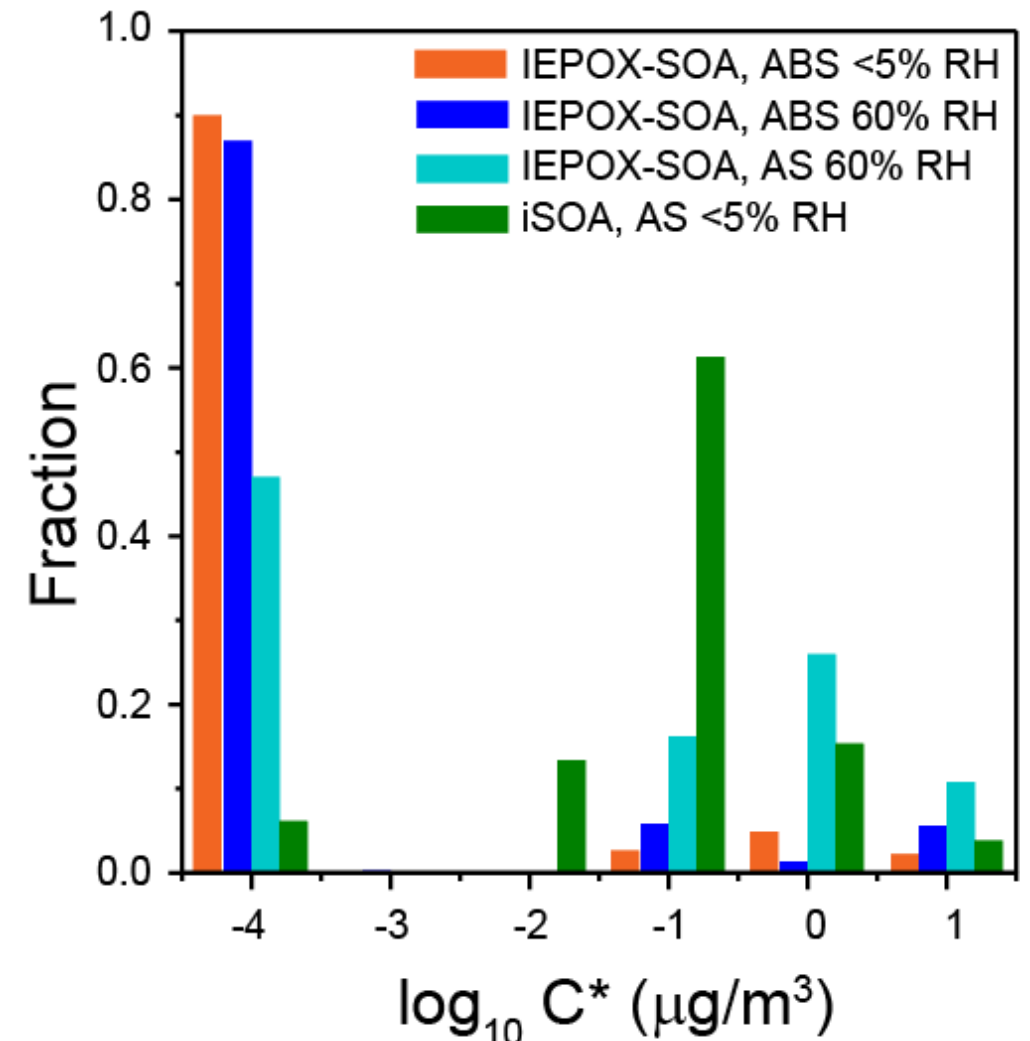
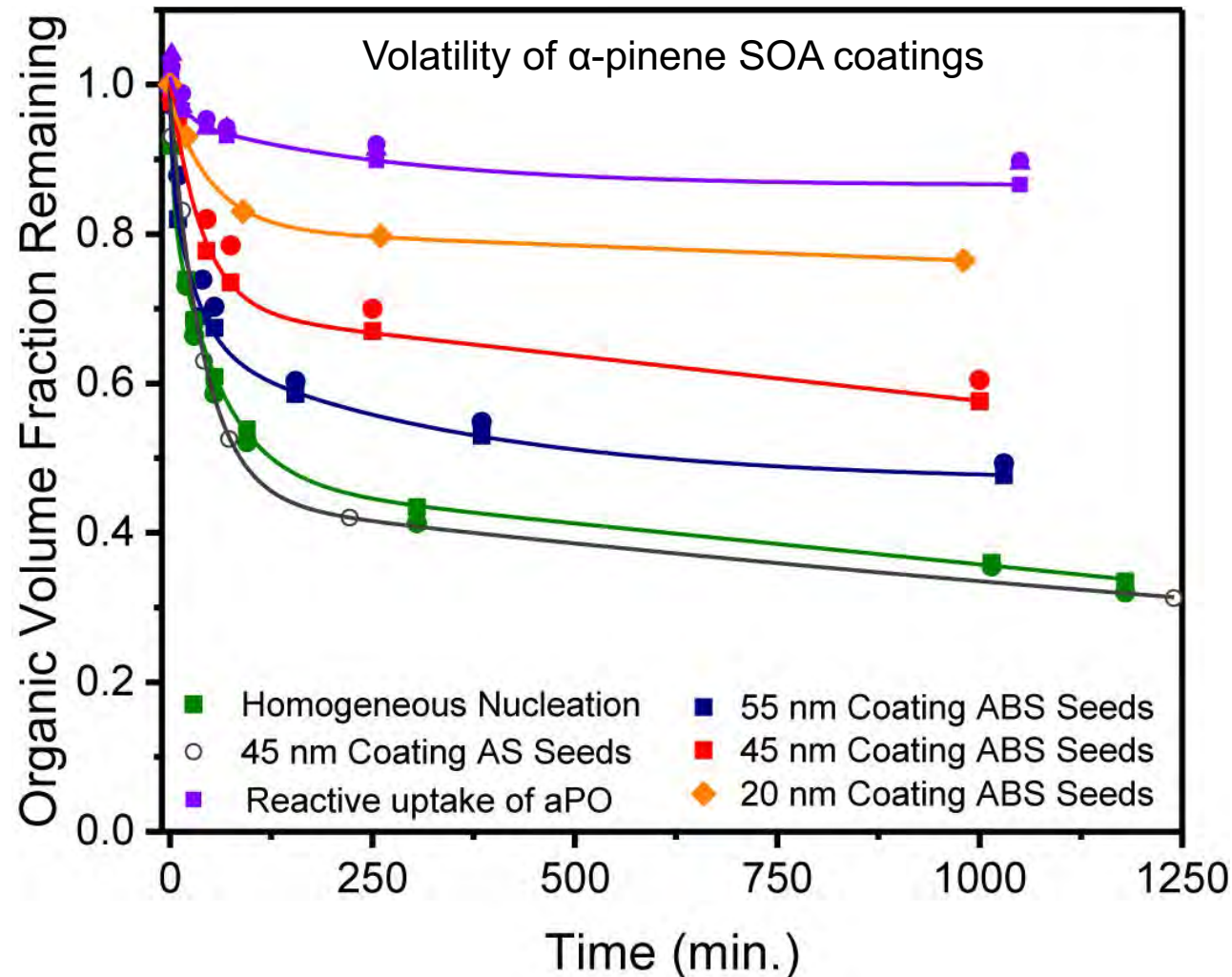
Estimated effective bulk diffusion coefficients for aged a-pinene SOA as a function of RH

Zaveri, R. A., J. E. Shilling, A. Zelenyuk, M. A. Zawadowicz, K. Suski, S. China, D. M. Bell, D. Veghte, and A. Laskin, Particle-phase diffusion modulates partitioning of semivolatile organic compounds to aged secondary organic aerosol, **Environ. Sci. Technol.**, (2020).

Impacts

- SVOCs favor growth of small particles due to low diffusivity inside larger, aged secondary organic aerosols
- Facilitates rapid growth of ultrafine particles to climatically-active sizes

The Effect of Aerosol Acidity on the Composition and Volatility of Monoterpene and Isoprene-derived SOA



- Multiphase chemistry between isoprene- and monoterpene-oxidation products and acidic (ABS) sulfate particles leads to the formation of low-volatility products, i.e. organosulfates and oligomers, and a decrease of HOMs
- The non-volatile fraction of α -pinene SOA coatings formed on ABS seeds increases with decrease in coating thickness
- The non-volatile fraction of IEPOX-SOA formed on ABS seeds is twice as large as that observed for non-acidic seeds