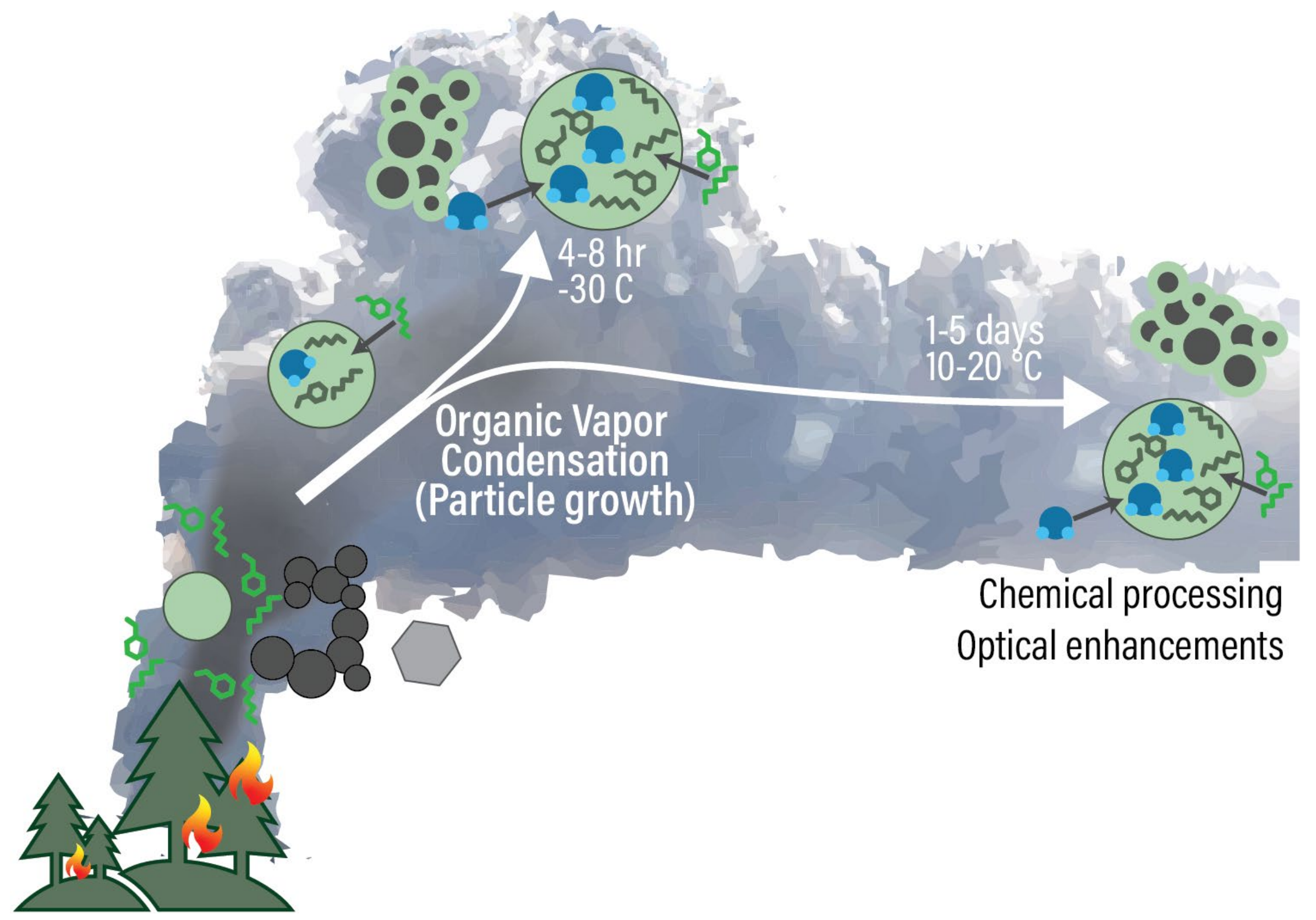
Evidence of secondary organic aerosol formation by non-methane hydrocarbons condensation in Pyro-Cumulonimbus (pyroCb)

LA-UR-21-25763

K.B. Benedict, K. Gorkowski, J. Lee, M. Dubey, E. Koo , J. Reisner | *Los Alamos National Laboratory*
I. Simpson, B. Barletta, D.R. Blake | *University of California Irvine* J. Katich | *CIRES/NOAA* J. Schwarz | *NOAA*

Observations of the rapid chemistry that occurs in pyroCb plumes are limited



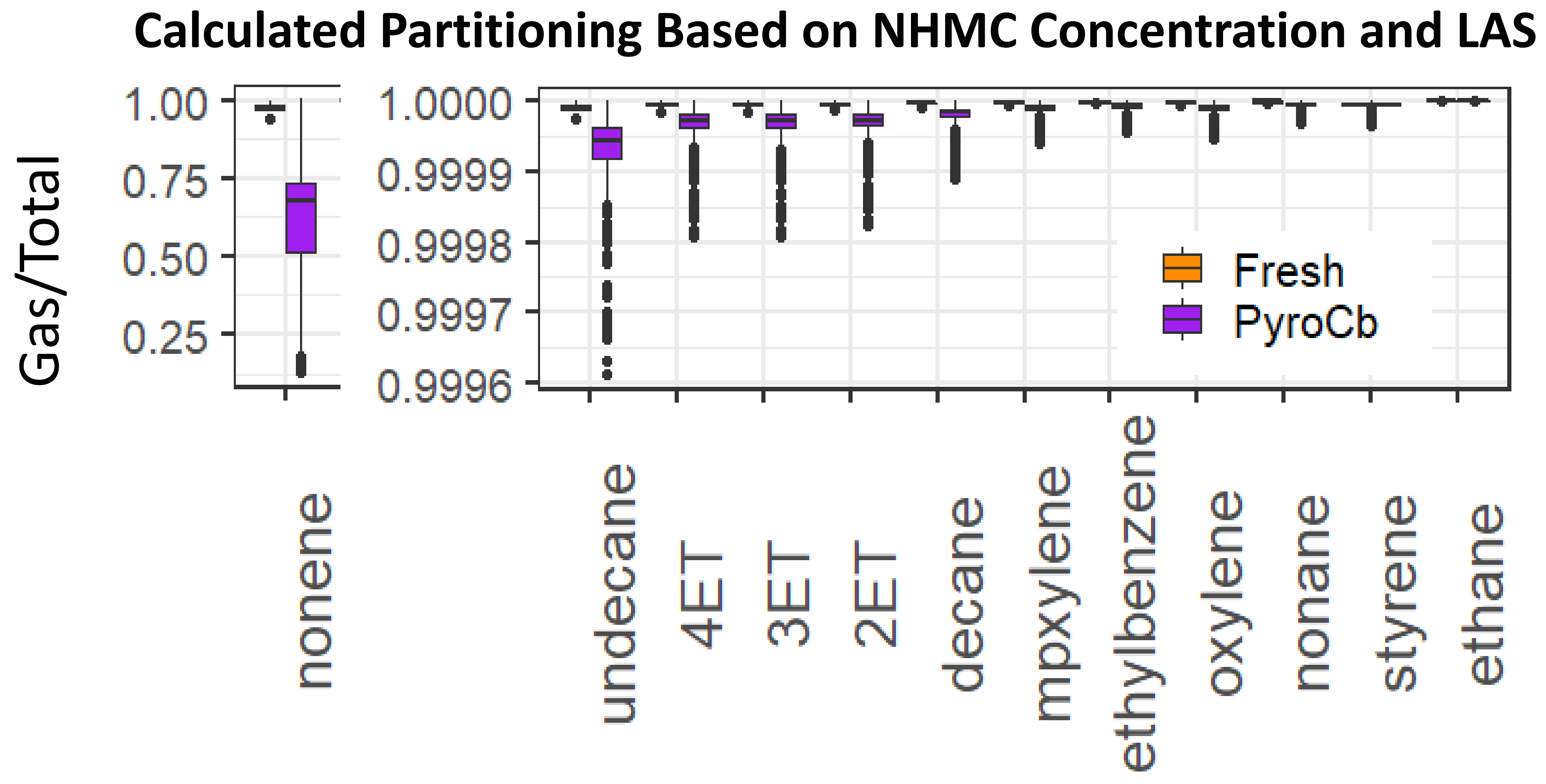
FIREX-AQ observed pyroCb smoke during the Williams Flats Fire.

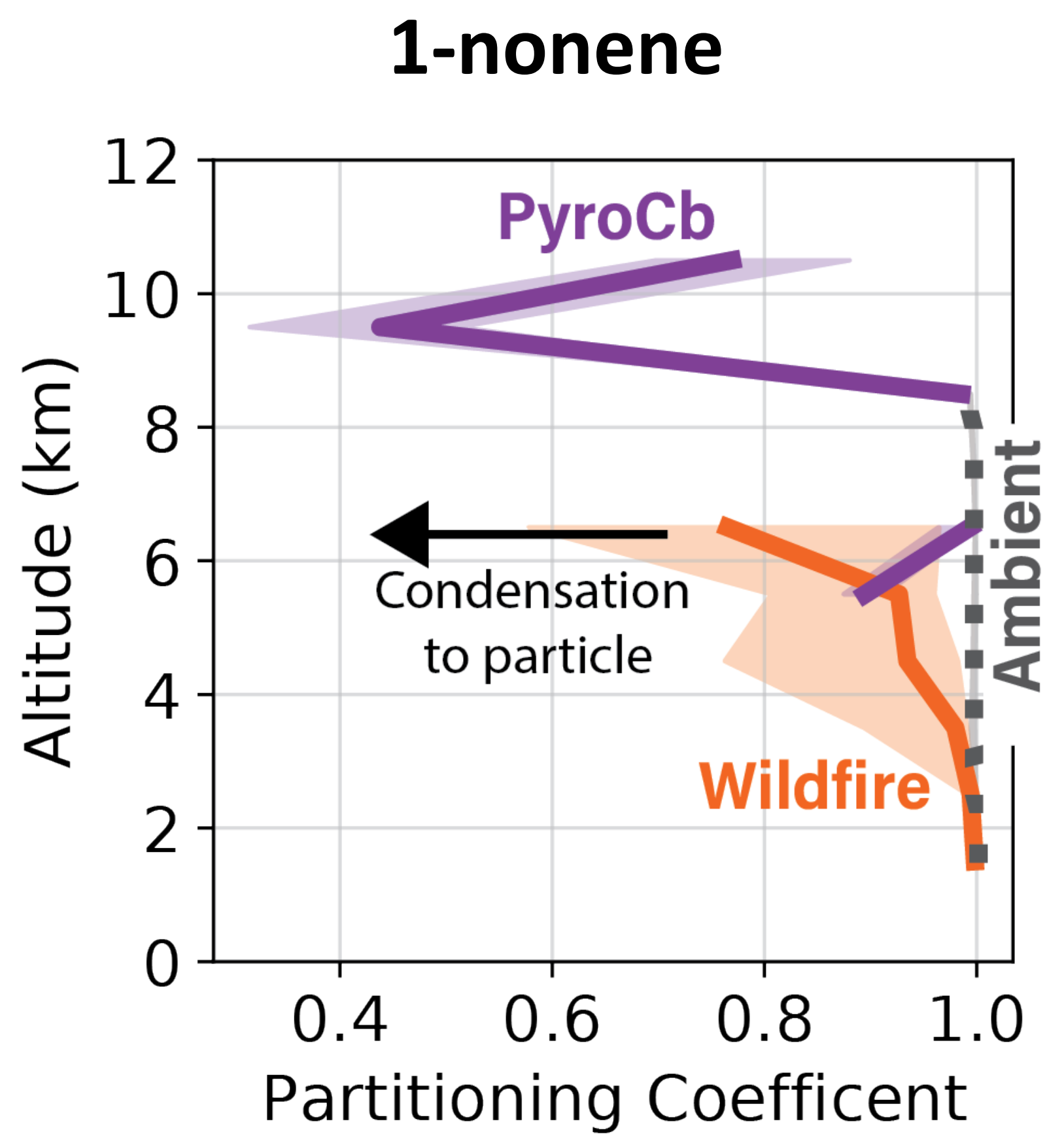
- NOAA/NASA DC-8 Campaign
  - Whole Air Samples – NMHCs
  - Black Carbon (SP2)
  - Size distributions (LAS)
- Calculate Partitioning Faction for each gas phase compound (gas/Σgas+aerosol) using partitioning theory.

Observational Evidence

Gas Phase:

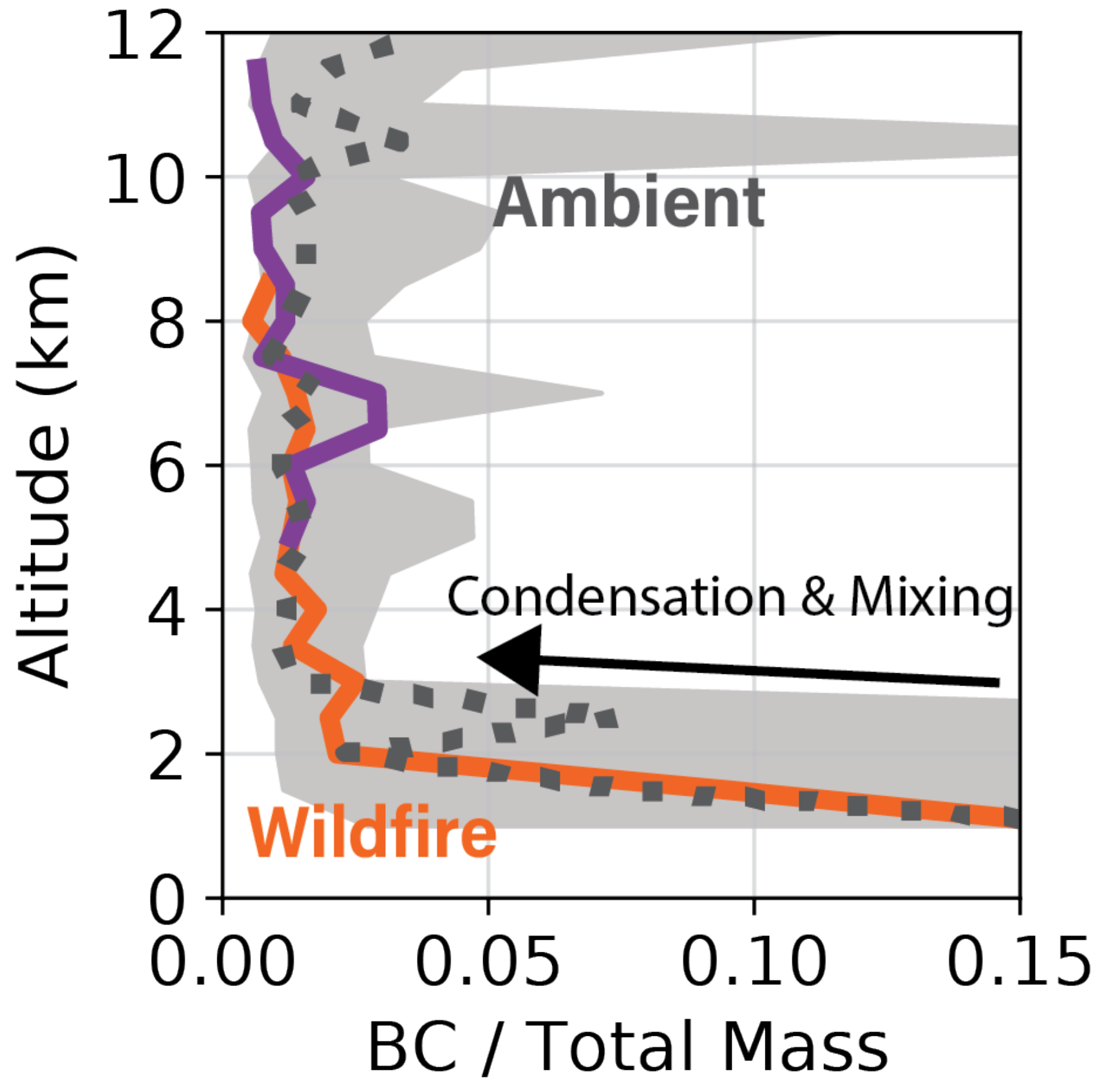
- 1-nonene is the only compound that shows significant changes to the gas aerosol partitioning.
- Vapor pressure is the main driver of condensation.

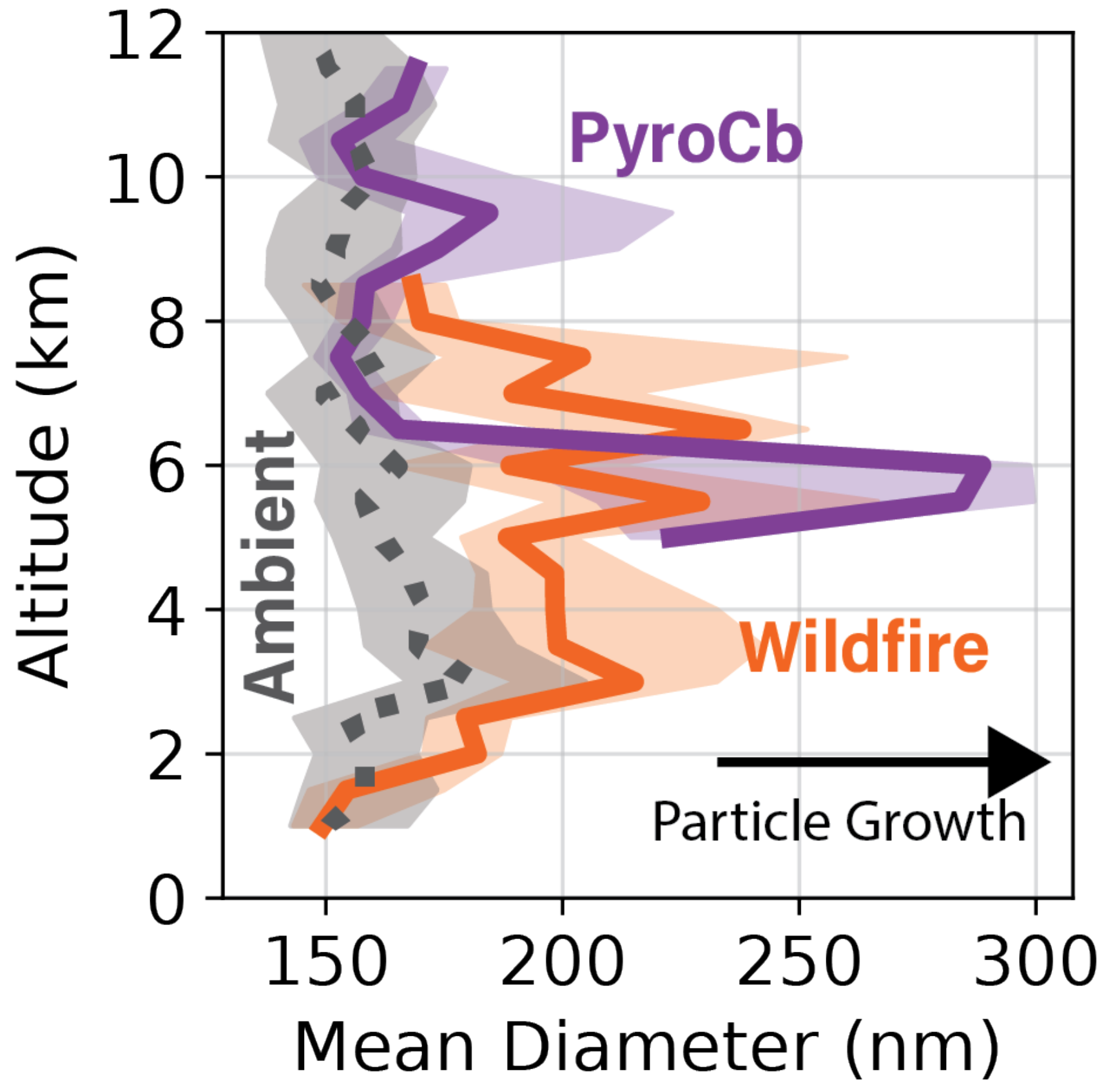




Particle Phase:

- Lower Black Carbon/total mass = more coatings on OA or BC
- Above ~3km fire impacted aerosol indicate more condensation than in ambient aerosol.
- Mean diameter increases with elevation.

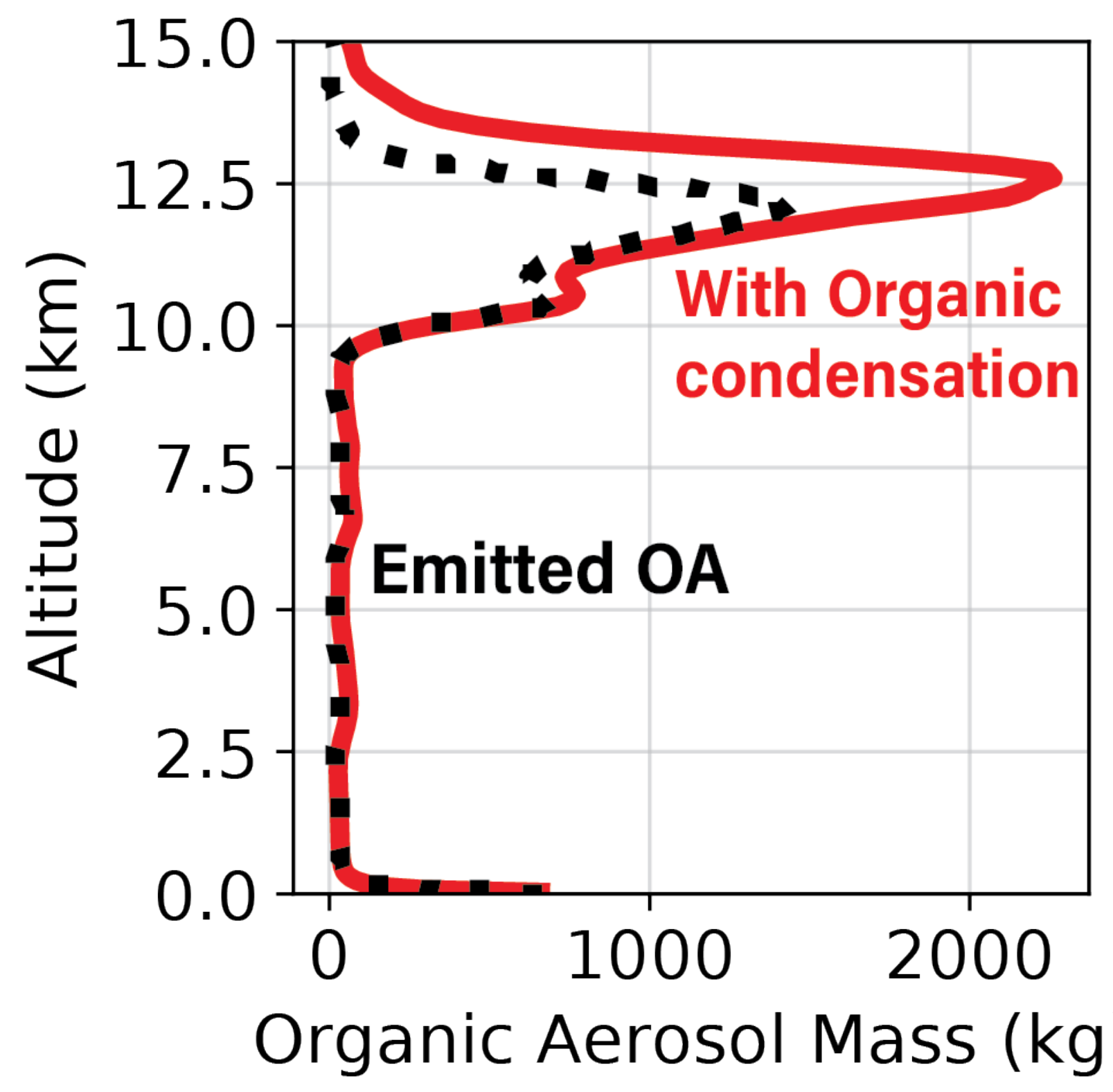




Adding a condensation mechanism to fire models

HIGRAD (High Gradient Applications model)

- Wildfire modeled as a circular time-dependent source (radius = ~1km).
- Snapshot from 125 minutes. Organic condensation parameterization based on volatility, is concentration and temperature dependent.
- The additional organic condensation increases the altitude and OA concentration of the plume.



Acknowledgements
Special thanks to the FIREX-AQ NOAA/NASA team and instrument PIs.

Vapors are Lost to Walls, Not to Particles on the Wall:

Development of Artifact-Corrected Parameters and Implications for Global Secondary Organic Aerosol

Kelsey R. Bilsback,[1*] Yicong He,[1] Arthur W. H. Chan,[2] Jeffrey R. Pierce,[1] Nga L. Ng,[3] John Seinfeld,[4] Shantanu H. Jathar[1**]

[1]Colorado State University, [2]University of Toronto, [3]Georgia Institute of Technology, [4]California Institute of Technology

Chamber experiment artifacts include: losses of particles to the walls and the losses of vapors to the particles on the wall and the wall directly.

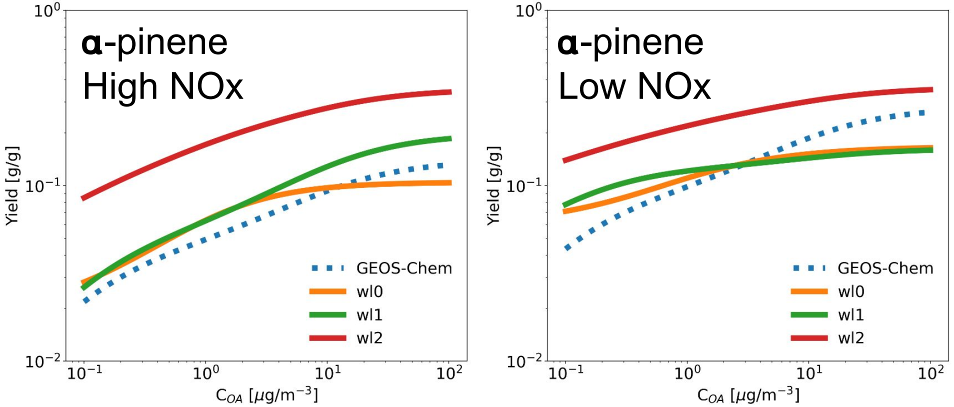
<u>We developed a systematic method for generating artifact-corrected SOA parameters.</u>

Step 1) **Fit** the chamber data using the SOM-TOMAS box-model, which accounts for chamber artifacts.

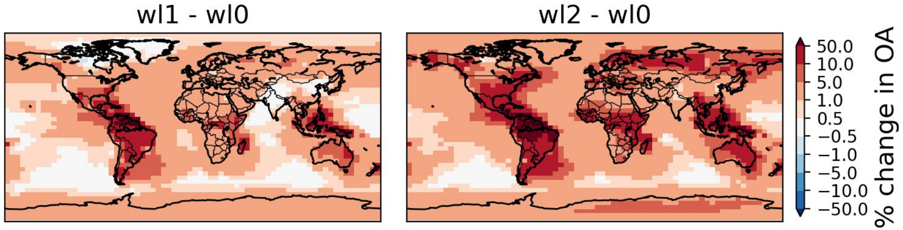
Step 2) **Model** VBS parameters using a pseudo atmospheric model that captures atmospherically relevant OA concentrations.

Step 3) **Model** OA concentrations in the atmosphere using the VBS parameters from Step 2 and GEOS-Chem.

*Kelsey.Bilsback@colostate.edu, **Shantanu.Jathar@colostate.edu



Step 2: Our updated schemes tended to substantially impacted the SOA mass yield, depending on conditions.



Step 3: Updating the yield parameters for α-pinene alone can change estimated OA by up to 22% in some regions.

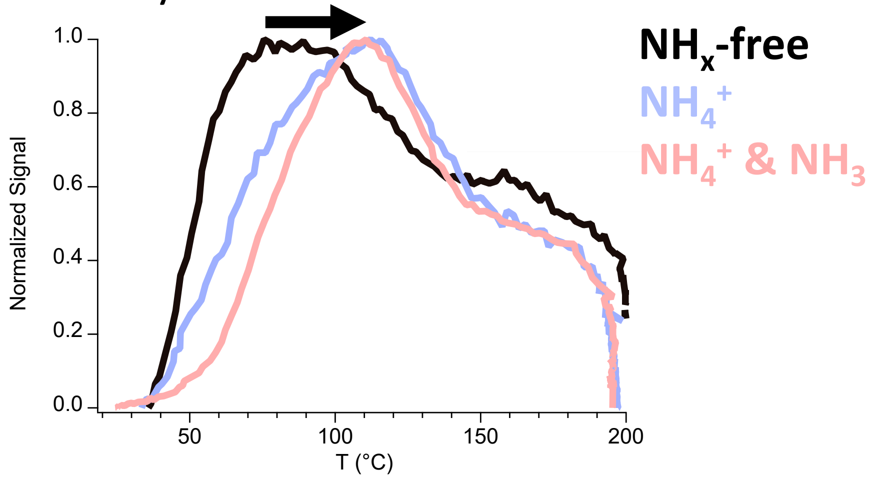
Effects of ammonia aging on the composition and volatility of biogenic SOA

Experimental Overview

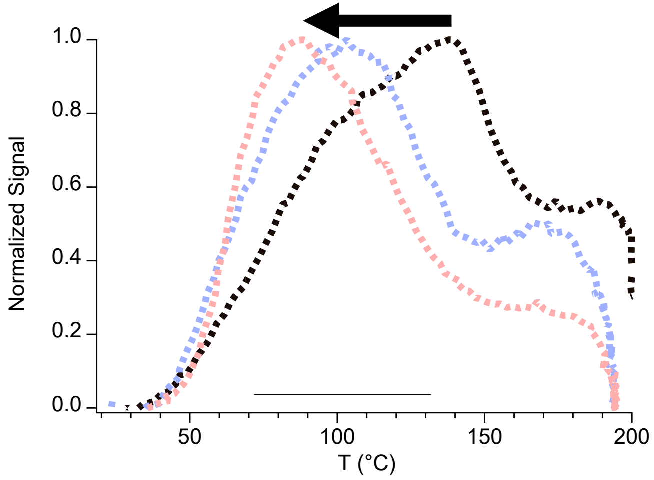
- α-pinene + O_3 SOA in presence of inorganic seed
- 3 conditions
  - NH_x-free
  - NH_4^+ in inorganic seed
  - ~20 ppb NH_3 addition following SOA formation (NH_4^+ containing seeds)
- FIGAERO-CIMS with protonated ethanol clusters as the reagent ion

*Effective volatility of **CHO** compounds is sensitive to N and RH*

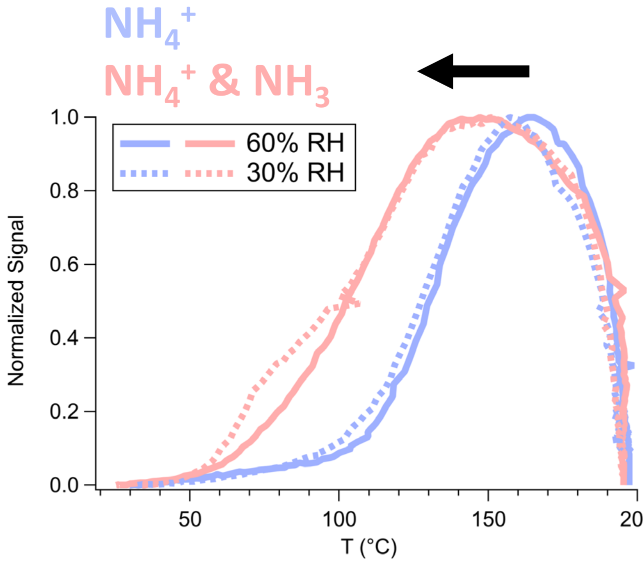
60% RH: N addition **decreases** effective volatility



30% RH: N addition **increases** effective volatility



***CHON** compounds are <u>less</u> volatile and <u>less</u> sensitive to RH changes compared to CHO compounds*



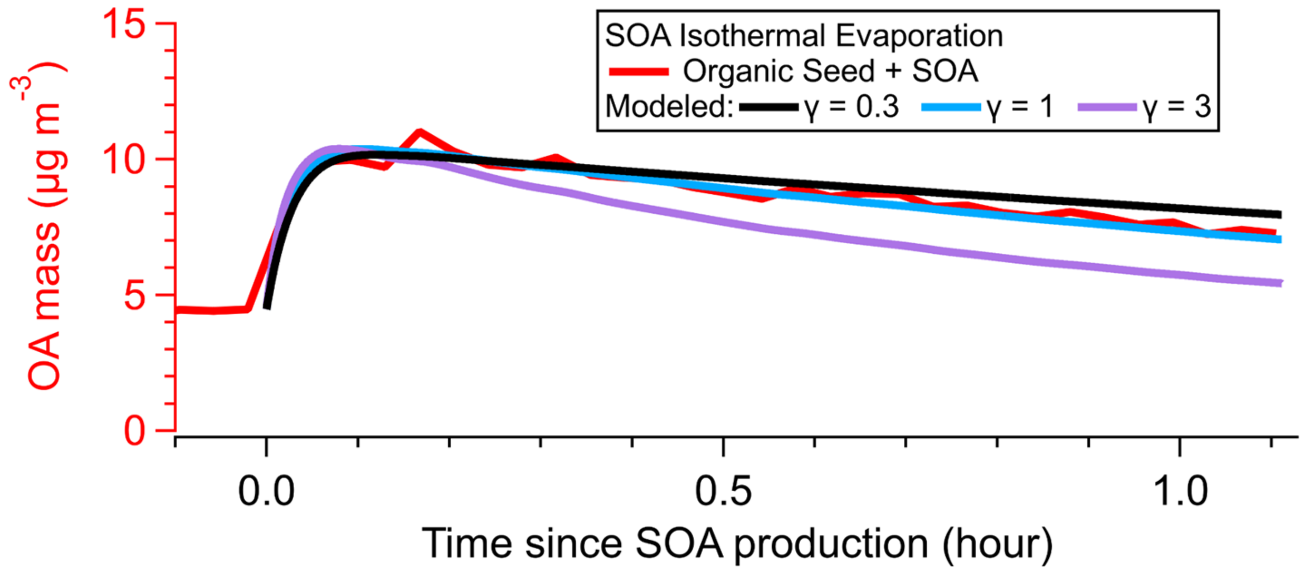
Addition of reduced N dramatically alters SOA composition and effective volatility with minimal impacts on aerosol mass

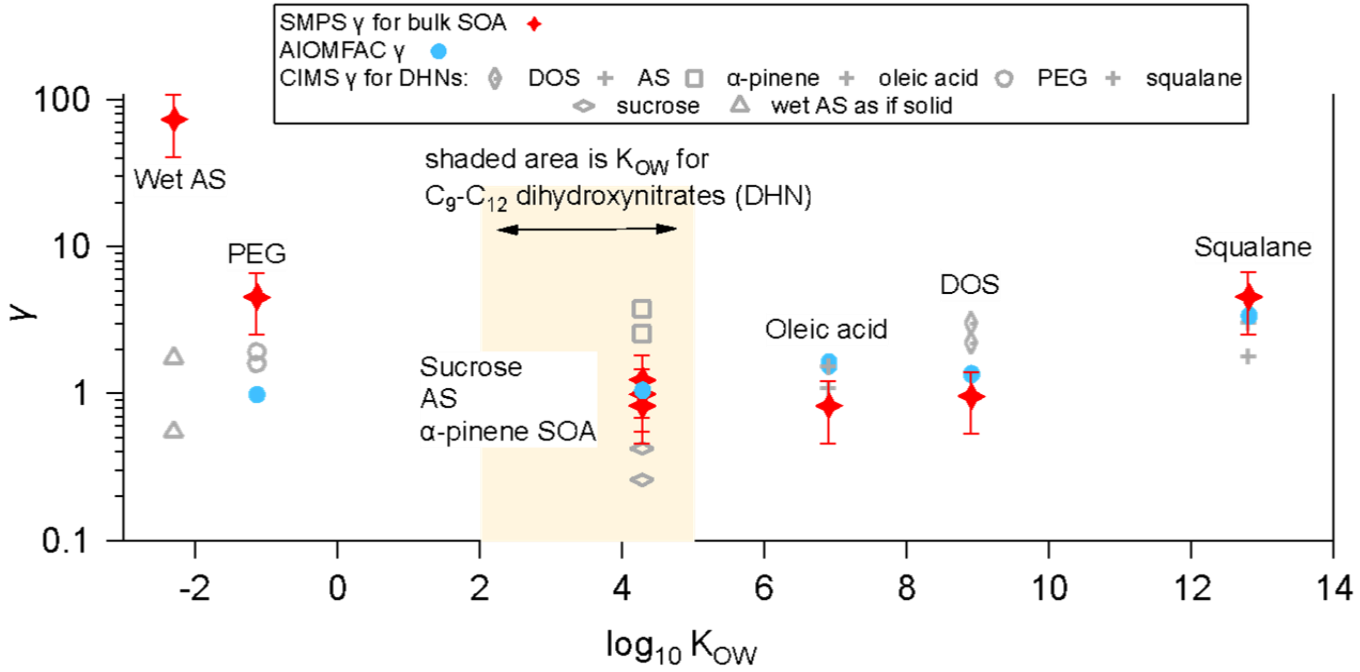
CU Boulder: Aroob Abdelhamid, Ellie Browne (eleanor.browne@colorado.edu)
University of Eastern Finland: Angela Buchholz, Iida Pullinen, Siegfried Schobesberger, Annele Virtanen

Funding: NSF GRFP & GROW fellowships

SOA Gas/Particle Partitioning: Activity Coefficients

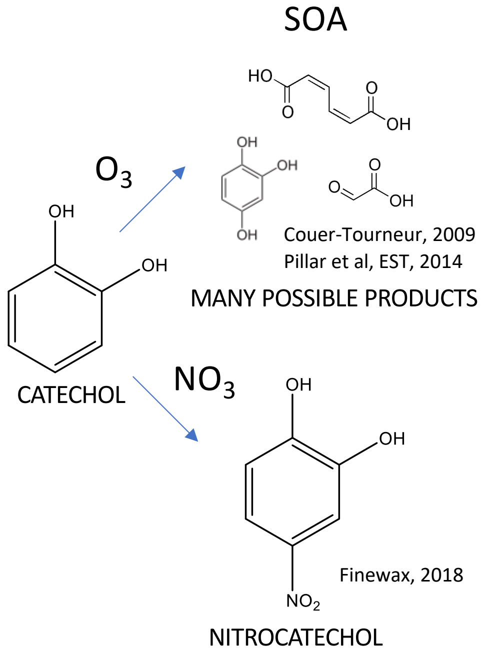
- Few measurements of organic compounds' activity coefficients (γ)
- Isothermal evaporation of SOA measured, γ quantified for bulk SOA and individual compounds in wide variety of seed particles
- γ increased (~1 to ~5) as polarity of SOA molecules and pre-existing seed diverged — making SOA formation less favorable
- High computed γ value of 74 for wet ammonium sulfate-SOA system indicates phase separation
- Bulk SOA *γ* not explained by simplified speciated SVOC-seed interactions — more detailed molecular information of the mixtures needed





X. Liu, D.A. Day, J.E. Krechmer, P.J. Ziemann, J.L. Jimenez. Determining Activity Coefficients of SOA from Isothermal Evaporation in a Laboratory Chamber. *Environ. Sci. Technol. Lett.*, 8, 3, 212–217, 2021. https://doi.org/10.1021/acs.estlett.0c00888.

Nitrocatechol condenses onto existing organic aerosol via new mechanism:



SOA

O_3

Couer-Tourneur, 2009
Pillar et al, EST, 2014

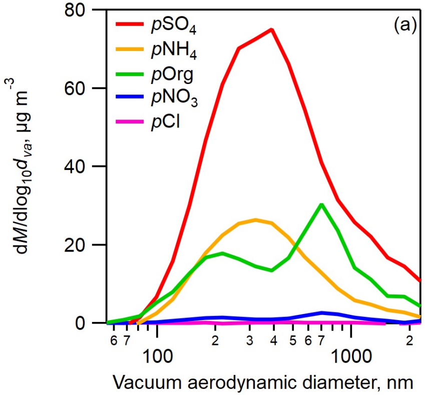
MANY POSSIBLE PRODUCTS

CATECHOL

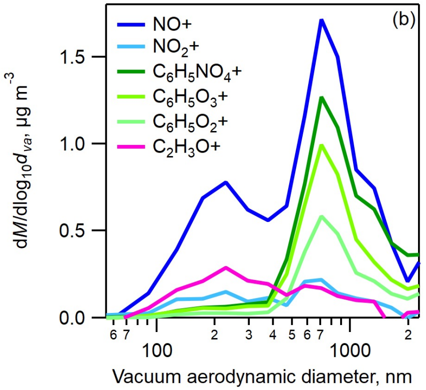
NO_3

Finewax, 2018

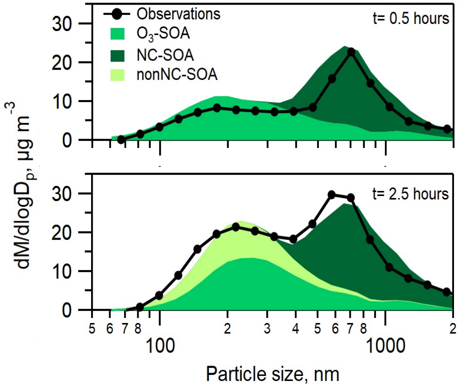
NITROCATECHOL



Organic aerosol in bimodal distribution different from ammonium sulfate seed

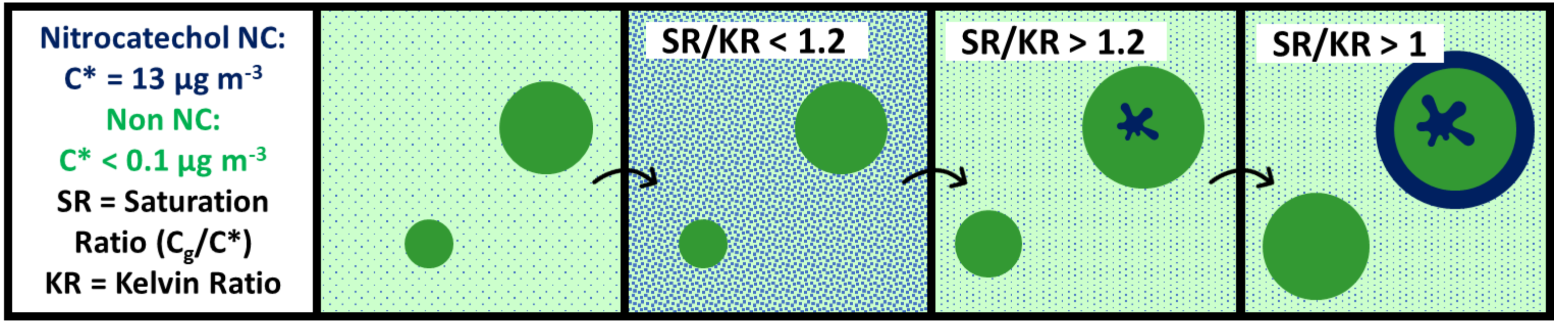


Nitrocatechol appears almost exclusively in the large organic mode



Reproduced in aerosol microphysics model (SOM-TOMAS)

Heterogeneous condensation



Nitrocatechol NC:
C* = 13 μg m^{-3}
Non NC:
C* < 0.1 μg m^{-3}
SR = Saturation Ratio (C_g/C*)
KR = Kelvin Ratio

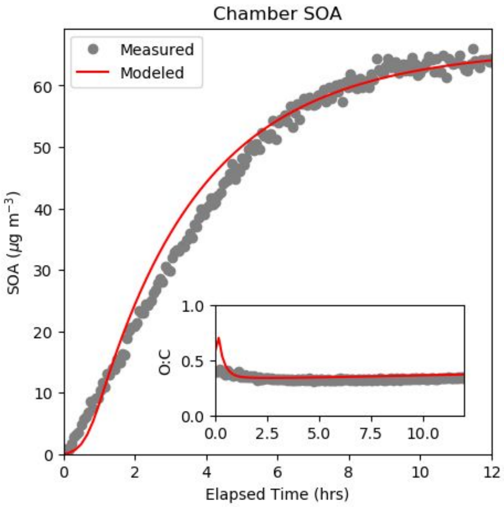
Modeling Secondary Organic Aerosol in Oxidation Flow Reactors: **Constraining the Nucleation Rate using Size Distributions**

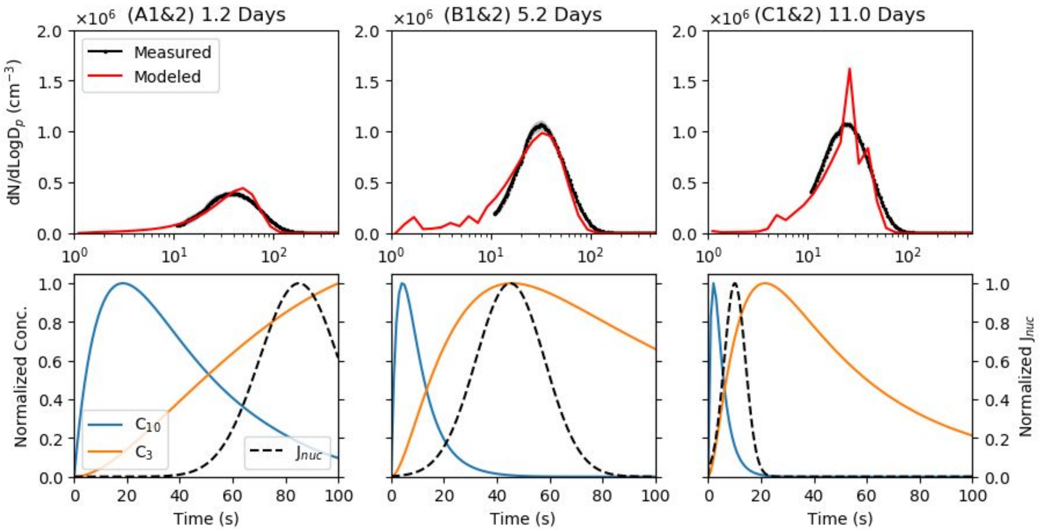
CHARLES HE[1], Andrew Lambe[2], Beth Friedman[1], Delphine K. Farmer[1], John Seinfeld[3], Jeffrey R. Pierce[1], Shantanu Jathar[1]

[1]Colorado State University
[2]Aerodyne Research Inc.
[3]California Institute of Technology

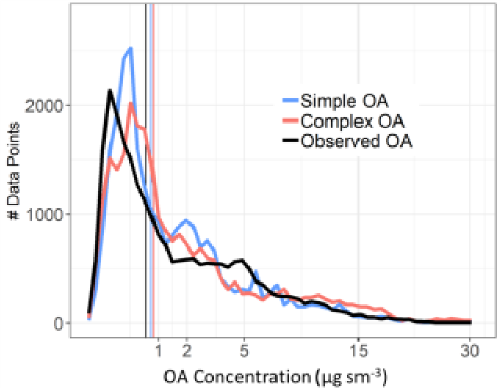
ASR
Atmospheric System Research

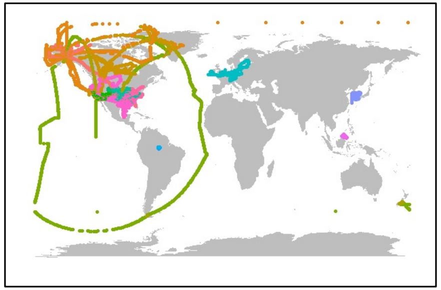
- We applied the SOM-TOMAS model to study SOA formation in OFR (*α*-pinene), by simulating gas-phase oxidation (with HOMs), gas/particle partitioning (with phase state), particle-phase reactions, heterogeneous oxidation, nucleation and wall loss.
- We constrained gas-phase oxidation parameters by fitting SOM-TOMAS to chamber SOA; $D_b = 4\times10^{-19}$ m^2 s^{-1}; $\gamma_{OH} = 0.6$; particle wall loss from measured transmission efficiencies; nucleation rate pre-calculated and optimized to give best agreement with measured size distributions.
- **For the lower OH exposures, the nucleation rate profile must be delayed wrt. the 1st-generation products.**

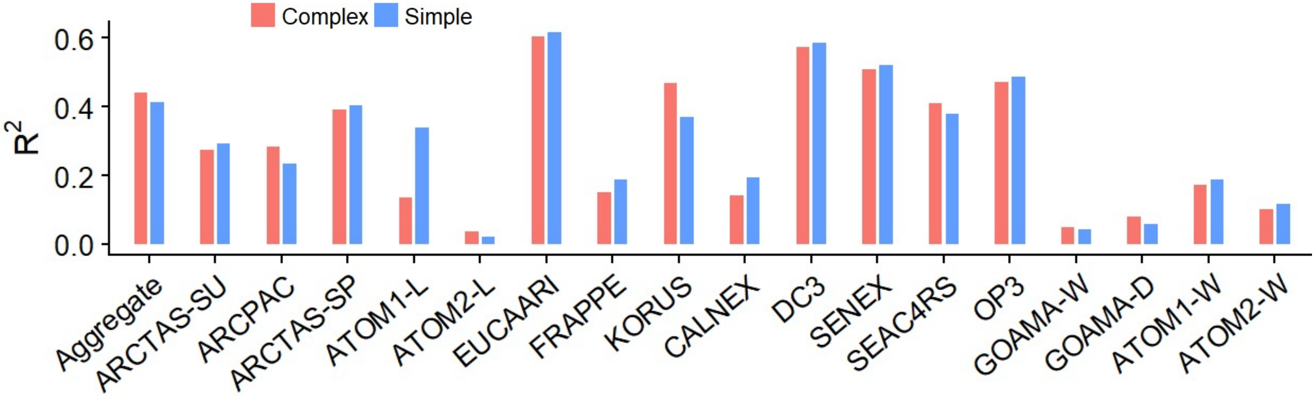




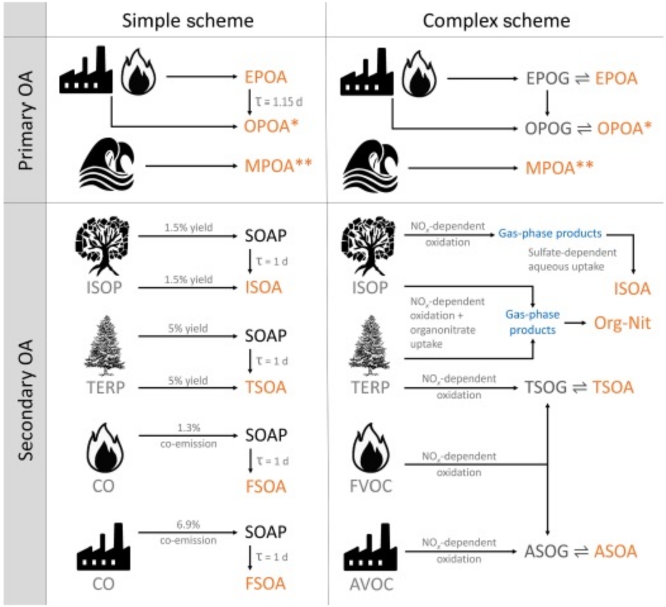
Global Model with Varying Complexity Schemes Has Similar Performance: Implications for Representation of SOA?







GEOS-Chem



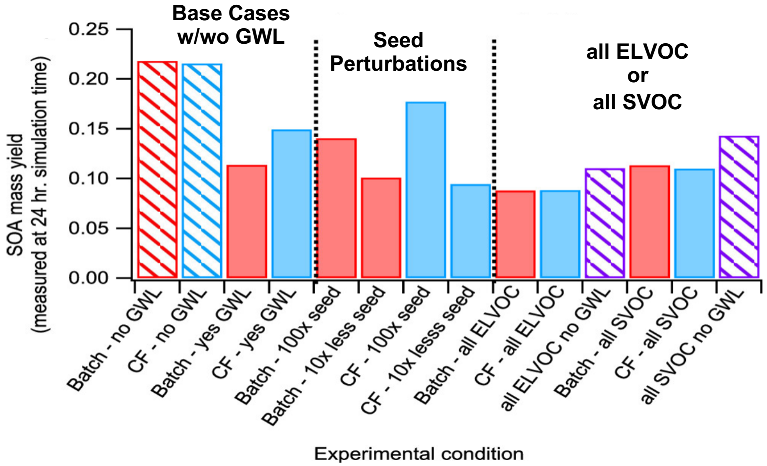
*Measurements are all AMS (Jose Jimenez, Hugh Coe, John Shilling, Roya Bahreini)

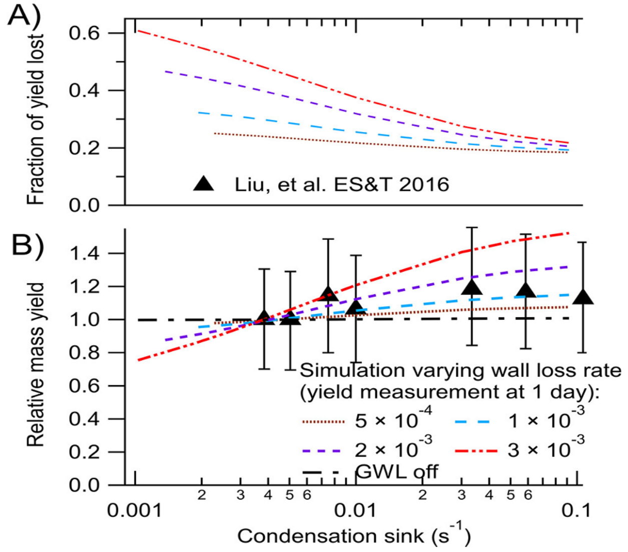
[Pai, Heald, et al., ACP, 2020]

University of Colorado Boulder

Gas-Wall Loss in Teflon Chambers: Continuous vs Batch

- Historically, most chambers have operated in “batch” mode. Increasing “continuous flow” (CF) mode
- Literature: belief that SOA yields measured in CF chambers are not affected by GWL, shown by low seed-dependence of yield
- Experimentally-constrained box model: GWL occurs in both types of chambers. Both require correction for accurate yields, even with substantial pre-existing seed
- GWL effects on yields result from rapid ELVOC (irreversible) gas loss to walls (vs particles) and long timescales (2-3 days) for SVOC to reach equilibrium with walls





J.E. Krechmer, D.A. Day, J.L. Jimenez. Always Lost but Never Forgotten: Gas-Phase Wall Losses Are Important in All Teflon Environmental Chambers. *Environ. Sci. Technol.*, 54, 20, 12890–12897, 2020. https://doi.org/10.1021/acs.est.0c03381

Multiphase OH Oxidation of Amorphous Organic Aerosol for Tropospheric Conditions

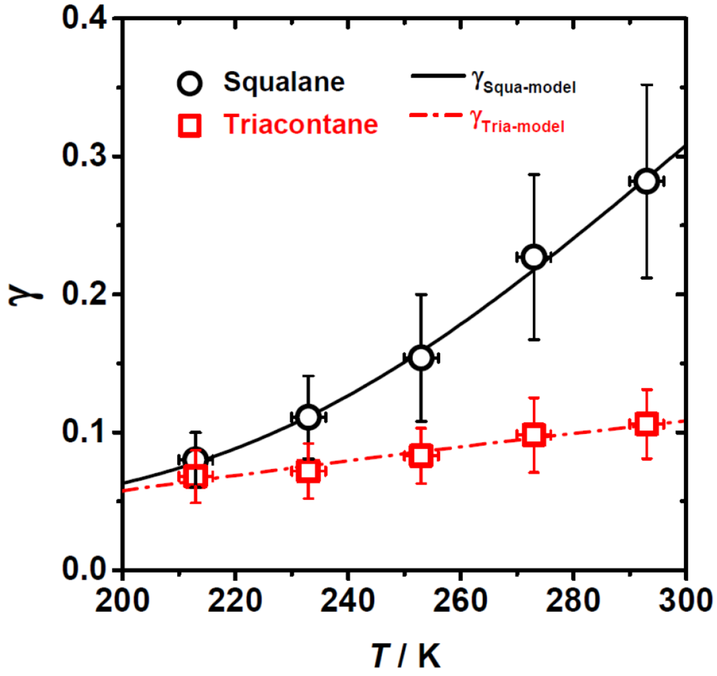
Jienan Li and Daniel A. Knopf, Representation of Multiphase OH Oxidation of Amorphous Organic Aerosol for Tropospheric Conditions, *Environ. Sci. Technol.*, 55, 7266-7275, 2021. doi: 10.1021/acs.est.0c07668

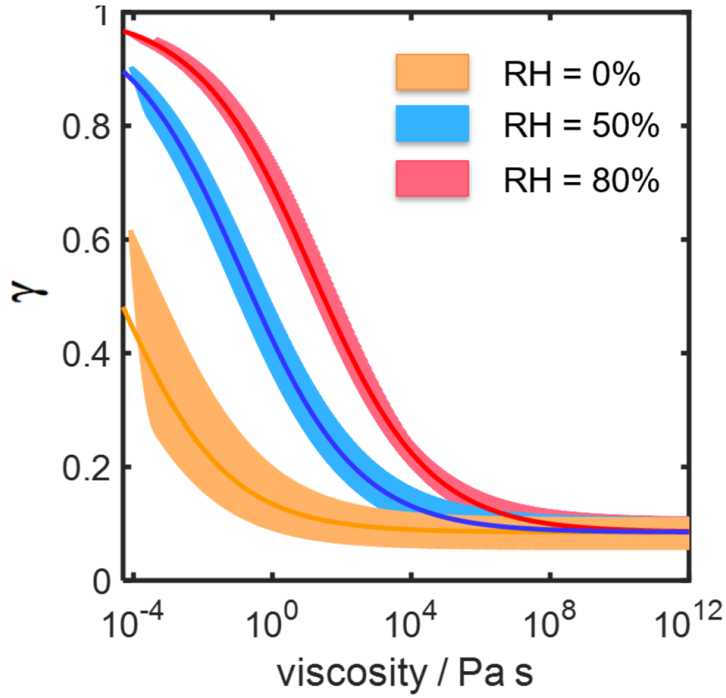
Objective

- *Determine multiphase oxidation kinetics for typical tropospheric temperatures considering amorphous phase changes of organic condensed-phase species.*

Key Findings

- *Reactive uptake most sensitive when the organic phase transitions from semisolid to liquid.*
- *Established resistor model representation.*
- *Temperature-dependent data allows to decouple thermodynamic and physical parameters, e.g., desorption energy and surface reaction rate constant.*
- *Derivation of Henry's law constant for OH dissolution into aliphatic organics: 2 orders of magnitude smaller than typical assumptions.*
- *Computational efficient parameterization of initial oxidation step of OA as a function of particle viscosity.*





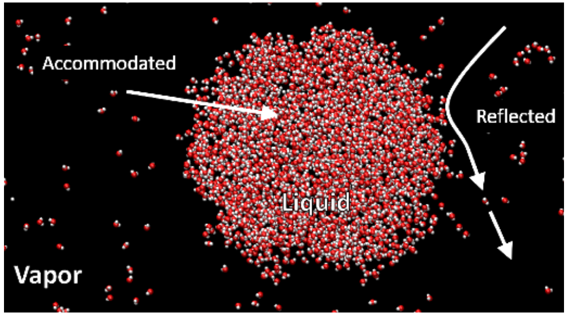
Atomistic Modeling of the Growth, Structural Evolution, and Properties of Nanoscale Droplets and Particles

Jennifer Lukes (jrlukes@seas.upenn.edu)

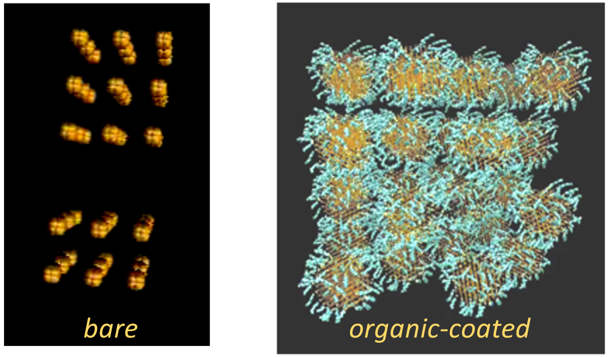
Single particle modeling capabilities:

- Surface tension
- Viscosity
- Diffusion coefficient
- Uptake of various species
- Heat of condensation
- Species spatial distribution and concentration
- Different compositions, temperatures, pressures, humidities

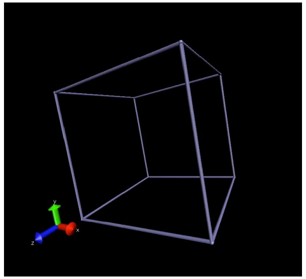
Scale: few nm – 100 nm



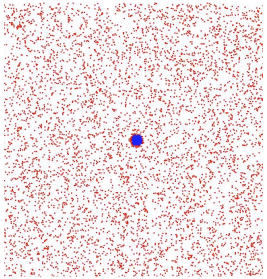
Mass accommodation – water droplet[1]



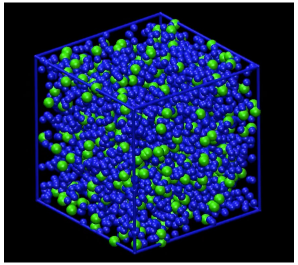
Structural evolution in clusters of nanoparticles[2]



Droplet nucleation and coalescence[3]



Vapor condensation and droplet growth on an insoluble particle[1]



Multicomponent phase segregation[4]