

# Phase, Viscosity, Morphology, and Room Temperature Evaporation Rates of SOA Particles at Low and High Relative Humidities, and their Interaction with Hydrophobic Organics

Alla Zelenyuk<sup>1</sup>, Dan Imre<sup>2</sup>, Josef Beránek<sup>1</sup>, Jacqueline Wilson<sup>1</sup>, Evan Abramson<sup>3</sup>, and Manishkumar Shrivastava<sup>1</sup>

<sup>1</sup>Pacific Northwest National Laboratory, <sup>2</sup>Imre Consulting, <sup>3</sup>University of Washington



Pacific Northwest  
NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

## Abstract

Formation, properties, transformations, and temporal evolution of secondary organic aerosol (SOA) particles strongly depend on particle phase. Semi-volatile molecules that comprise SOA particles were assumed to form a low viscosity solution that maintains equilibrium with the evolving gas phase by rapid evaporation condensation. However, studies by our group indicate that laboratory-generated SOA particles and ambient SOA characterized in a recent field campaign are in a semi-solid, highly viscous phase, and their evaporation rates are orders of magnitude slower than predicted.

Given that atmospheric relative humidity (RH) can change particle phase, it is important to investigate the effect of RH on the phase and evaporation kinetics of SOA particles. To this end SOA particles were generated at low and high (~50% and 90%) RH, and their evaporation kinetics and phase were characterized as a function of RH.

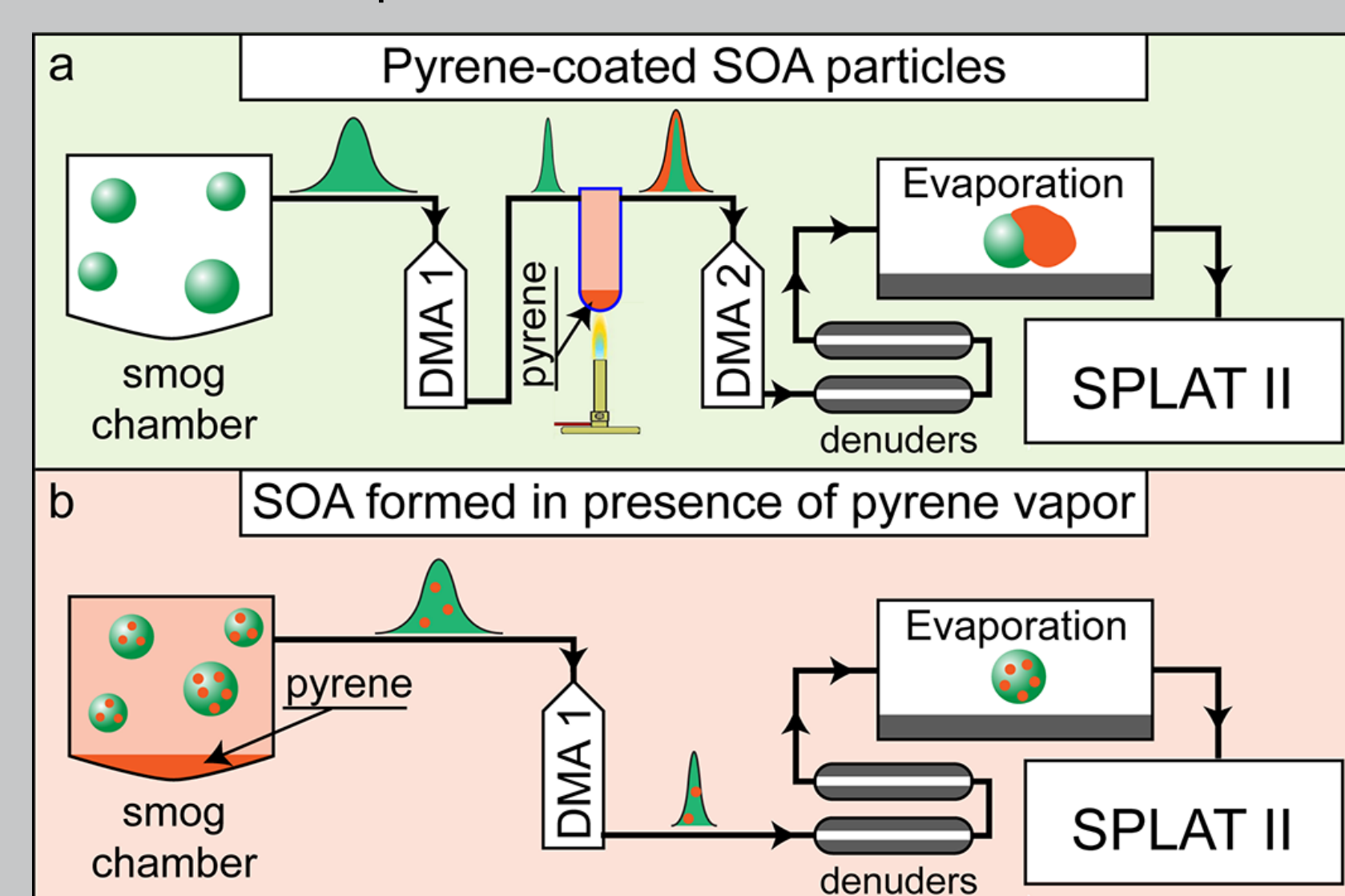
In the ambient atmosphere SOA particles form in the presence of a mixture of different organic compounds, which are present at or below their equilibrium vapor pressure, and thus have been ignored. However, our data show that these compounds can adsorb to the surface of particles during SOA formation, becoming trapped in the highly viscous SOA, and affect particle properties. We examine the interaction between SOA particles and different hydrophobic organics representing typical anthropogenic emissions by making SOA in the presence of the vapors of these hydrophobic organics and characterizing their properties. We find that the interaction between SOA and hydrophobic organics leads to a symbiotic relation, in which trapped hydrophobic organics are protected from evaporation and the oxidizing atmosphere, and the presence of hydrophobic organics virtually stops SOA evaporation.

We also demonstrate that it is possible to directly measure the diffusion rates of these molecules in SOA, and use them to calculate a reasonably accurate value for the SOA viscosity, from which particle coalescence rates are calculated. Using pyrene as the tracer molecule and SOA derived from alpha-pinene ozonolysis, we find that it takes ~24 hours for half the pyrene to evaporate. Based on the observed pyrene evaporation kinetics we estimate a diffusivity of  $2.5 \times 10^{-21} \text{ m}^2 \text{ s}^{-1}$  for pyrene in SOA. Similar measurements on SOA doped with fluoranthene and phenanthrene yield diffusivities comparable to that of pyrene.

Assuming a Stokes-Einstein relation, an approximate viscosity of  $10^8 \text{ Pa s}$  can be calculated for this SOA. Such a high viscosity is characteristic of tars and is consistent with published measurements of SOA particle bounce, evaporation kinetics, and the stability of two reverse-layered morphologies. We show that a viscosity of  $10^8 \text{ Pa s}$  implies coalescence times of minutes, consistent with the findings that SOA particles formed from coagulation are spherical on the relevant experimental timescales. Measurements on aged SOA particles doped with pyrene yield an estimated diffusivity ~3 times smaller, indicating that hardening occurs with time, which is consistent with the increase in SOA oligomer content, decrease in water uptake, and decrease in evaporation rate previously observed with aging.

## Method

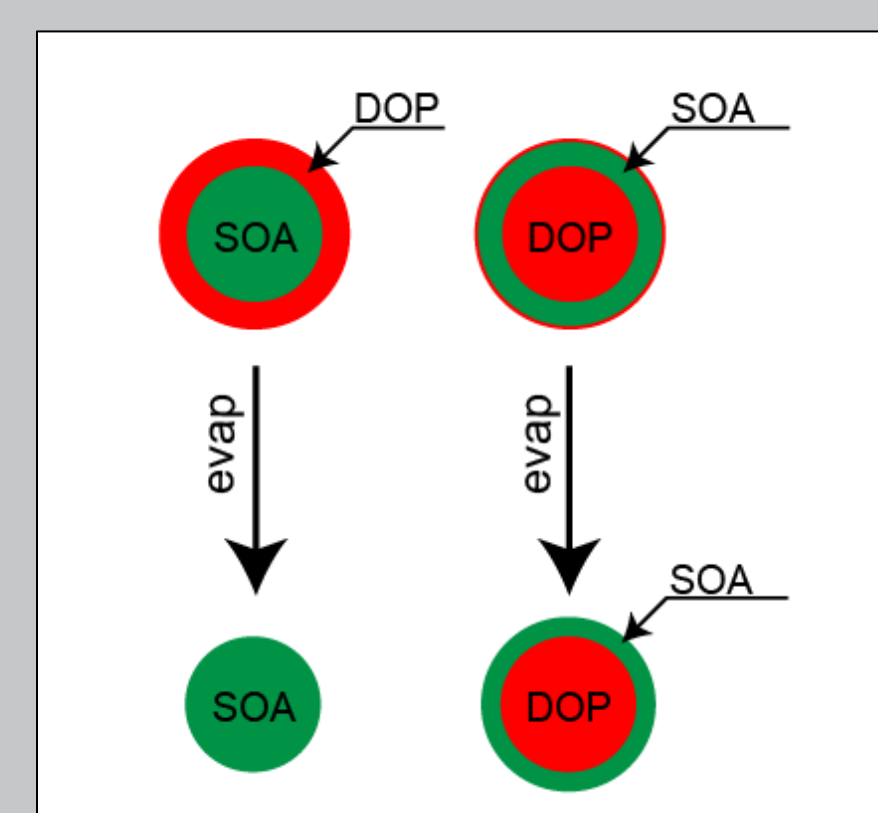
Schematic of the SOA formation, coating, RT evaporation, and characterization experiments.



Single particle mass spectrometer, SPLAT II, was used to monitor changes in particle size, composition, density, shape, and morphology as function of evaporation time.

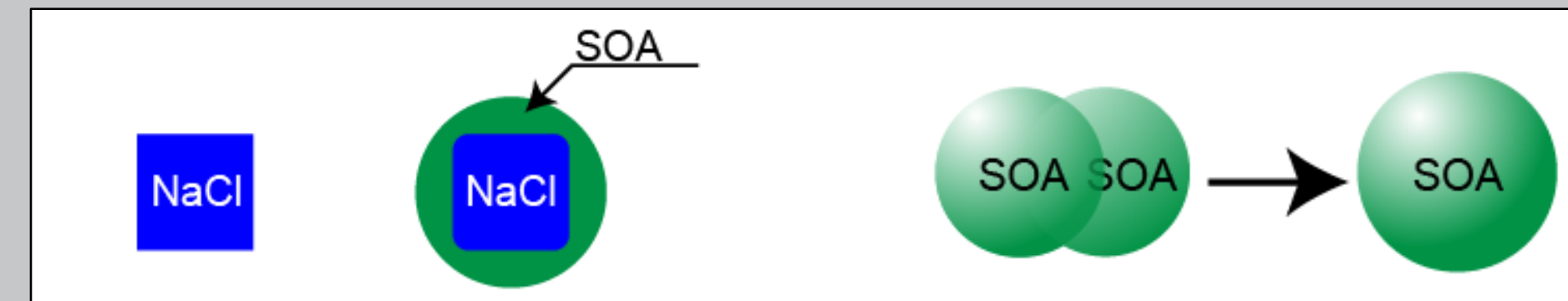
## SOA Particles are Semisolids

- Particles with two opposite morphologies are stable for many hours
- DOP coating on SOA seeds evaporates very fast
- When coated with SOA, DOP does not evaporate
- The mass spectra of SOA do not change with evaporation



- SOA particles bounce more than crystalline ammonium sulfate particles
- SOA evaporation rates are nearly size-independent
- Concentrations of organic nitrates in SOA are *inconsistent* with equilibrium partitioning between gas and liquid particles phases

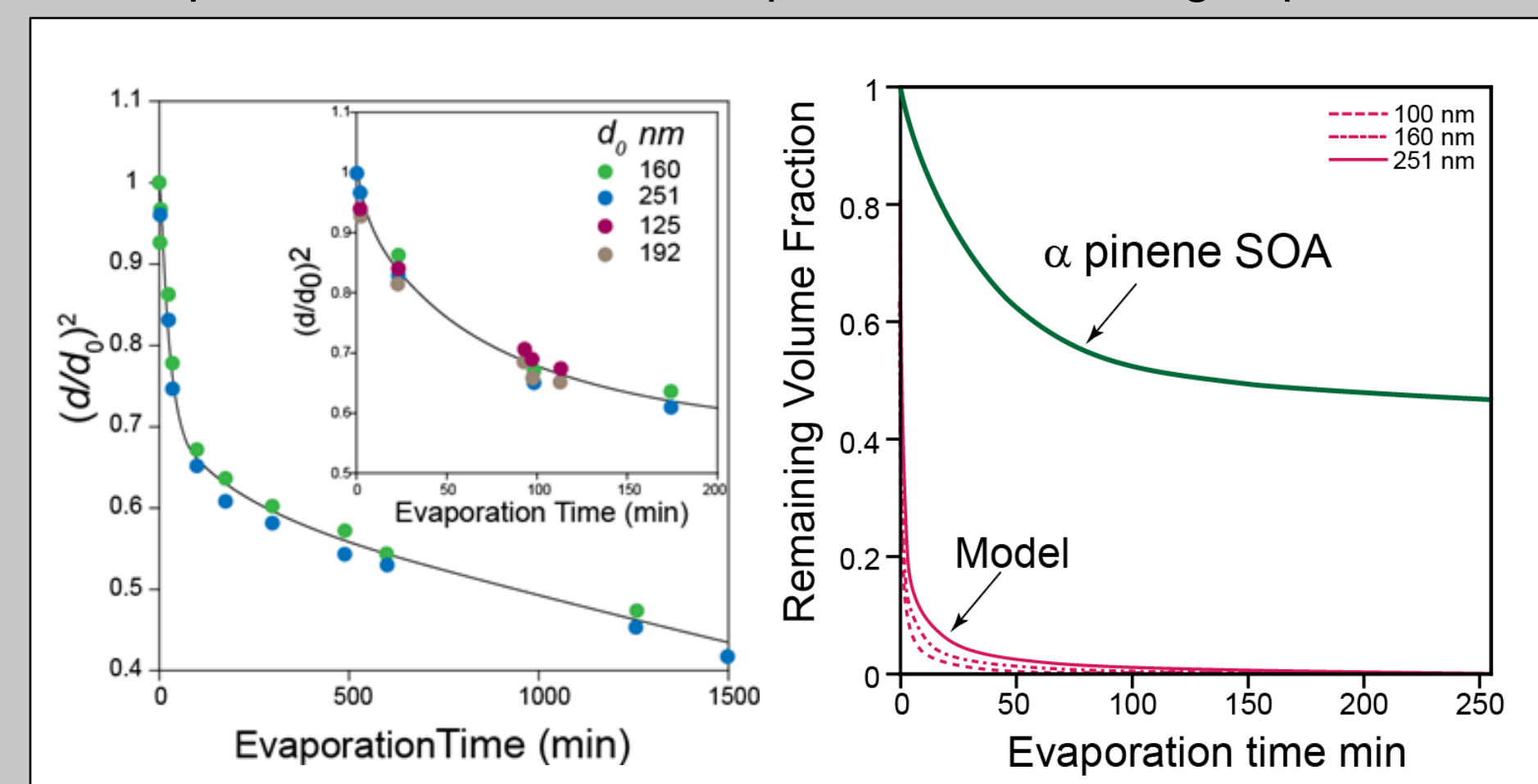
- SOA Particles are not rigid solids:



- SOA particles are spherical even after coagulation
- SOA coating transforms cubic NaCl seed particles into spherical particles

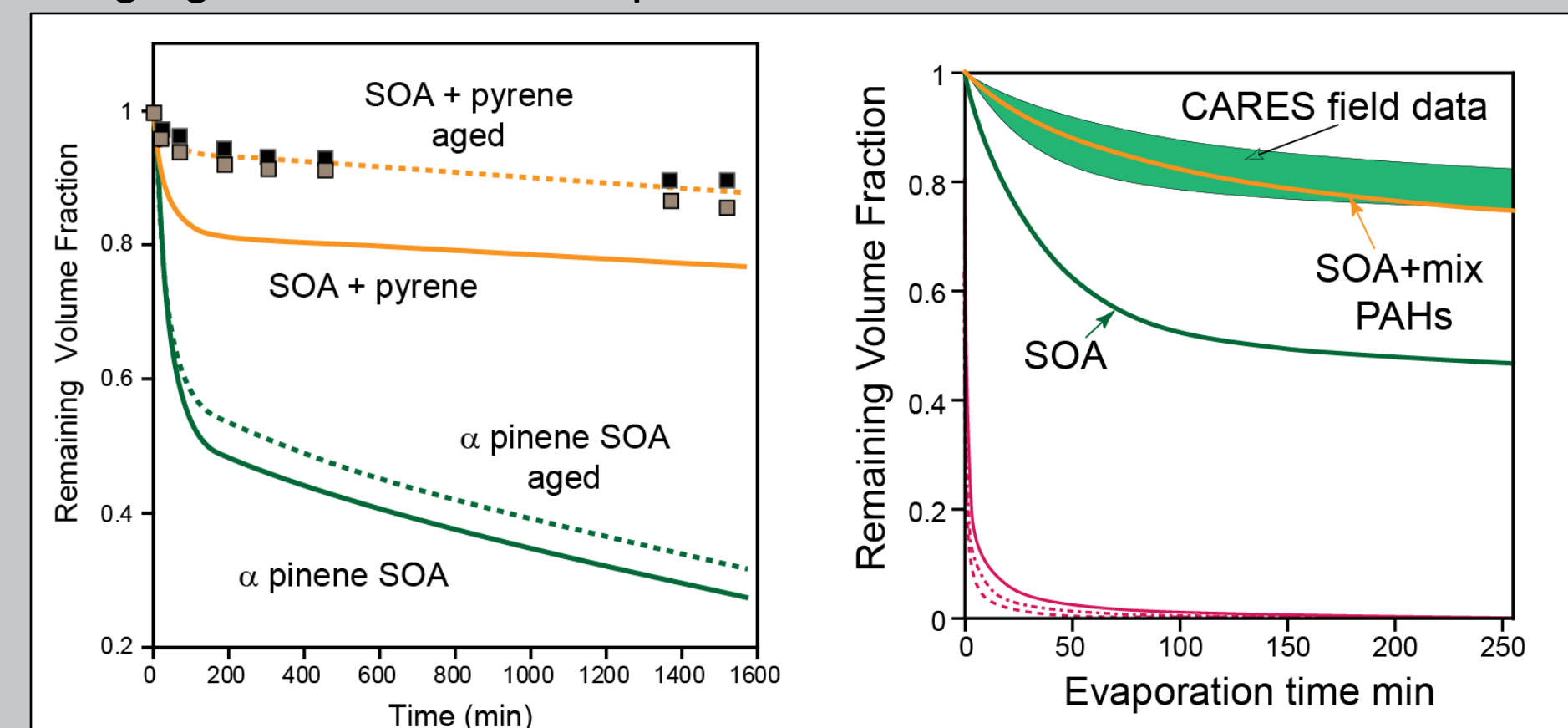
## RT Evaporation Kinetics

- Measured RT evaporation of size-selected particles for ~24 hrs
- Evaporation is orders of magnitude slower than models predict
- Contrary to models it is nearly size-independent
- Particles are not liquids
- SOA particles are not in the equilibrium with the gas phase

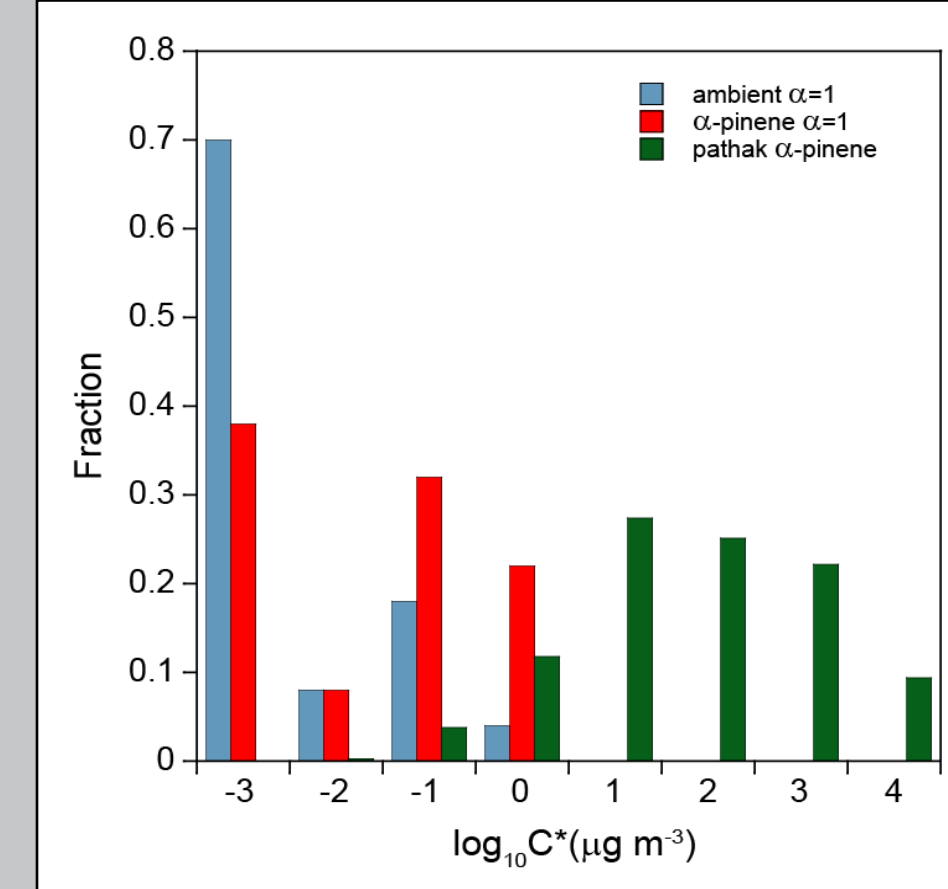


## Effect of Hydrophobic Organics & Aging

- SOA particles formed in the presence of hydrophobic organic vapors evaporate slower
- Aging further slows evaporation

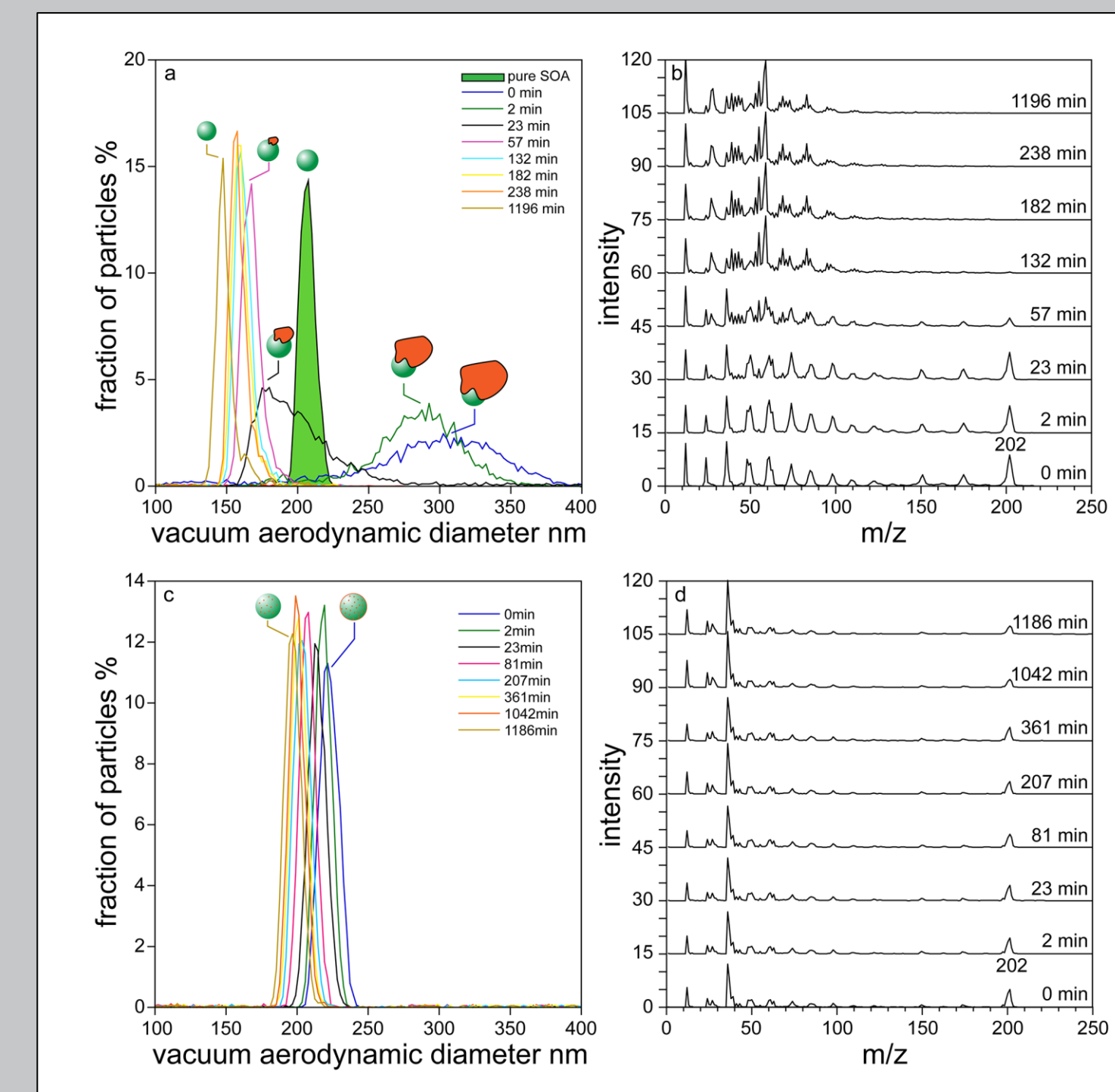


- Evaporation of ambient size-selected SOA looks like the slowest laboratory SOA data
- Comparison of experimental data against predictions of detailed kinetic mass transfer model using 7-products VBS developed to fit SOA formation shows large differences



## Pyrene-Containing Particles

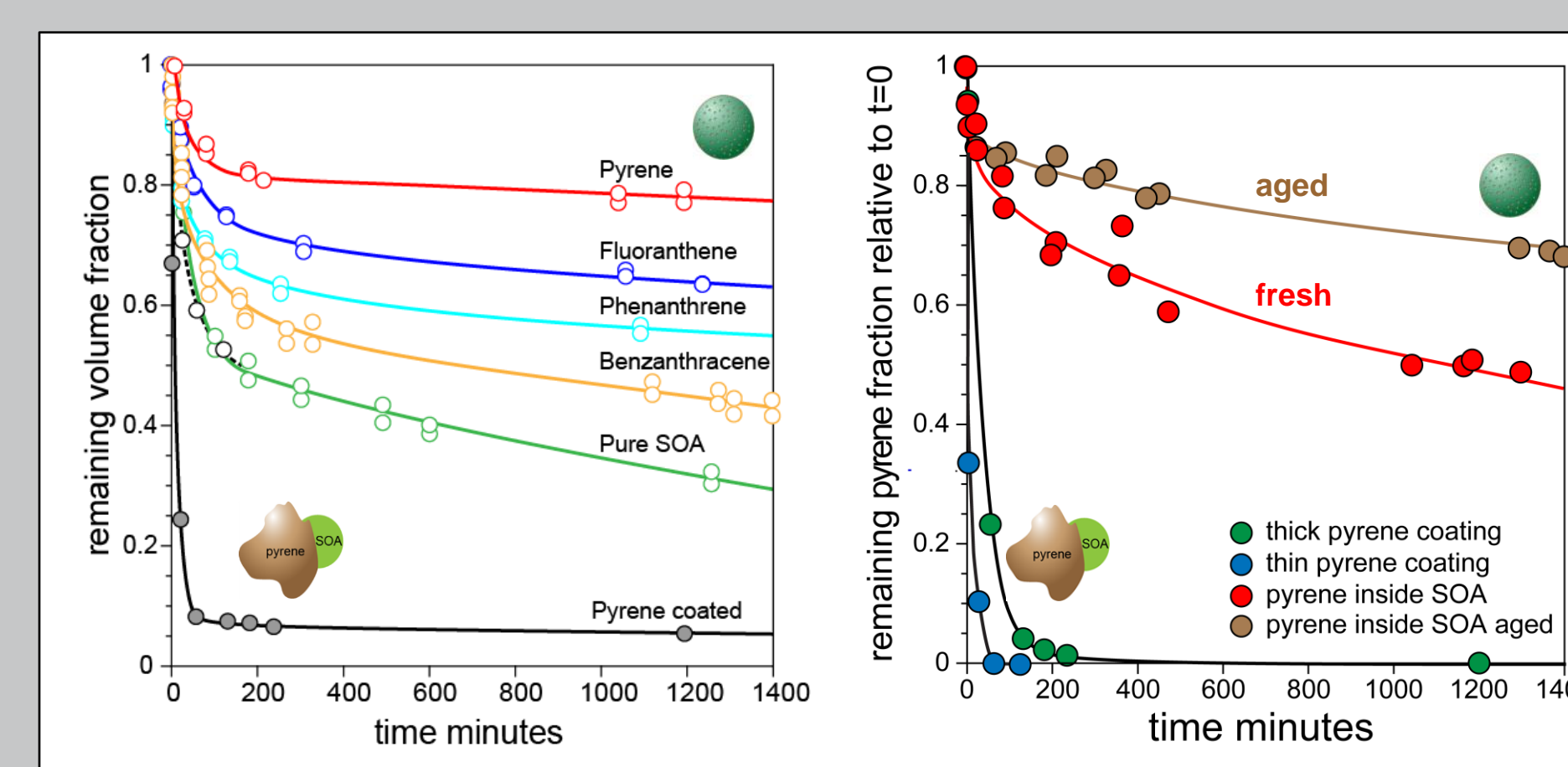
- Pyrene-coated particles are aspherical
- Pyrene coating evaporates fast and completely



- SOA particles formed in the presence of pyrene vapor are spherical
- Pyrene trapped inside highly viscous SOA takes days to evaporate

## Synergy between SOA and PAHs

- PAHs, acquired during SOA formation, significantly slow SOA evaporation
- PAHs trapped inside viscous SOA cannot evaporate and are shielded oxidation
- Discovered synergistic relationship between SOA and PAHs that may explain *long range transport (LRT)* of toxic substances like PAHs and other persistent organic pollutants (POPs)

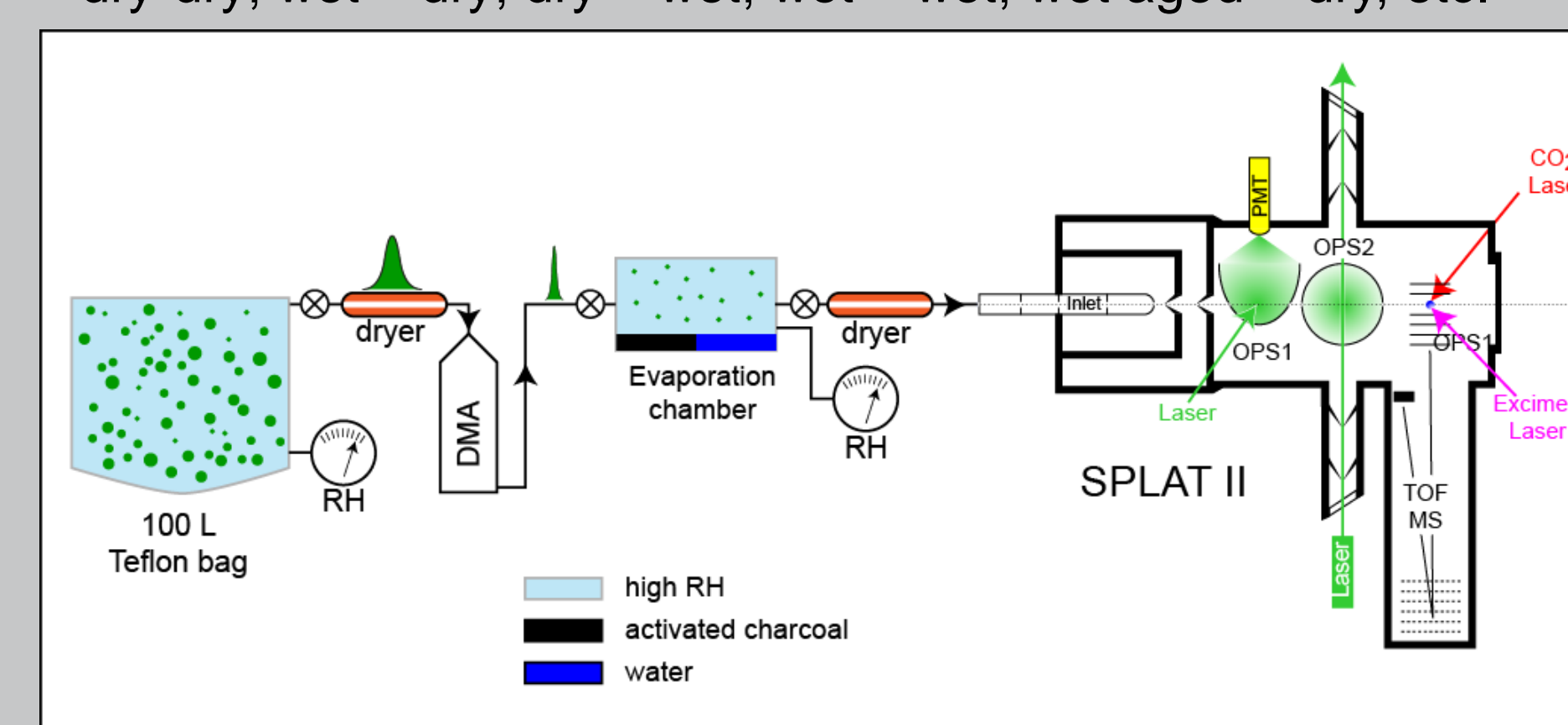


## SOA Phase and Viscosity

- Measuring PAHs evaporation rates yields chemical diffusivity and SOA viscosity
- First direct measurements of SOA diffusivity and viscosity: pyrene diffusivity in SOA:  $D = 2.5 \times 10^{-21} \text{ m}^2/\text{s}$ , SOA viscosity:  $\eta = 10^8 \text{ Pa s}$ , characteristic of tars
- Measurements on aged SOA yields an estimated diffusivity ~3 times smaller, indicating that hardening occurs with time
- Calculated coalescence rates are consistent with spherical SOA

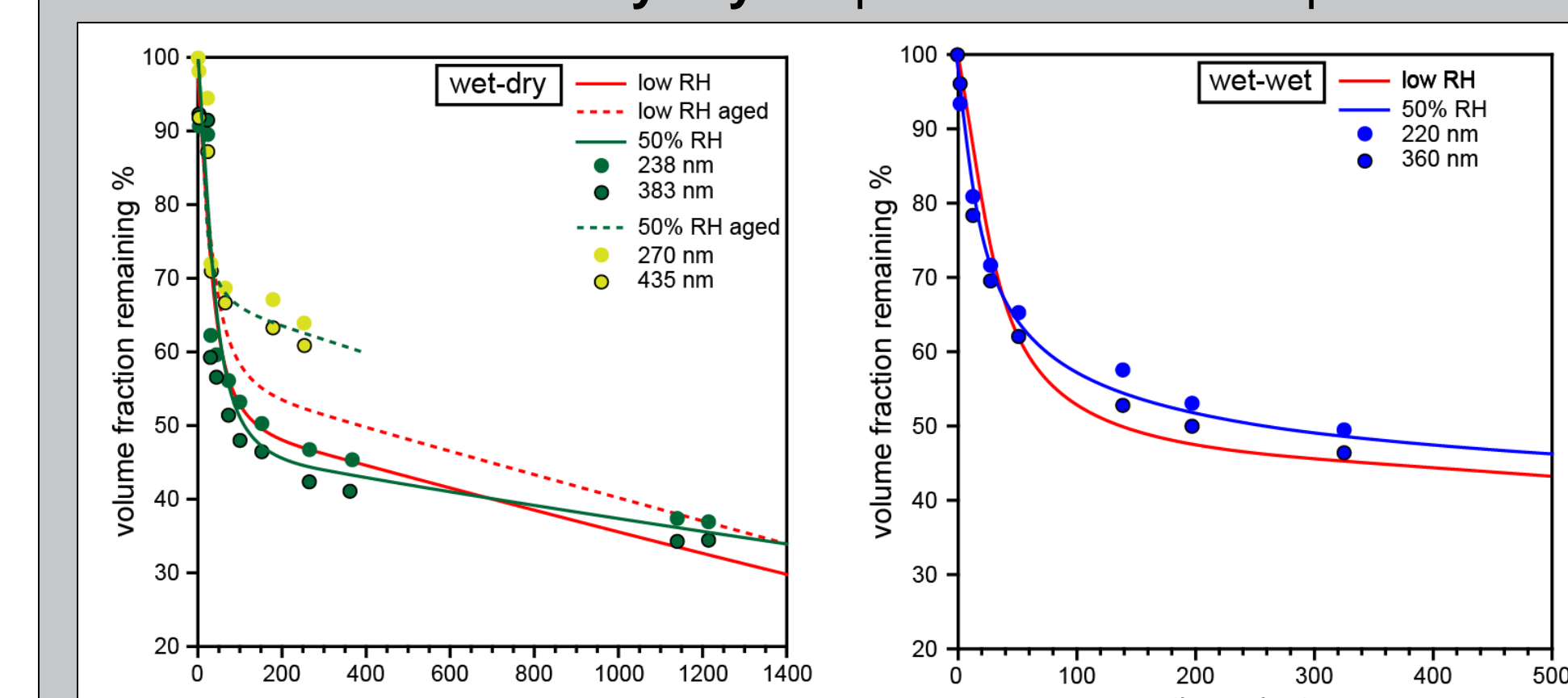
## SOA Evaporation at Higher RH

- We modified our experimental system to allow studies of the RT evaporation of size-selected SOA particles at higher RH
- We present here studies in which SOA was made and its evaporation characterized in a number of combinations: dry-dry; wet - dry; dry - wet; wet - wet; wet aged - dry, etc.

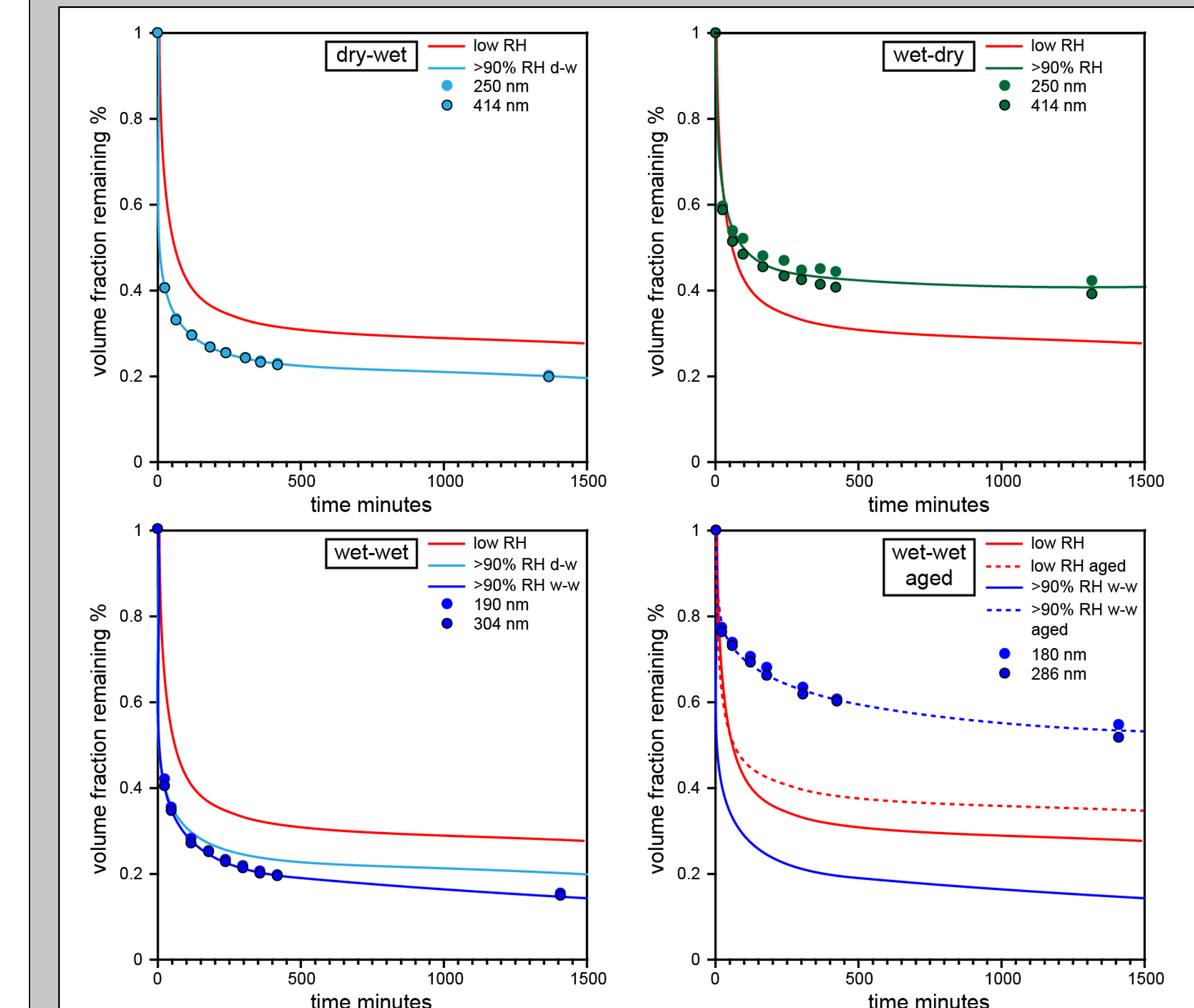


## SOA Evaporation at Higher RH

- The evaporation kinetics data show almost no change between dry-dry, wet-dry, and wet-wet experiments
- Red line: measured **dry-dry** evaporation rates for  $\alpha$ -pinene SOA

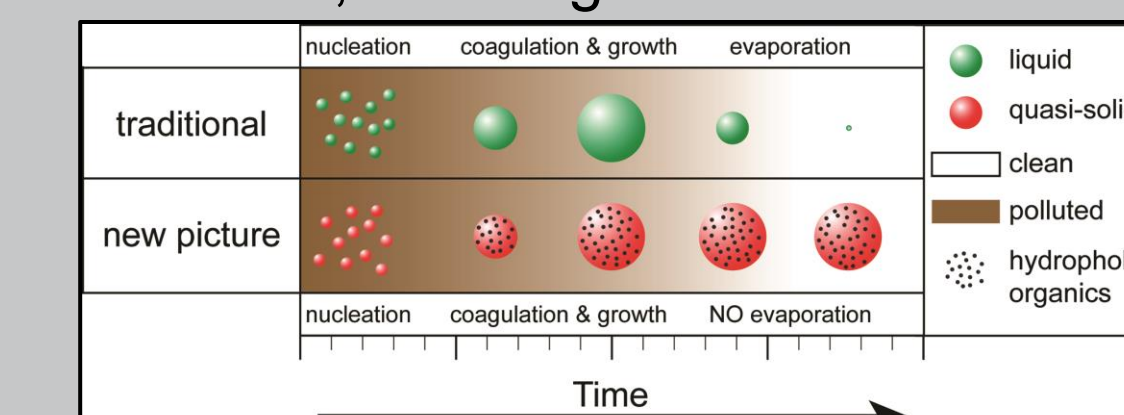


- The data show that under very high RH (>90%) we get more evaporation in the fast phase
- For all cases **evaporation** remains nearly **size-independent**
- Aging has a very large effect of wet particles

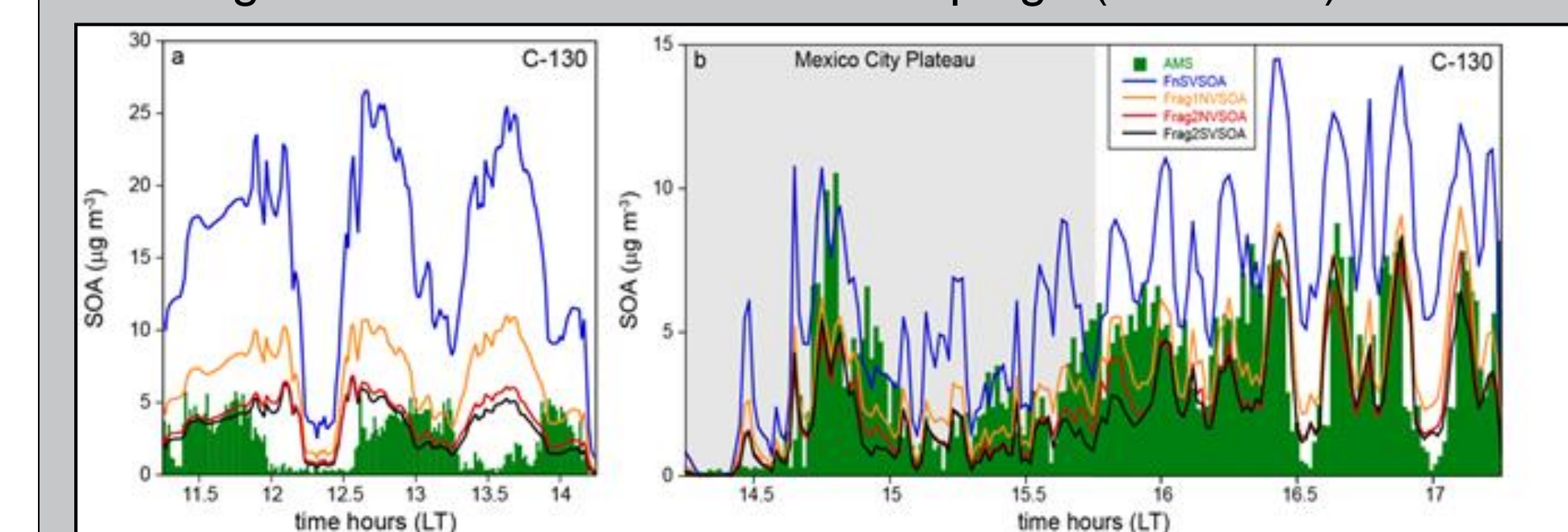


## New SOA Modeling Approaches

- New SOA modeling approaches must take into account new experimental findings about SOA phase, volatility, non-equilibrium behavior, and fragmentation reactions



- Our recent SOA modeling study includes non-absorbing, low effective volatility SOA, and for the 1<sup>st</sup> time incorporates fragmentation reactions in 3D models
- It shows significant improvement in the performance of the model, especially downwind of Mexico City
- Below WRF-Chem-calculated vs. AMS-measured SOA loadings during the 2006 MILAGRO field campaign (March 10)



## Acknowledgements

This work was supported by the U. S. DOE Office of Basic Energy Sciences, Chemical Sciences Division and Office of Biological and Environmental Research (Atmospheric Research Program). This research was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the DOE Office of Biological and Environmental Research at Pacific Northwest National Laboratory (PNNL).