Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

The Surprising Role of Semivolatile Organics in the Growth of Ultrafine Particles

Rahul Zaveri

Pacific Northwest National Laboratory

John Shilling[1], Alla Zelenyuk-Imre[1], Jiumeng Liu[1], David Bell[1], Emma D'Ambro[2], Cassandra Gaston[2], Joel Thornton[2], Jaqueline Wilson[1], Alex Laskin[1], Peng Lin[1], Jian Wang[3], Richard Easter[1], John Seinfeld[4], Allan Bertram[5], Scot Martin[6], Chongai Kuang[3], Daniel Cziczo[7], Ari Setyan[8], Qi Zhang[9], Timothy Onasch[10], and Douglas Worsnop[10]

[1]Pacific Northwest National Laboratory, [2]University of Washington, [3]Brookhaven National Laboratory, [4]California Institute of Technology, [5]University of British Columbia, [6]Harvard University, [7]Massachusetts Institute of Technology, [8]Empa - Switzerland, [9]University of California at Davis, [10]Aerodyne Research, Inc.

ASR Science Team Meeting, Tysons Corner, May 4, 2016

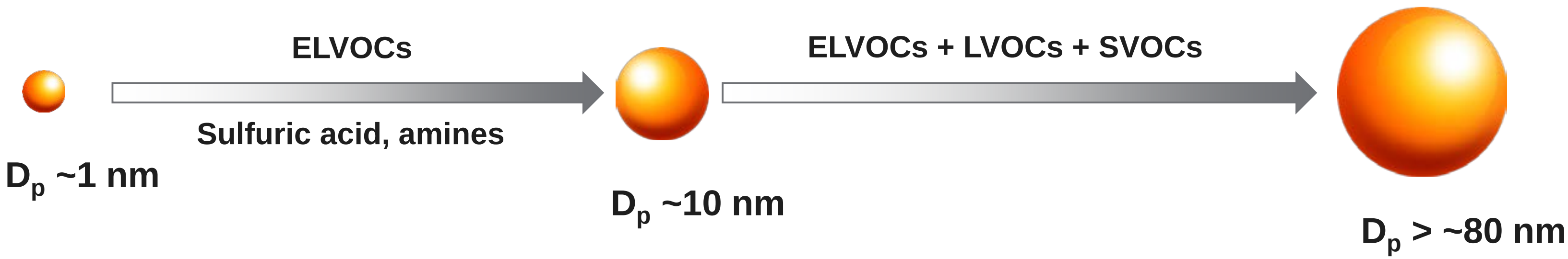
U.S. DEPARTMENT OF ENERGY

ARM CLIMATE RESEARCH FACILITY

ASR Atmospheric System Research

EMSL

Motivation



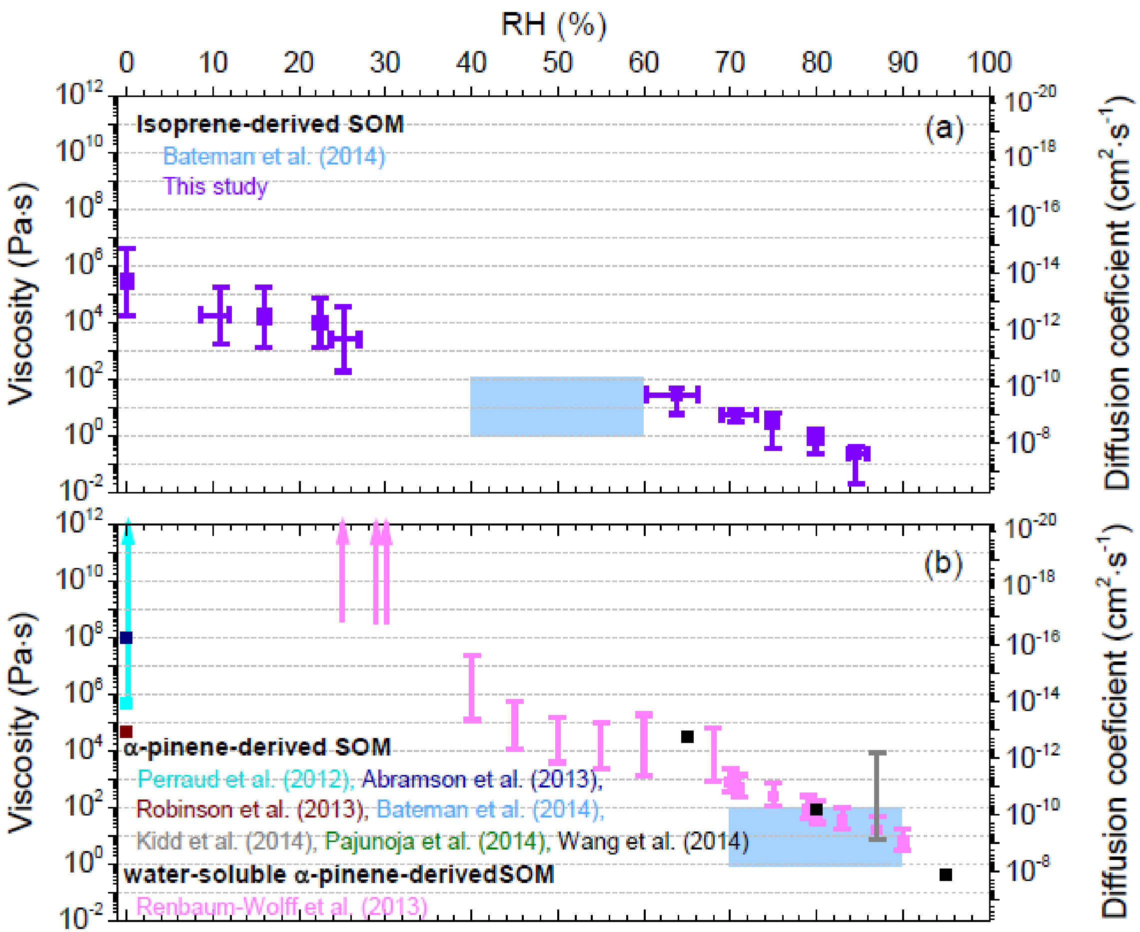
- Aerosol particles larger than ~80 nm influence Earth's radiation balance
- Particles smaller than ~80 nm dominate the number concentration
  - New particle formation
  - Emissions from fossil fuel combustion
- Growth is controlled by condensation of oxidation products of biogenic and anthropogenic VOCs forming secondary organic aerosol (SOA):
  - Extremely Low Volatile Organic compounds **(ELVOCs):** **$C^* < 3 \times 10^{-4}$ µg m^{-3}**
  - Low Volatile Organic Compounds **(LVOCs):** **$3 \times 10^{-4} < C^* < 0.3$ µg m^{-3}**
  - Semivolatile Organic Compounds **(SVOCs):** **$0.3 < C^* < 300$ µg m^{-3}**

Motivation

- Physicochemical mechanisms governing particle growth and size distribution dynamics of SOA are still not fully understood.
- Traditional view:
  - Kinetic condensation of **ELVOCs** and **LVOCs** proportional to Fuch's corrected surface area distribution → **Favors growth of ultrafine particles**.
  - Rapid gas-particle equilibrium of **SVOCs** (**neglecting condensed-phase diffusion limitation**) → **Favors growth of large particles**.

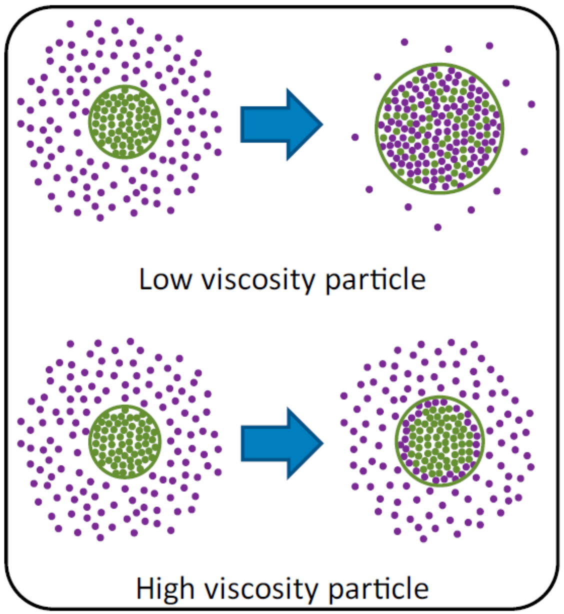
Particle Viscosity and Diffusivity

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*



Song et al., 2015, ACP

High viscosity will slow down SVOC condensation



Renbaum-Wolff et al., 2013, PNAS.

Chamber Experiments

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by **Battelle** *Since 1965*

Ultrafine Seed (40 nm) Ammonium Sulfate

VOC, H_2O_2

T, RH

NO_x, O_3, PTRMS

Aerosol samples for evaporation kinetics

Evaporation Chamber

SPLAT II

SMPS, BNL FIMS

AMS
UW FIGAERO-CIMS

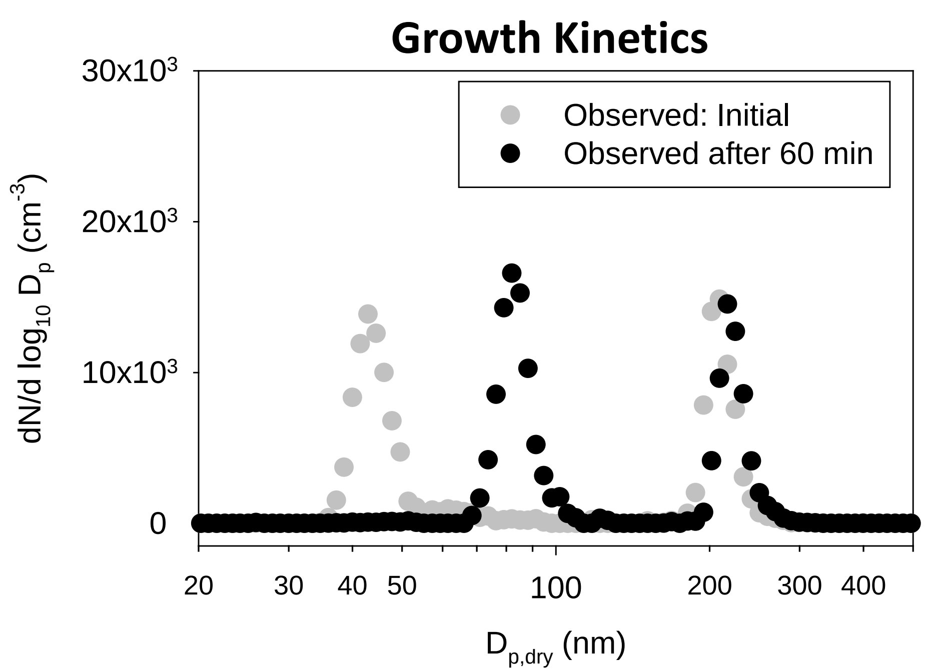
Filter samples for nano-DESI-HRMS analysis (EMSL)

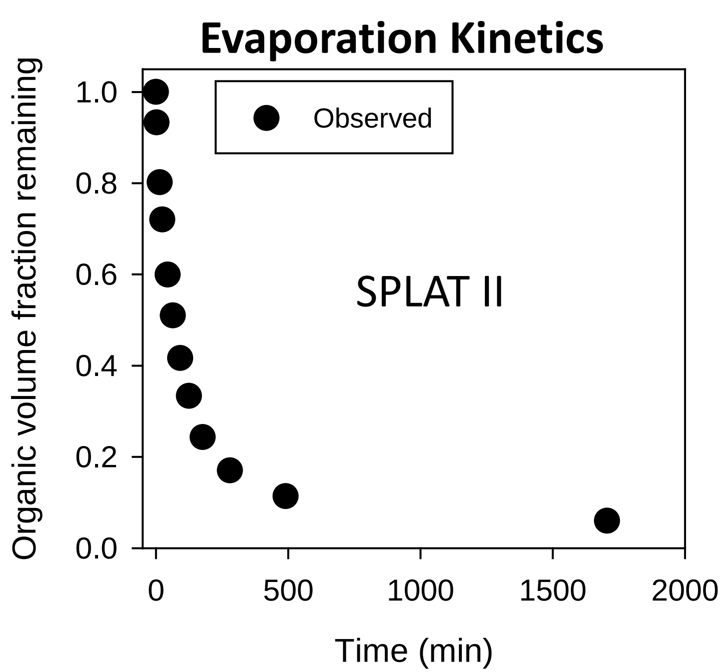
Aerosol Composition

Approach

Phase 1: Make large isoprene SOA seed and inject ultrafine ammonium sulfate (AS) seed

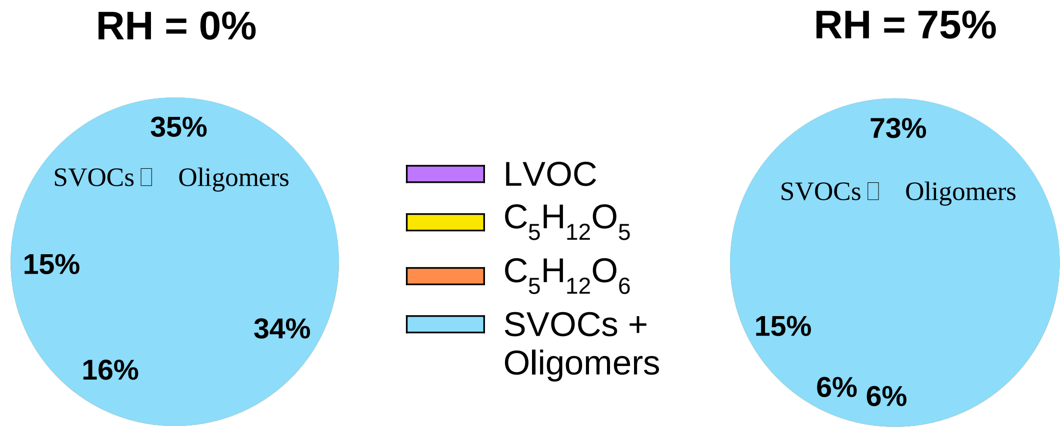
Phase 2: The two seeds are grown by condensing vapors formed from photooxidation of isoprene.



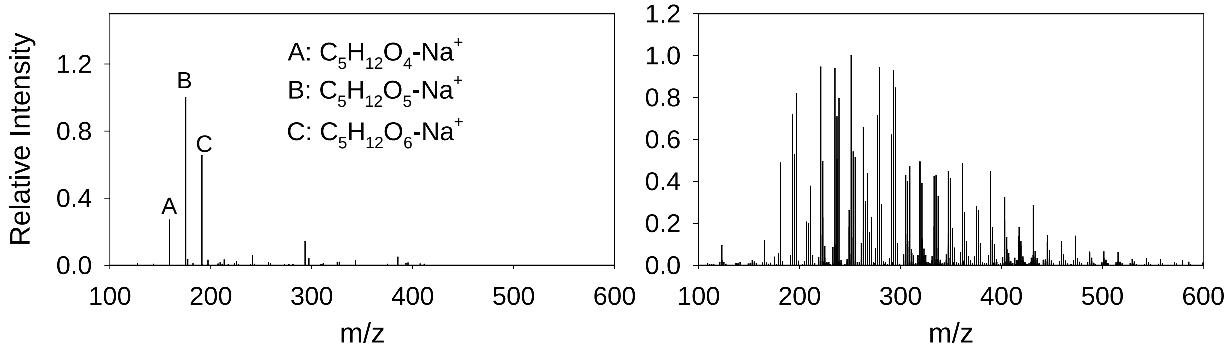


Isoprene SOA Composition

SOA species mass fractions based on FIGAERO-CIMS measurements.



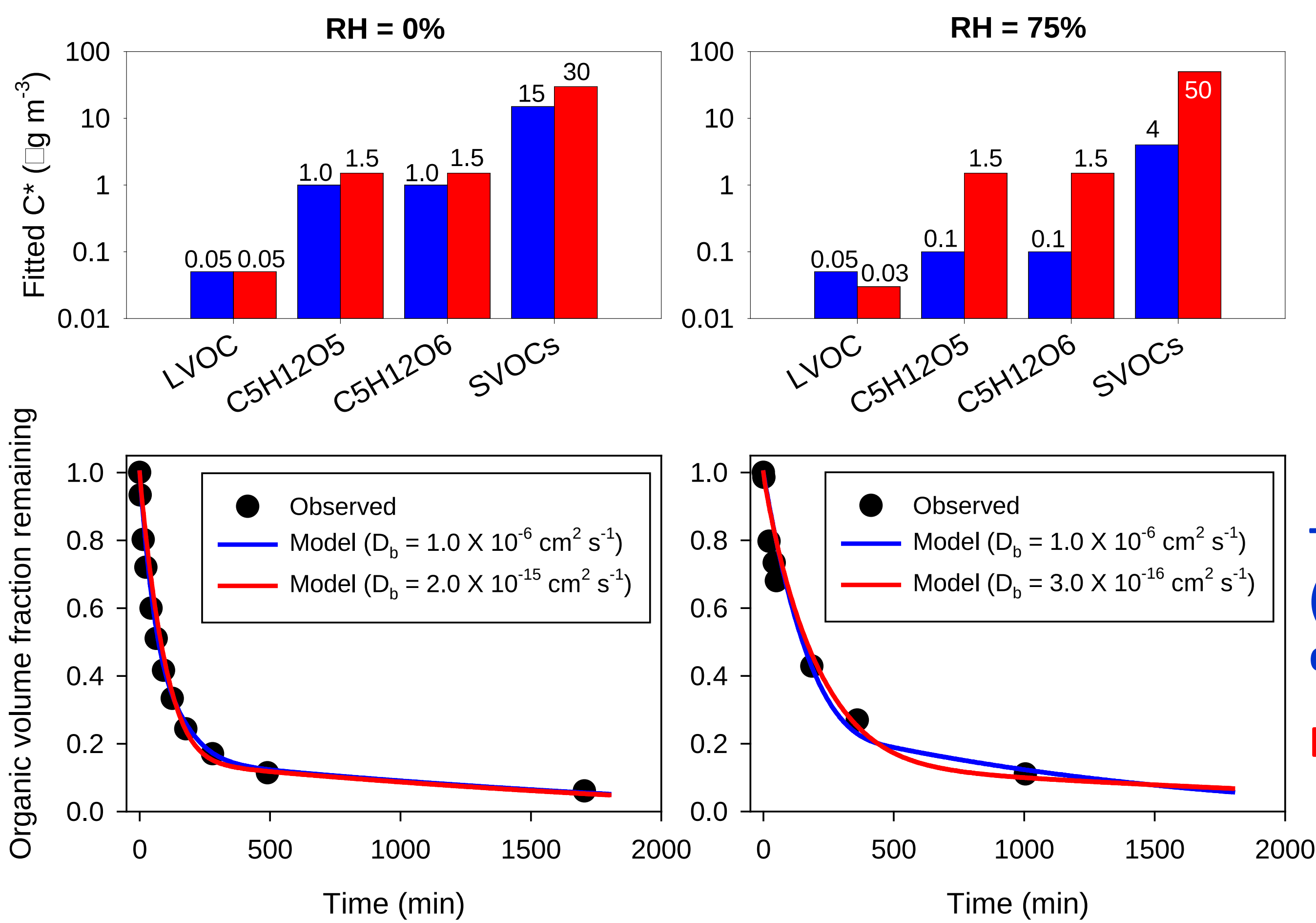
(+)nano-DESI-HRMS mass spectra shows presence of oligomers in both dry and humid air SOA samples.



$$\mathrm{SVOC} + \mathrm{SVOC} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Dimer}$$

Assumed time scale ~10 min

Volatility from Evaporation Kinetics



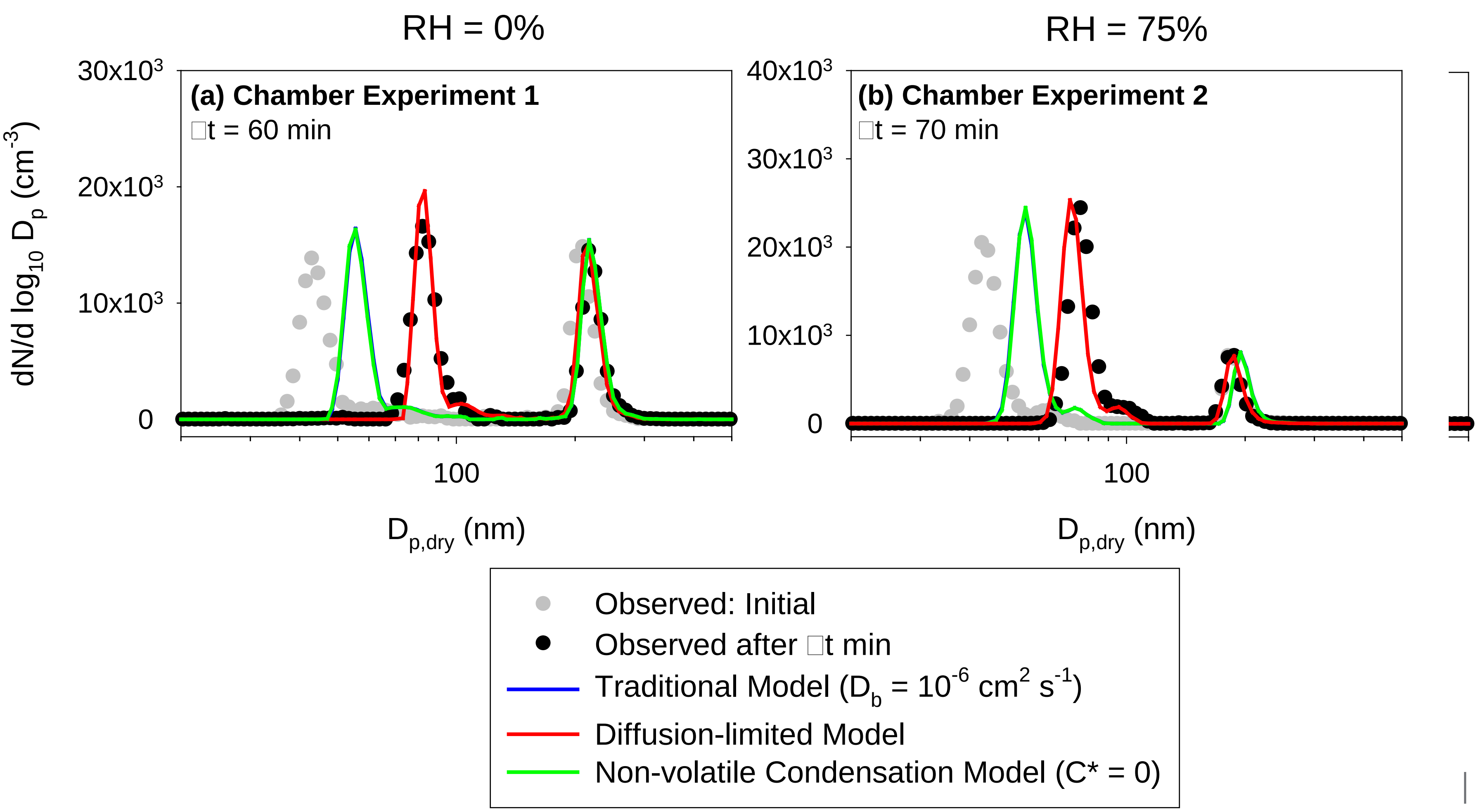
Traditional Model (negligible particle-phase diffusion)

Diffusion-limited Model

Modeling Growth Kinetics

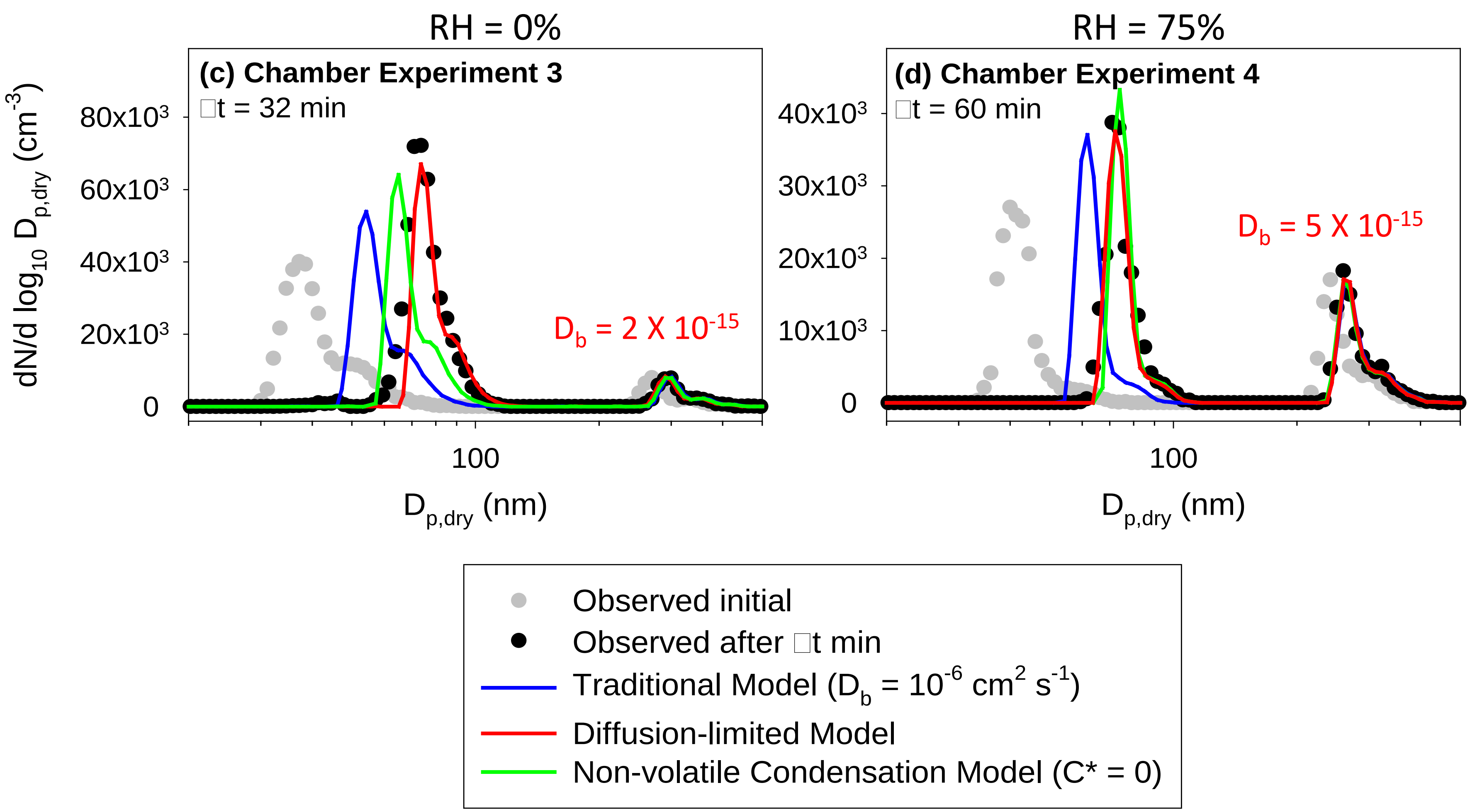
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Traditional Model vs. Diffusion-limited Model

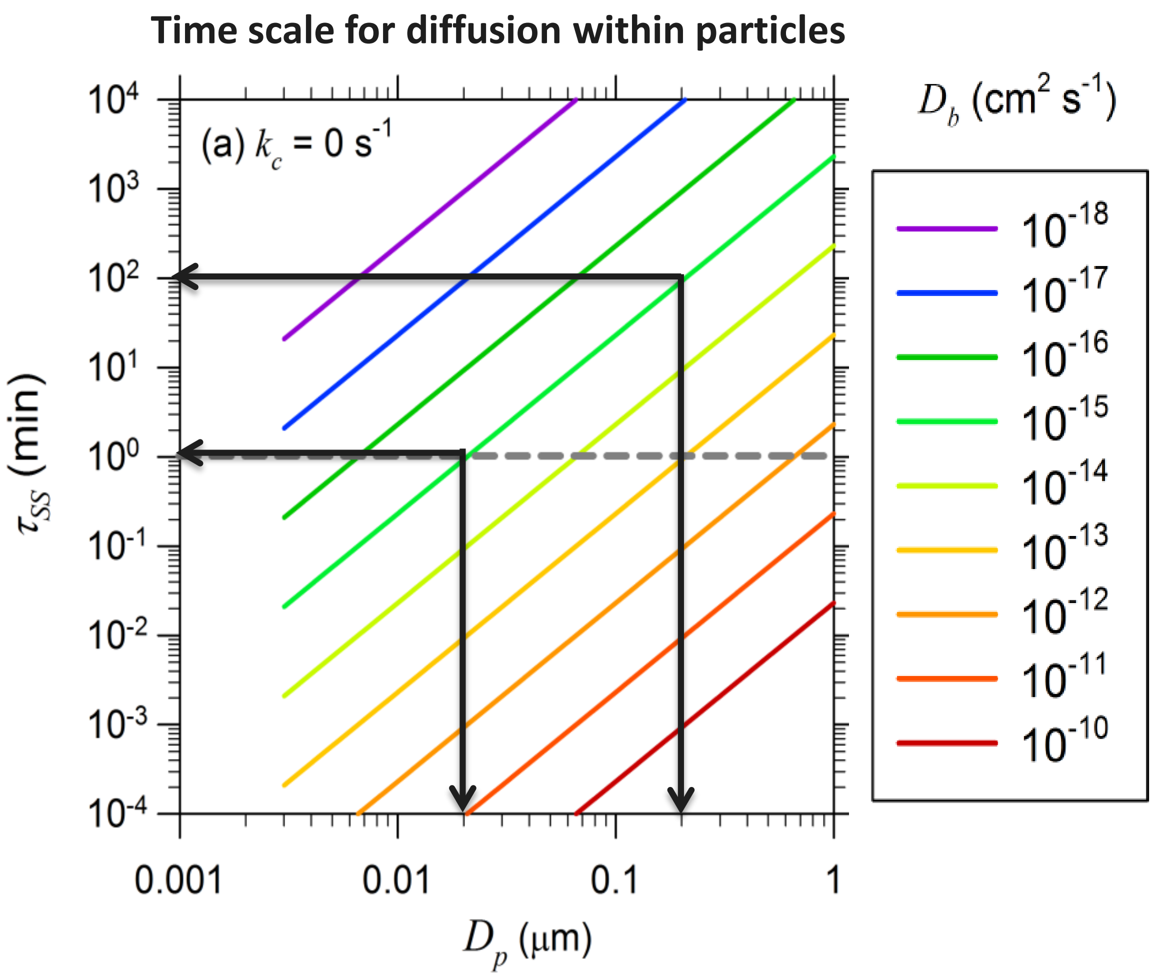


Modeling Growth Kinetics

Large seed: aged α-pinene SOA



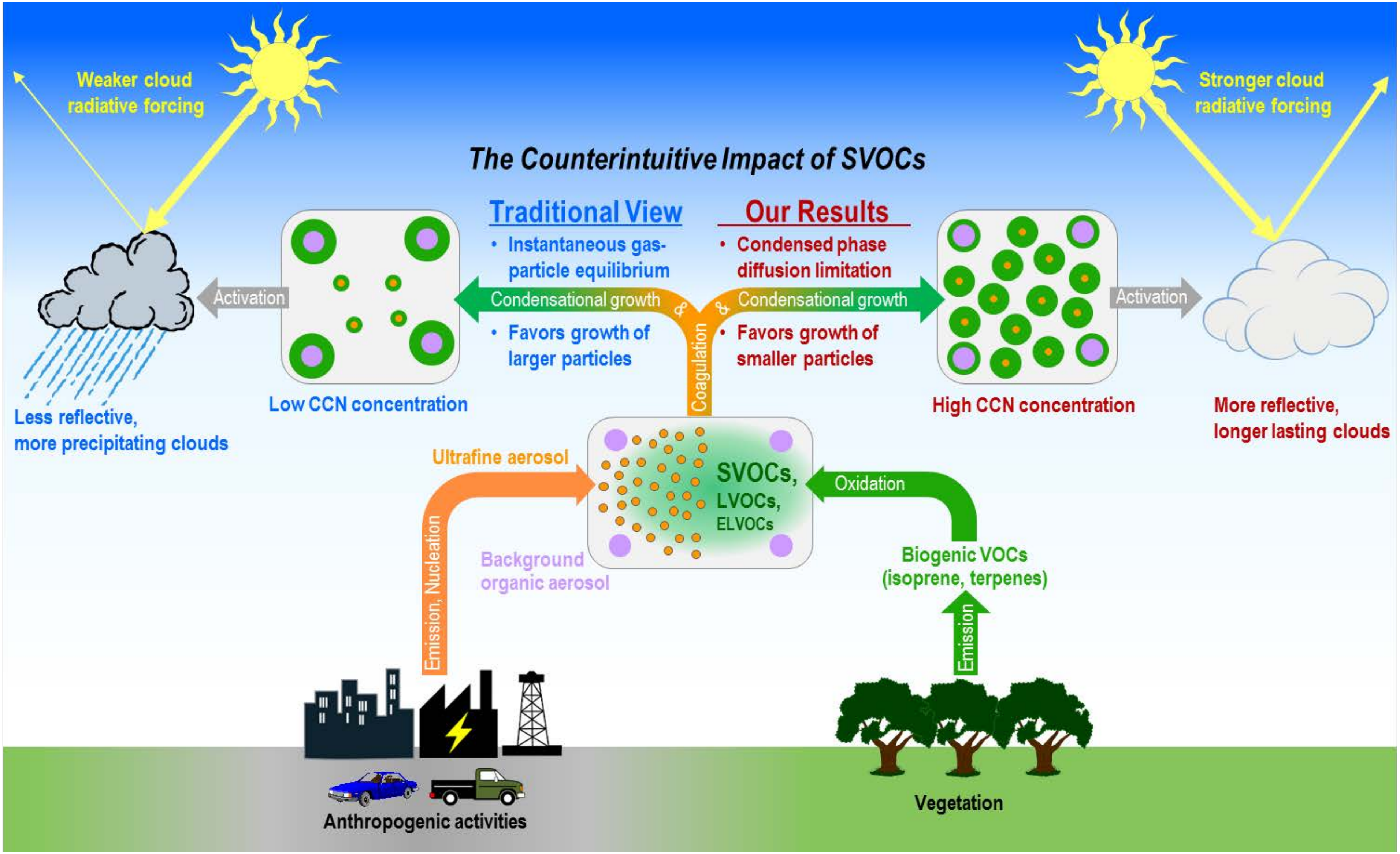
Effect of Particle Size on Diffusion Timescale



Large variation in diffusion time scales with size has a profound effect on the SOA size distribution dynamics and the growth of ultrafine particles!

Zaveri et al., 2014, ACP.

The Big Picture



Conclusions & Future Work

- Aged isoprene and α-pinene SOA containing oligomers show diffusion-limited growth up to 75% RH.
- This phenomenon slows down growth of large particles, but in turn favors growth of ultrafine particles that can more effectively compete for the available SVOCs.
- This counterintuitive behavior needs to be examined at higher RH and for other SOA precursors that form SVOCs.
- Need to develop model parameterizations that capture SOA growth dynamics for all key precursors over the full RH and temperature range.

Acknowledgements

This work was supported by:

- DOE Atmospheric System Research (ASR) Program
- DOE ARM Climate Research Facility
- PNNL Environmental Molecular Sciences Laboratory (EMSL)

ARM
CLIMATE RESEARCH FACILITY

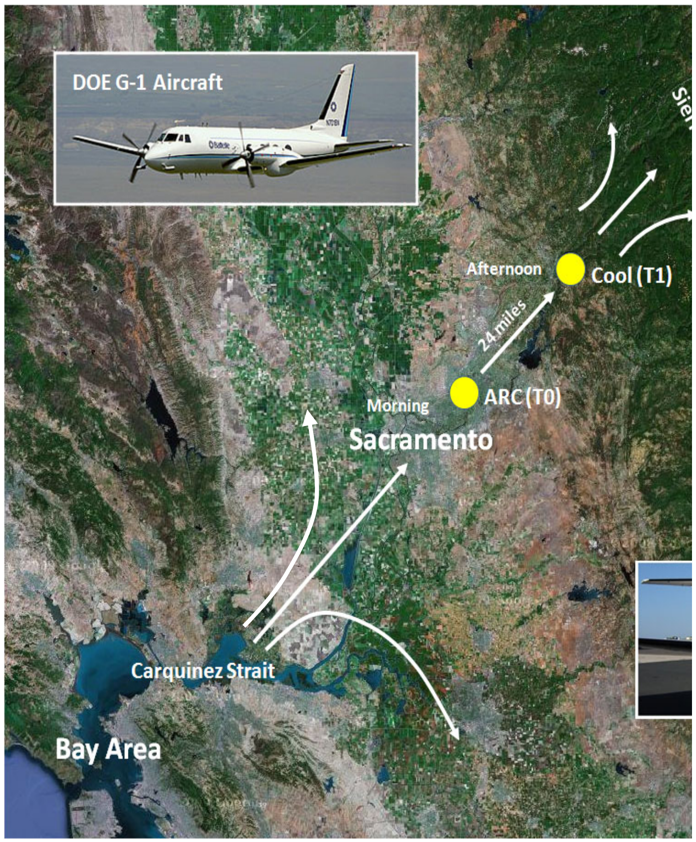
ASR
Atmospheric
System Research

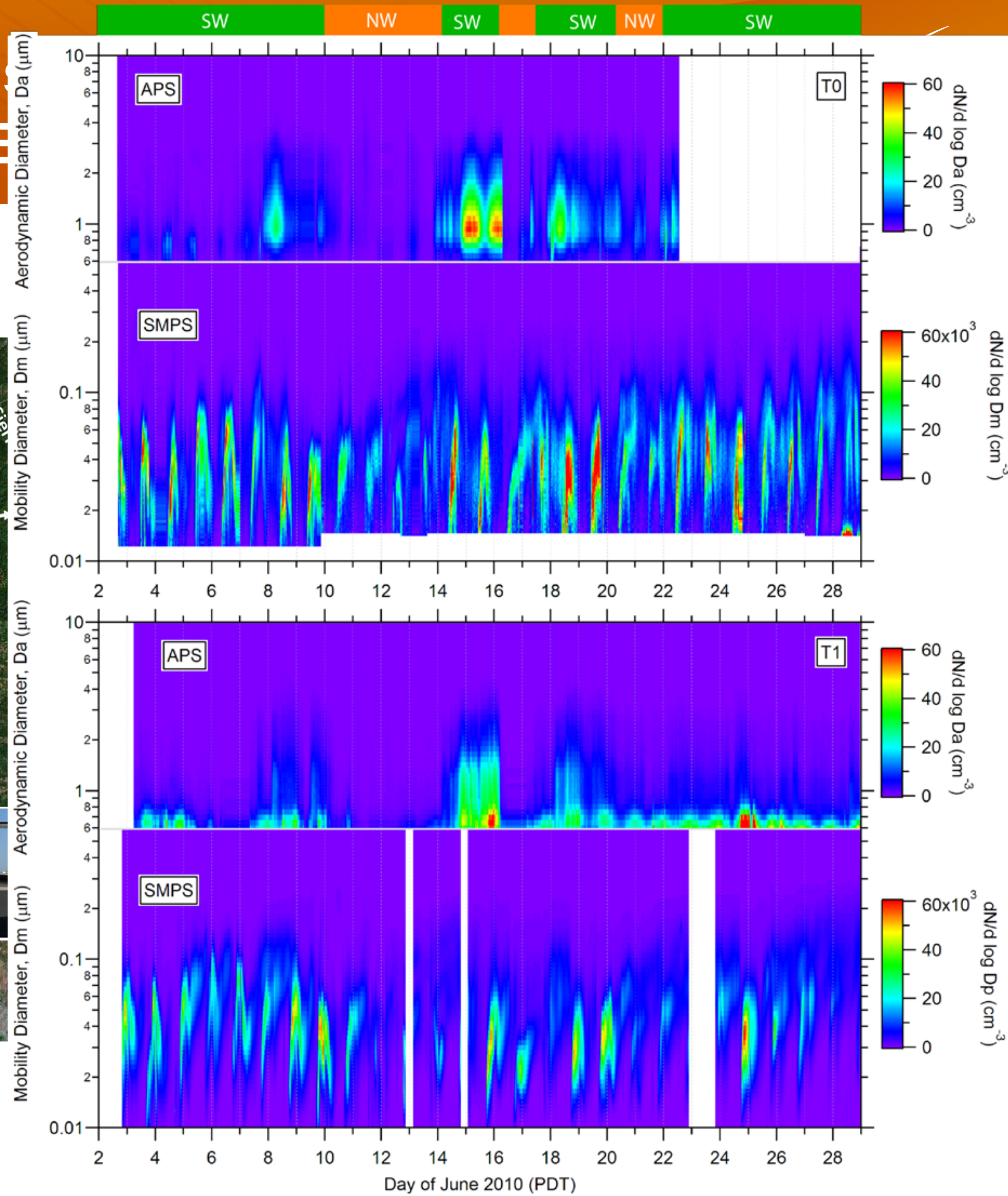
EMSL

Carbonaceous Aeros
Effects Study (CARE

ARM
CLIMATE RESEARCH FACILITY

June 2010

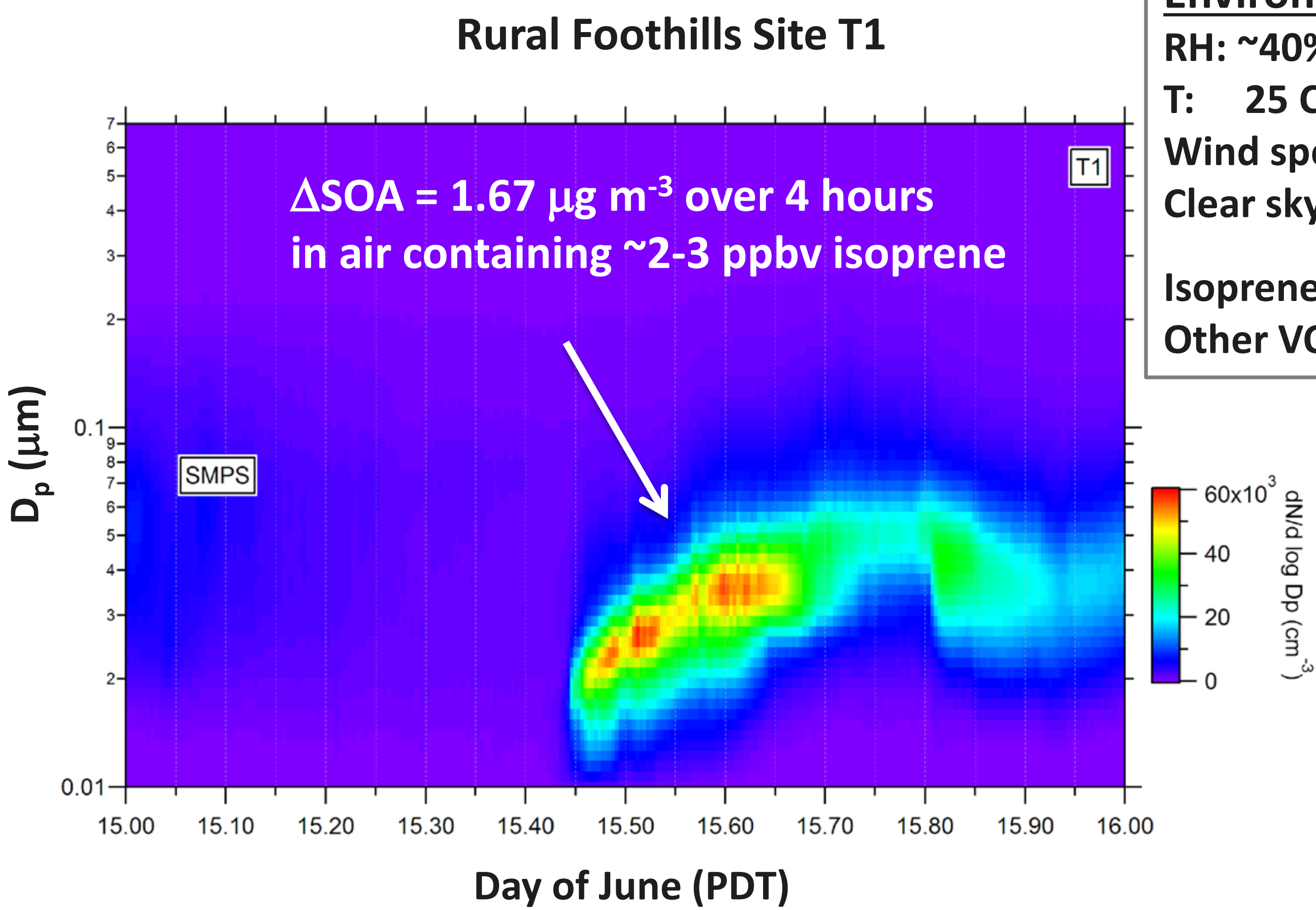




Zaveri et al., 2012, ACP.

Episode of June 15

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965



Environmental Conditions

RH: ~40%

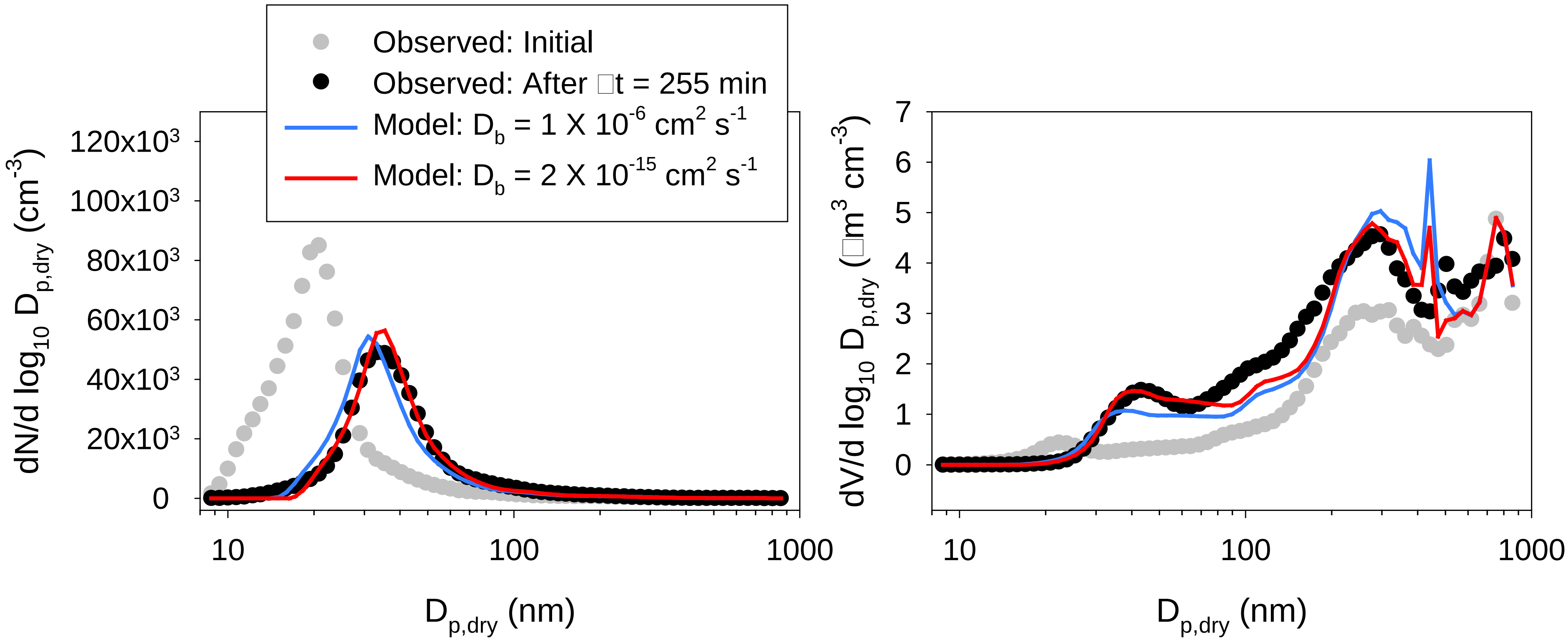
T: 25 C

Wind speed: 2-3 m/s

Clear sky

Isoprene: 2-3 ppbv

Other VOCs: < detection



Observed: Initial
Observed: After □t = 255 min
Model: D$_b$ = 1 X 10^{-6} cm^2 s^{-1}
Model: D$_b$ = 2 X 10^{-15} cm^2 s^{-1}
dN/d log$_{10}$ D$_{p,dry}$ (cm^{-3})
120x10³
100x10³
80x10³
60x10³
40x10³
20x10³
0
10
100
1000
D$_{p,dry}$ (nm)
dV/d log$_{10}$ D$_{p,dry}$ (□m^3 cm^{-3})
7
6
5
4
3
2
1
0
10
100
1000
D$_{p,dry}$ (nm)