

US EPA ARCHIVE DOCUMENT

UCR



Understanding the Hygroscopic Properties of BC/OC Mixing States: *Connecting Climate and Health Impacts of Anthropogenic Aerosol*

[Akua Asa-Awuku: akua@enqr.ucr.edu](mailto:akua@enqr.ucr.edu)



EPA Black Carbon STAR grants kick-off
Tuesday, May 22th, 2012

¹*Dept of Chemical and Environmental Engineering*

²*Bourns College of Engineering Center of Environmental Research and Technology*

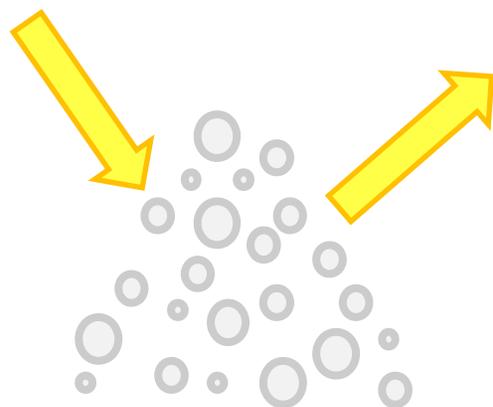
UNIVERSITY OF CALIFORNIA, RIVERSIDE

Hypothesis:

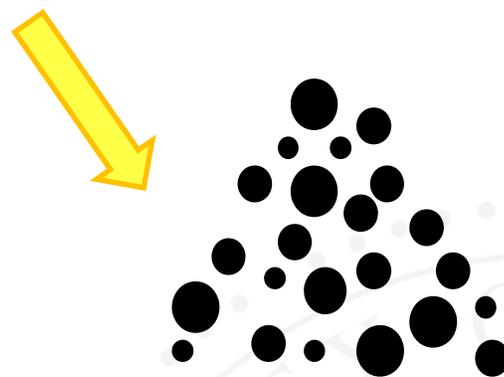
If BC is well mixed with organic hygroscopic material, it will significantly alter droplet growth rates and sizes.

This will impact **droplet deposition** rates in the lungs and influence **radiative forcing** estimates of the aerosol-indirect effect.

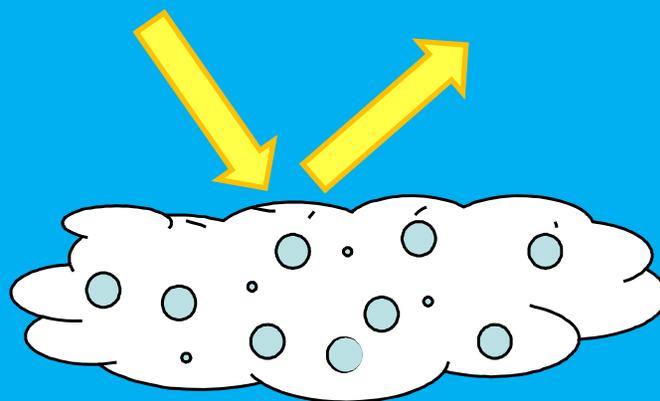
The connection between aerosols and climate



DIRECT COOLING



DIRECT WARMING



INDIRECT

The ability to *cool* or *warm* effects the **global** energy balance

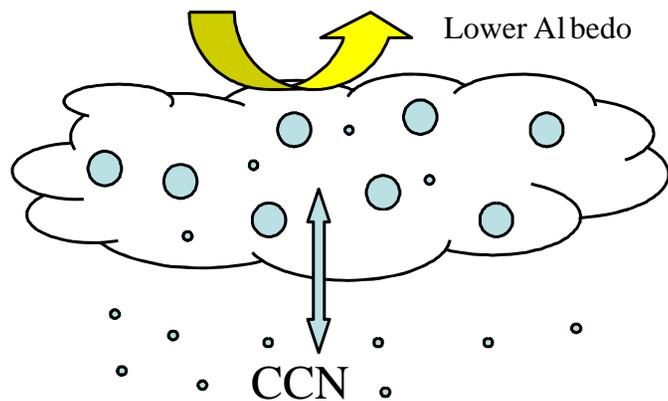
4 Key Aerosol Factors

- a. Number
- b. Size
- c. Composition
- d. Hygroscopicity

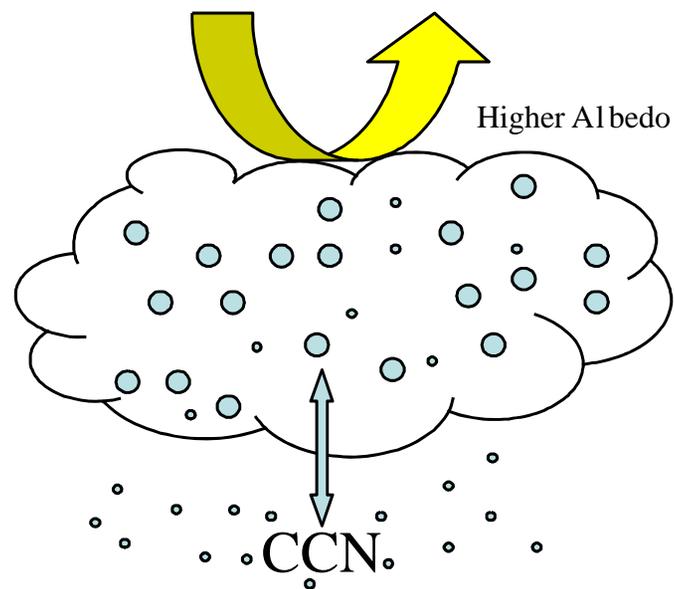
INDIRECT

DROPLET SIZE AND GROWTH

Aerosols that **activate** and become droplets are called **Cloud Condensation Nuclei (CCN)**



Clean Environment
(few CCN)



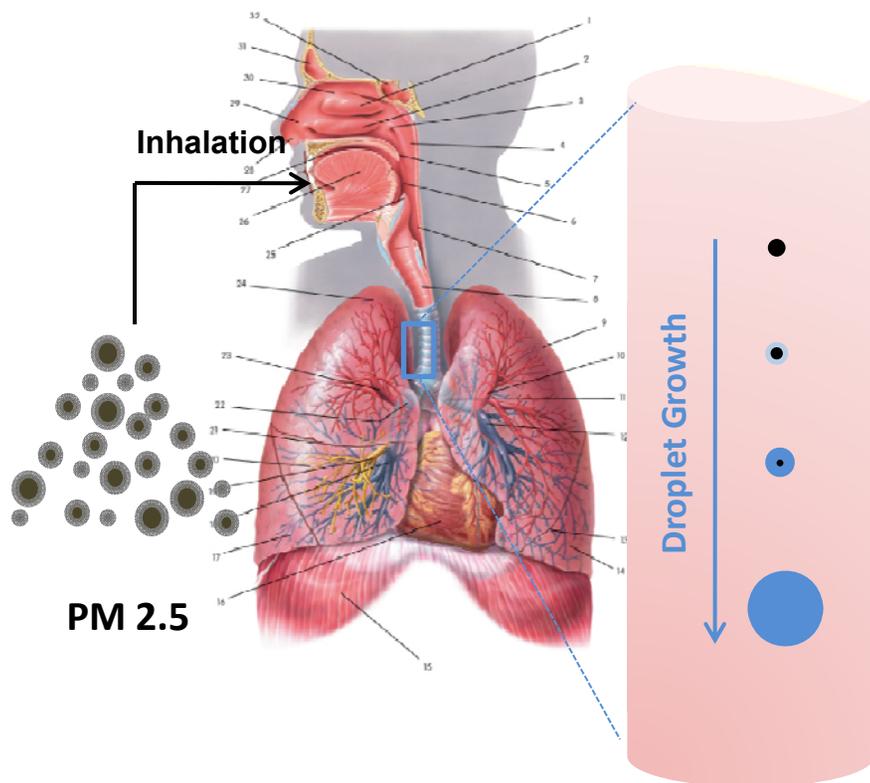
Polluted Environment
(more CCN)

Aerosols impact clouds and hence climate

T

In addition to understanding CCN (dry particle) properties it is important to measure and characterize droplet growth

THE IMPORTANCE OF AEROSOL WATER-VAPOR INTERACTIONS



Enhanced Condensational Growth of Particles affects lung deposition rates

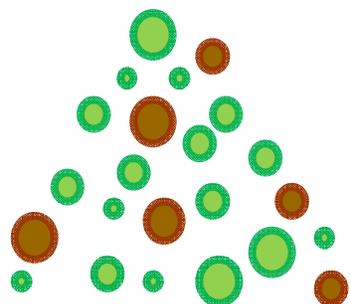
The ability of aerosol to uptake water (hygroscopicity) has the potential to impact health

Hygroscopicity affects the deposition rates of particles in the lung

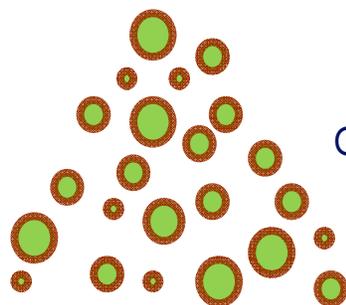
The hygroscopicity of complex aerosol, pollutant mixtures, needs to be characterized

THE IMPORTANCE OF BC WATER-VAPOR INTERACTIONS

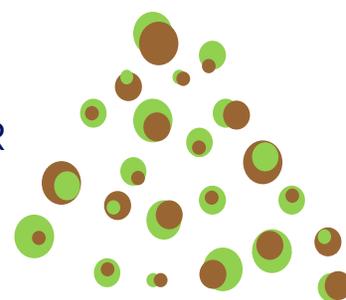
Organic components contribute the greatest variability to ambient aerosol hygroscopicity and droplet growth



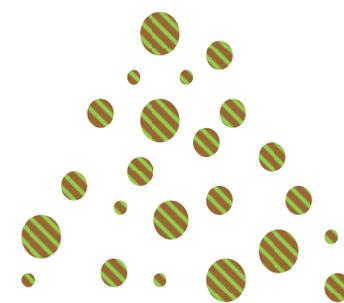
No mixing



OR



Weak Mixing
2-phase System



Strong Mixing
1-phase System

(1) What is the mixing state of BC/OC

(2) Do BC/OC mixing states evolve in ageing systems?

(3) How will the mixing state of BC impact water-uptake?

Soluble Mass

Mixing State

Droplet Size

Form Biogenic SOA in Chamber from
Terpene pre-cursors

α -pinene (α P)

- Semi-Volatile Organics
- Dark ozonolysis
- O_3 and OH

Quickly Inject Anthropogenic POA

Motor Oil (MO)

- Semi-Volatile Organics
- Heated Injector System

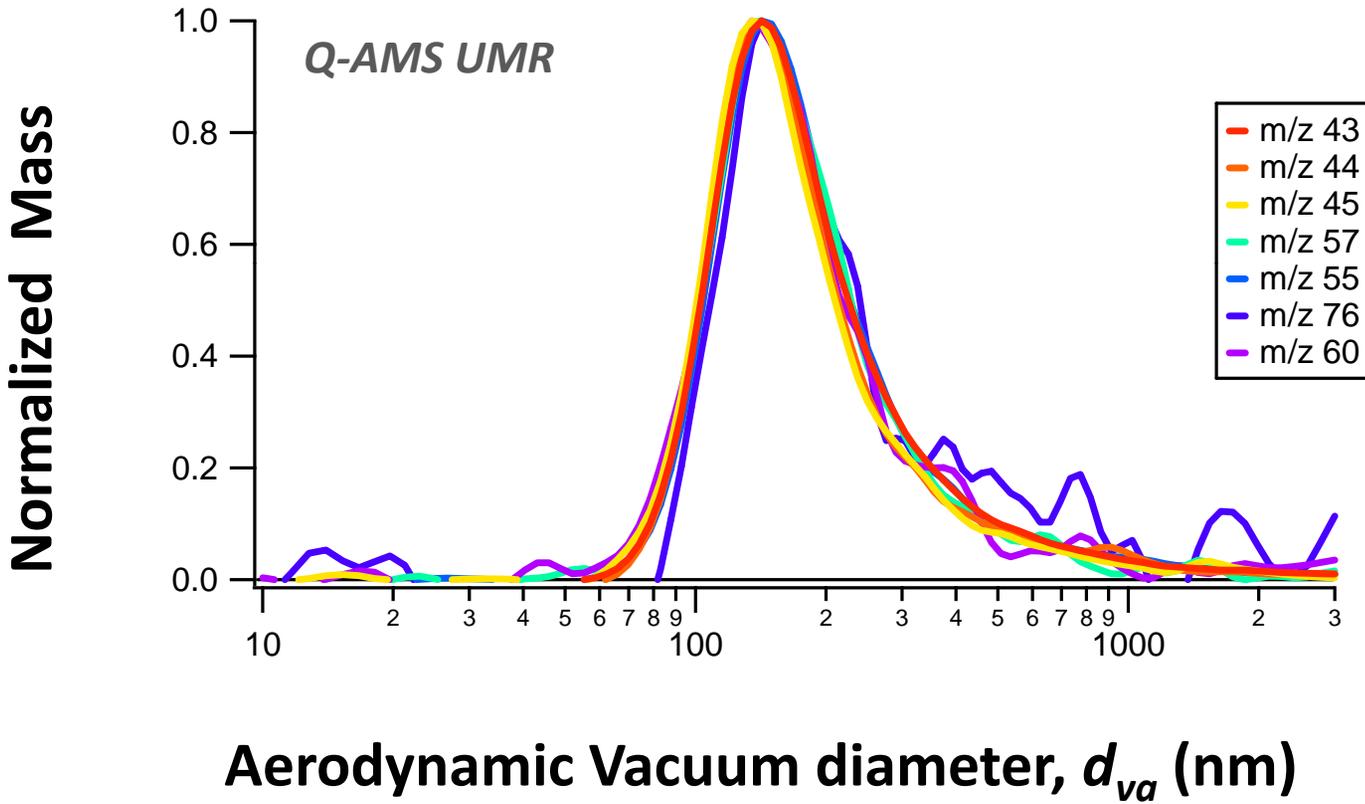
Diesel Exhaust (DL)

- Semi-Volatile Organics
- Diesel Generator



α -pinene SOA

(a) α -pinene SOA (Before Mixing)

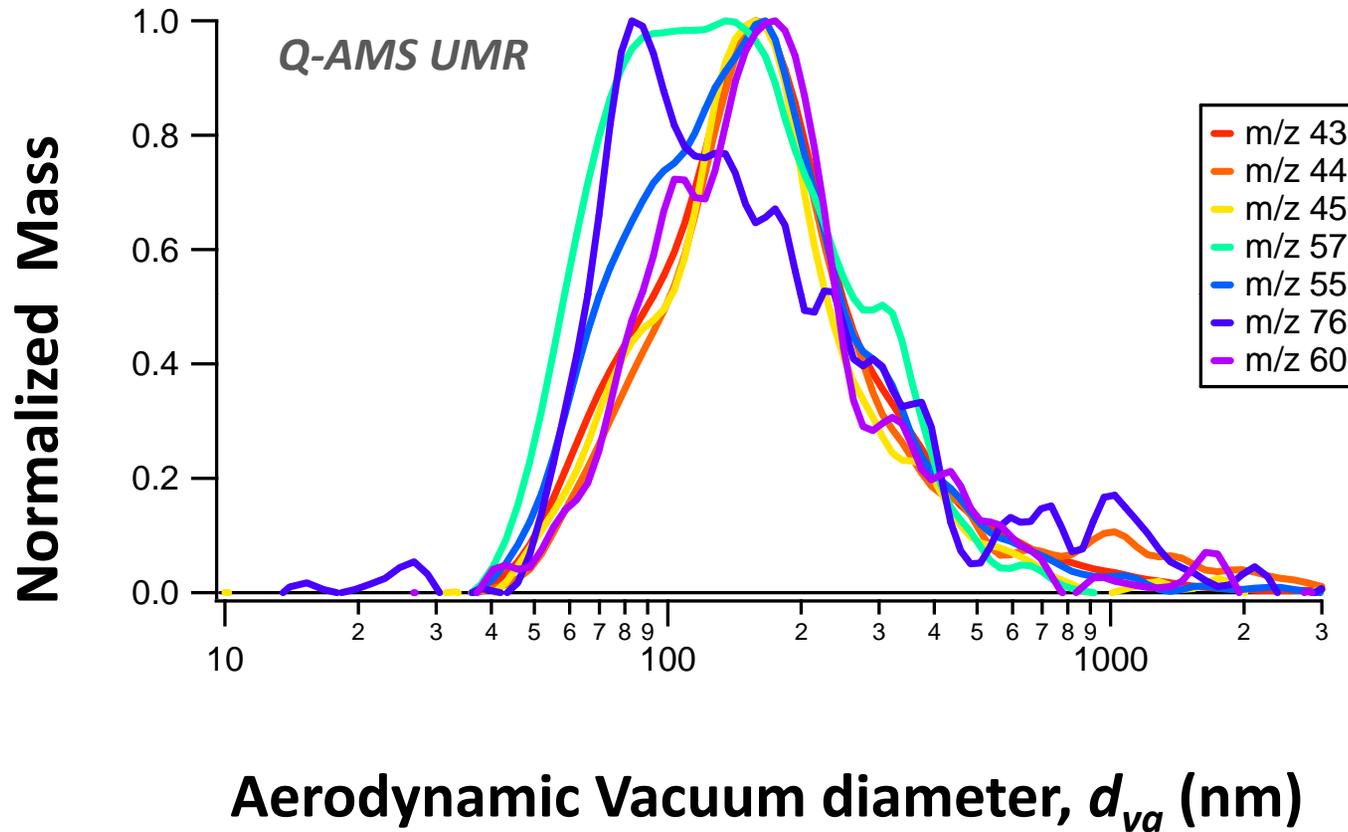


Asa-Awuku et al, 2009

α -pinene SOA

+ Diesel Exhaust POA

(b) α -pinene SOA + DL POA (After 15 min)



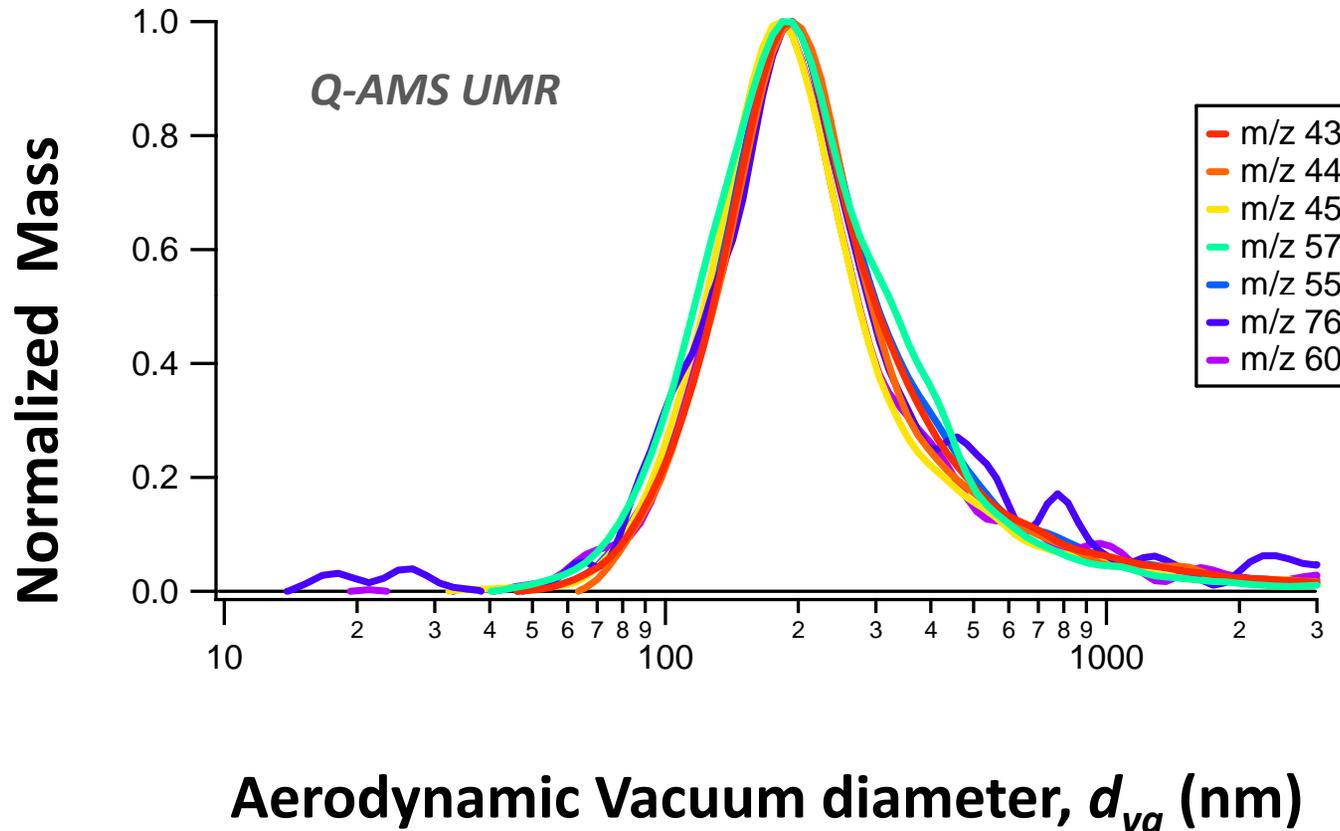
Asa-Awuku et al, 2009

STRONG / 1-PHASE MIXTURE

α -pinene SOA

+ Diesel Exhaust POA

(c) α -pinene SOA + DL POA (After 1 hour 15 min)

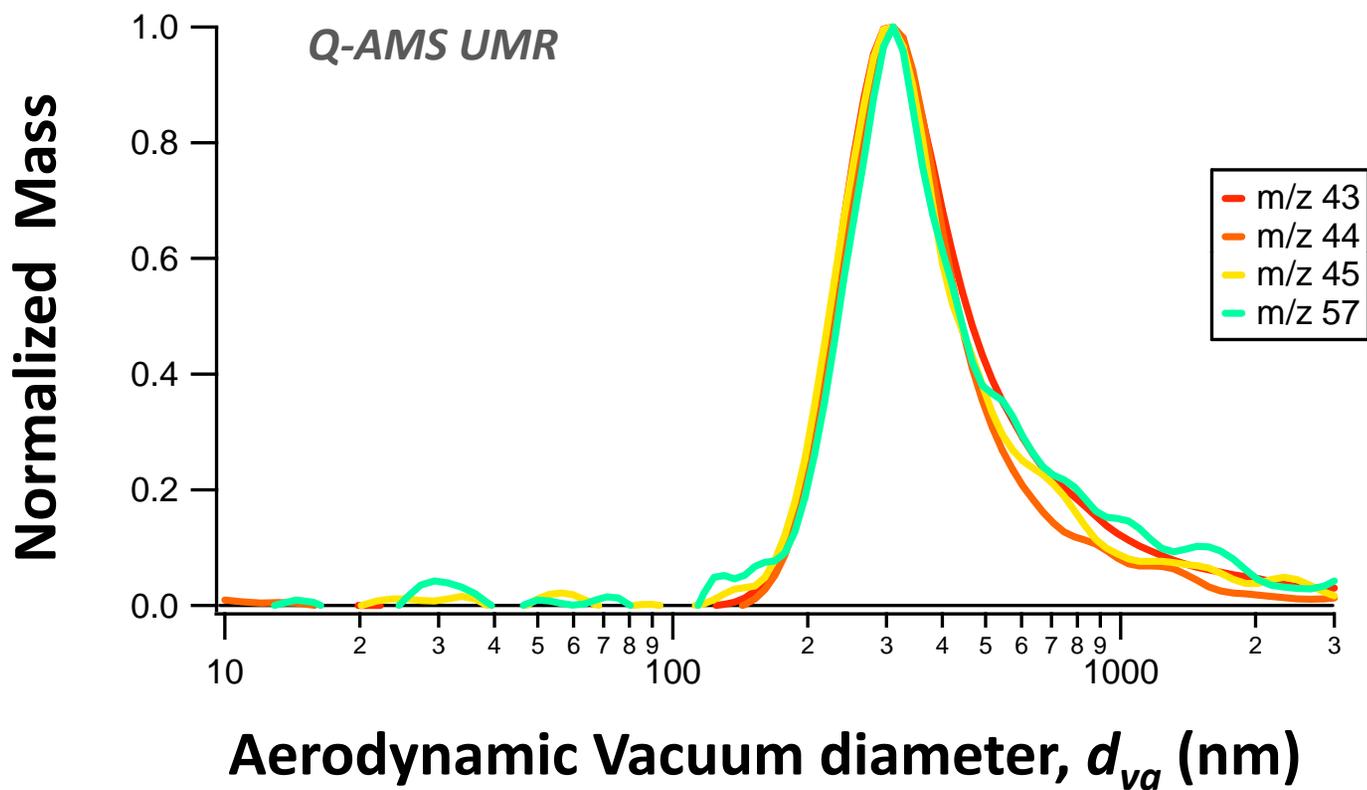


Asa-Awuku et al, 2009

STRONG / 1-PHASE MIXTURE

α -pinene SOA

(a) α -pinene SOA (Before Mixing)



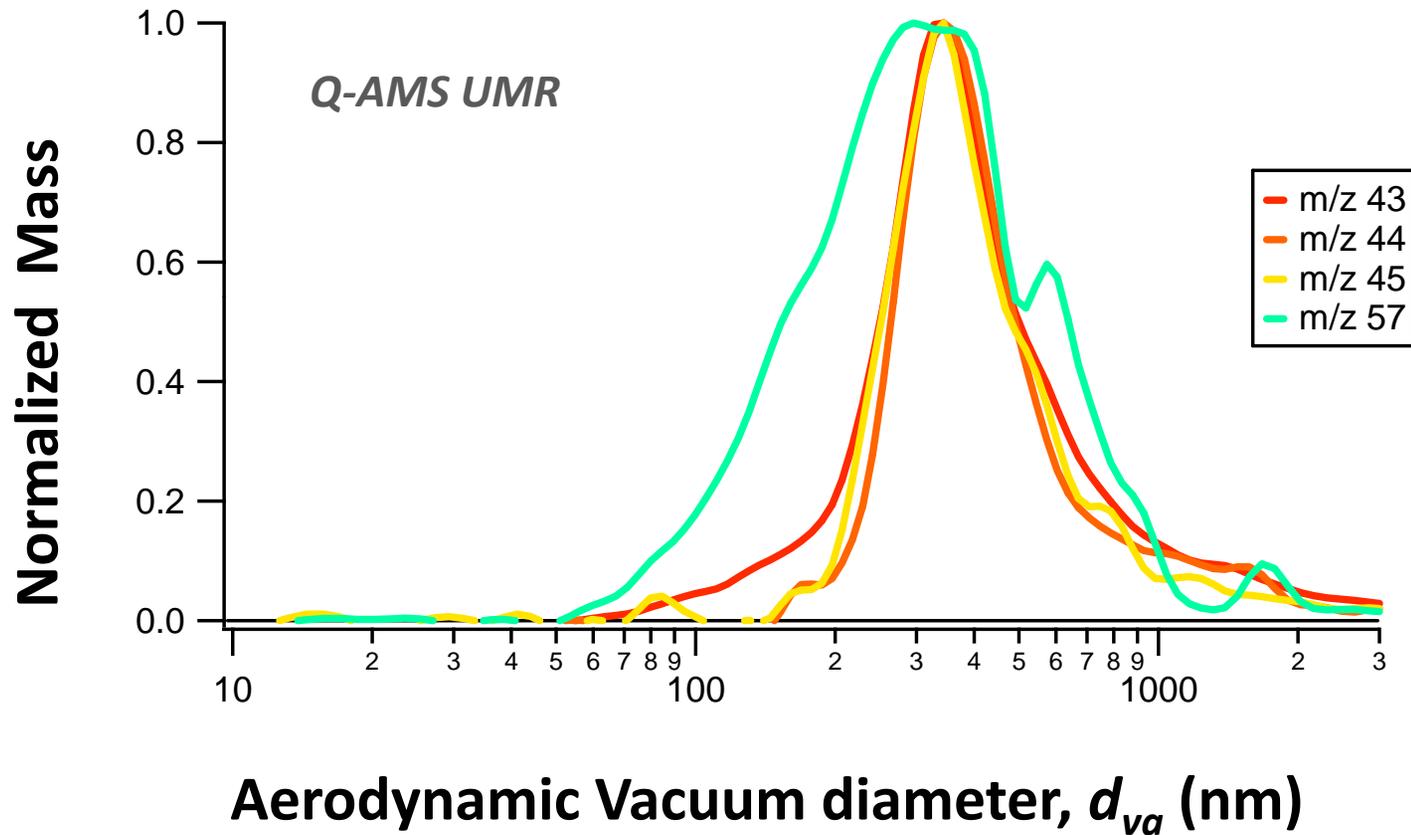
Asa-Awuku et al, 2009

α -pinene SOA



Motor Oil-Fuel POA

(b) α -pinene SOA + MOF POA (After 15 min)



Asa-Awuku et al, 2009

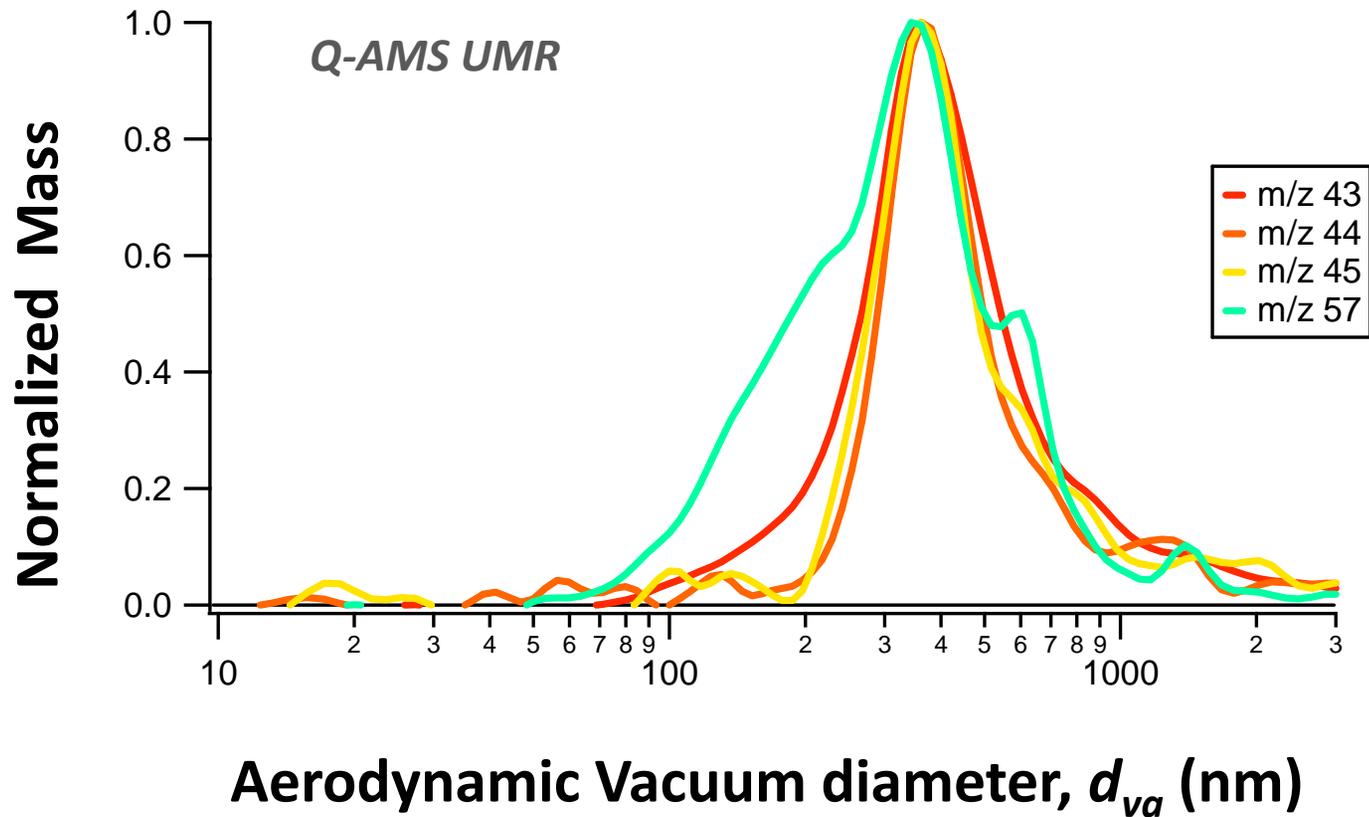
WEAK / 2-PHASE MIXTURE

α -pinene SOA



Motor Oil-Fuel POA

(c) α -pinene SOA + MOF POA (After 4 hours)



Asa-Awuku et al, 2009

WEAK / 2-PHASE MIXTURE

MIXING OBSERVATIONS

- **Diesel exhaust (DL) POA** *readily* mixes with **α -pinene (α P) SOA** and forms a one phase mixture of lower volatility semi-volatile compounds
 - The mixing process occurs rapidly and takes one hour to form a singular phase in the chamber
 - The components of DL are more similar to α -pinene SOA than motor-oil
 - In terms of VBS, they are closer in the 2-D space and are thus more likely to favor each other
- **Motor Oil (MO) POA** plus **α -pinene SOA** form a weak two phase mixture
 - Some motor oil vapors will condense on the surface of α -pinene SOA
 - However once saturated, the remaining Motor Oil stays in its own phase

DROPLET FORMATION FROM REALISTIC AEROSOL

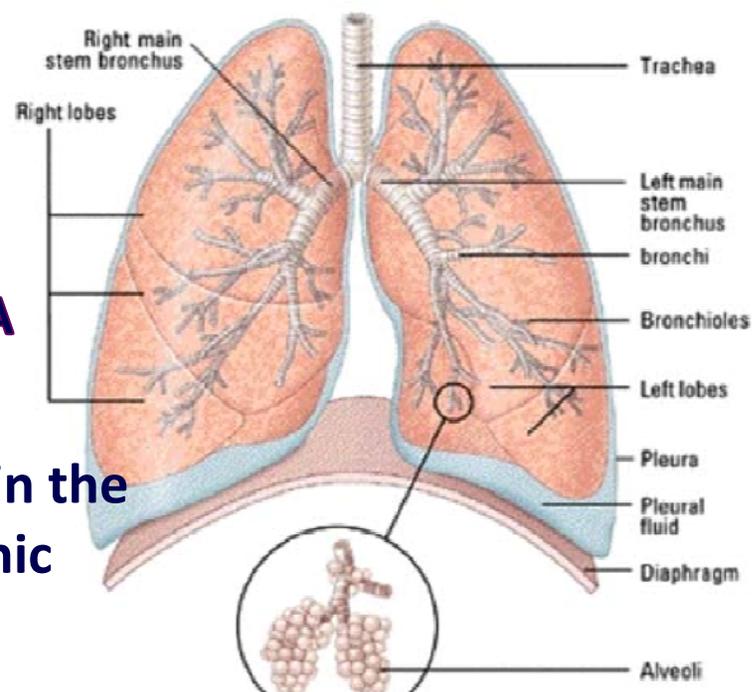
The aerosol hygroscopicity impacts the ability to form stable water droplet

Primary organic aerosol (POA) is emitted directly into the atmosphere

e.g. vehicular particulate emissions

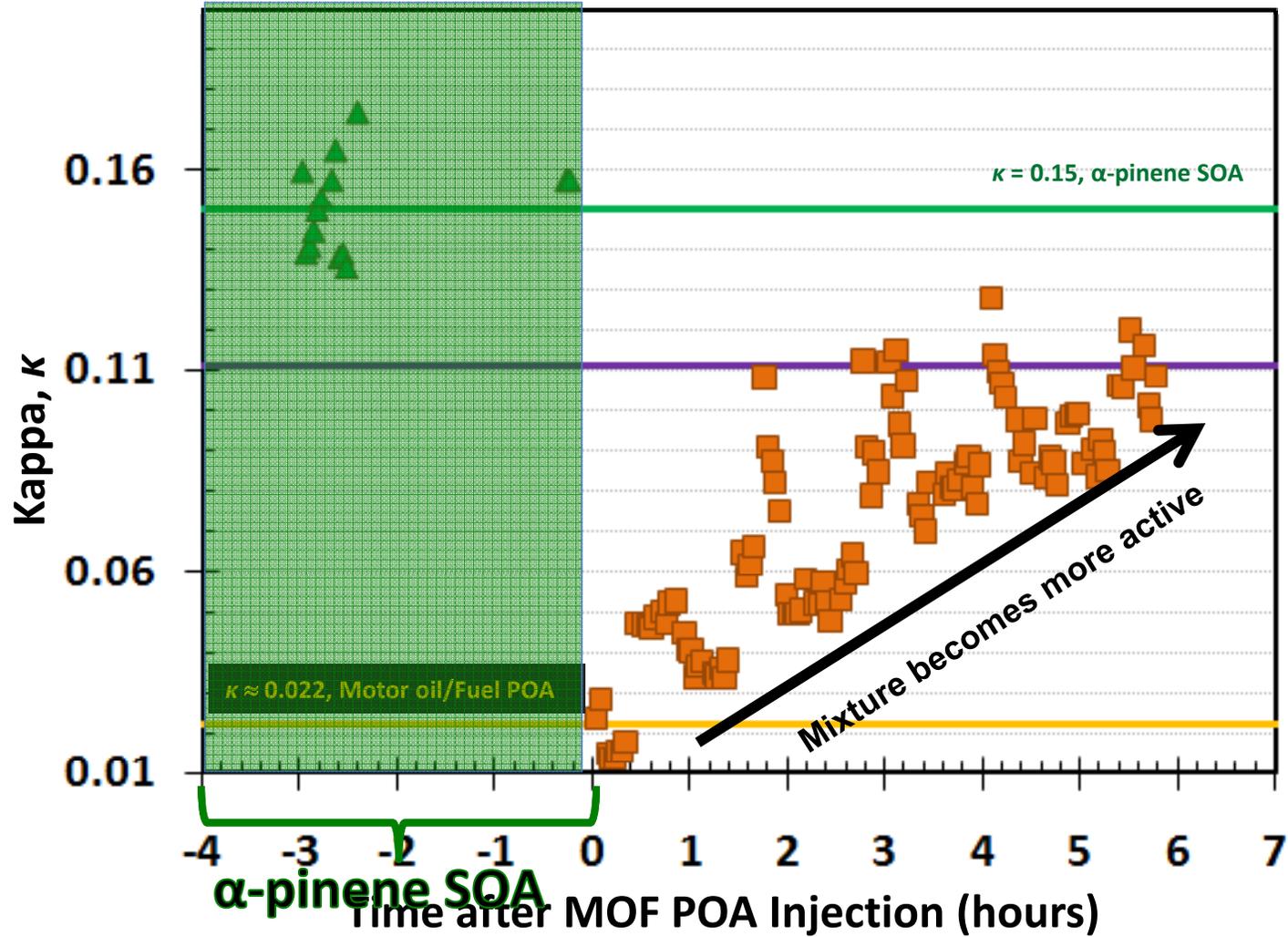
Motor Oil POA & Diesel Exhaust POA

Secondary organic aerosol (SOA) is formed in the atmosphere via reactions with volatile organic compounds



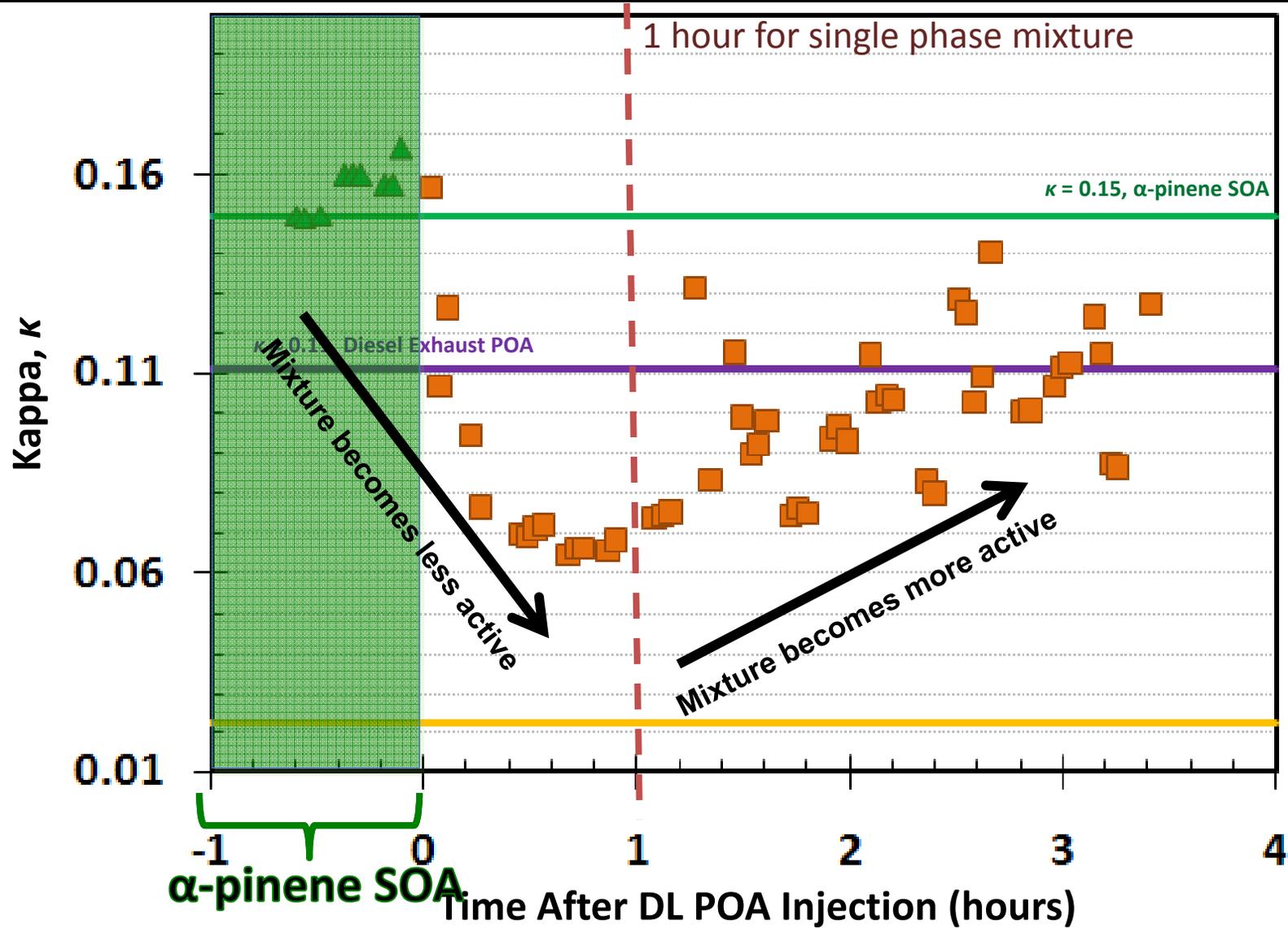
The ability of aerosol to form droplets at a given supersaturation is governed by aerosol size and aerosol chemistry

2. The mixture quickly becomes active after injection



WEAK/ 2-PHASE MIXTURE

3. After one phase is formed, hygroscopicity increases

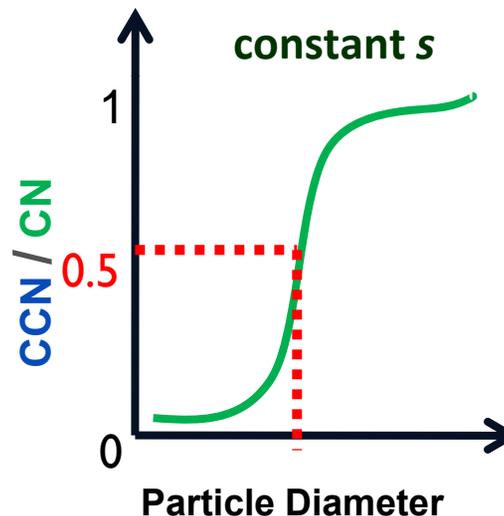
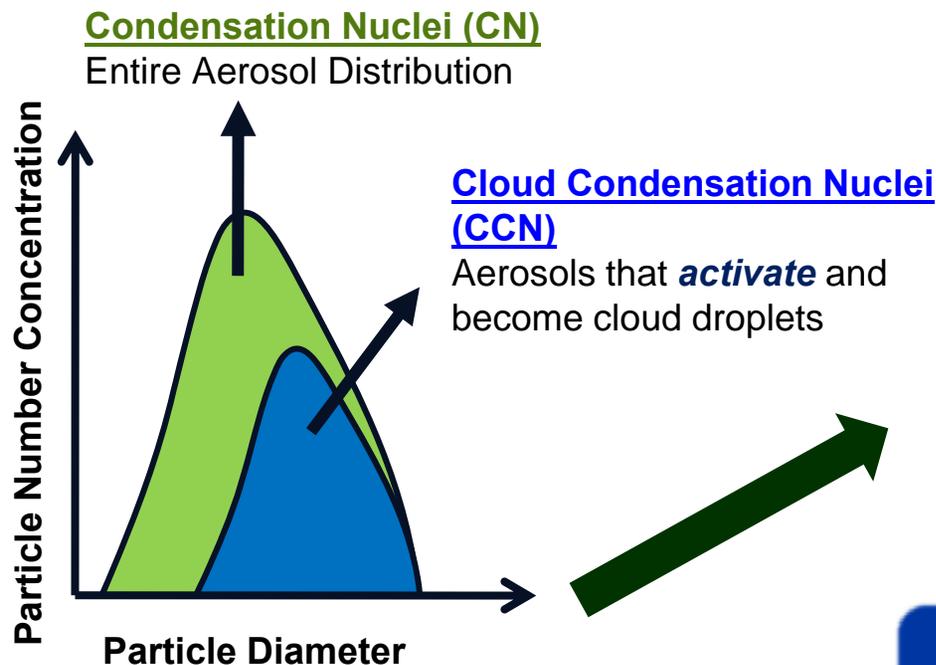


STRONG / 1-PHASE MIXTURE

CCN & DROPLET MEASUREMENTS



DMT Continuous Flow Stream-wise Thermal Gradient CCN Counter

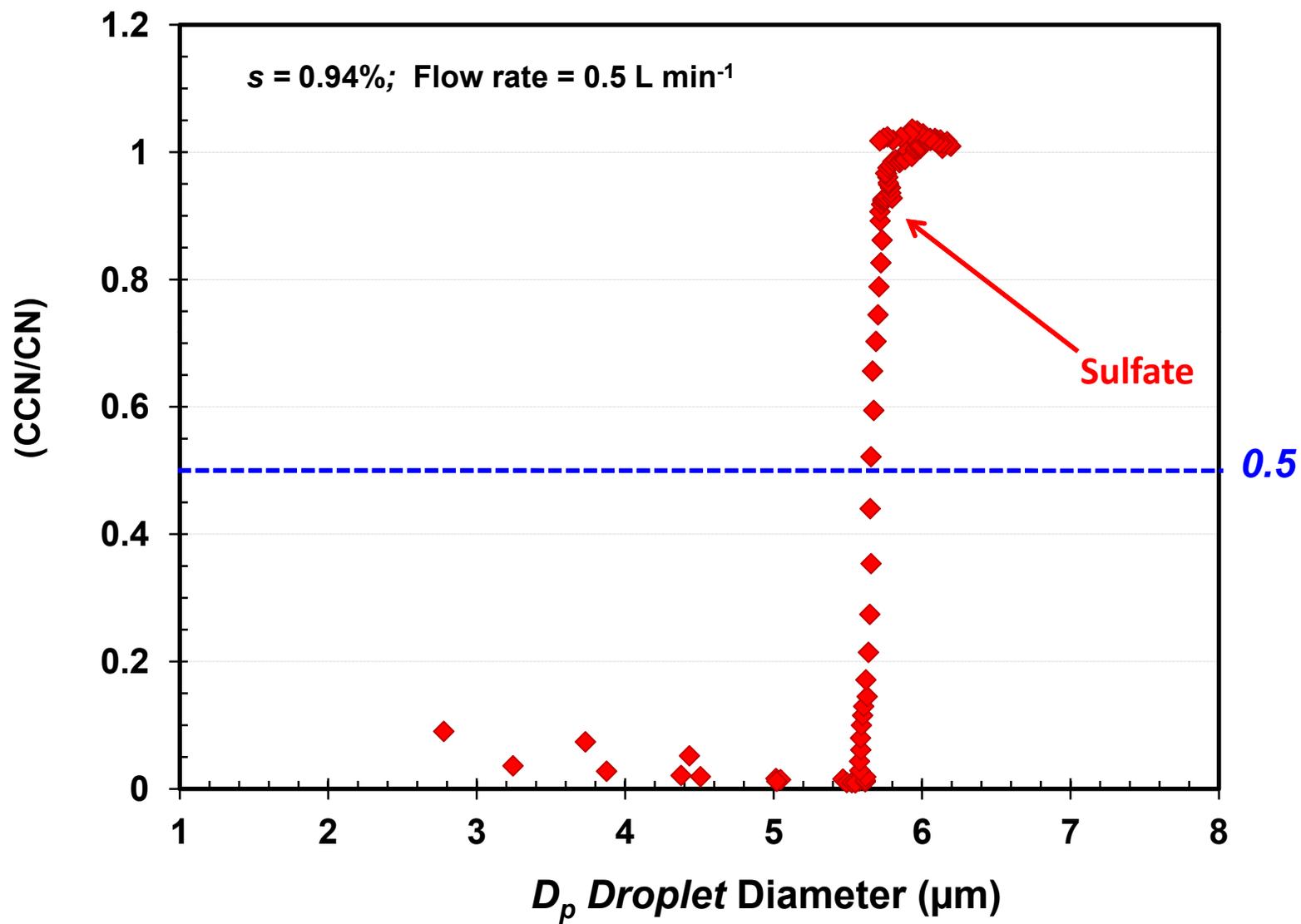


We can apply this concept for dry and wet particle diameters!

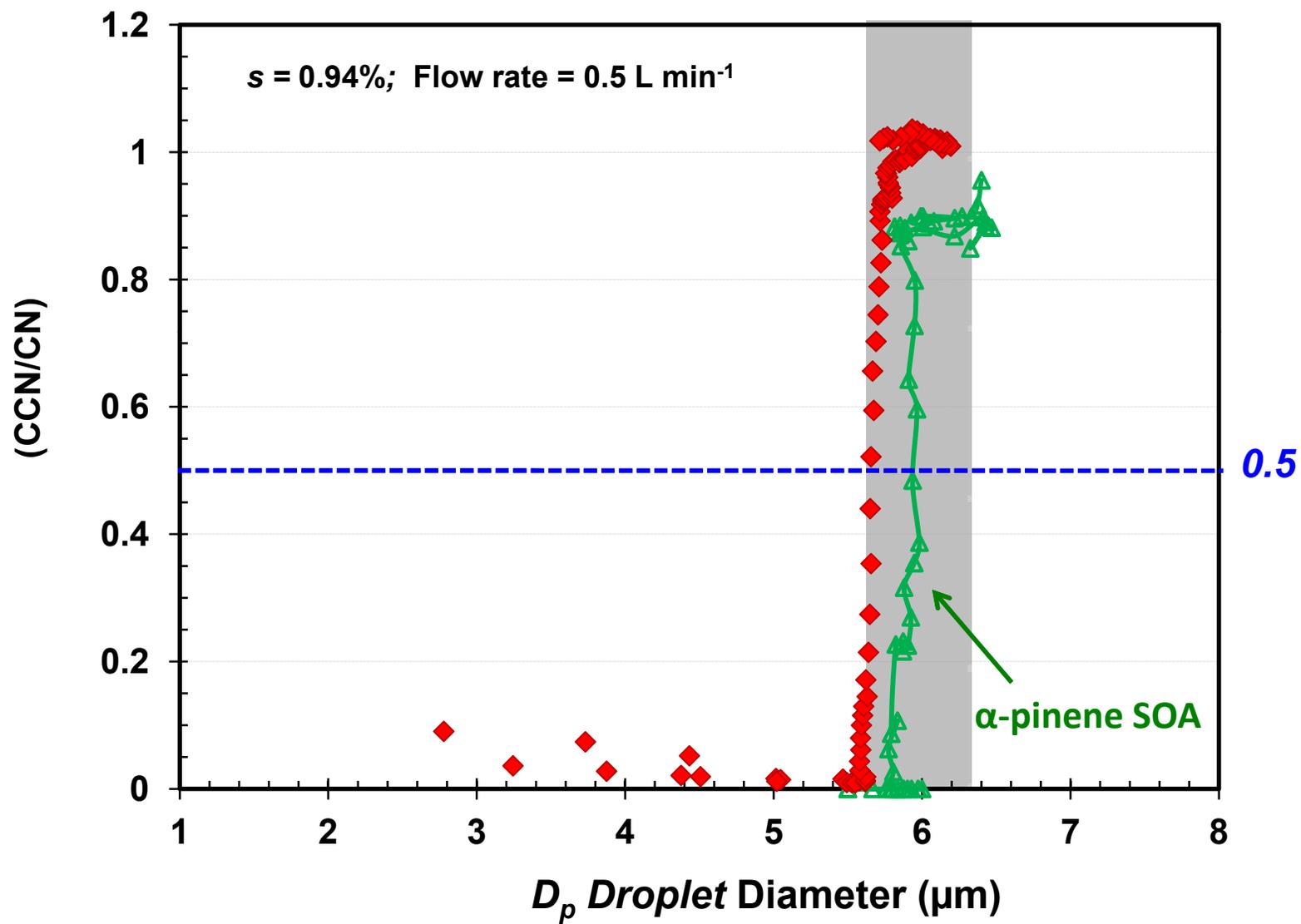
Scanning Mobility CCN Analysis

Moore, Nenes and Medina, 2010

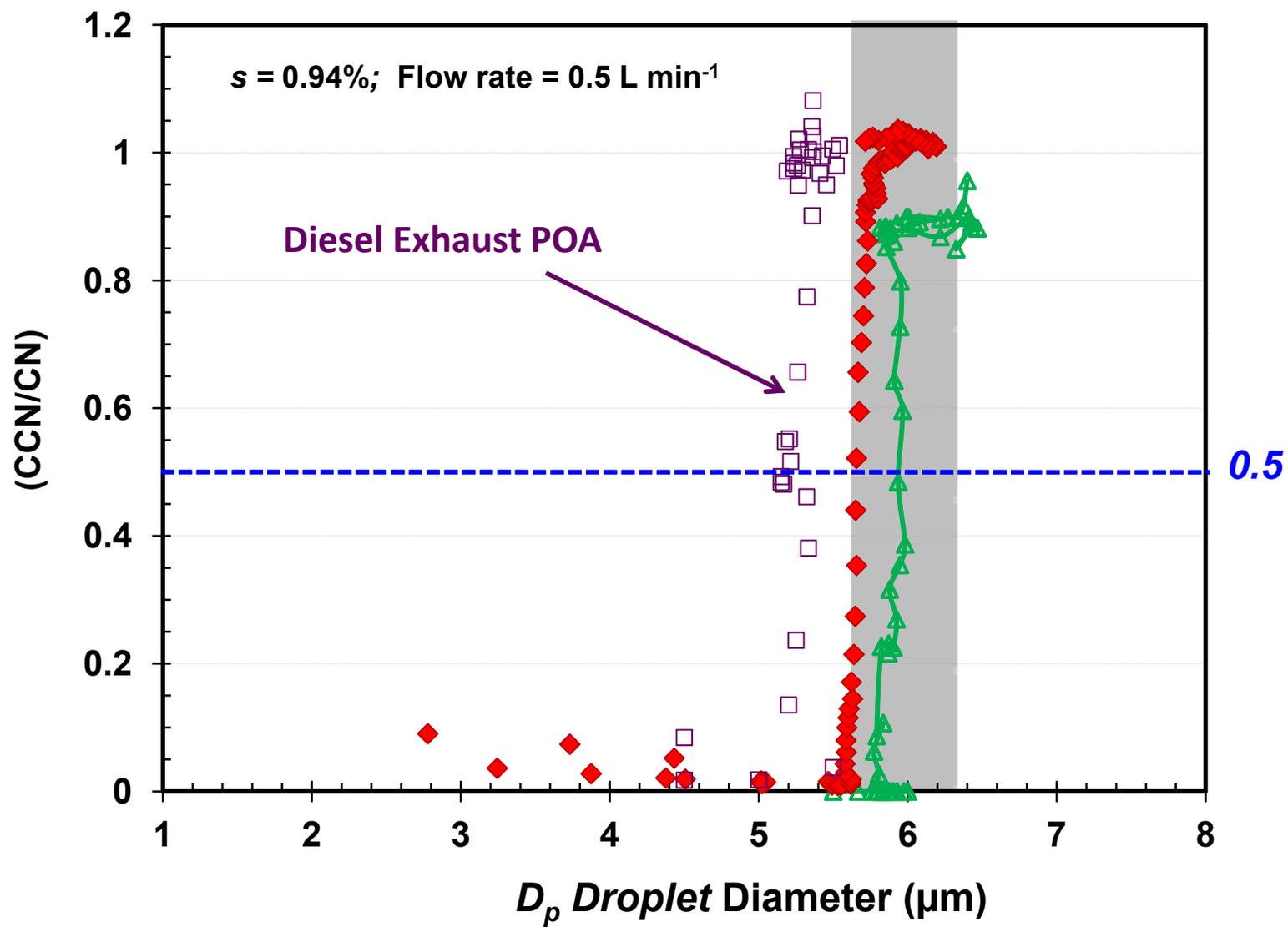
DROPLET GROWTH KINETICS



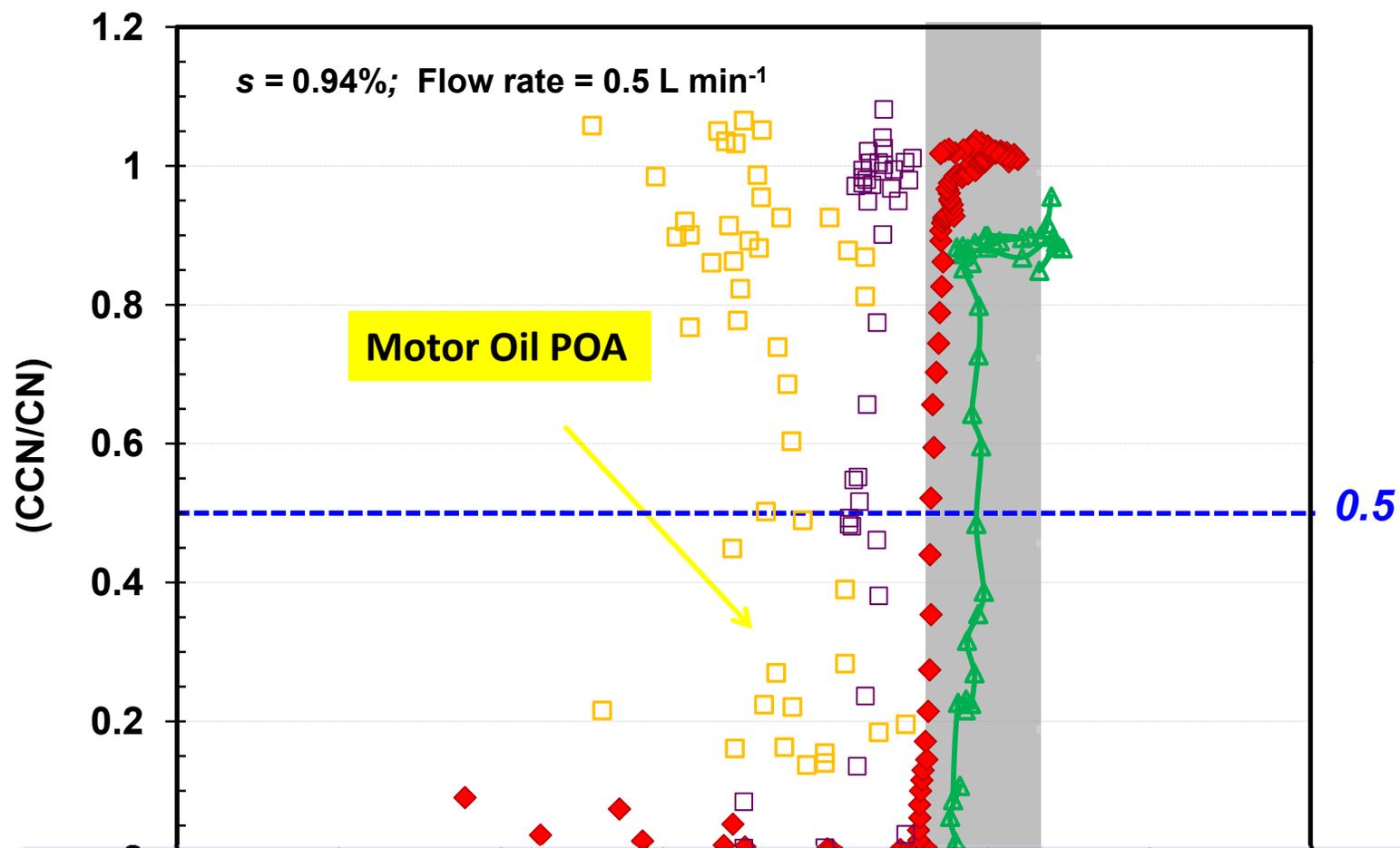
DROPLET GROWTH KINETICS



DROPLET GROWTH KINETICS

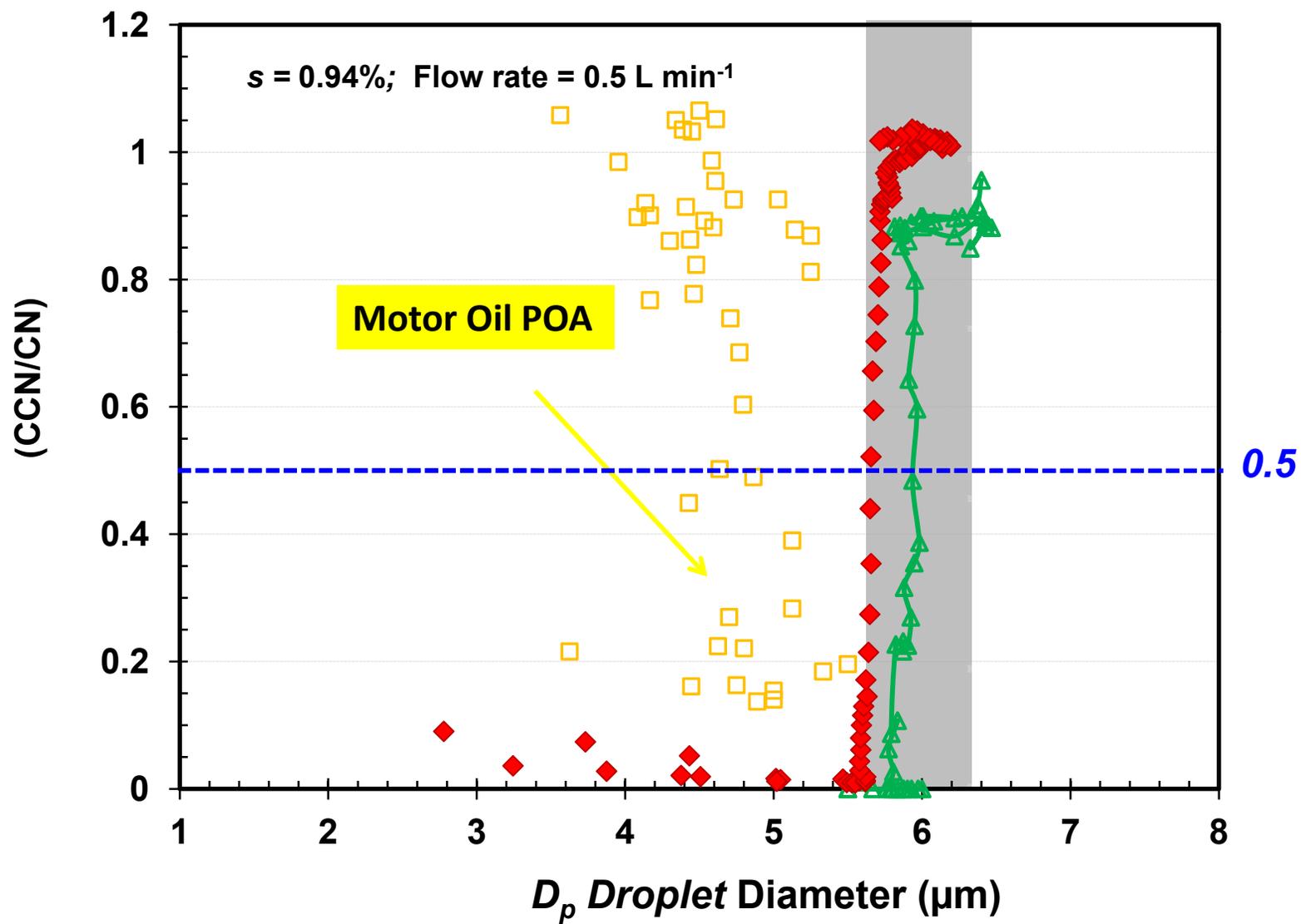


DROPLET GROWTH KINETICS



What happens when we mix?

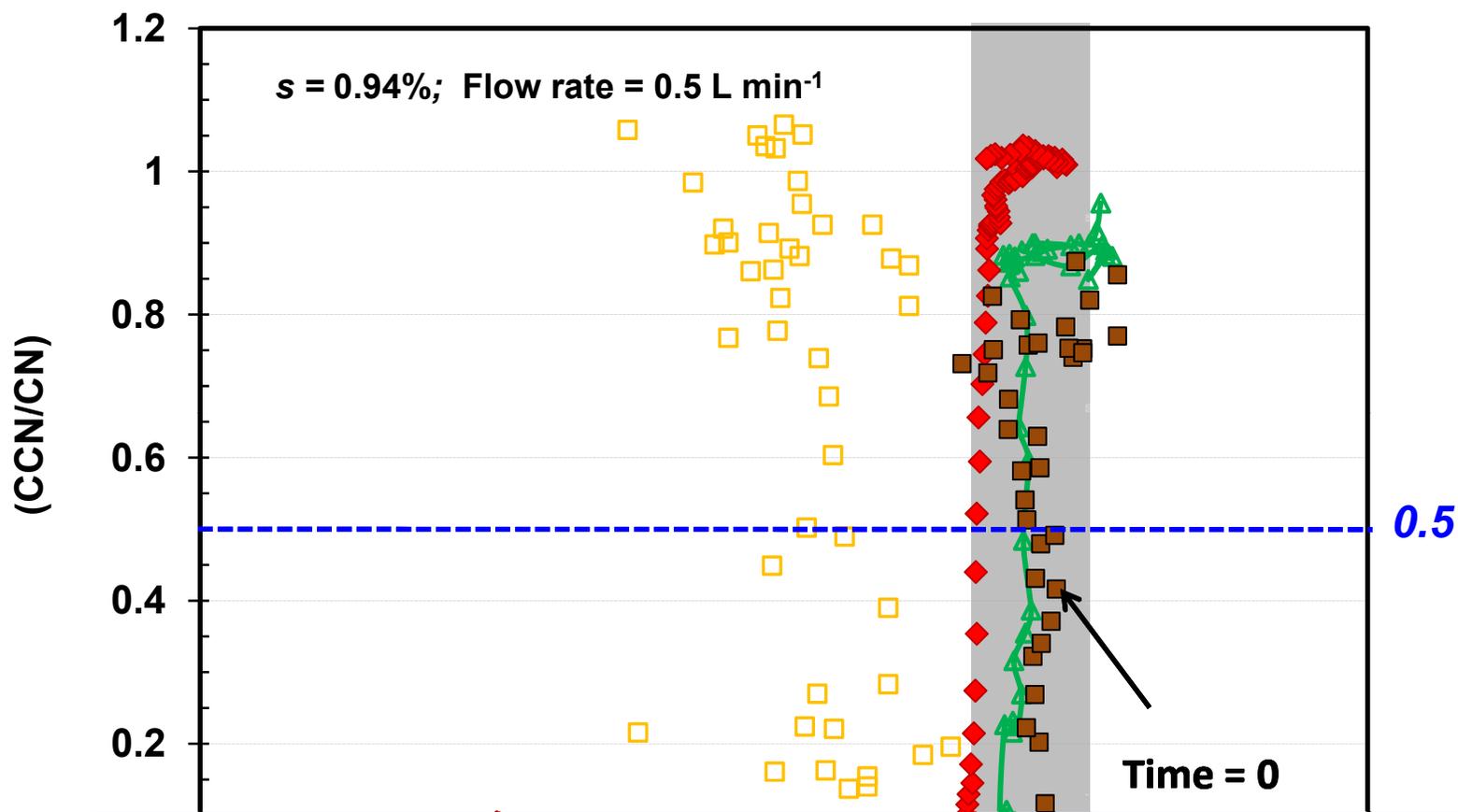
DROPLET GROWTH KINETICS



α -pinene SOA



Motor Oil POA



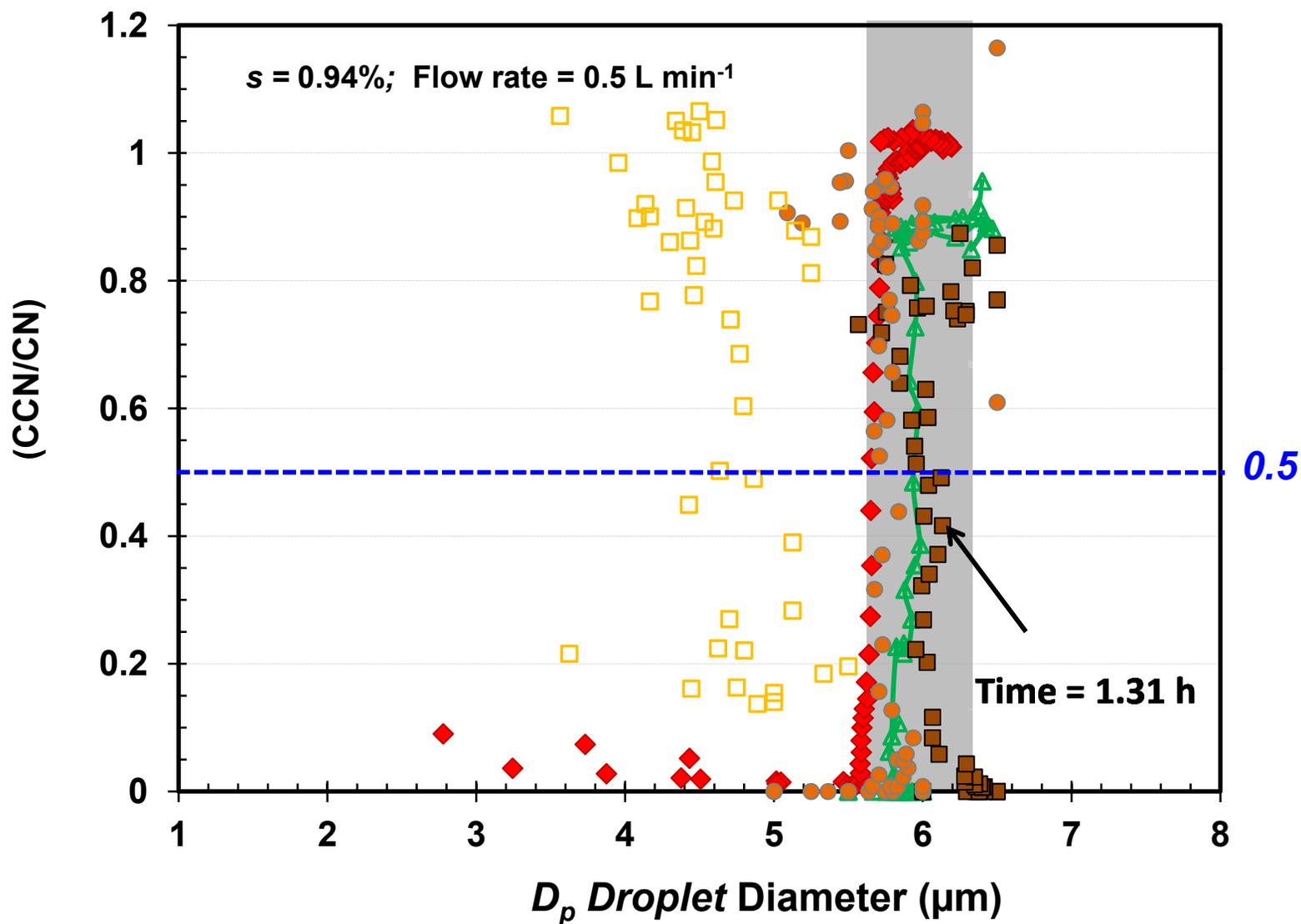
Enough hygroscopic material is available for organic droplets to grow to similar sizes as sulfate and α -pinene SOA

WEAK / 2-PHASE MIXTURE

α -pinene SOA



Motor Oil POA

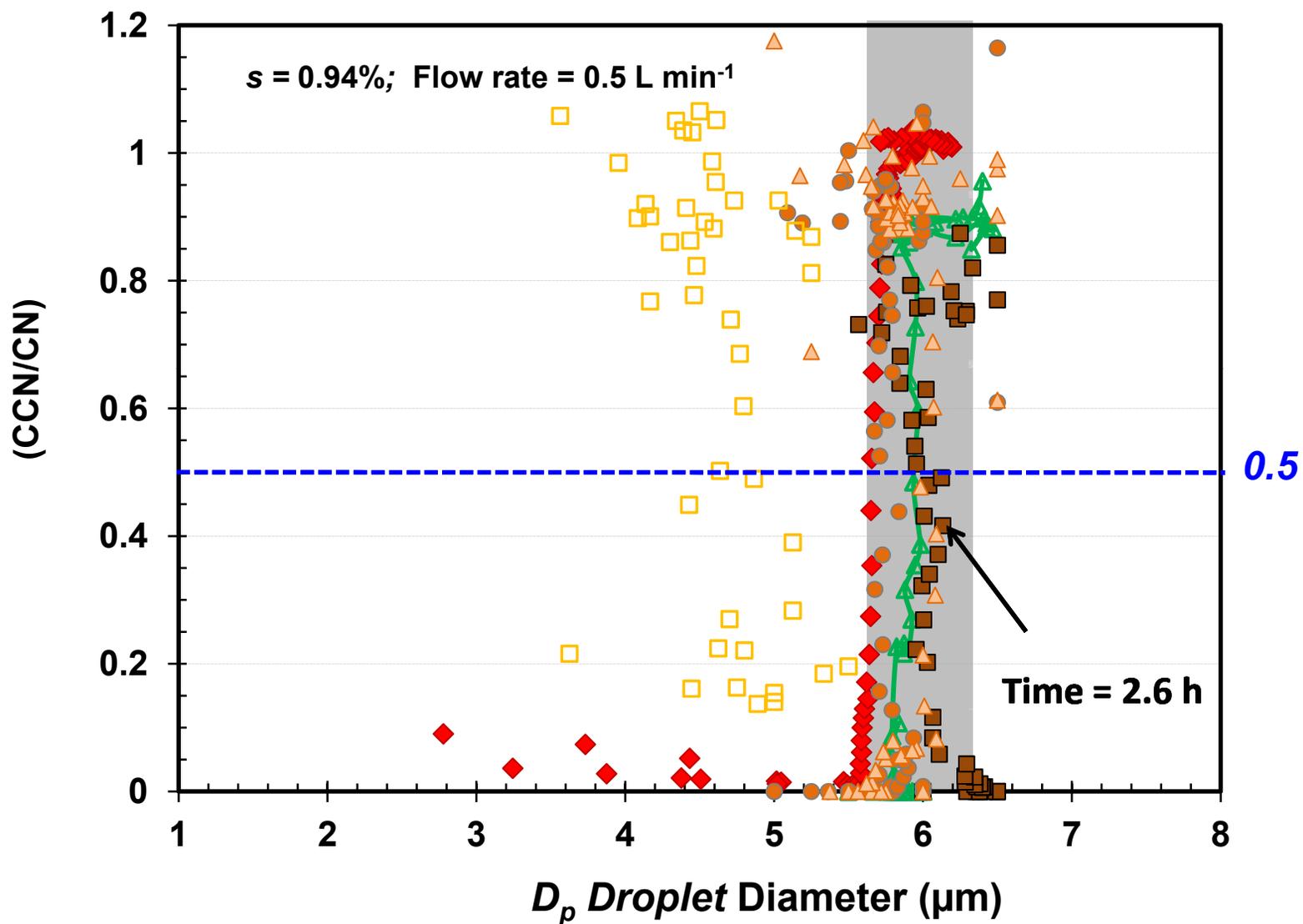


WEAK / 2-PHASE MIXTURE

α -pinene SOA



Motor Oil POA

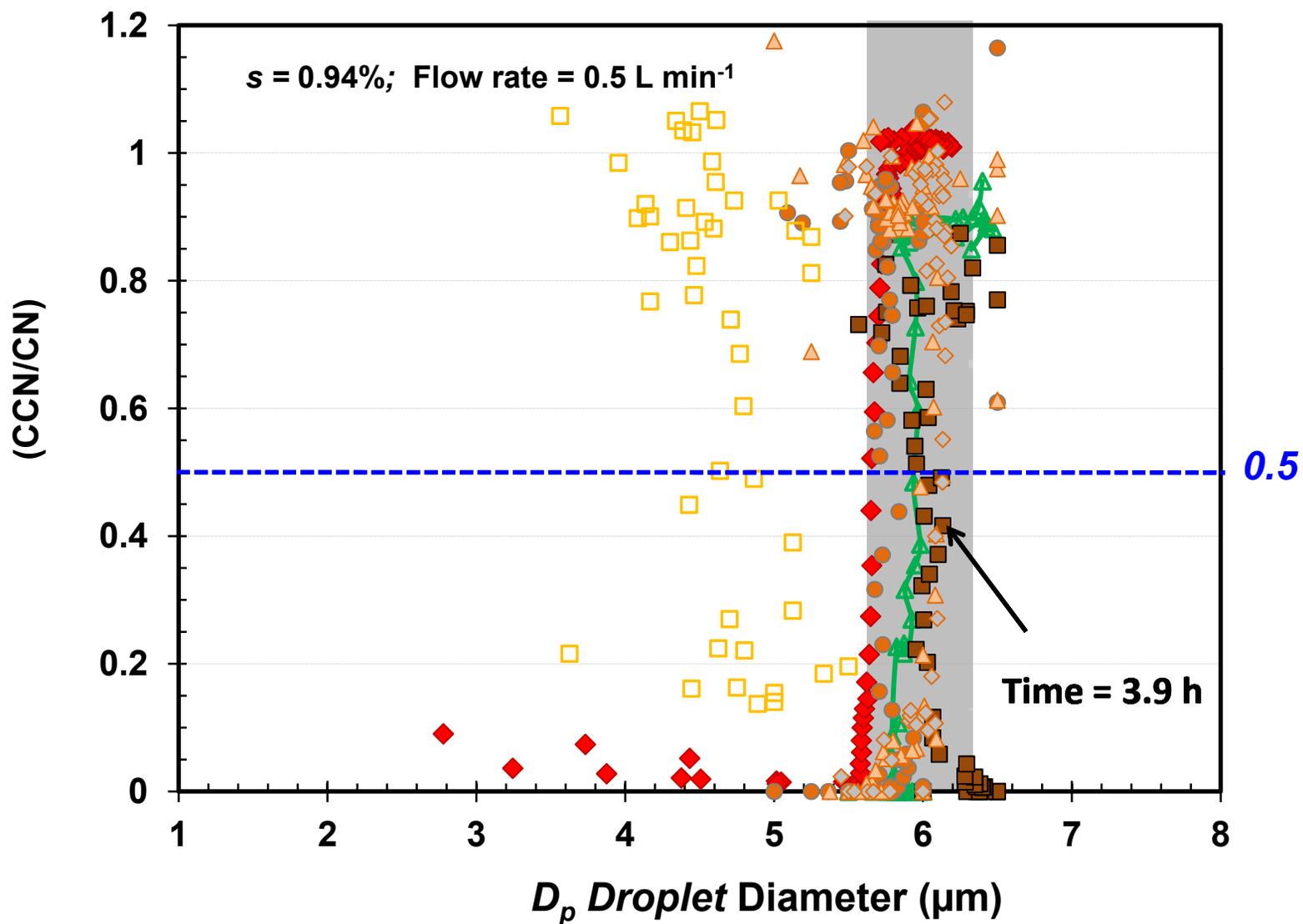


WEAK / 2-PHASE MIXTURE

α -pinene SOA



Motor Oil POA

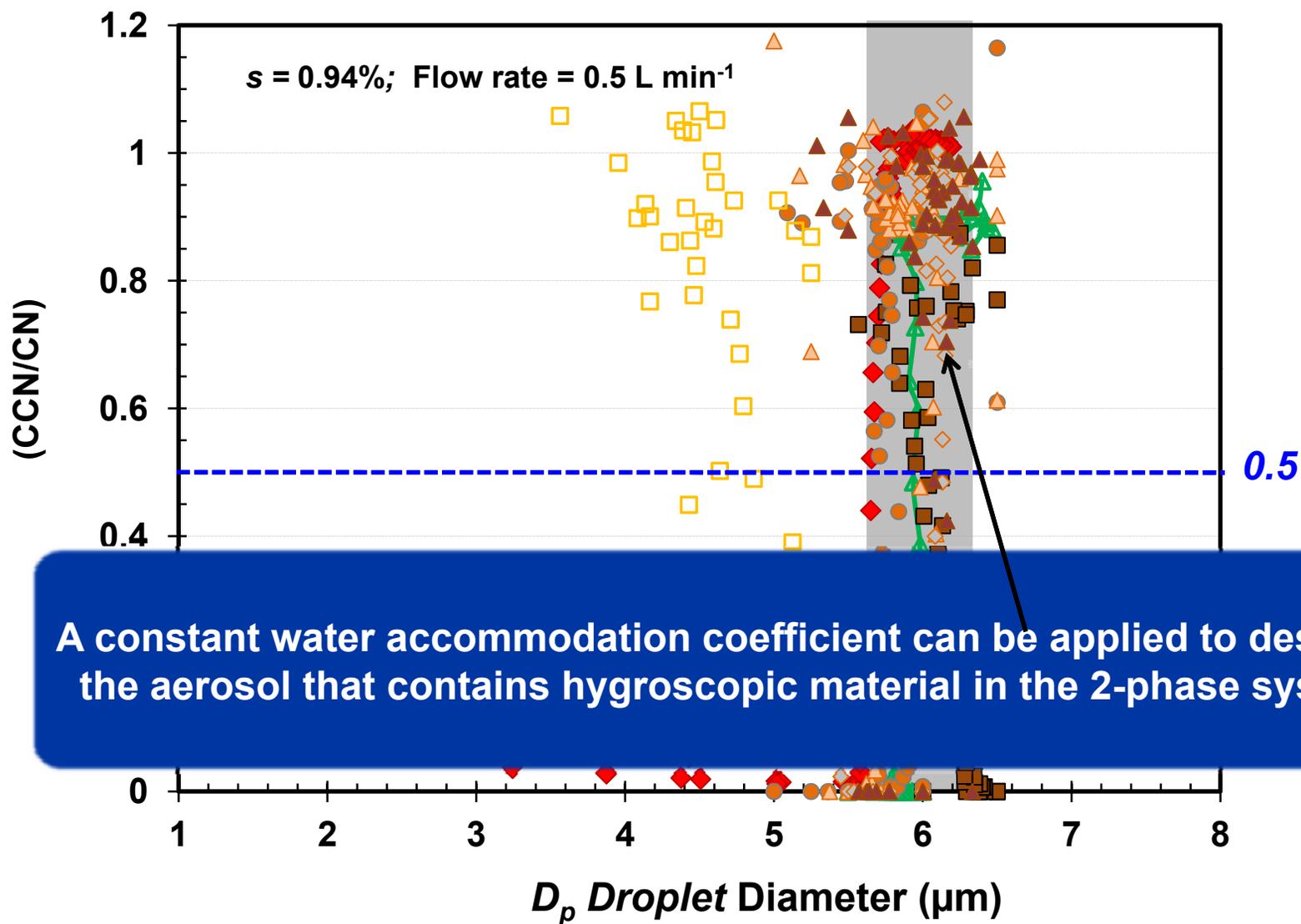


WEAK / 2-PHASE MIXTURE

α -pinene SOA



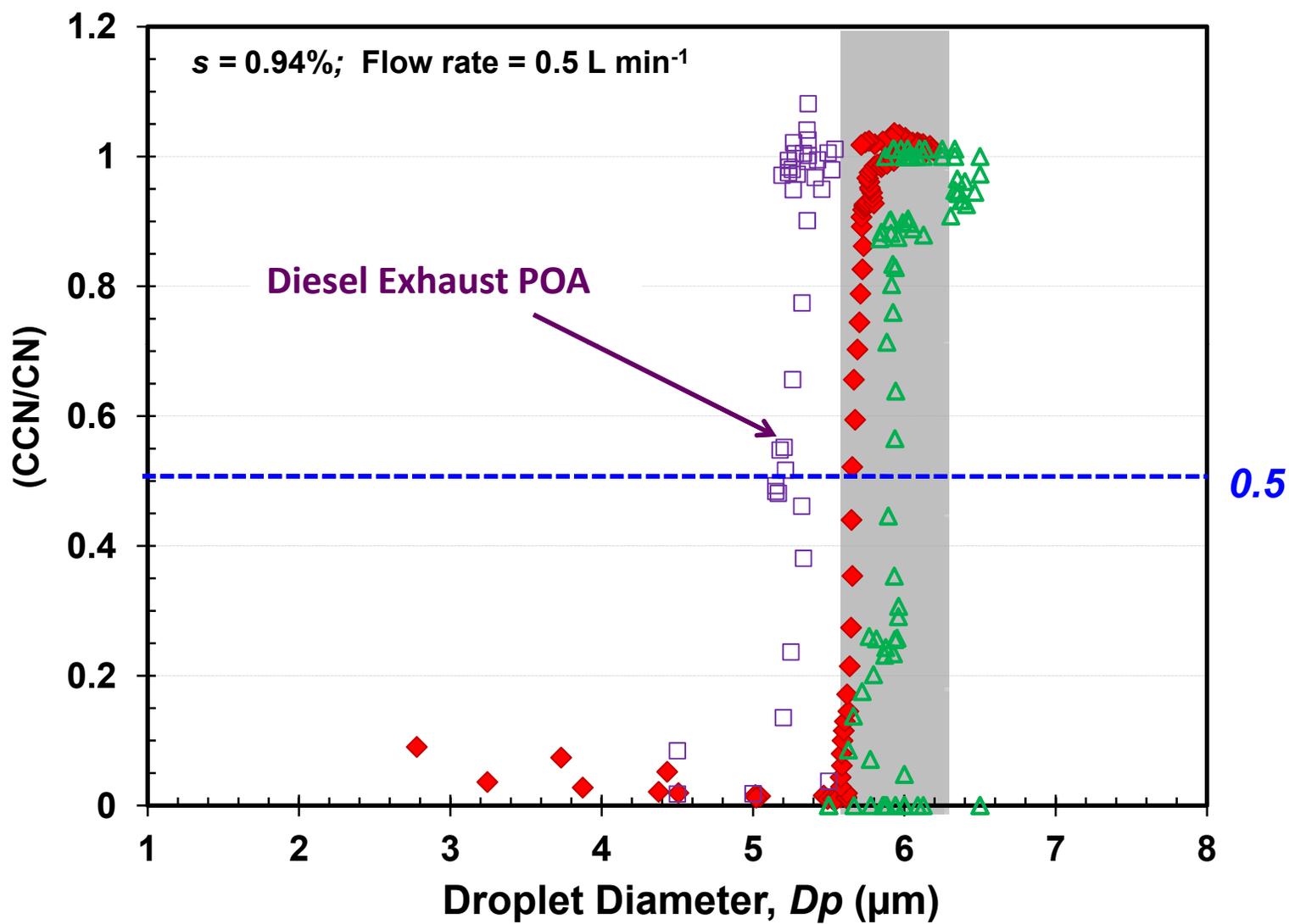
Motor Oil POA



A constant water accommodation coefficient can be applied to describe the aerosol that contains hygroscopic material in the 2-phase system

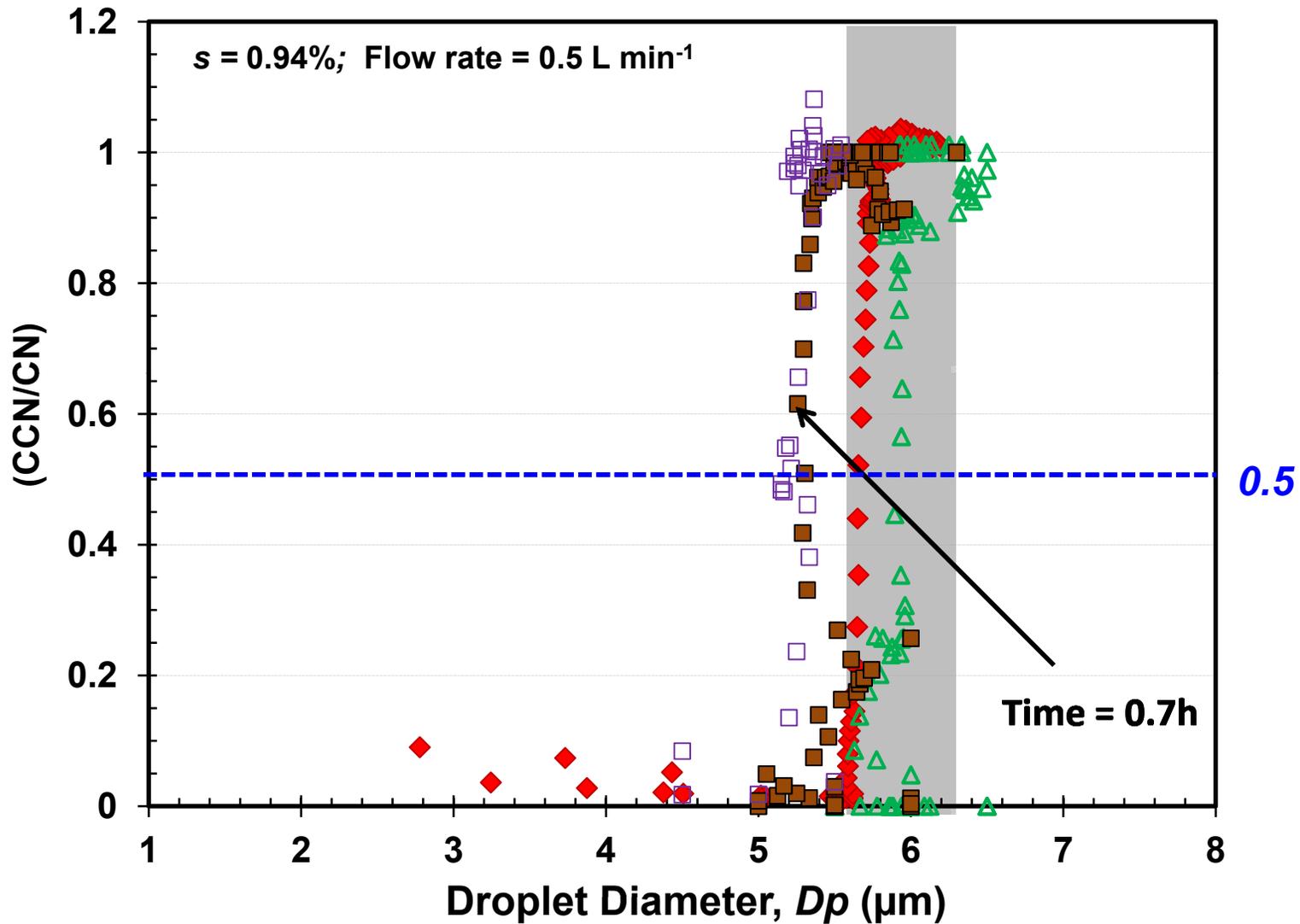
WEAK / 2-PHASE MIXTURE

DROPLET GROWTH KINETICS



α -pinene SOA

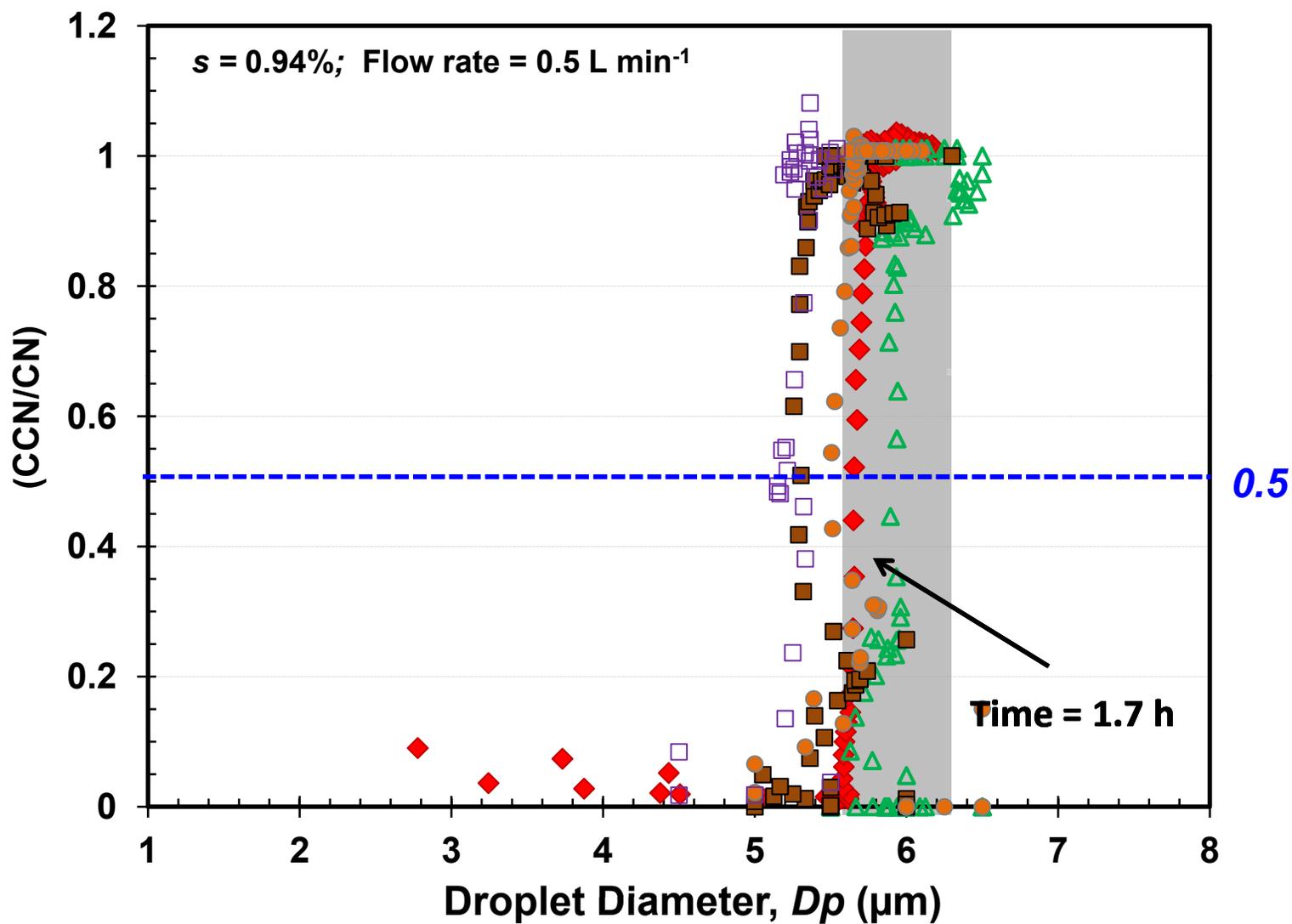
+ Diesel Exhaust POA



STRONG / 1-PHASE MIXTURE

α -pinene SOA

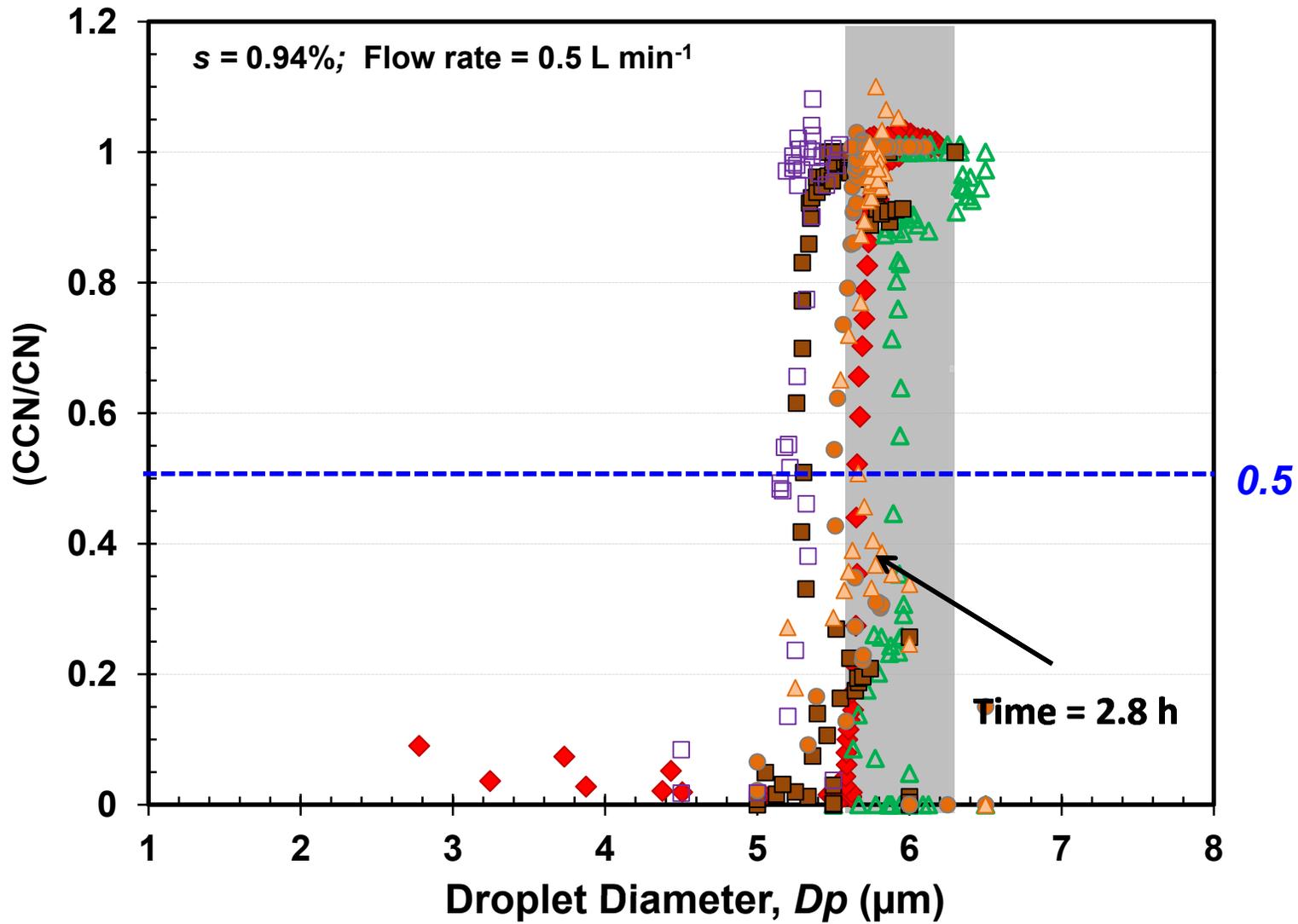
+ Diesel Exhaust POA



STRONG / 1-PHASE MIXTURE

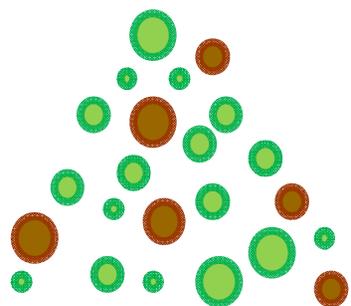
α -pinene SOA

+ Diesel Exhaust POA

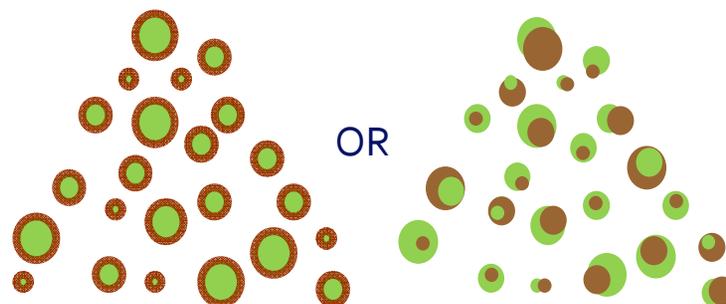


STRONG / 1-PHASE MIXTURE

MIXING STATE MATTERS

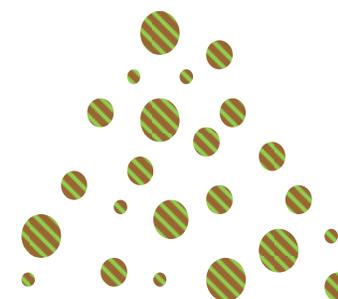


No mixing



OR

Weak Mixing
2-phase System



Strong Mixing
1-phase System

The mixing state of the aerosol is important.

The extent of mixing will substantially modify CCN activation parameters and droplet growth rates

The presence of hygroscopic materials will promote droplet growth

Soluble Mass

Mixing State

Droplet Size

I. Design apparatus to control and modify BC/OC aerosol mixing states

II. Identify Online and Offline techniques to characterize BC water uptake and droplet growth

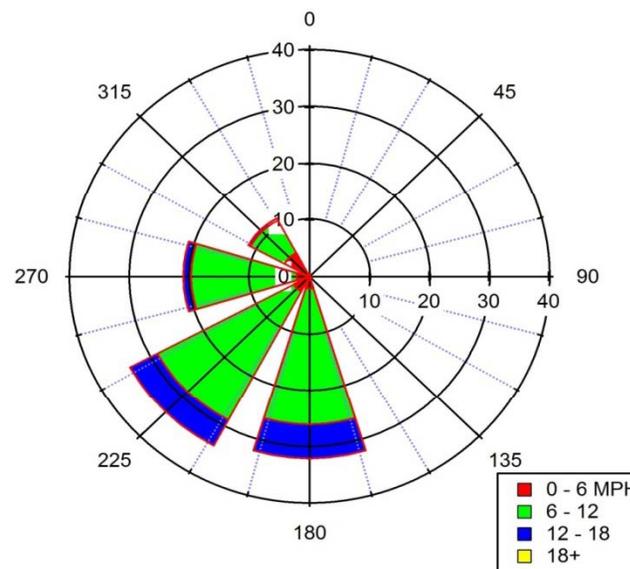
III. Test the ability to promote water uptake of BC aerosol containing particles through oxidative ageing properties

IV. Measuring the cloud droplet ability of BC engine emissions from diesel & alternative fuel sources

V. Quantify droplet growth for climate and health.

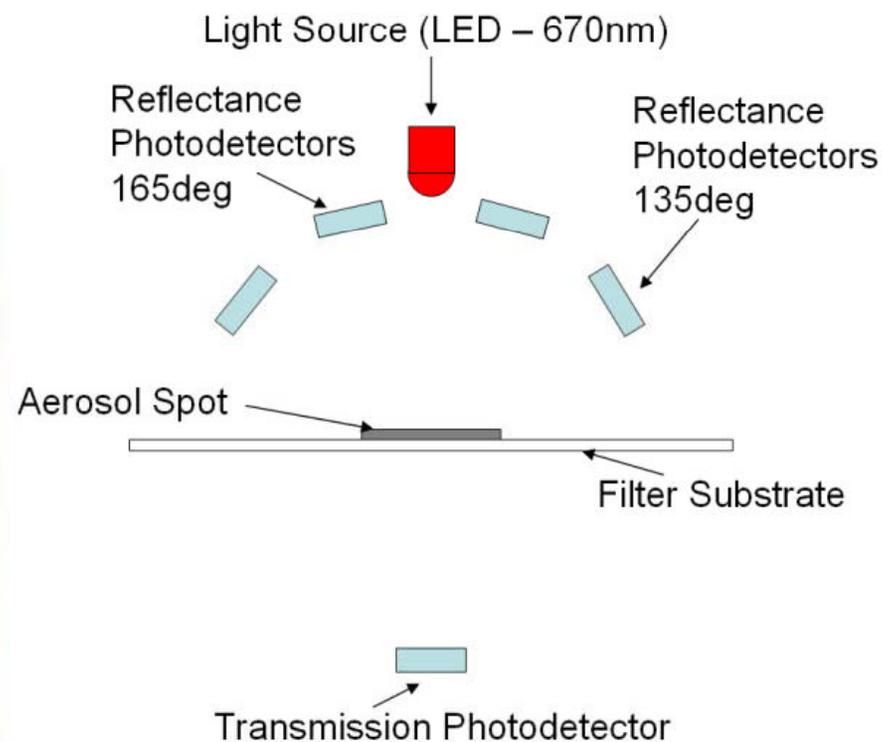
I-710 Field Site

- ★ In Collaboration with AQMD
- ★ Instrument trailer was located 15 meters downwind of freeway



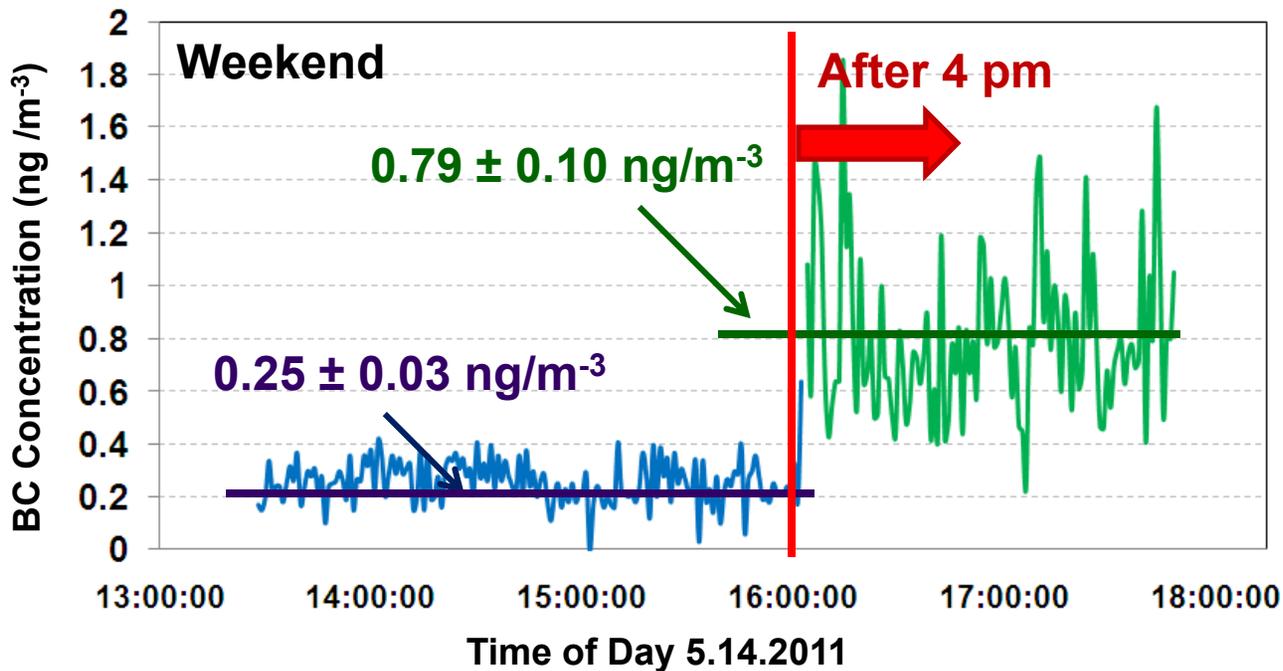
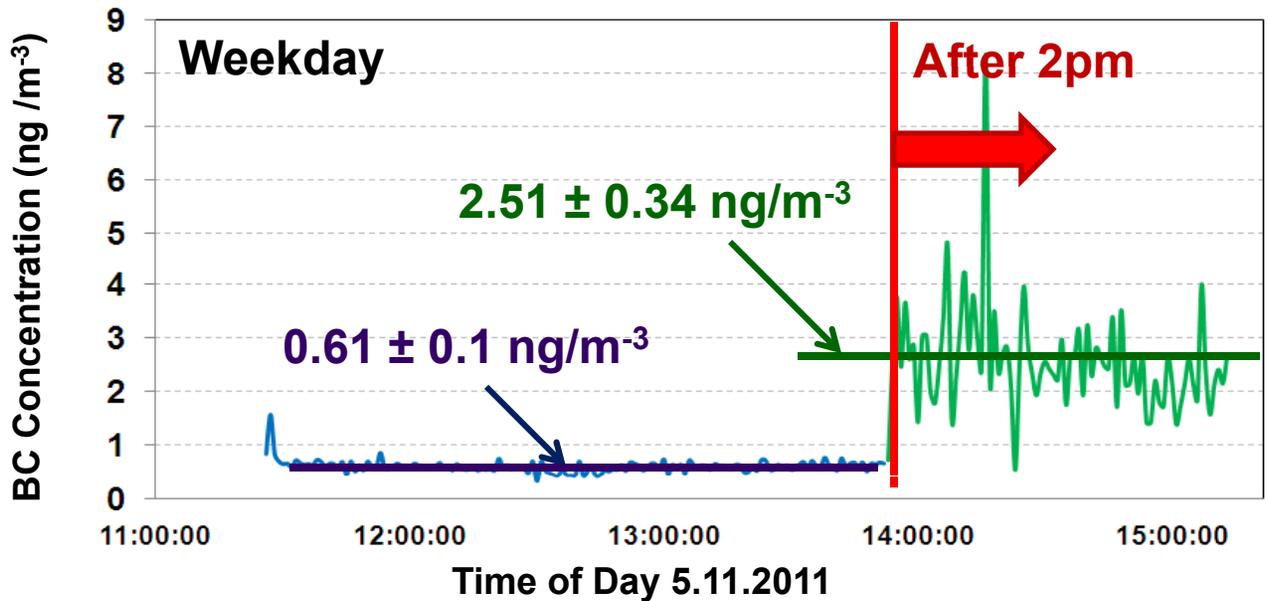
Multi-Angle Absorption Photometer

- Black Carbon (**BC**) is measured with a Multi-Angle Absorption Photometer (MAAP)
- BC tends to be insoluble
- The MAAP uses multiple light sources to determine the reflective aerosol properties



*University of Manchester, Centre for Atmospheric Science

Changes in BC Concentration due to Wind Direction

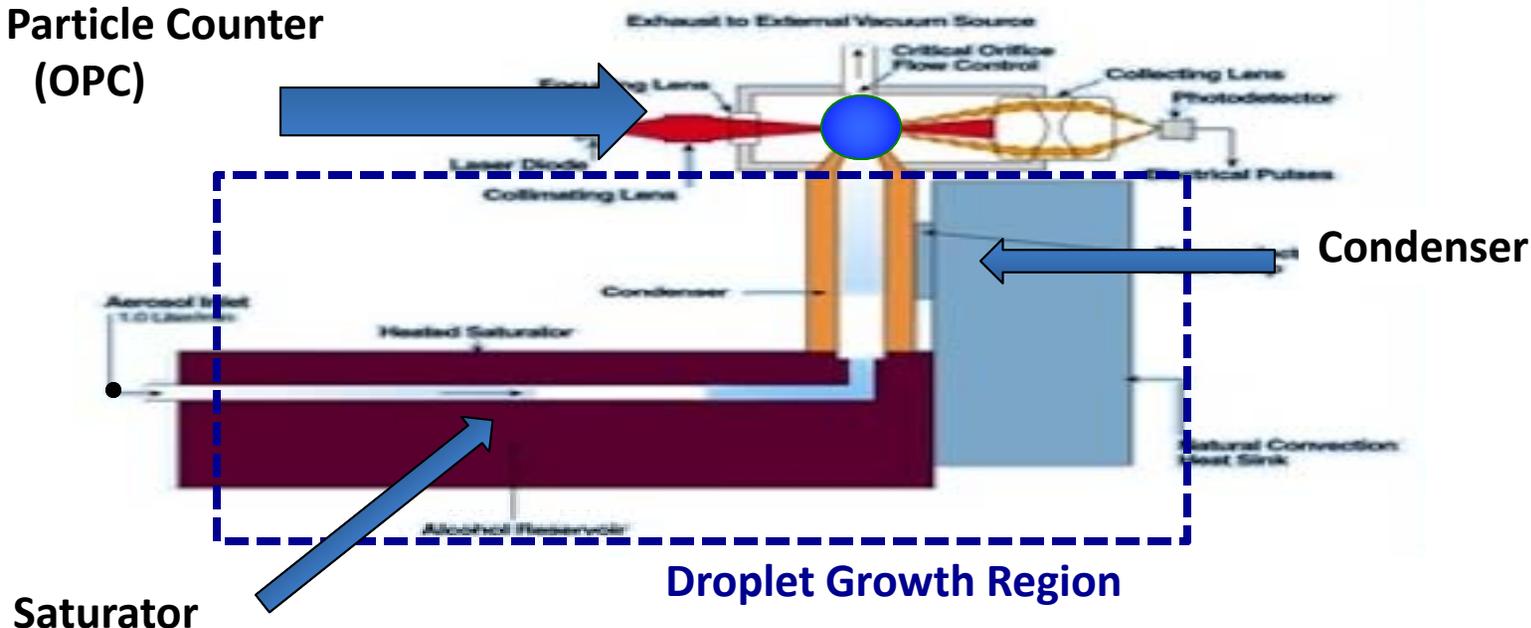


Weekday
Aerosol
contains ~ 3x
as much BC as
Weekend BC
concentrations

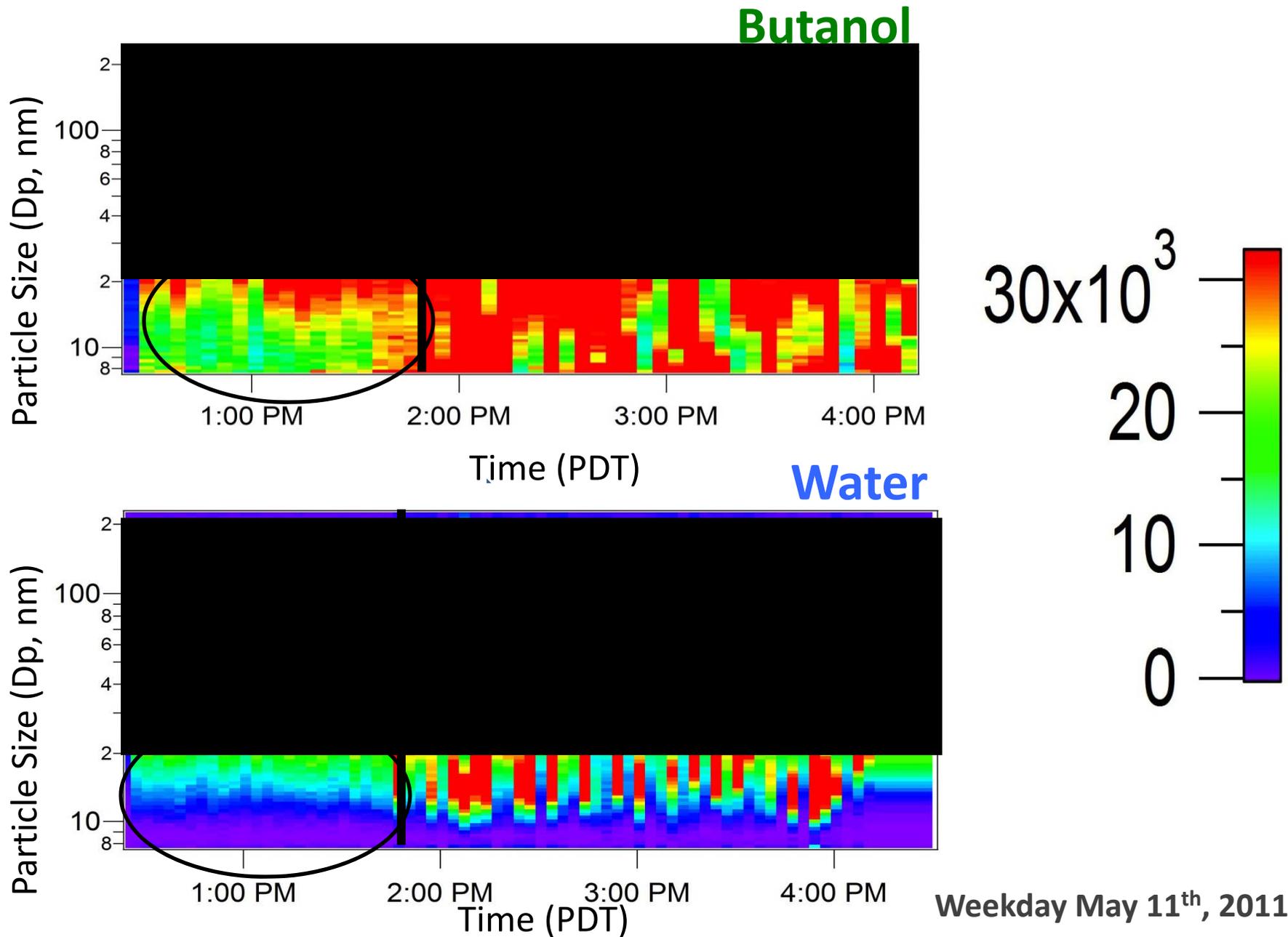
How are Particles counted?

- Dry nanoparticles are exposed to a supersaturation region in which wetted droplets are grown to micron sizes
- Condensational Particle Counters (CPC) detects larger micron size droplets with an optical particle counter (OPC)
- CPC supersaturation is generated with two different working fluids, **Butanol (TSI 3772)** and **Water (TSI 3785)**

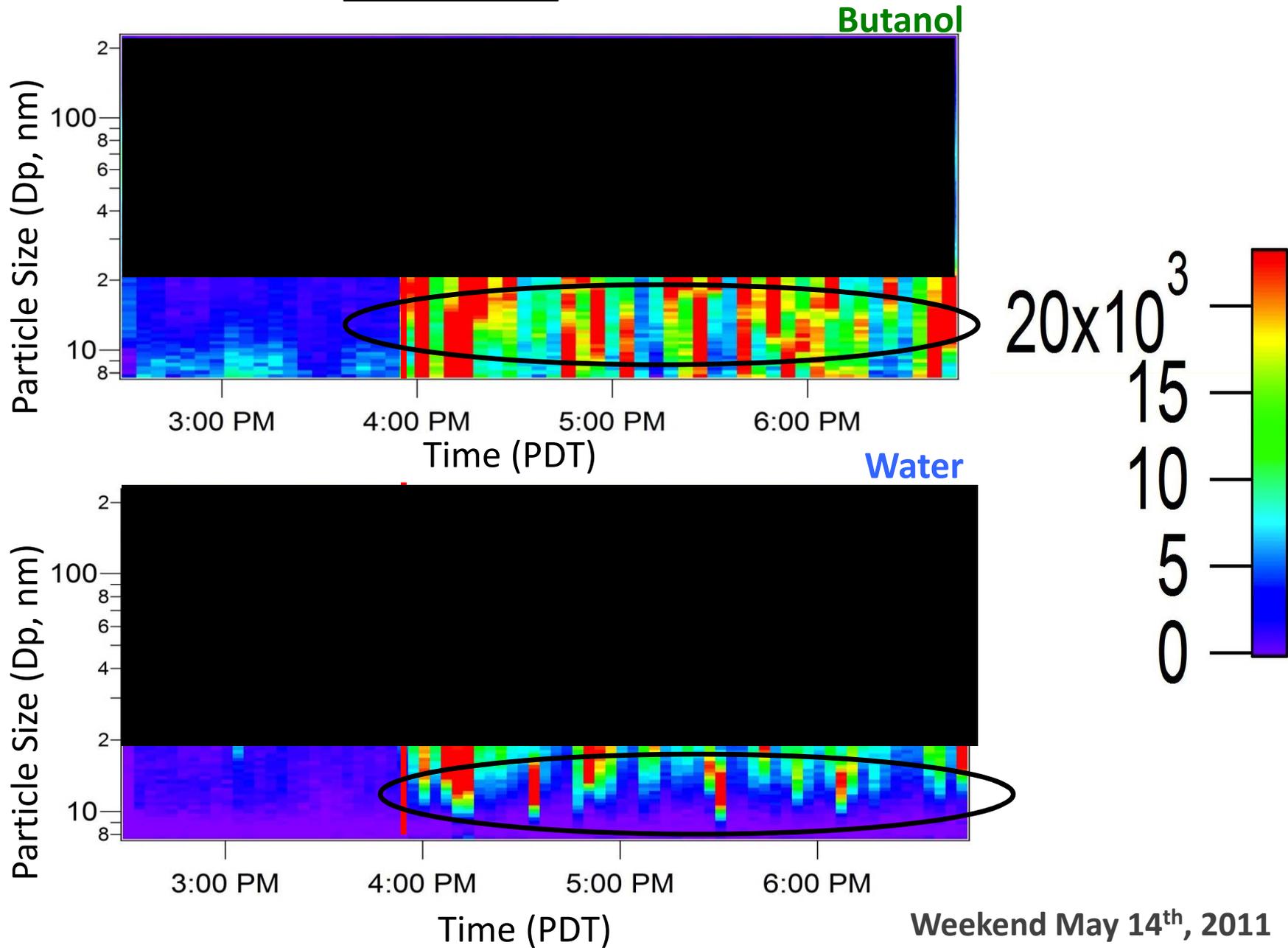
Optical Particle Counter (OPC)



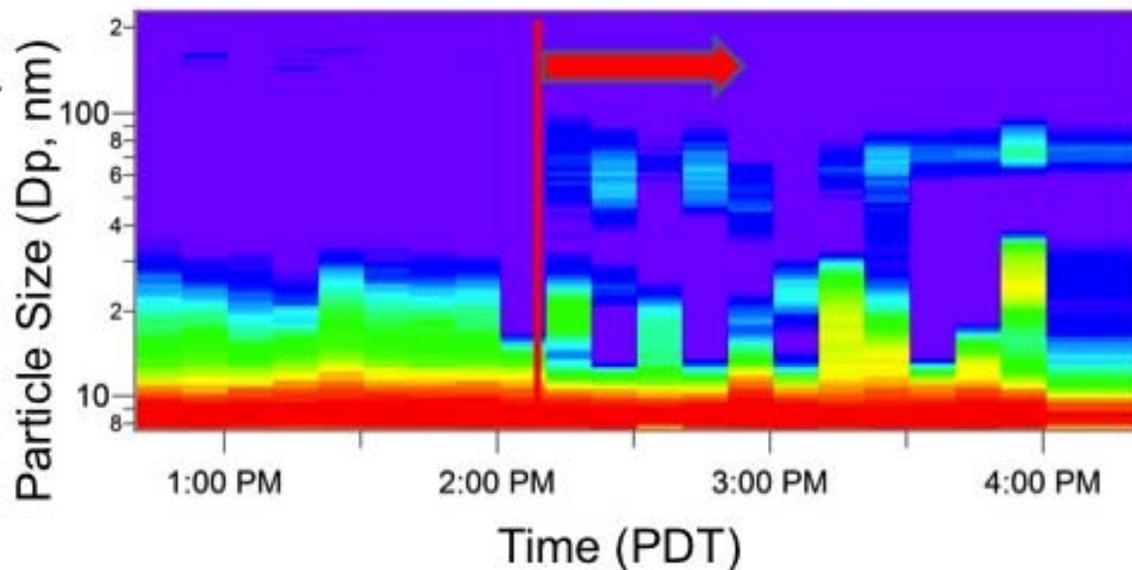
Differences in Weekday Particle Distribution



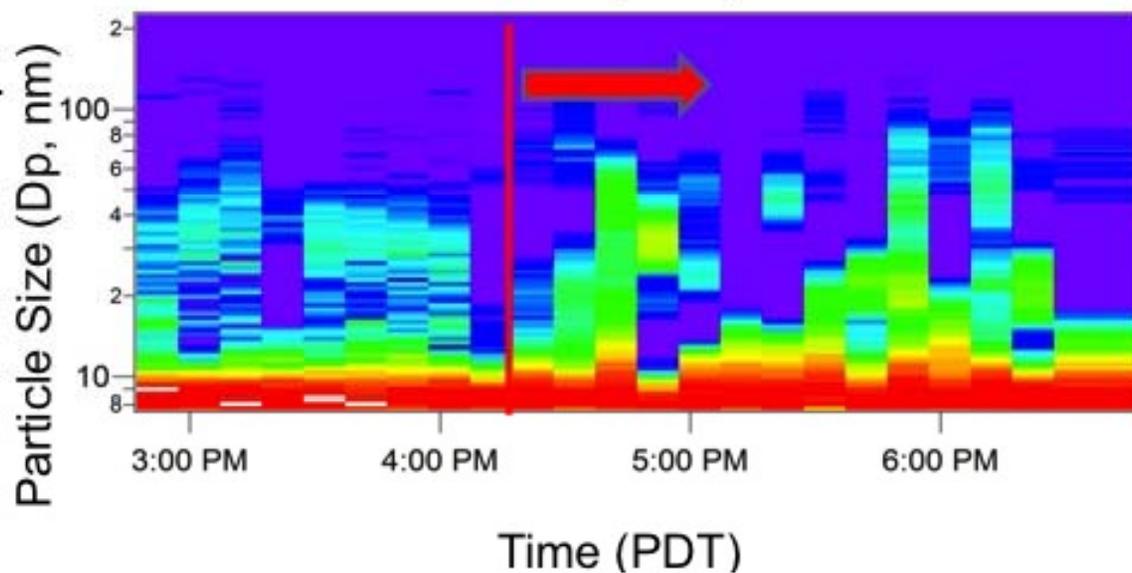
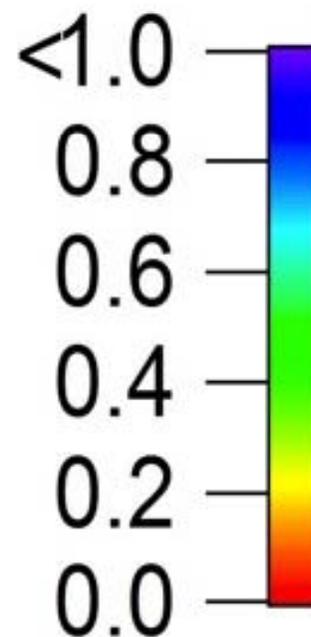
Differences in Weekend Particle Distribution



Counting Efficiency, Ratio of Water / Butanol

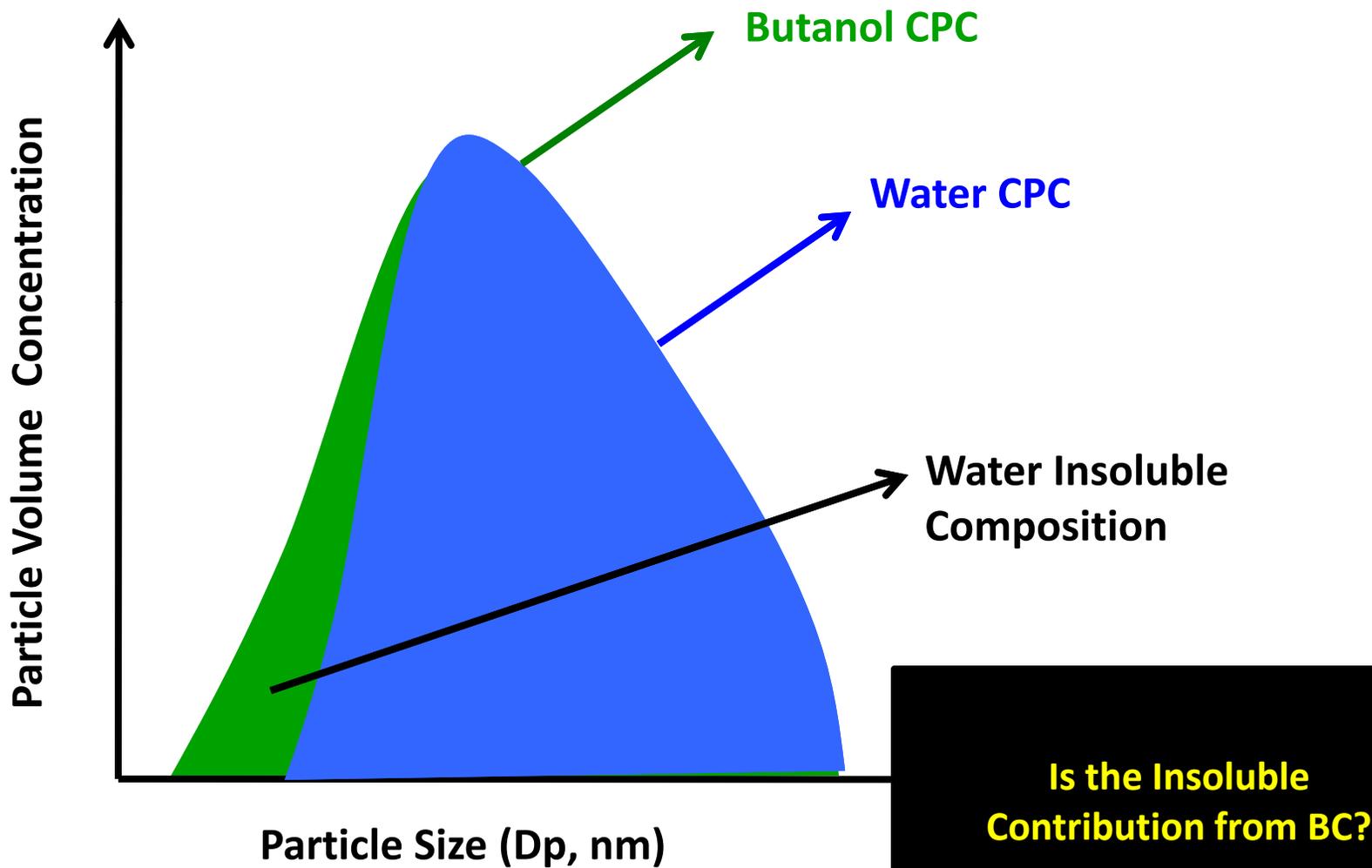


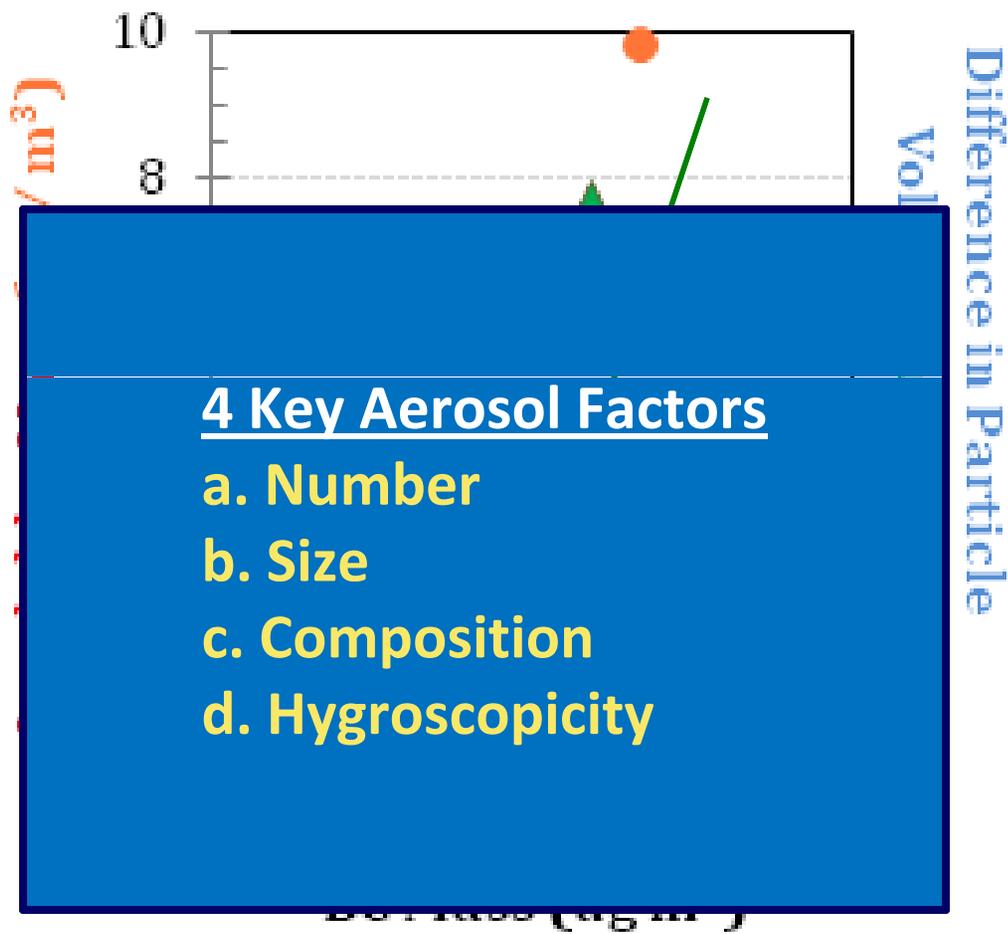
May 11th, 2011



May 14th, 2011

Why the Difference?





4 Key Aerosol Factors

- a. Number
- b. Size
- c. Composition
- d. Hygroscopicity



**Real Time
measurement to
Infer Soluble Mass
Composition of
Particles**

Ongoing BC and CCN Studies

- Controlled Mixing State Apparatus
- BC from Biomass Burning
- Biodiesel Fuel Emissions (*CARB - TD, GK*)
- Aromatic Fuel Emissions (*API – TD, GK, RLR*)

Source: NASA : *Black Carbon
Cloud Droplets (artist
rendition)*





Aerosol-Climate Effects



Michael Giordano, Daniel Short, Xiaochen Tang, and Diep Vu

Correspondence: akua@engr.ucr.edu