

# UCR



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

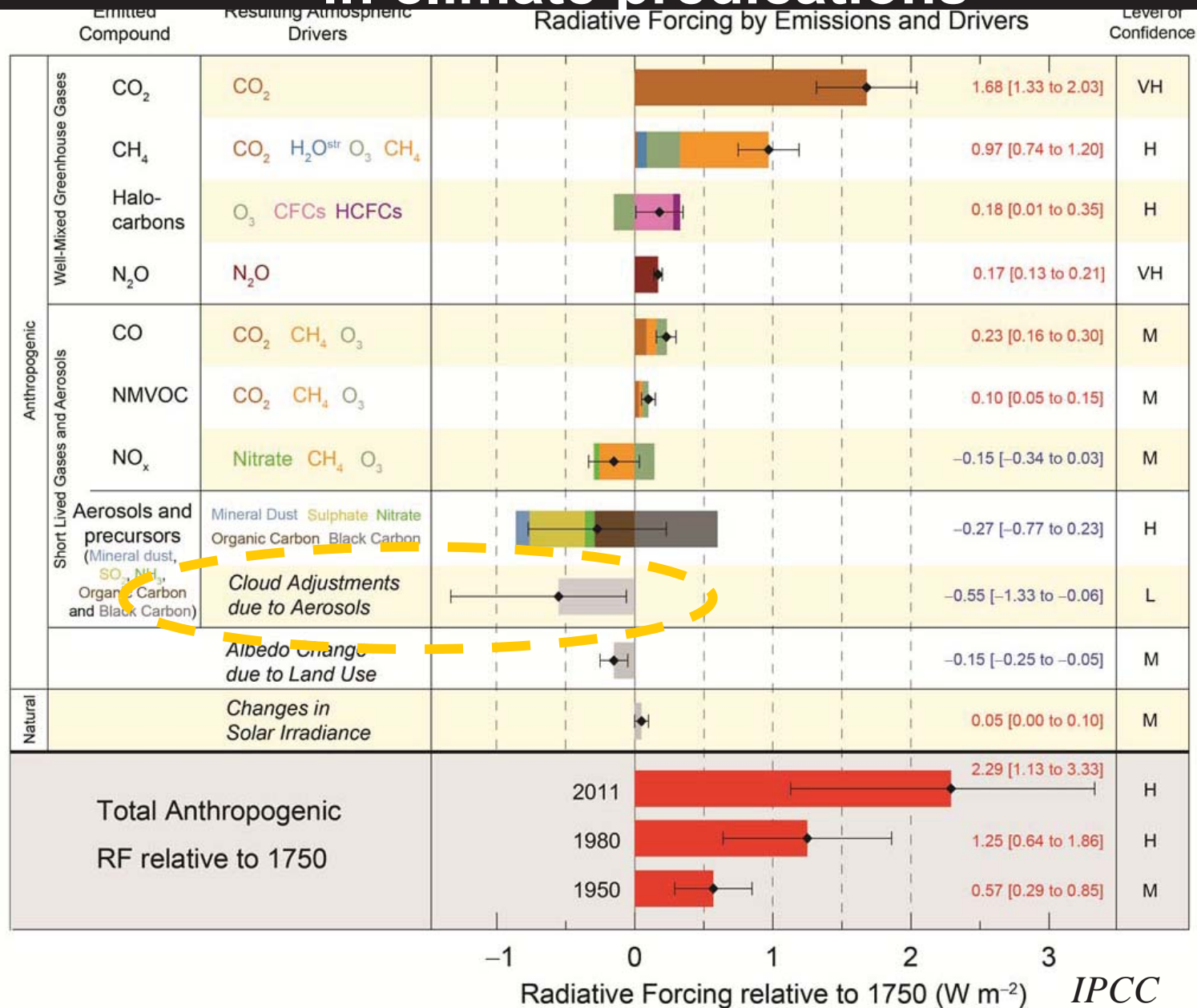
*Akua Asa-Awuku*

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Bourns College of Engineering  
Center of Environmental Research and Technology

Funding: EPA Black Carbon STAR

November 13<sup>th</sup>, 2014  
UNIVERSITY OF CALIFORNIA, RIVERSIDE

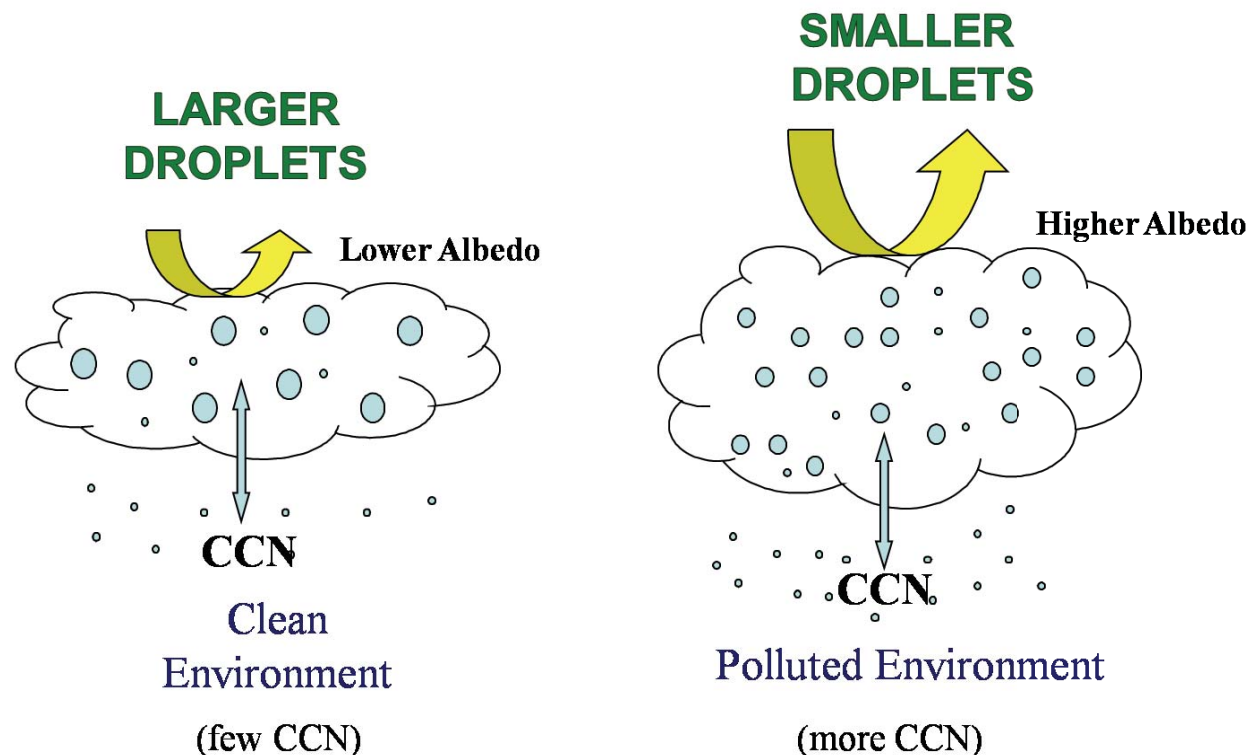
# Clouds contribute the greatest uncertainty in climate predications



## RELEVANT PROPERTIES OF COMPLEX CCN

Cloud condensation nuclei (CCN) activate and become cloud droplets

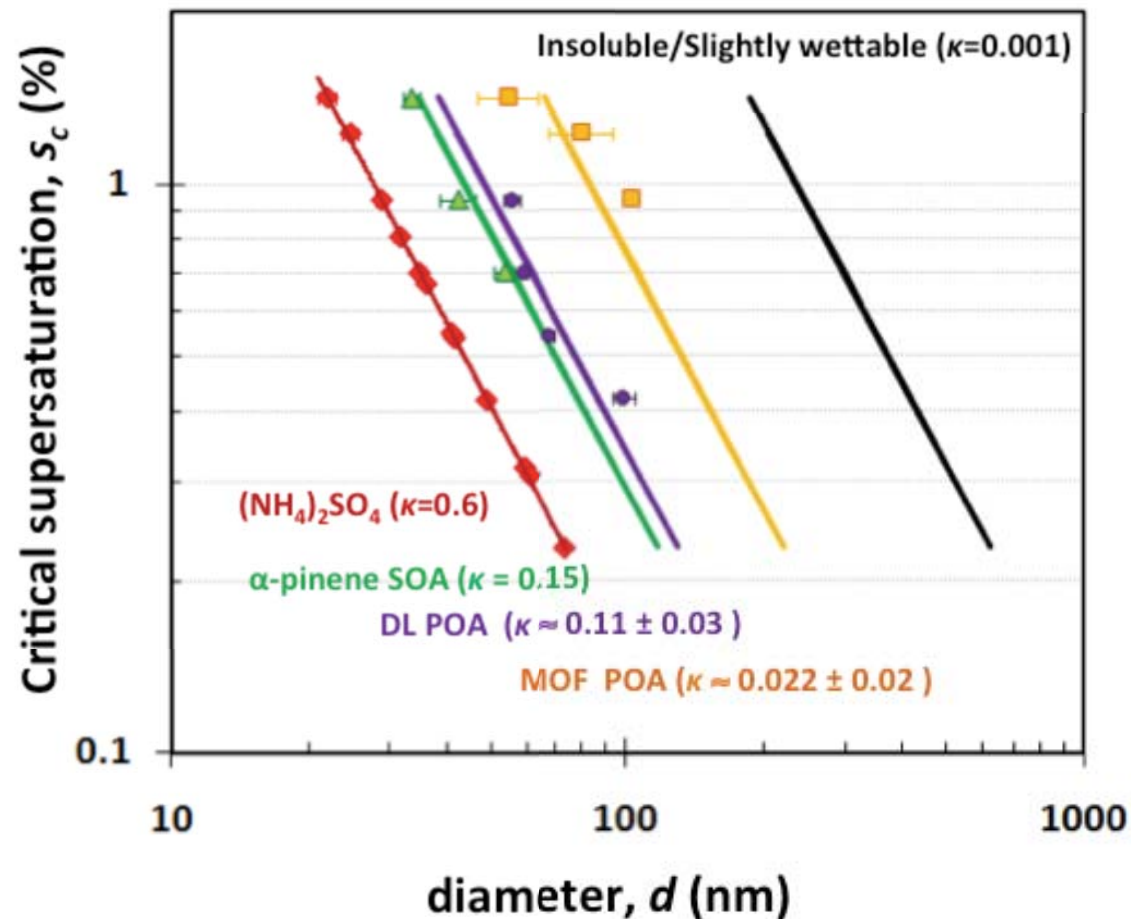
The ability to be CCN depends on particle size and chemistry



## RELEVANT PROPERTIES OF COMPLEX CCN

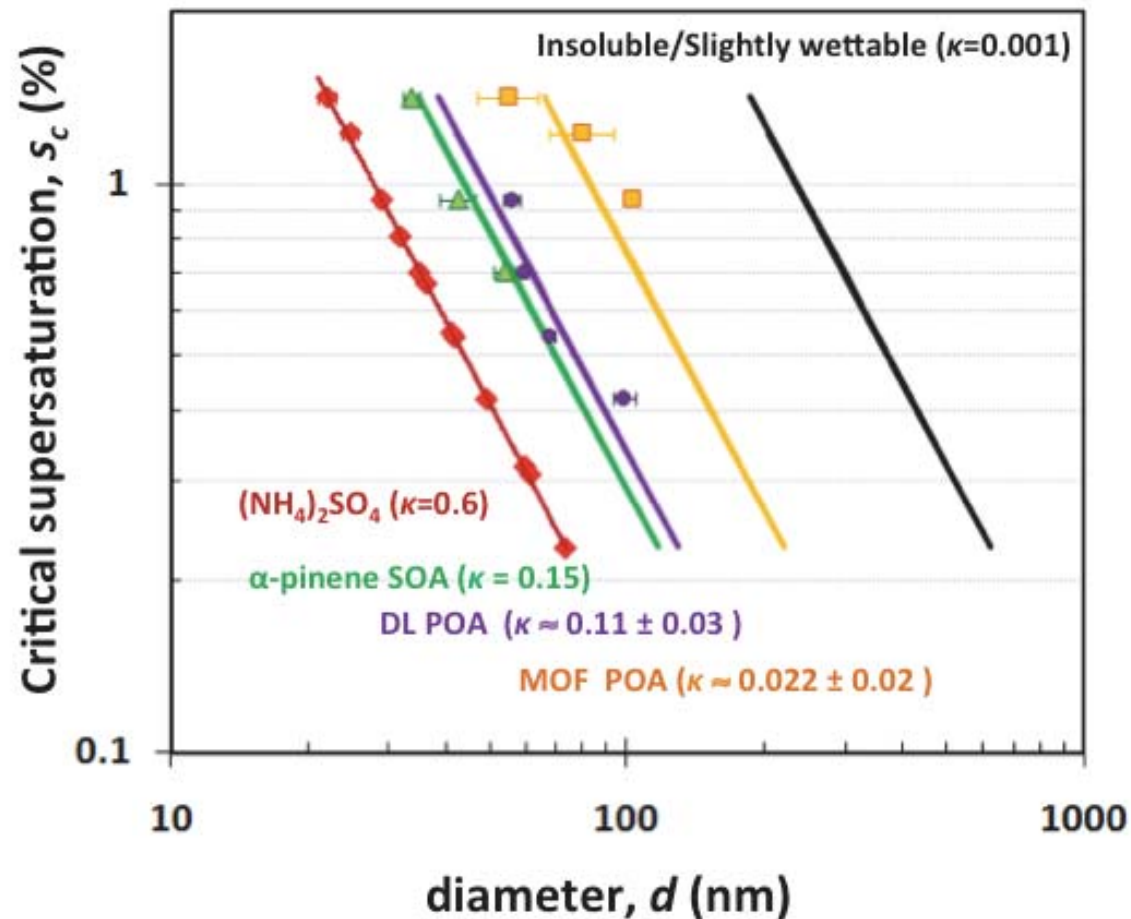
Cloud condensation nuclei (CCN) activate and become cloud droplets

The ability to be CCN depends on particle size and chemistry





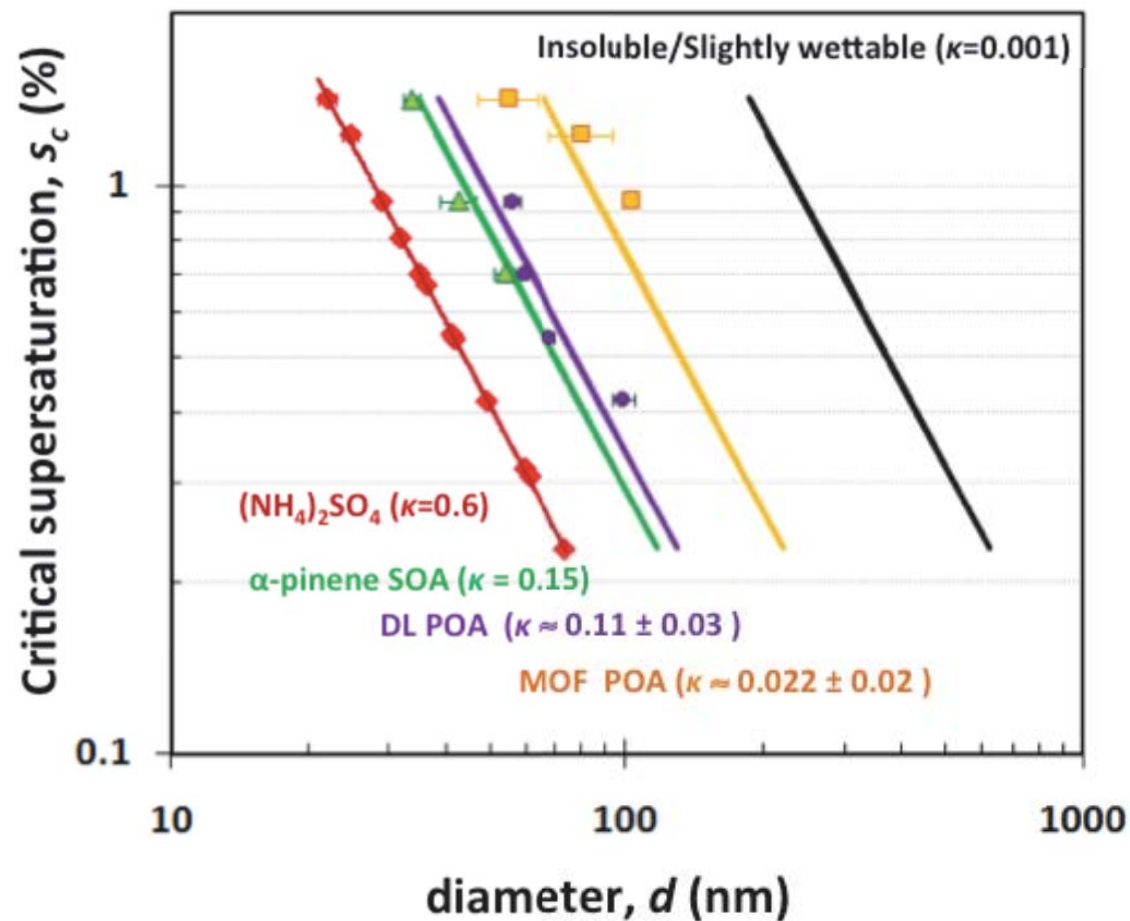
The more complex the aerosol source,  
the more difficult it becomes to characterize the changing  
chemical and physical properties of the CCN.



## RELEVANT PROPERTIES OF COMPLEX CCN

The apparent hygroscopicity of complex CCN can be modified

Prevalent assumptions can shift the perceived the single hygroscopicity parameter  $\kappa$  for complex CCN by 100% or more



**Field Testing**



**NEAR-ROAD TESTING**



**SHIP EMISSIONS**

**Real World Simulations**



**CHASSIS DYNAMOMETER**



**ENVIRONMENTAL CHAMBER**

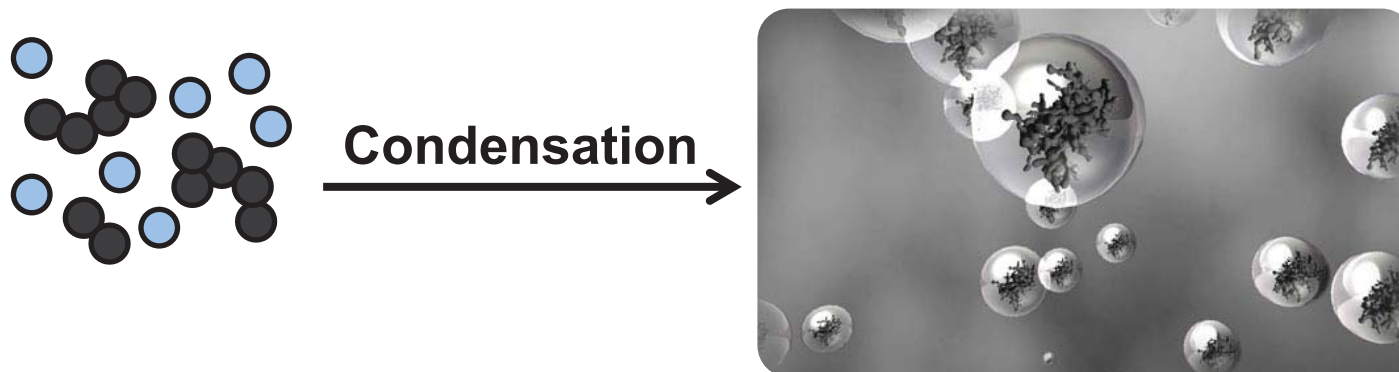
**Lab Tests**



**MIXING STATE FLOW TUBE**

**Increasing Level of  
Aerosol BC Composition Complexity**

## OUR APPROACH TO COMPLEX HYGROSCOPIC PARTICLES



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

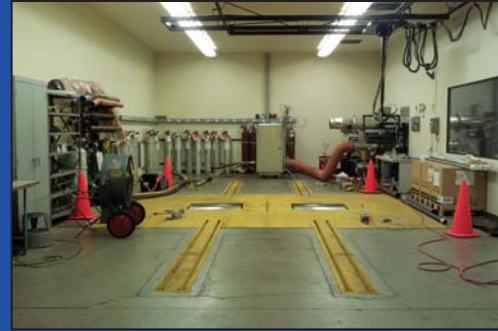
**(1) Provide Fast Measurement Techniques for Real-World BC Sources**

**(2) Characterize changes in Physical and Chemical Properties that can alter perceived Hygroscopicity of BC sources**

**(3) Refine Analysis Methods for complex CCN Mixing States**



**NEAR-ROAD TESTING**



**CHASSIS DYNAMOMETER**

# Part 1: Vehicle Emission Sources

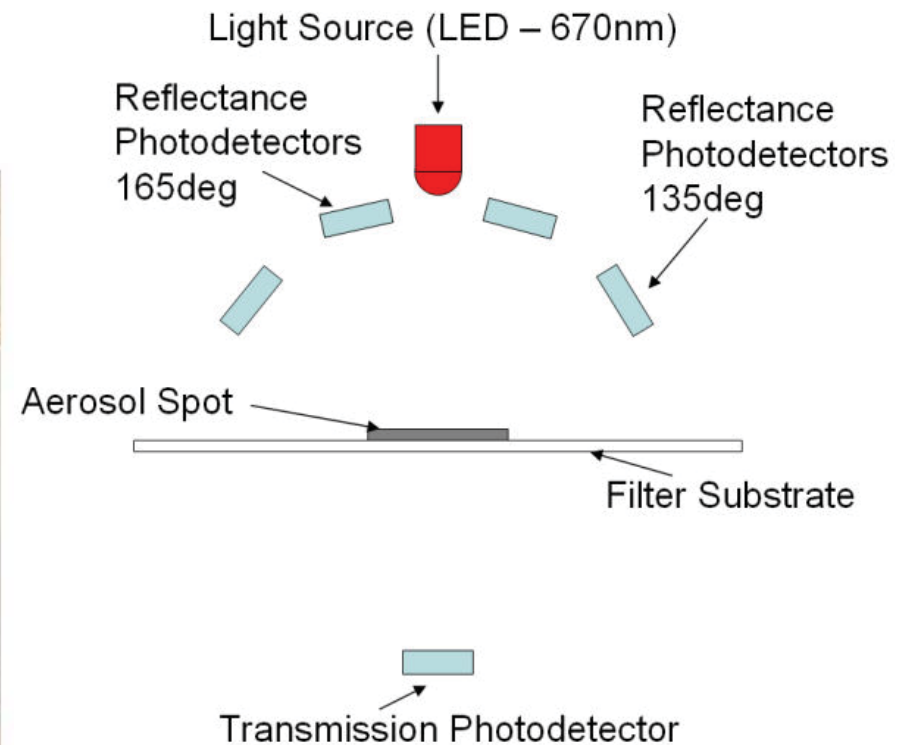
- 1) Traffic-related sources are a known emitter of particulate matter and black carbon aerosol
- 2) Exposure within 30 m of roadway traffic has been known to affect respiratory functions



# Multi-Angle Absorption Photometer

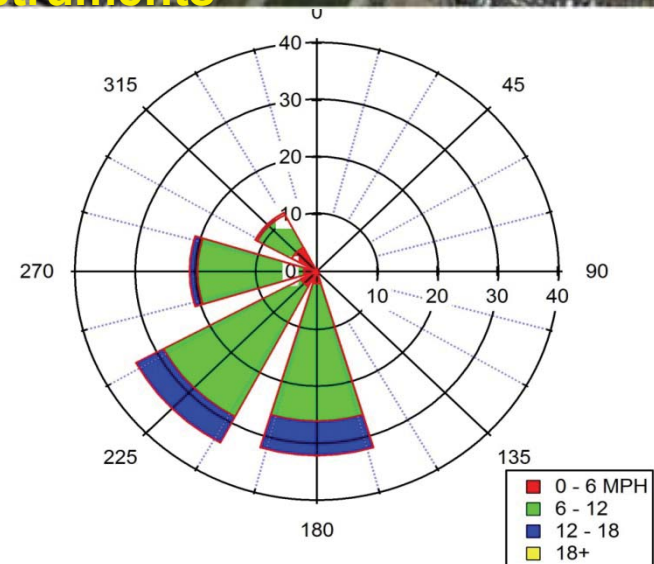


- ★ Black Carbon (BC) is measured with a Multi-Angle Absorption Photometer (MAAP)
- ★ The MAAP uses multiple light sources to determine the reflective aerosol properties

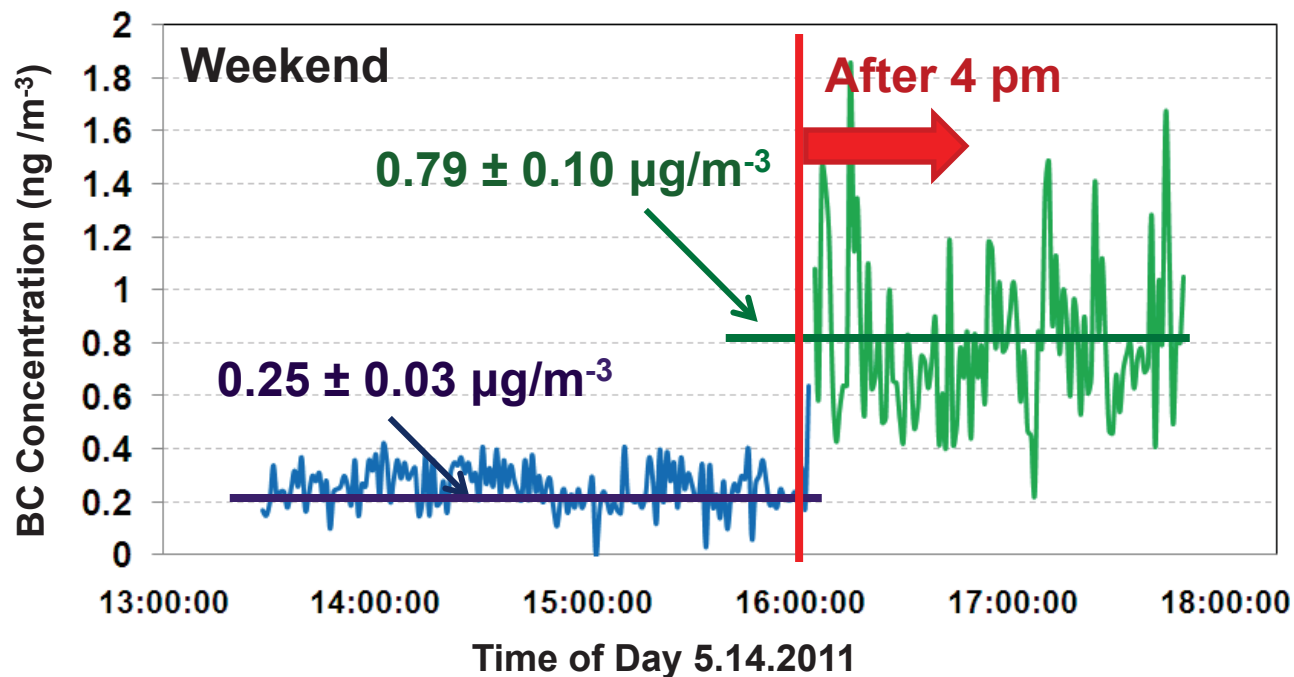
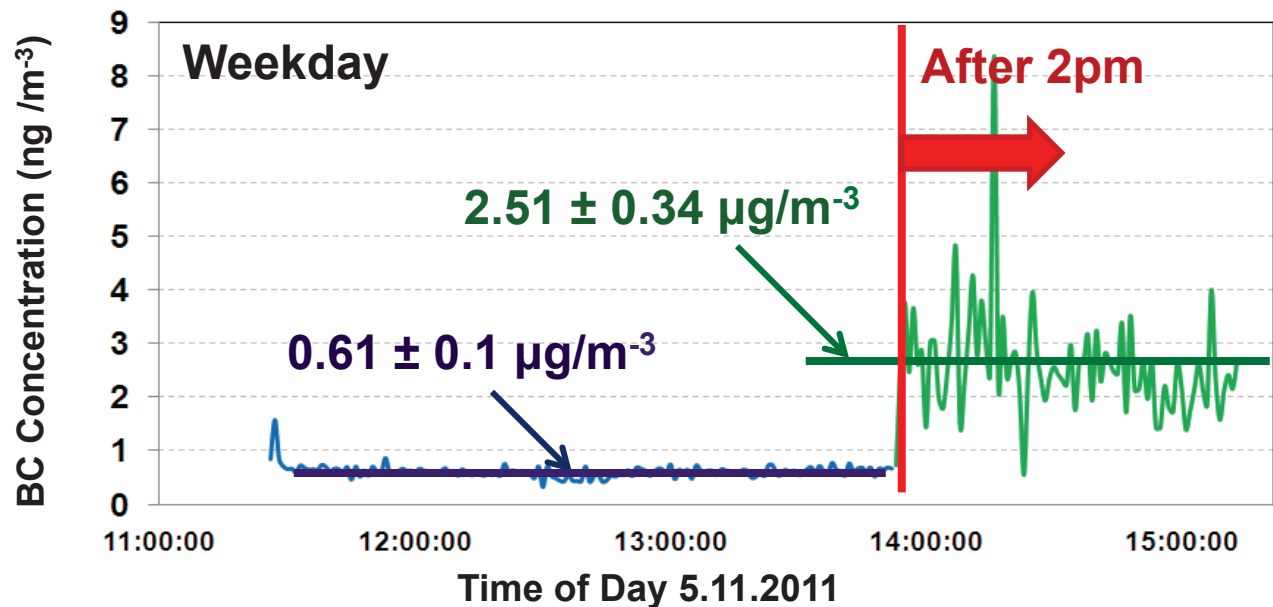


# I-710 Highway Field Measurements

- ★ Instrument trailer was located 15 meters downwind of freeway
- ★ Study focuses on measurements from two different days
  - ★ **Weekday - May 11<sup>th</sup> and**
  - ★ **Weekend - May 14<sup>th</sup>**



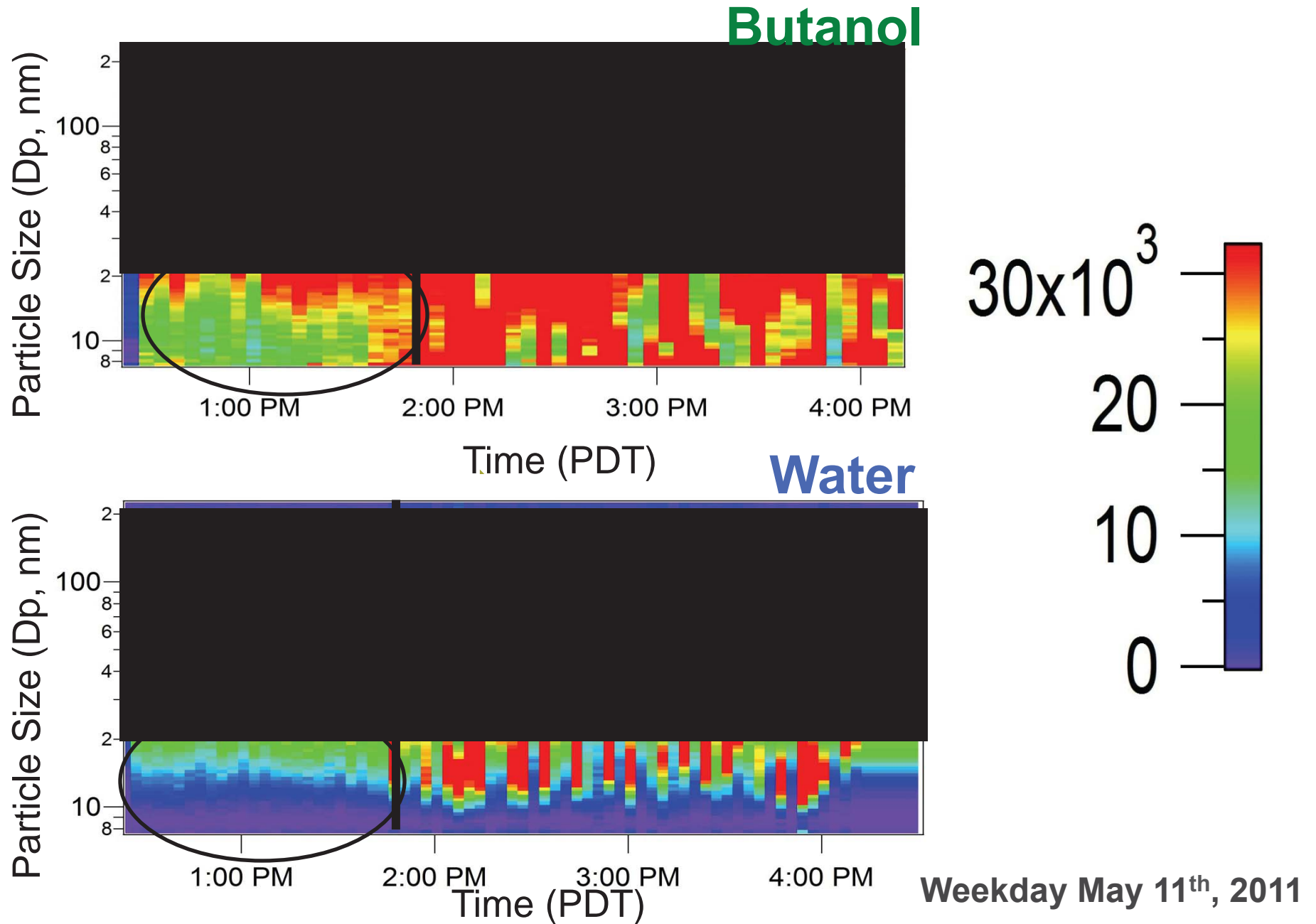
# Changes in BC Concentration due to Wind Direction



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

- ★ All instruments capture change in air mass
- ★ **Changes in Particle Number Concentration (size) and BC Mass Concentration (composition) correlate to changes in wind direction**

# Differences in Weekday Particle Distribution



# How are Particles sized?



**TSI 3081 Electrostatic Classifier**

- ★ Dry Particles are first size selected with an electrostatic classifying system

## **Scanning Mobility Particle Sizer (SMPS)**

- ★ Long DMA (TSI 3081) selects sizes in the range of 5 to 350 nm
- ★ Uses a Kr-85 radiation source to charge the aerosol
- ★ Then applies a voltage in which electron mobility will size select the particles

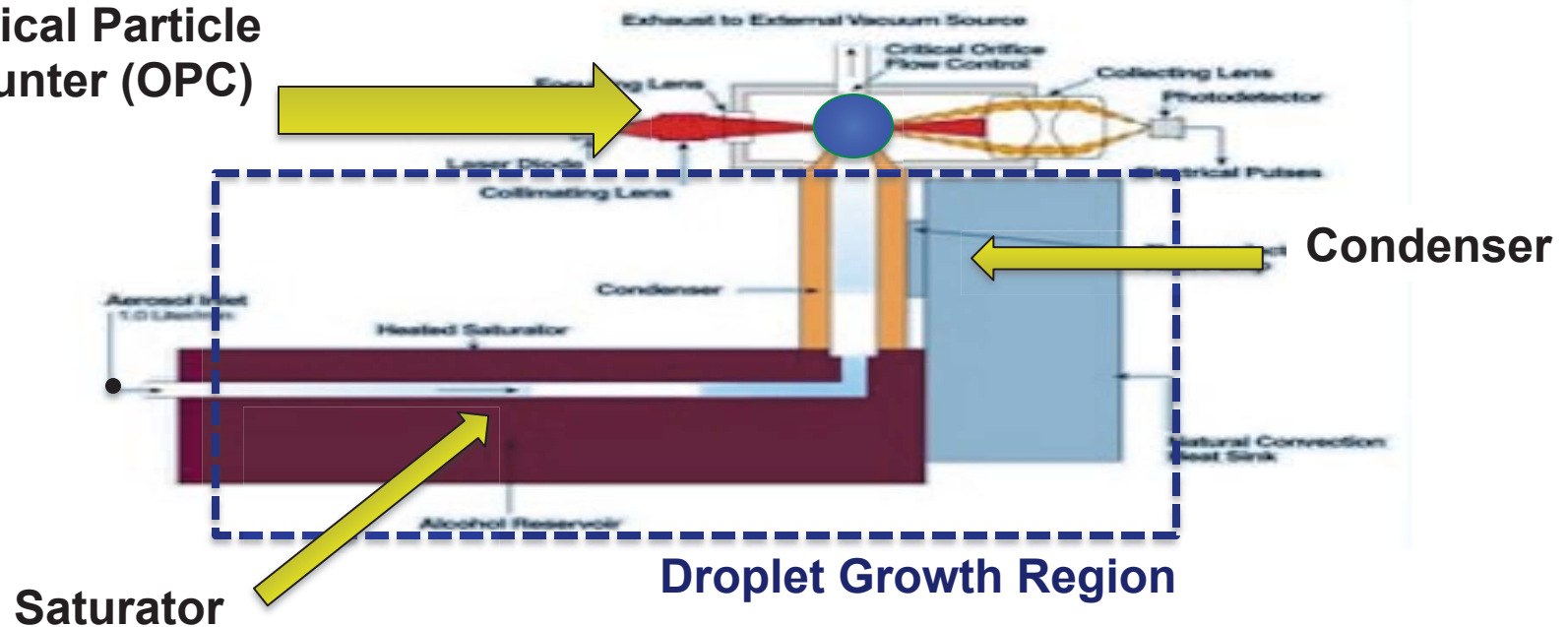
Mono-disperse particles then flow into the Condensational Particle Counter (CPC) to be counted



# 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)**

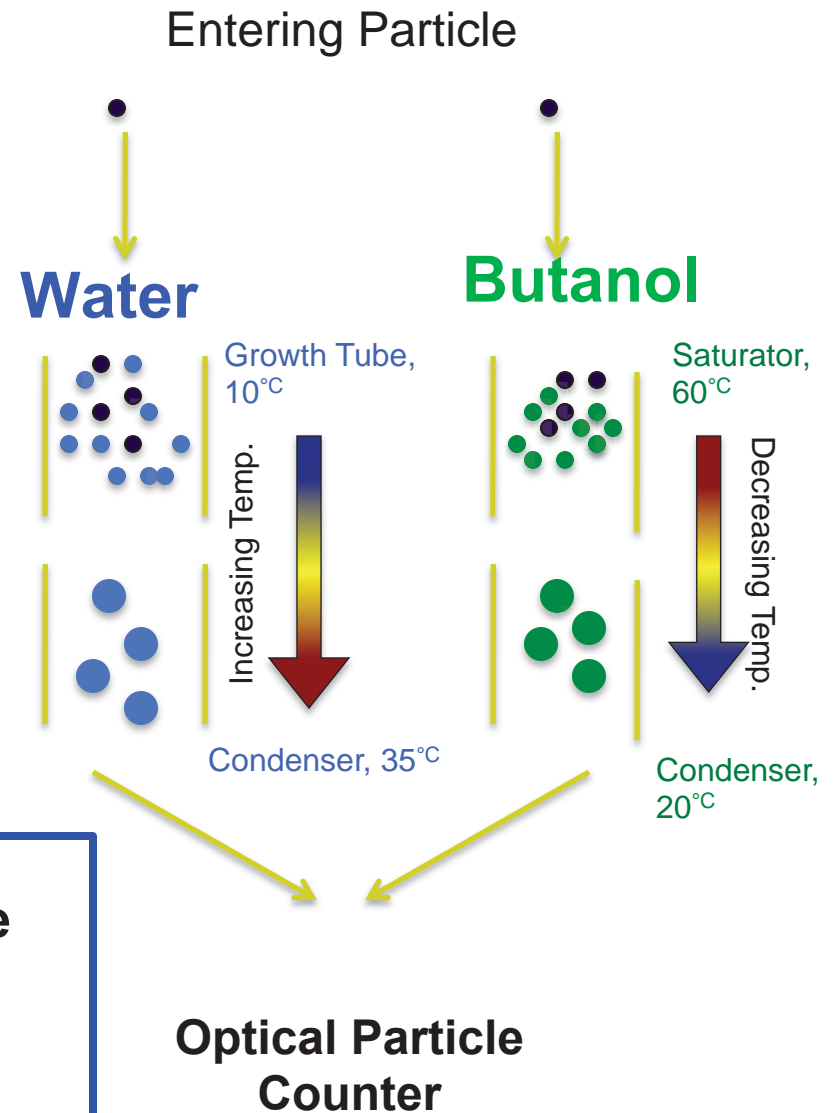
## Optical Particle Counter (OPC)



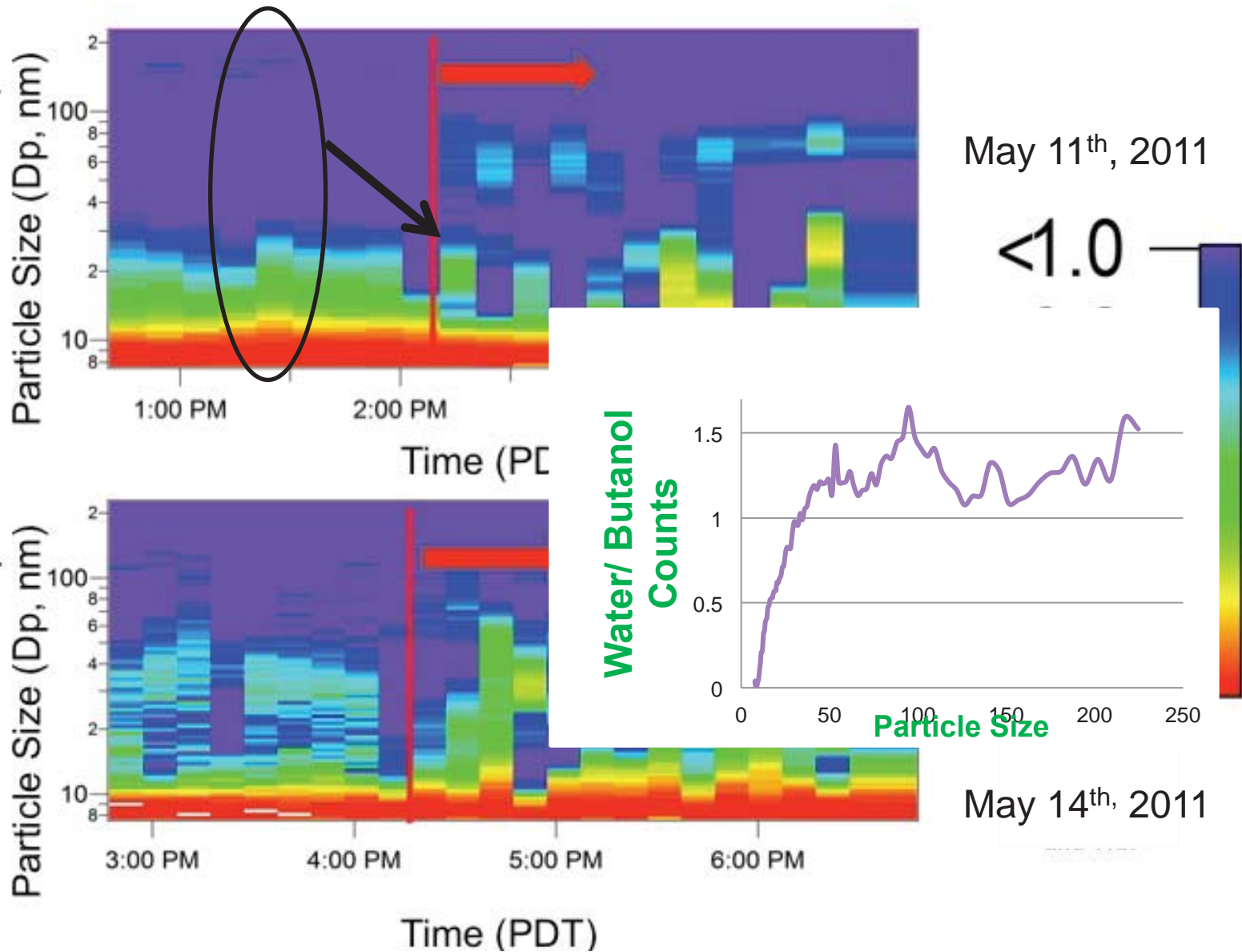
# Understanding Particle Counters

- ★ Water and Butanol CPCs exploit temperature and mass transfer principles to grow droplets
- ★ **Butanol** has a lower vapor pressure than and is larger in size (> Mol. wt) than air
- ★ Larger **Butanol** vapors diffuse more slowly than both air and water
- ★ Butanol vapors are cooled to condense and grow droplets

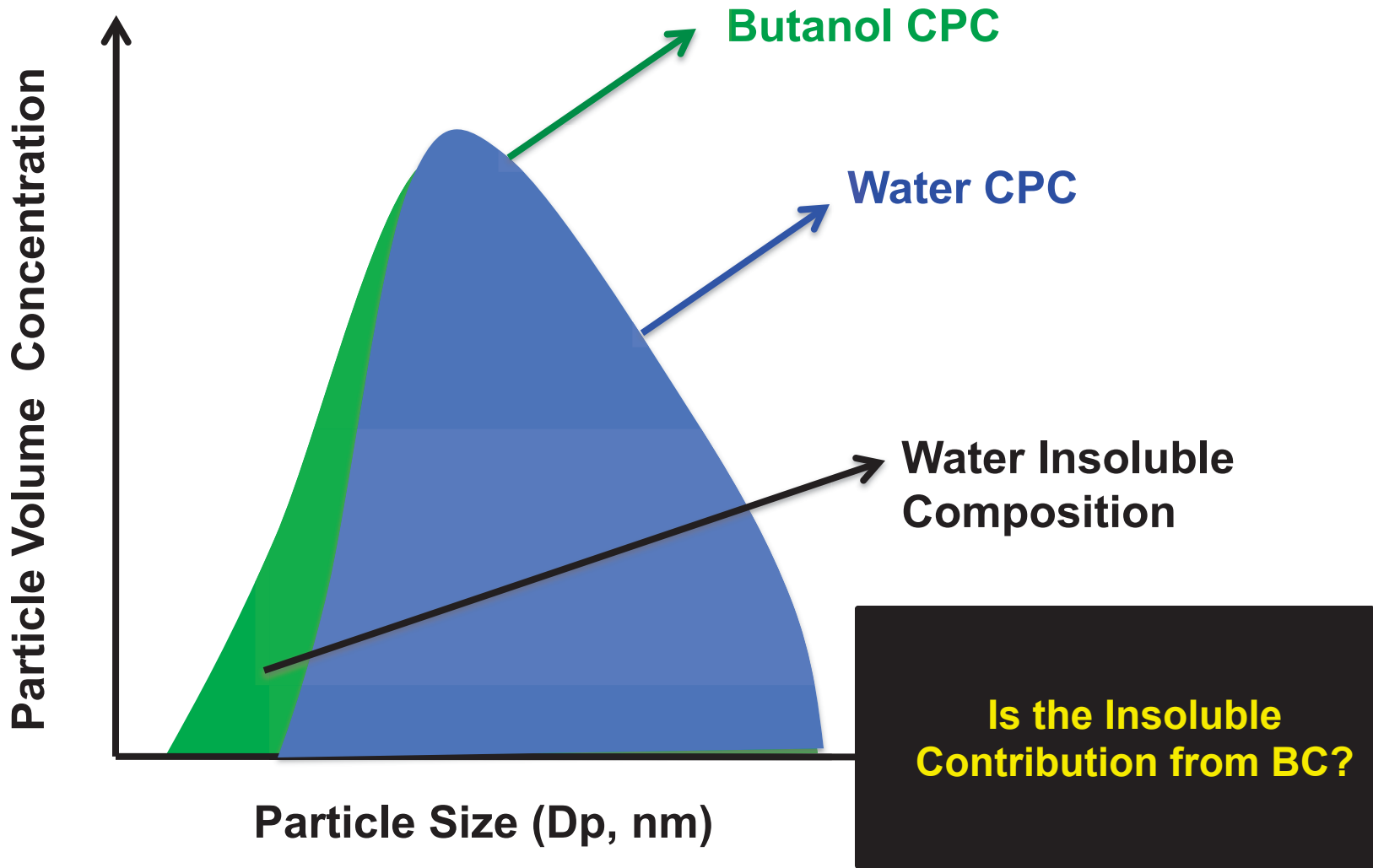
**Water** vapor from wetted walls diffuse *faster* than air and must be heated to condense on dry particles



# Counting Efficiency, Ratio of Water / Butanol



# Why the Difference?



# Summary



## Aerosol Science and Technology

Publication details, including instructions for authors and subscription information:  
<http://www.tandfonline.com/loi/uast20>

### A Unique Online Method to Infer Water-Insoluble Particle Contributions

Daniel Short<sup>ab</sup>, Michael Giordano<sup>ab</sup>, Yifang Zhu<sup>c</sup>, Phillip M. Fine<sup>d</sup>, Andrea Polidori<sup>d</sup> & Akua Asa-Awuku<sup>ad</sup>

<sup>a</sup> Department of Chemical and Environmental Engineering, University of California—Riverside, Riverside, California, USA

<sup>b</sup> College of Engineering, Center for Environmental Research and Technology, University of California—Riverside, Riverside, California, USA

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<sup>d</sup> South Coast Air Quality Management District, Diamond Bar, California, USA

Accepted author version posted online: 23 Apr 2014. Published online: 25 Jun 2014.

- ★ **BC is prevalent at all times in near-roadway measurements**
- ★ **The Butanol (TSI 3772) and Water based (TSI 3785) CPCs report significantly different particle size and number concentrations for traffic-related aerosol.**



# Summary



## Aerosol Science and Technology

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### A Unique Online Method to Infer Water-Insoluble Particle Contributions

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Accepted author version posted online: 23 Apr 2014. Published online: 25 Jun 2014.

★ **On average, there are more butanol particle counts than there are water particle counts for sizes less than 100nm.**

★ Below 30nm, the W-CPC is less than 50% efficient

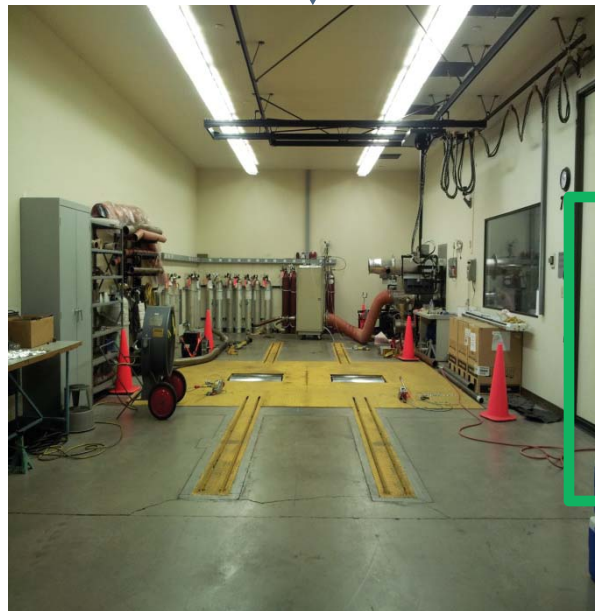
**Can we apply these measurements to controlled vehicle tests?**

# UCR CE-CERT Dynamometer Facilities

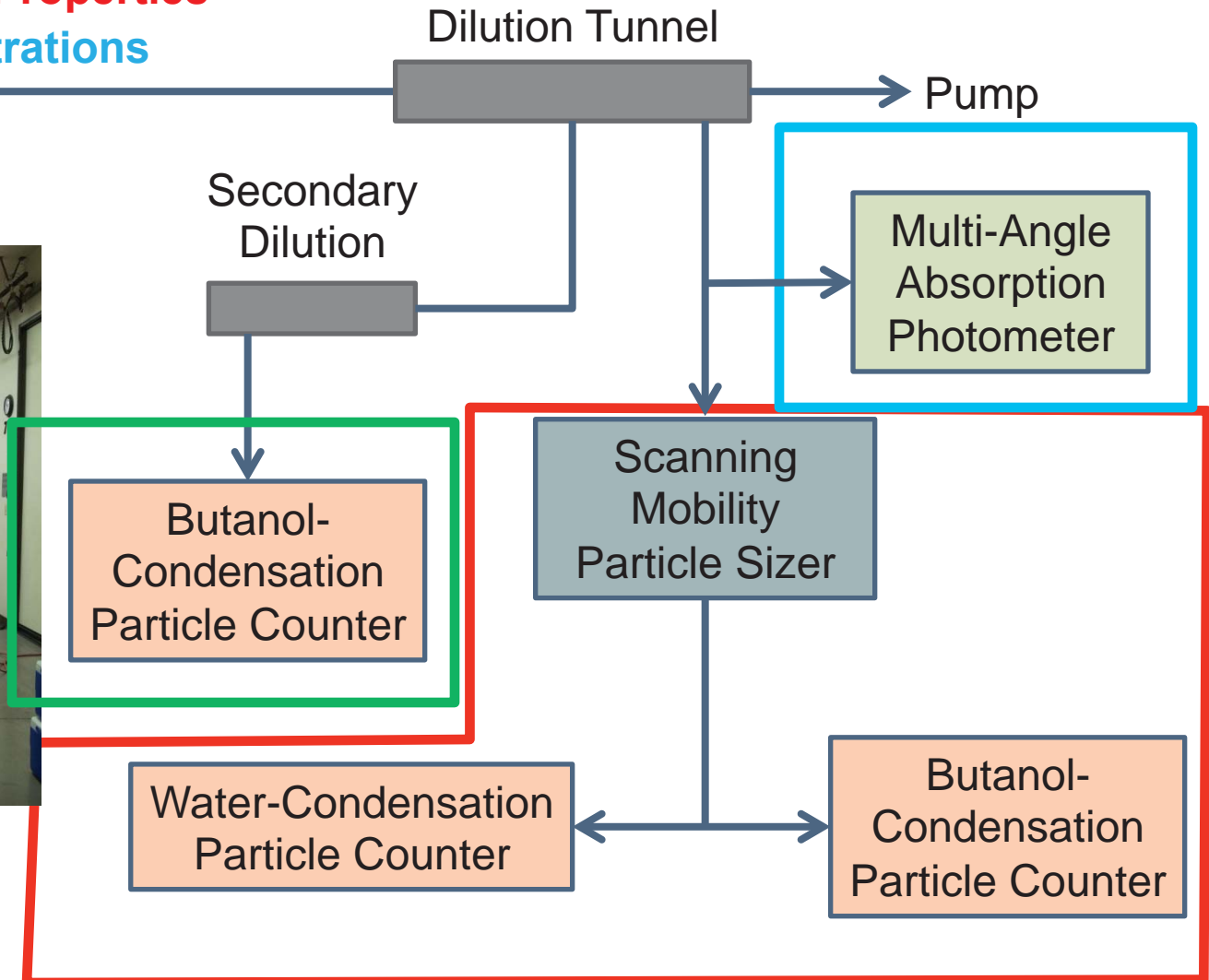
Total Particle Concentrations

Nucleation /Solubility Properties

Black Carbon Concentrations



Light Duty Chassis  
Dynamometer



# Impacts of BC Emissions



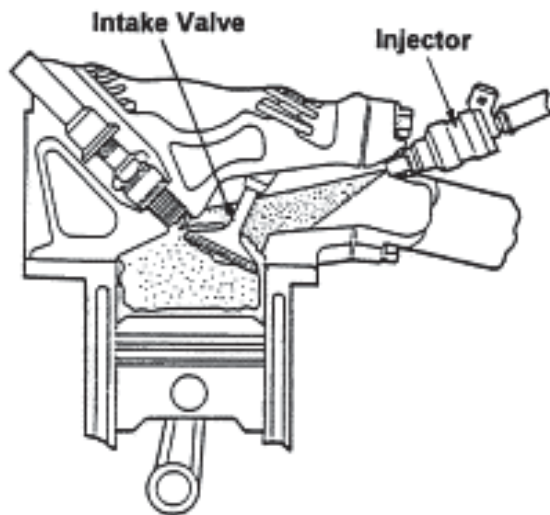
**How will changes in  
1) vehicle technology and  
2) fuels impact emissions?**

- ❖ Vehicles emit carbonaceous particles that can be water-insoluble and or black carbon concentration
  - ❖ Changes in water-insoluble/ BC composition will modify heterogeneous particle nucleating behavior
  
- ❖ Changes in fuel combustion will modify vehicular emissions
  - ❖ Gas phase, particle composition and concentration
  
- ❖ Changes in Vehicle Technology can modify vehicular emissions

## 2 Gasoline Engine Technologies Tested

### Port Fuel Injection (PFI)

### Gasoline Direct Injection (GDI)



PFI

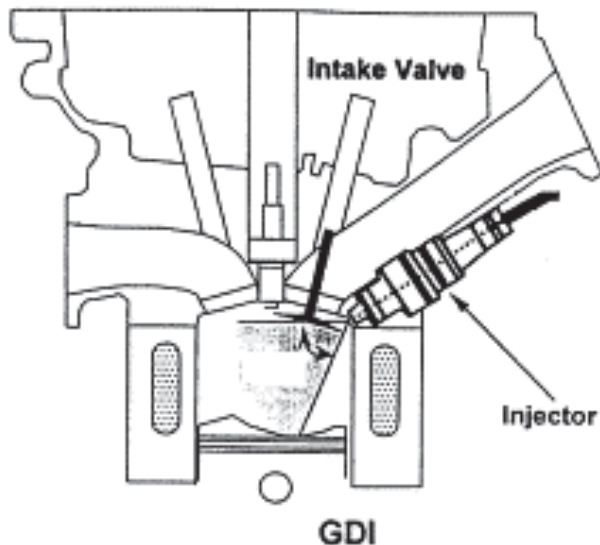
- **PFI is the most common light-duty engine system in use today**
  - Mixes fuel and air together before injection into the combustion chamber (Zhao et al. 1999)
- **Vehicles tested using this technology:**
  - 2007 Honda Civic and Dodge Ram
  - 2012 Toyota Camry



## 2 Gasoline Engine Technologies Tested

Port Fuel Injection (PFI)

Gasoline Direct Injection (GDI)

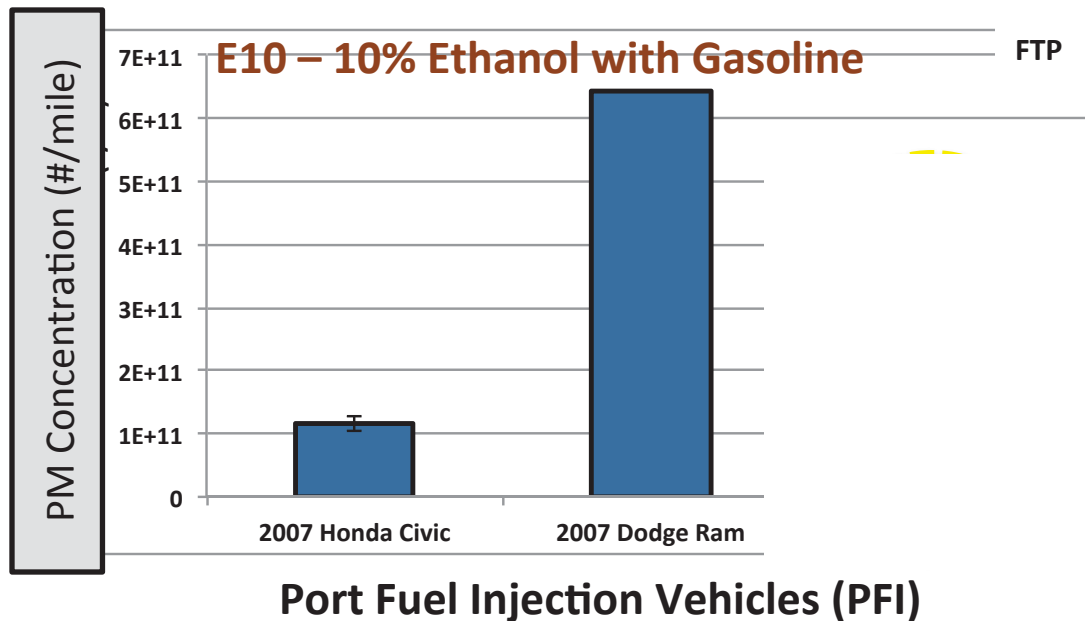


- **GDI Vehicles have increased fuel efficiency when compared to the typical PFI** (Zhao et al. 1999)
  - Gasoline and air are mixed in the combustion chamber;
- **Vehicles tested using this technology:**
  - 2012 Kia Optima
  - 2012 Chevy Impala



# PFI vs. GDI Engine Technology impacts PM Number

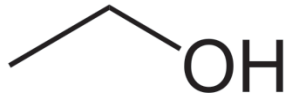
- **Larger Volume Engines will produce more Particles**
  - 2007 Dodge Ram- 5.7L 8-Cylinder Engine
  - 2007 Honda Civic- 1.8L 4-Cylinder Engine
- **The Newer PFI Technology can produce fewer particle emissions**
  - 2012 Toyota Camry- 3.5L 6-Cylinder Engine
- **PFI vehicles produce fewer particles than GDI.**
  - 10 times the order of magnitude of particle emitted by a GDI than a PFI





# Fuel Chemistry and Alcohol Blends

Ethanol



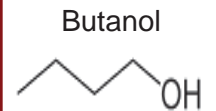
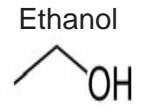
- ❖ Molecular Weight = 46.07 g mol<sup>-1</sup>
- ❖ Flash Point is 15°C
- ❖ Renewable Fuel made from corn and other biomaterials
- ❖ Pure Form has a higher Octane Number than Gasoline
- ❖ **95% of U.S. gasoline contains ethanol fuel blend (E10)**




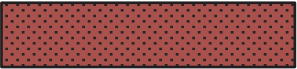
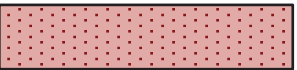
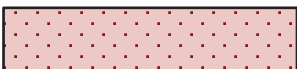

Butanol

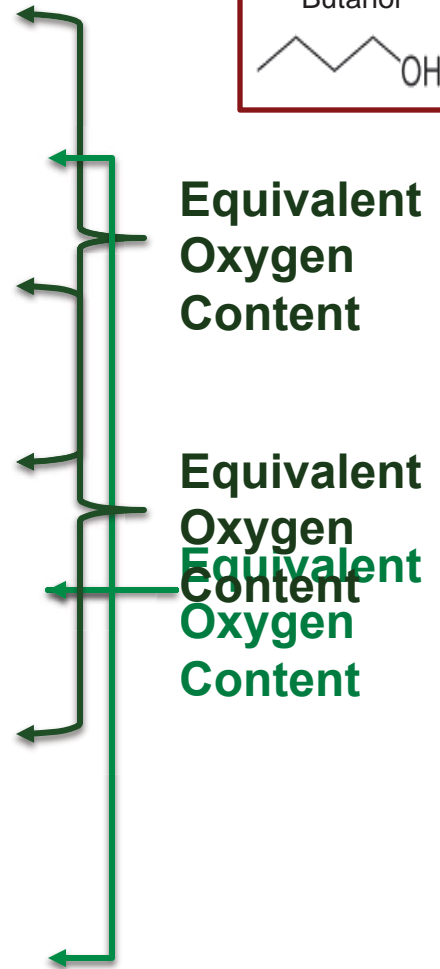


- ❖ Molecular Weight = 74.12 g mol<sup>-1</sup>
- ❖ Flash Point is 35°C
- ❖ Butanol can be produced using existing ethanol production facilities with few modifications
- ❖ **Butanol, compared to ethanol, has a lower vapor pressure and is more easily blended with gasoline**
- ❖ B16 is the oxygenated equivalent of E10 fuel

# Seven Alcohol Fuel Blends

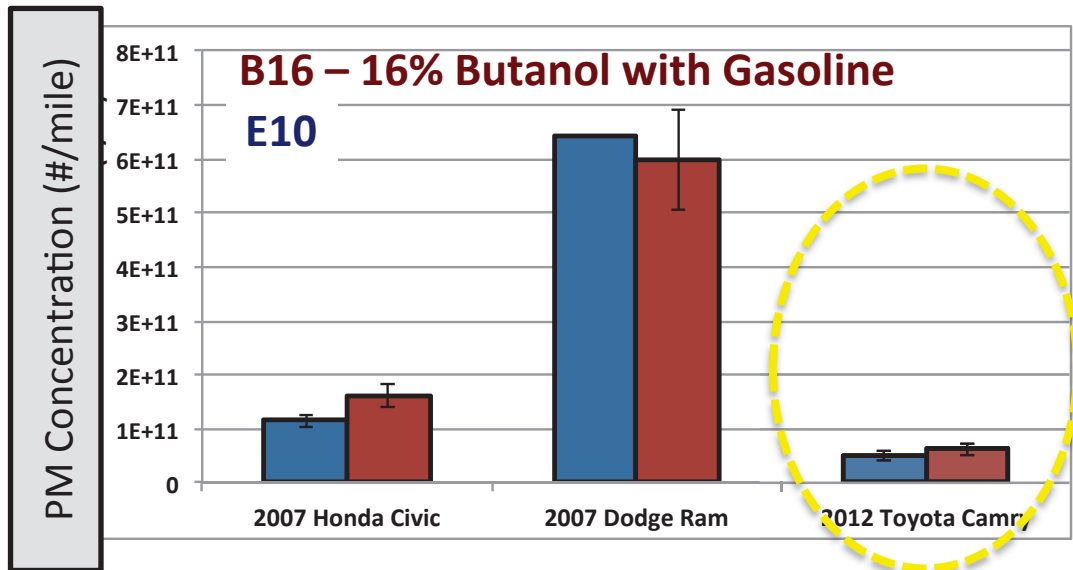


E10-		<b>10% Ethanol with 90% Gasoline</b>
E15-		<b>15% Ethanol with 85% Gasoline</b>
E20-		<b>20 % Ethanol with 80% Gasoline</b>
B16-		<b>16% Butanol with 84% Gasoline</b>
B24-		<b>24% Butanol with 76% Gasoline</b>
B32-		<b>32% Butanol with 6 % Gasoline</b>
E10/B8-		<b>10% Ethanol, 8% Butanol and 82% Gasoline</b>

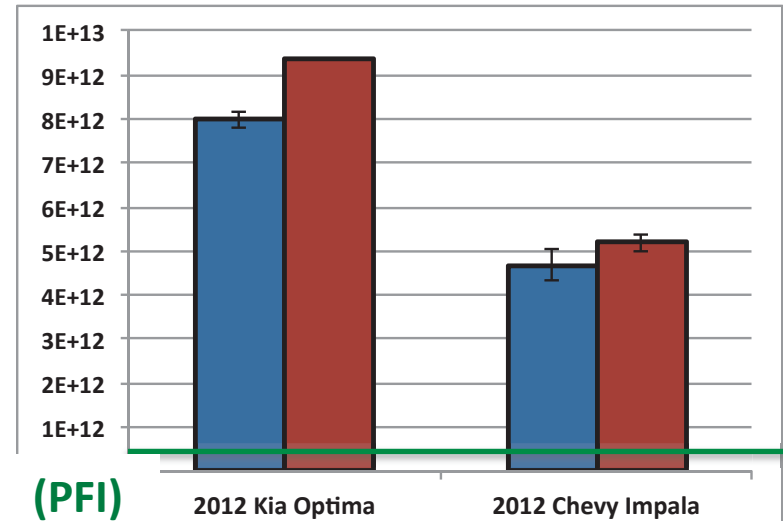


# B16 and E10 Emissions

- Again PFI vehicles produce fewer particles than GDI vehicles.
- B16 Fuel blends can produce more particles than E10 emissions
  - Butanol has a lower vapor pressure, easily mixed with gasoline, and more likely to form lower-vapor pressure products during combustion



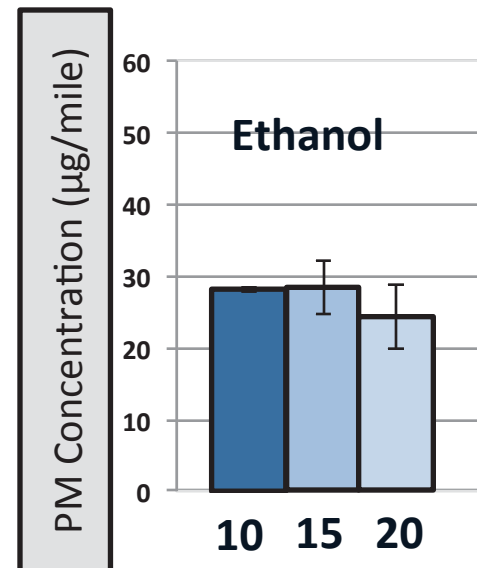
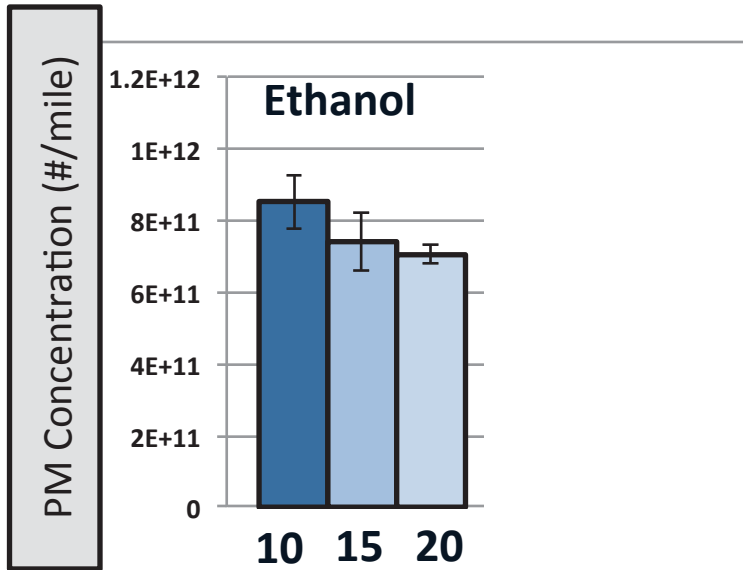
Port Fuel Injection Vehicles (PFI)



Gasoline Direct Injection (GDI)

# Fuel Blend Composition Affects PM Number

**Does Driving Cycle/  
Measurement Protocol  
Matter? Yes!**



Port Fuel Injection Vehicle (PFI)

- Higher Oxygenated Content for a given fuel blend reduces PM Number and Mass concentrations for the FTP cycle
- Equivalent oxygenated Butanol Fuels B24 and B32 produce less particles than Ethanol Blend Counterparts.

# Driving Cycles

- ❖ **Federal Test Procedure (FTP)**

- ❖ Developed by the Environmental Protection Agency



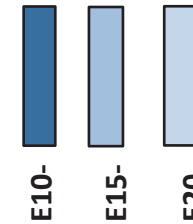
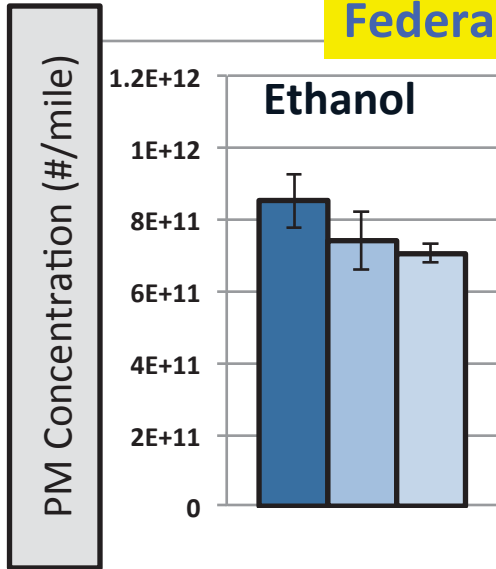
- ❖ **Unified Cycle (UC)-**

- ❖ Developed by the (California Air Resources Board)
  - ❖ better represents California driving styles

**AGGRESSIVE**

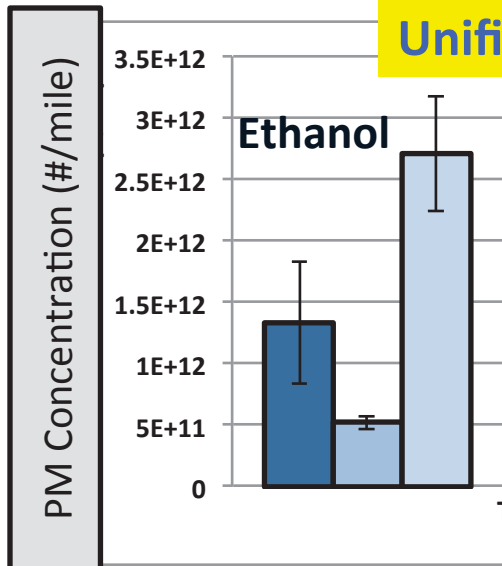
# Driving Cycle Affects PM Concentrations

## Federal Test Procedure



- More particles can be produced in the Unified Cycle with the Toyota Camry
- And there is a greater variation in fuel emission results

## Unified Cycle

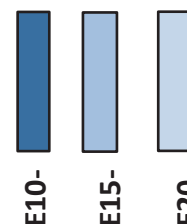
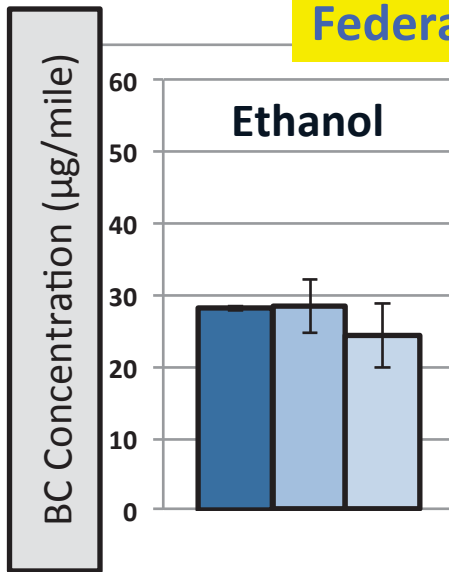


Port Fuel Injection Vehicle (PFI)



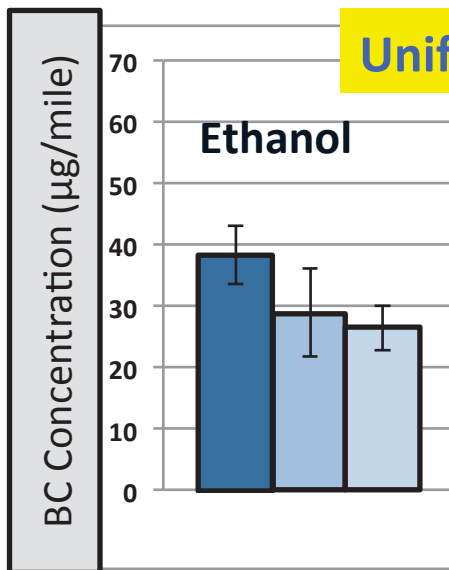
# Black Carbon Concentrations modified by Fuel Blends

## Federal Test Procedure



- More Black Carbon Produced in Unified Cycle; consistent with greater PN concentration

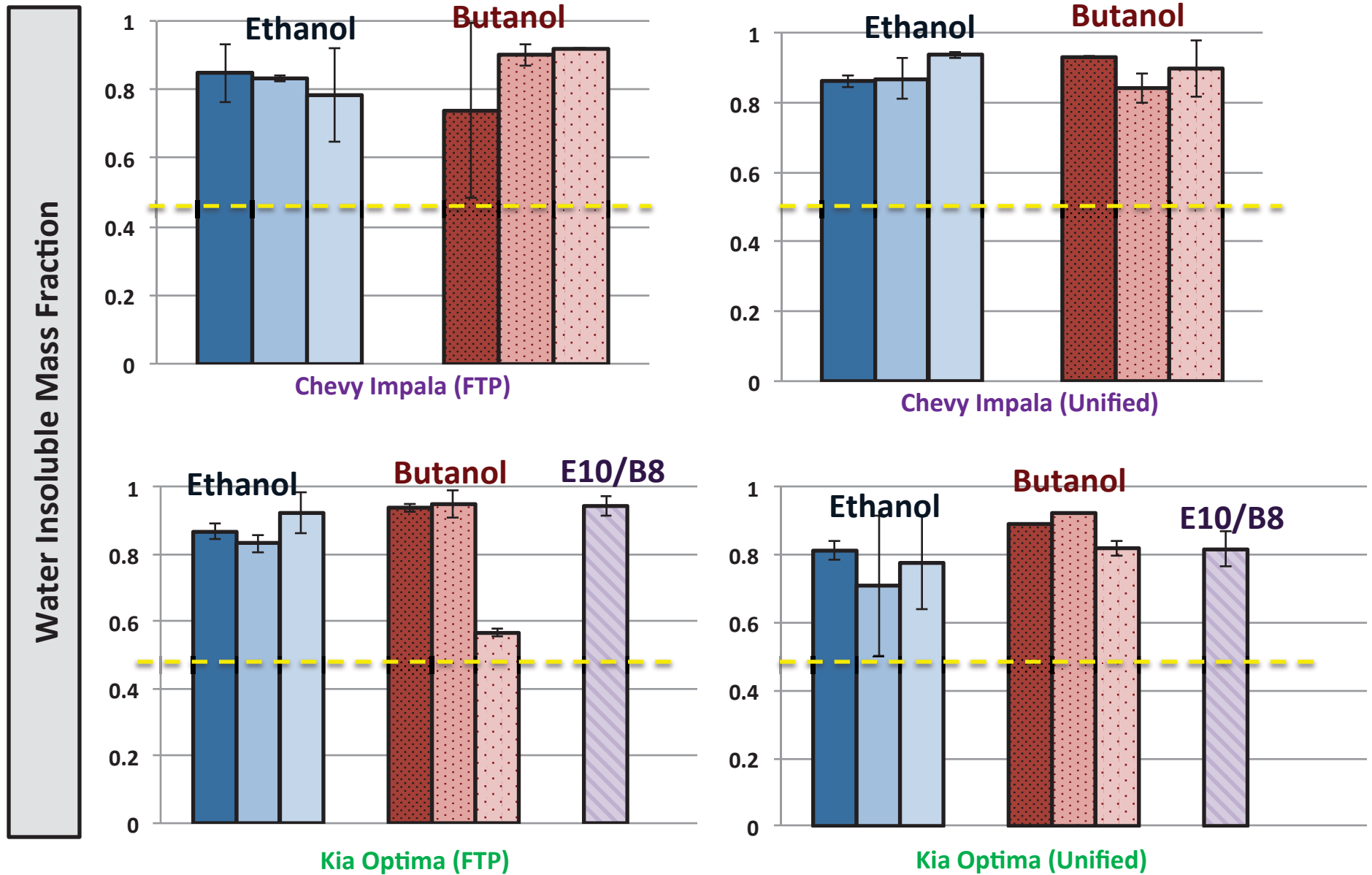
## Unified Cycle



Port Fuel Injection Vehicle (PFI)

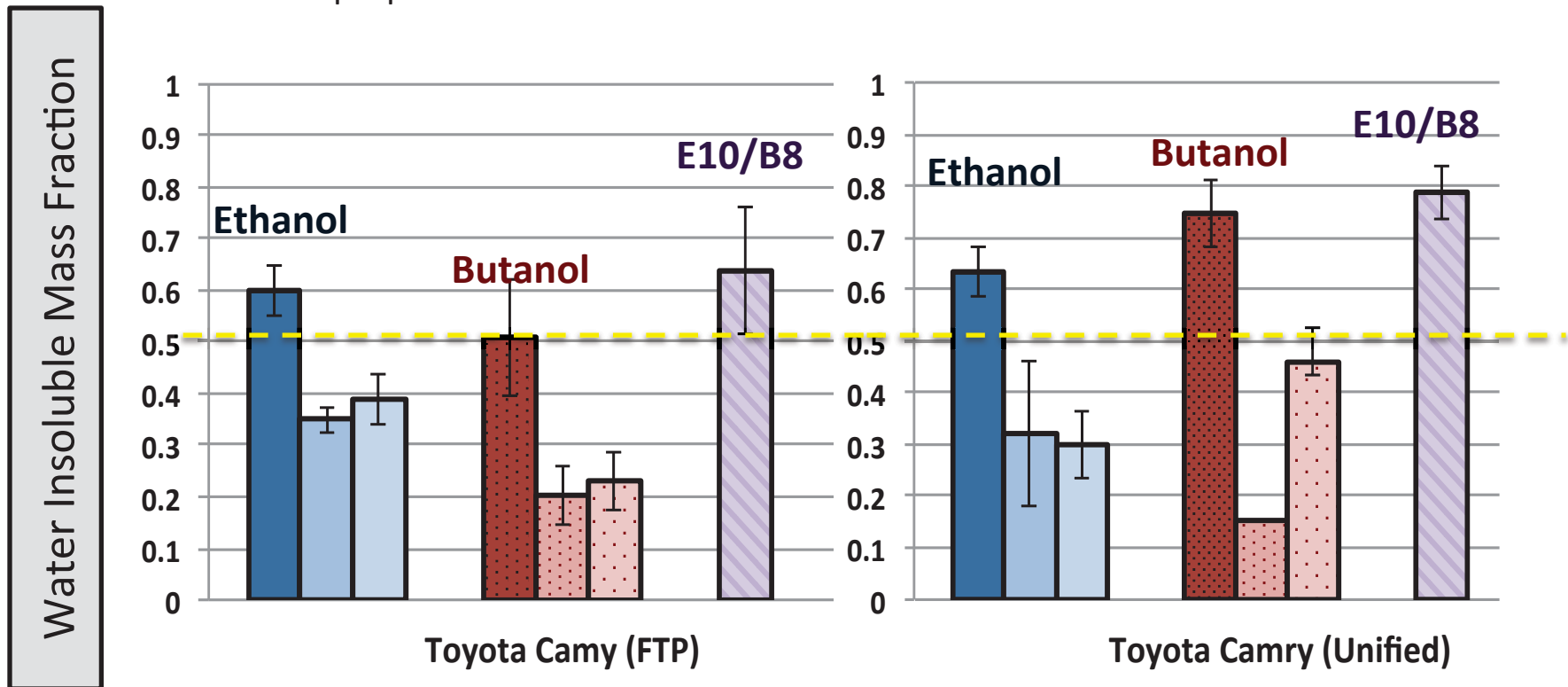
**The Particle Composition will vary by Fuel type and Driving Cycle**

# GDI Water Insoluble Mass Fraction

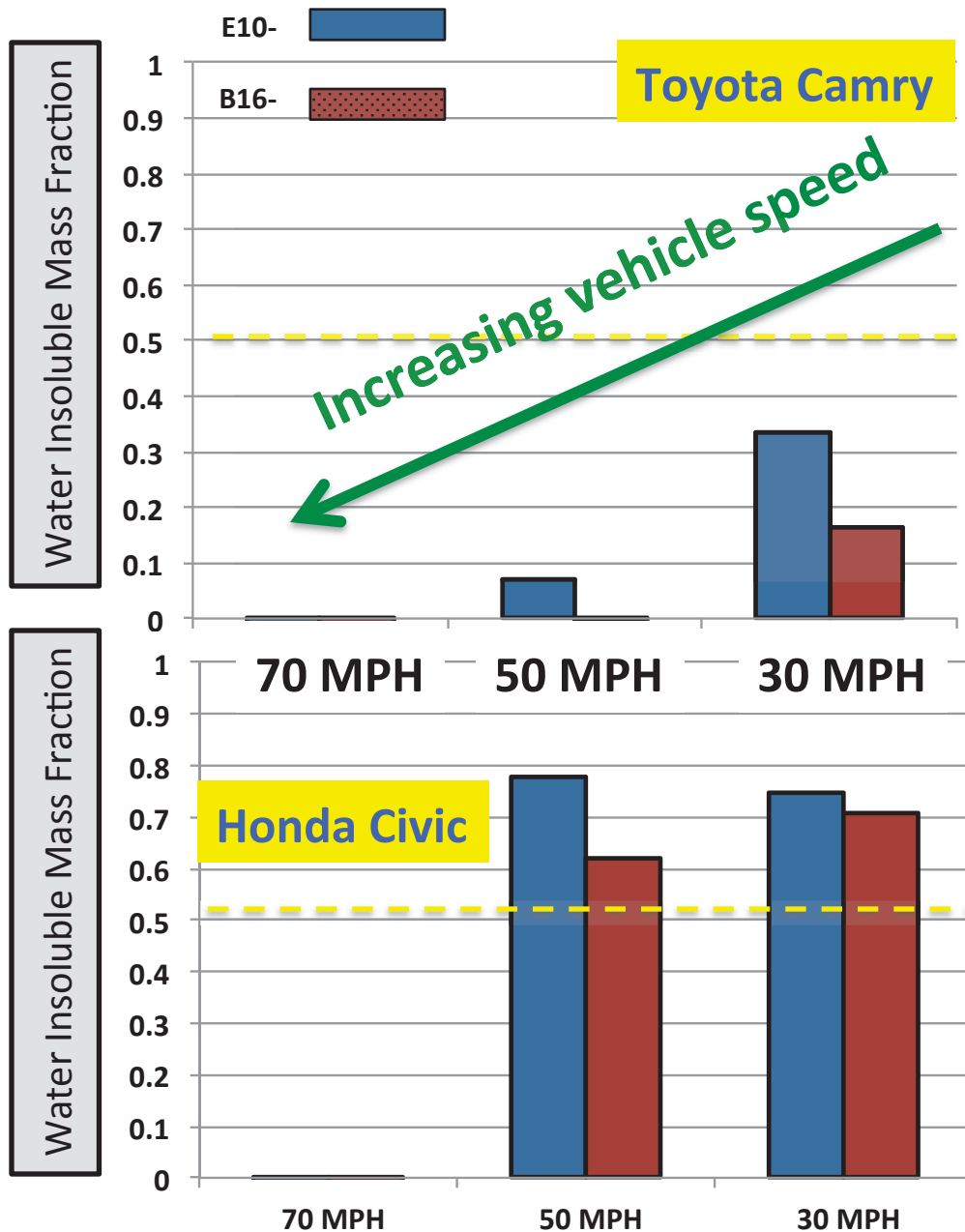


# PFI Water Insoluble Mass Fraction

- **2012 Toyota Camry produces mostly water soluble aerosol**
  - Oxygen content for and butanol the hygroscopicity of the particles
  - E10/B18 produces the most insoluble particles.
    - The properties of the fuels are not additive



# Higher speeds produce water-soluble particles



- The chemical composition of aerosol from steady-state emissions is **NOT** the same as the emissions tested on driving cycles.
- This is true for Varying Fuels, Vehicles, and Cycles

# Summary

- **On average, PN and BC concentrations were shown to decrease with larger concentrations of butanol and ethanol gasoline mixtures**
  - **Alcohol fuel blends can modify particle size, number, mass, and composition,**
- **GDI Vehicles emit 10 times more particles than PFI vehicles, even though they have better fuel economy.**
- **Of the vehicles tested the 2012 Toyota Camry had the fewest PM emissions for every fuel type**
- **PFI emissions can be more water-soluble compared to the GDI particle emissions**
- **Emission Particle hygroscopicity is dependent on vehicle speed.**

# Summary



## Evaluating Particulate Emissions from a Flexible Fuel Vehicle with Direct Injection when Operated on Ethanol and Iso-butanol Blends

2014-01-2768  
Published 10/13/2014

**George Karavalakis, Daniel Short, Vincent Chen, Carlos Espinoza, Tyler Berte, Thomas Durbin, Akua Asa-Awuku, and Heejung Jung**  
University of California

**Leonidas Ntziachristos and Stavros Amanatidis**  
Aristotle University of Thessaloniki

**Alexander Bergmann**  
Instrumentation and Control Systems

**CITATION:** Karavalakis, G., Short, D., Chen, V., Espinoza, C. et al., "Evaluating Particulate Emissions from a Flexible Fuel Vehicle with Direct Injection when Operated on Ethanol and Iso-butanol Blends," SAE Technical Paper 2014-01-2768, 2014, doi:10.4271/2014-01-2768.

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Fuel

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Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and iso-butanol blends



Georgios Karavalakis\*, Daniel Short, Diep Vu, Mark Villela, Akua Asa-Awuku, Thomas D. Durbin

University of California, Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), 1084 Columbia Avenue, Riverside, CA 92507, USA





ENVIRONMENTAL CHAMBER

## Part 2: BC from Biomass Burning Sources

# Biomass Burning (BMB)

- **Biomass burning is a widespread phenomena that is a major source of global aerosol emissions (2-5 petagrams C/yr)** (*Crutzen and Andreae, 1990*)
  - Burning can be anthropogenic: it is a common agricultural practice in land use management, especially in the tropics
  - It can also be biogenic: eg. Wildfires
- **Biomass burning emissions are a complex mixture gases and aerosols**



*The Rim Fire in Yosemite National Park (8/22/2013) which covered over 340 mi<sup>2</sup>.  
Source: NASA Earth Observatory*

- **Biomass burning aerosol emissions can directly absorb or scatter light**
- **Emissions from biomass can be cloud condensation nuclei (CCN) active** (*e. g. Englehart et al., 2012; Petters et al., 2009; Giordano et al 2013; 2014*)

# Getting closer to Ambient: *From Filters to Chambers*

★ Manzanita and Chamise are common shrubs in Southern California (Keeley and Davis, 2007)

★ in wildfires shrubs can account for nearly 80% of all biomass burned (Clinton et.al.,2006)

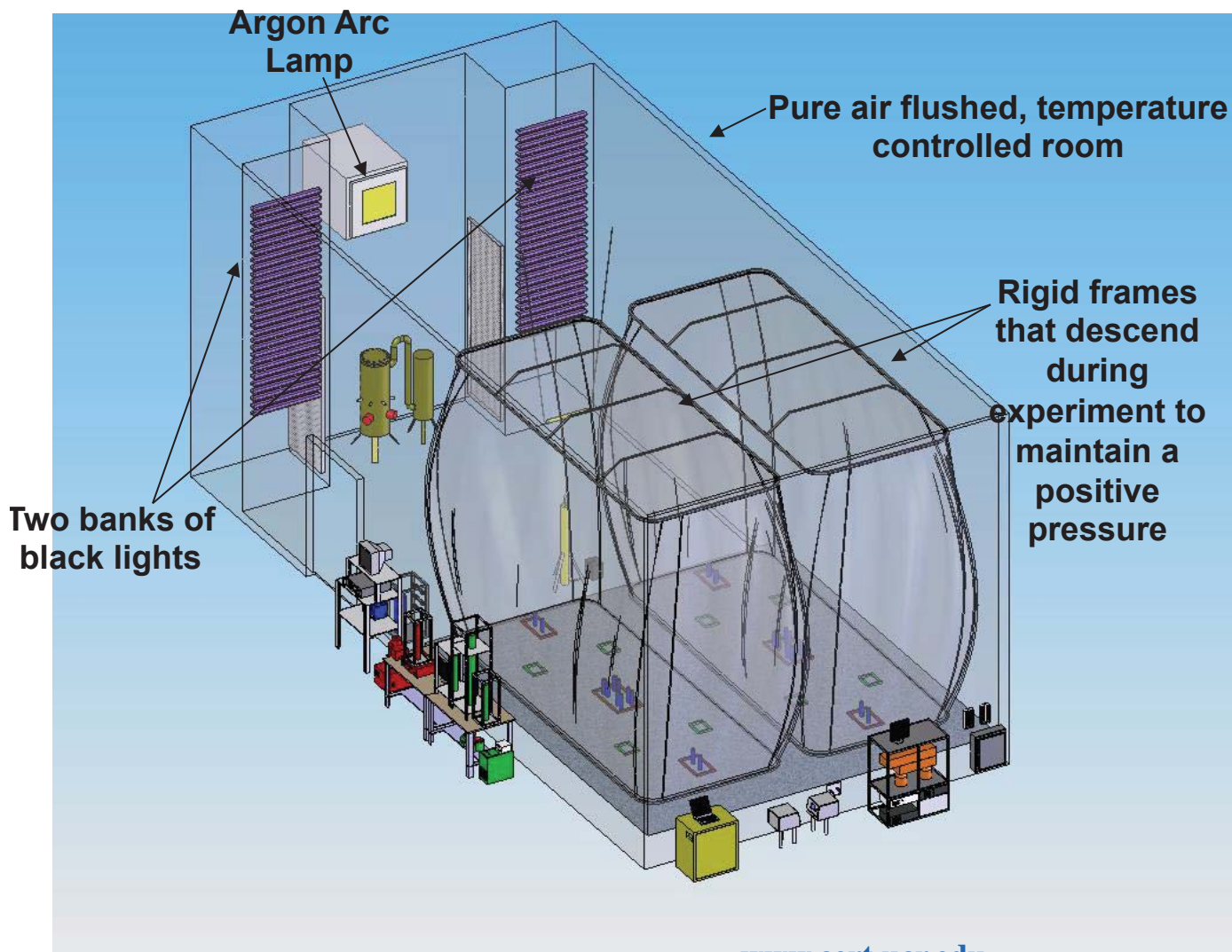


Manzanita  
Chamise

**We explore online aging of dilute concentrations of BMB aerosols with particular attention to CCN ability as a function of photochemical aging.**



# UCR/CE-CERT Environmental Chamber



- Dual 90 m<sup>3</sup> Teflon reactors
- Entire room is temperature controlled (5-45C ±1°C )
- 200 kW Argon arc lamp or 80 115 W 4-ft blacklights
- Humidification (dry <0.1 % to humid)
- Enclosure continually flushed with pure air

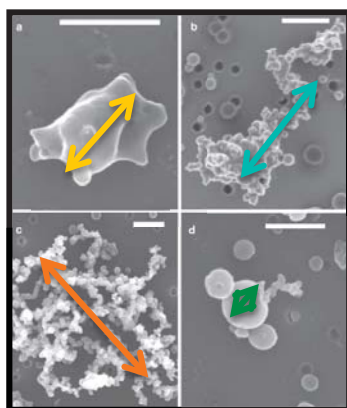


# CCN RELEVANT PROPERTIES OF BIOMASS BURNING



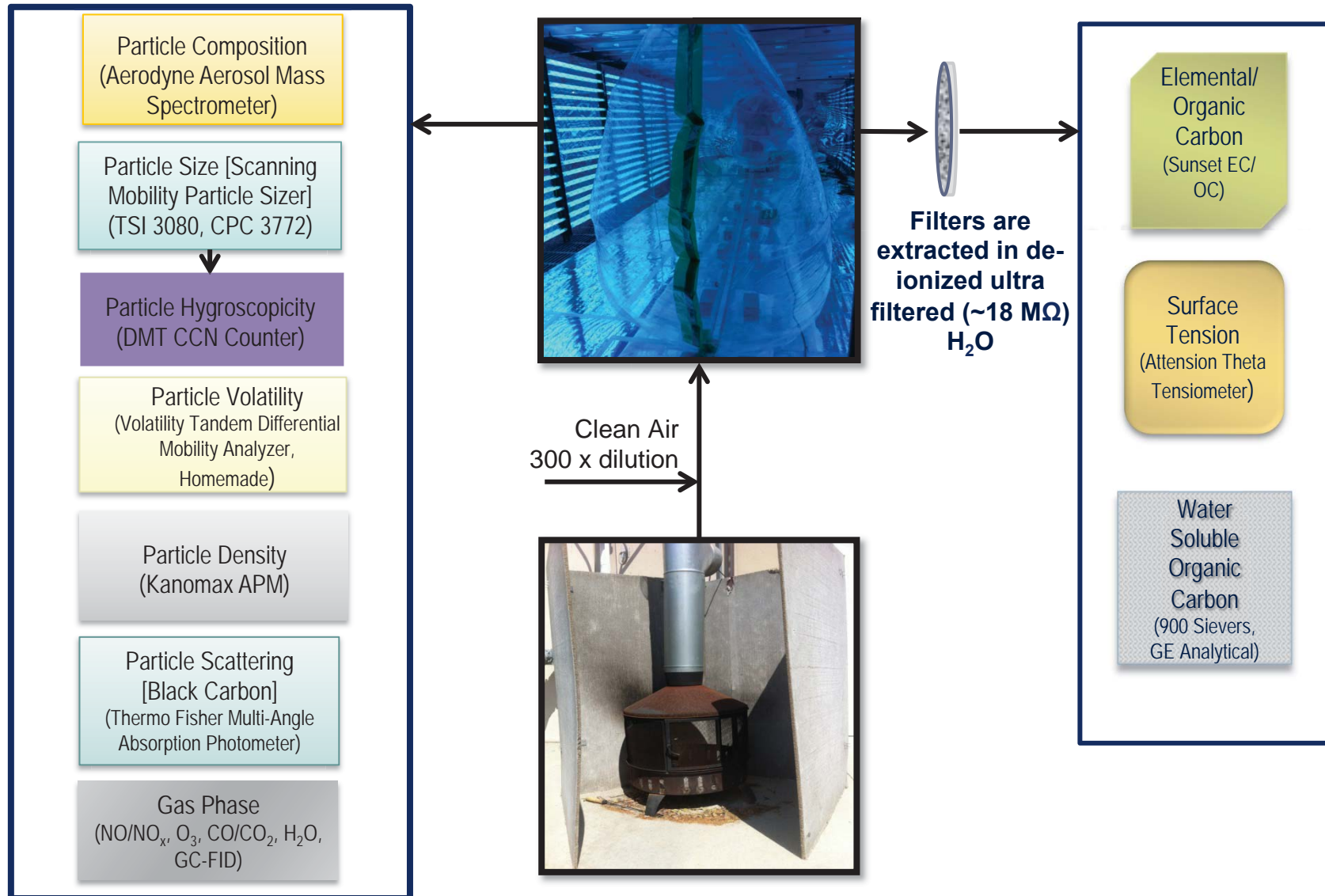
**(3) Time changes everything**

**(2) Chemistry is Important**



**(1) Size Does Matter**

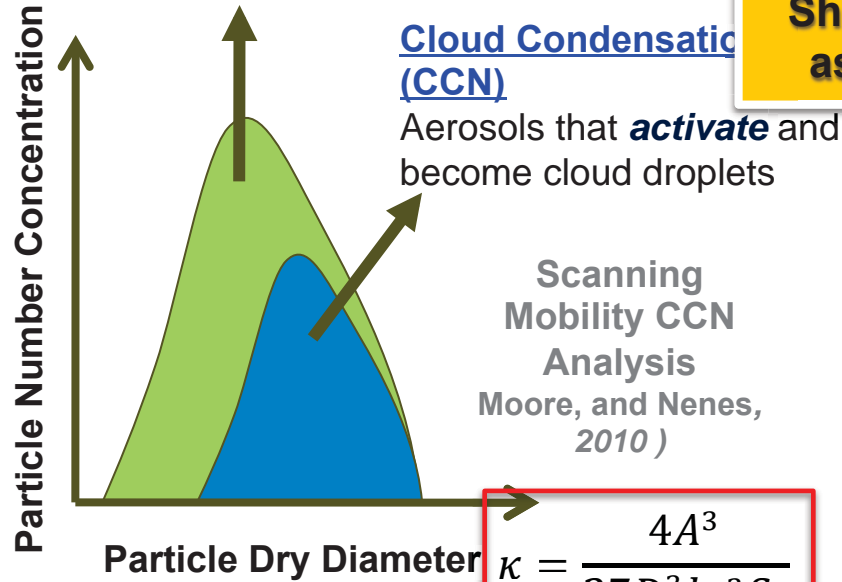
# Online Instrumentation Offline





# CCN Measurements

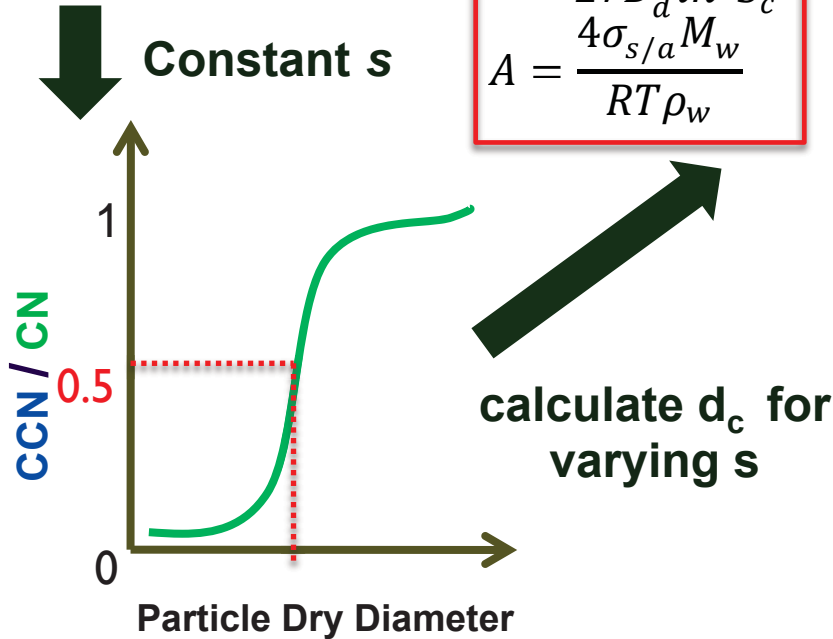
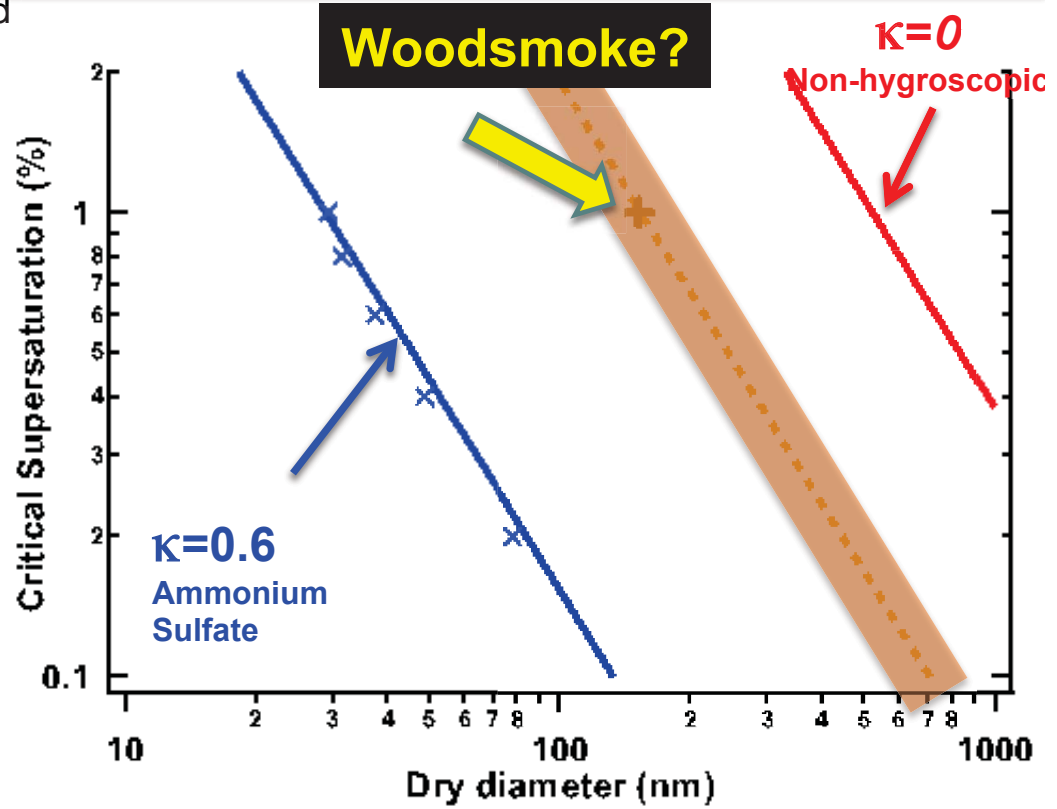
Condensation Nuclei (CN)  
Entire Aerosol Distribution



Shifts in **Kappa** are due to changes in composition, assuming constant water droplet surface tension

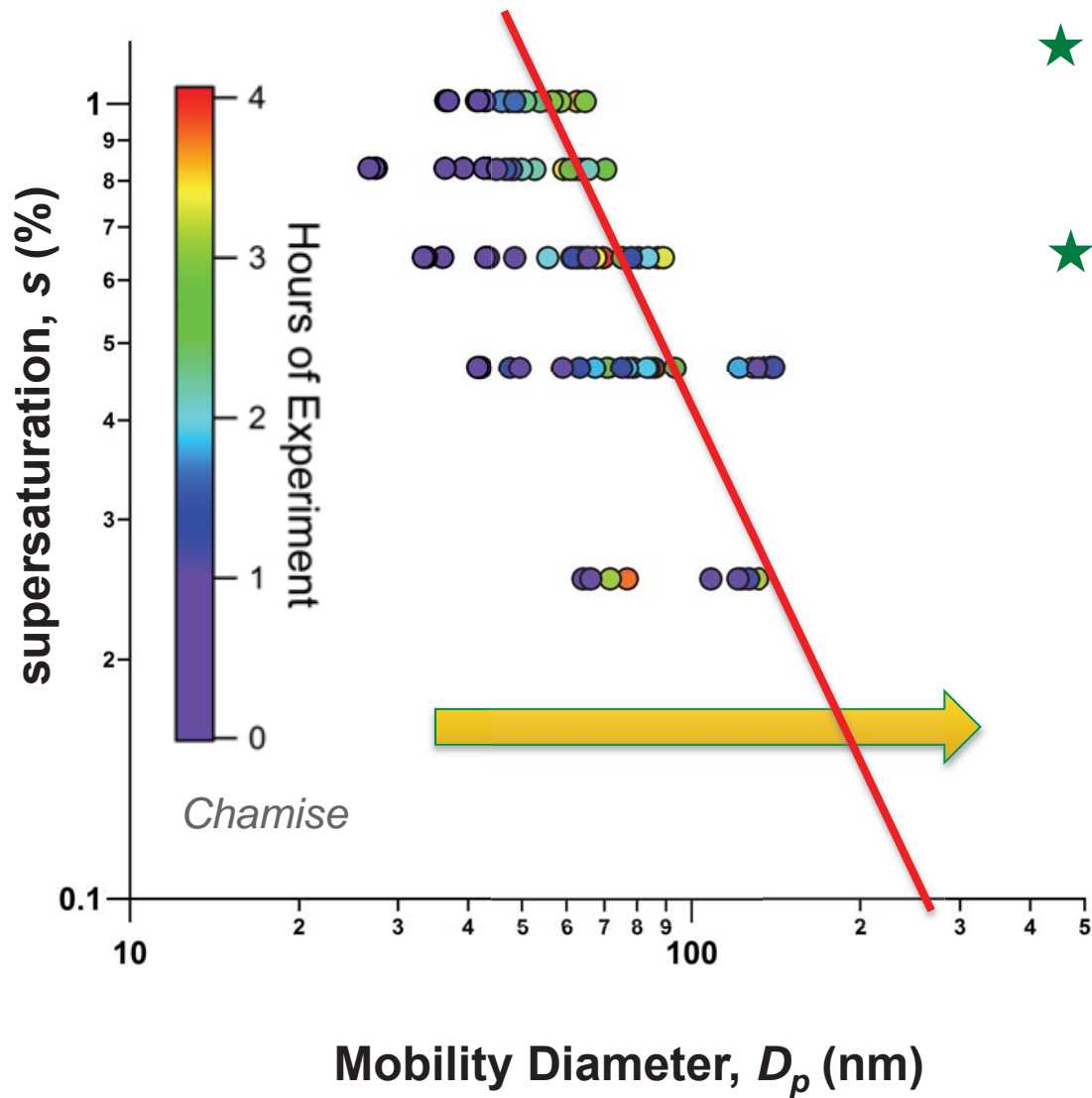
$$\kappa = \frac{4A^3}{27D_d^3 \ln^2 S_c}$$

$$A = \frac{4\sigma_{s/a} M_w}{RT\rho_w}$$



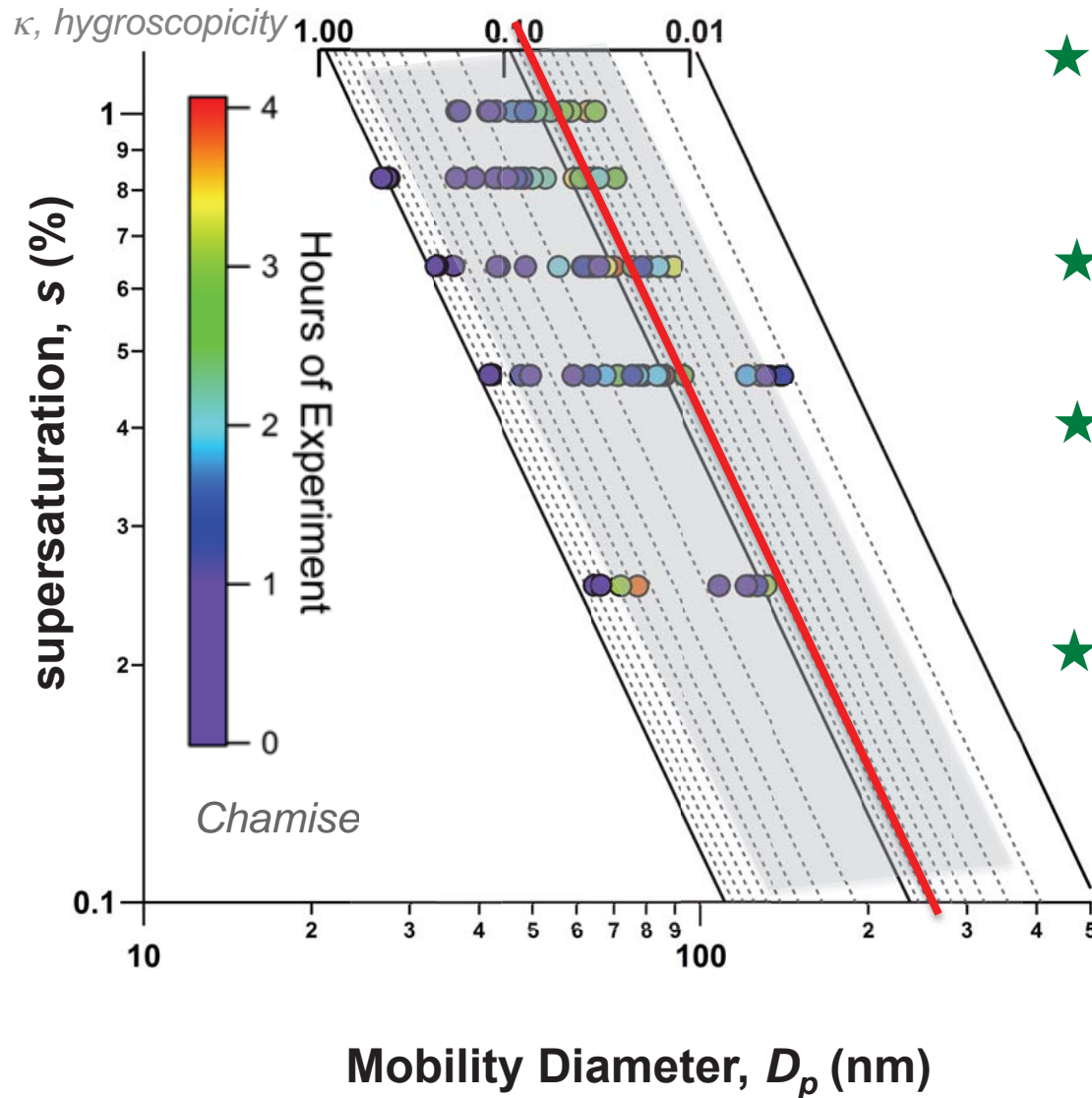
CCN Activity depends on:

- 1) Particle Size
- 2) Composition
- 3) Surface Tension

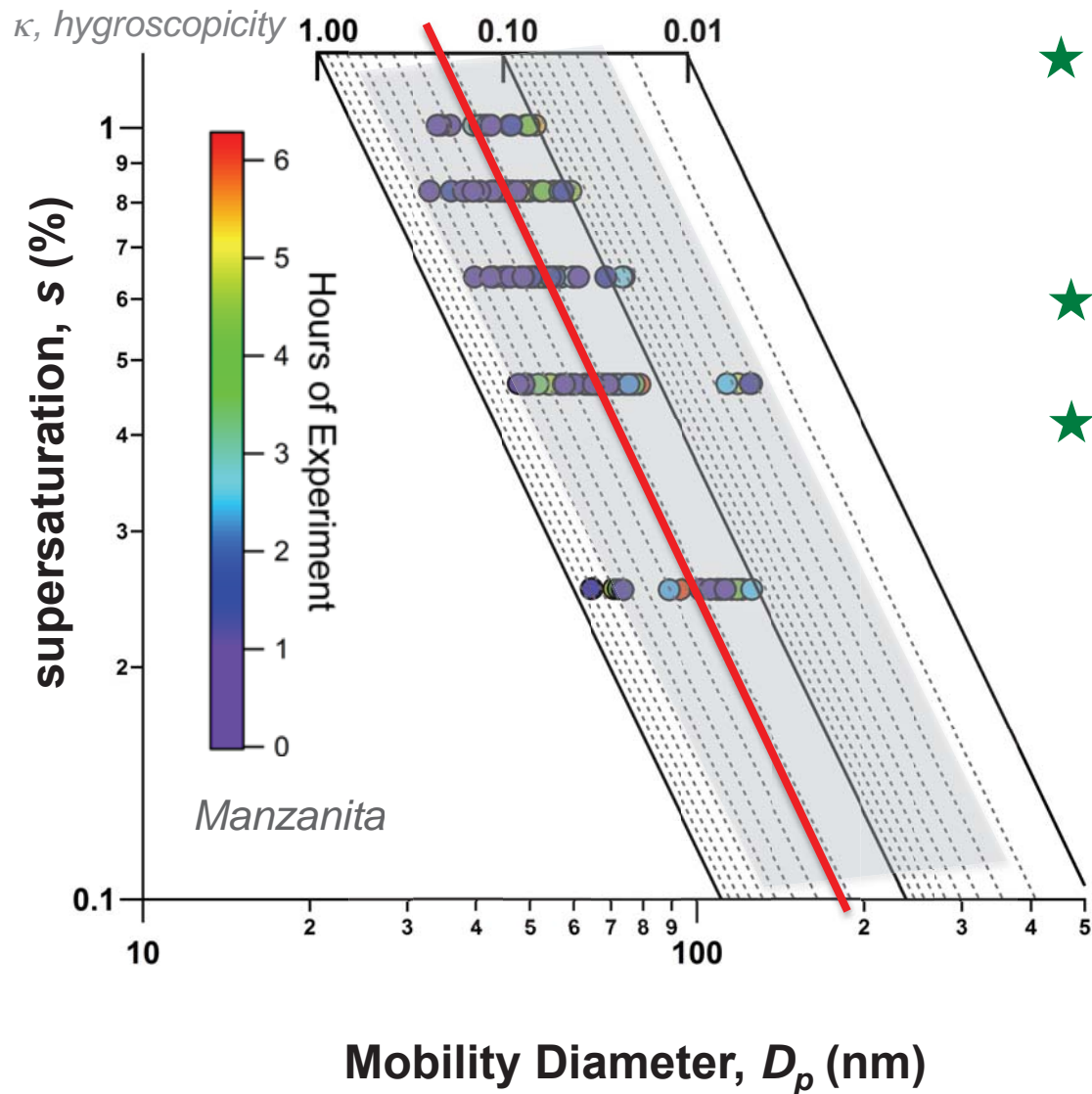


★ Chamise becomes less hygroscopic with time

★ Average  $\kappa \sim 0.098$



- ★ Chamise becomes less hygroscopic with time
- ★ Average  $\kappa \sim 0.098$
- ★ 2 OOM change in hygroscopicity,
- ★ Single Parameter,  $\kappa$ , can decrease from 1 to 0.04 within 4 hours of chamber ageing

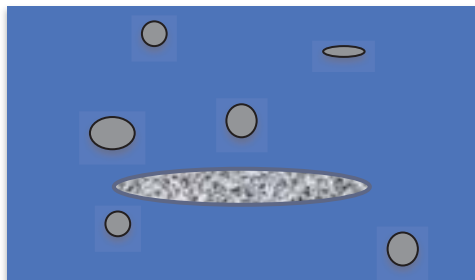
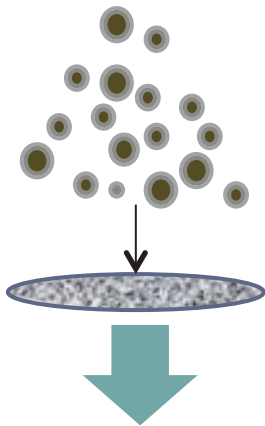


- ★ Manzanita also becomes less hygroscopic with time
- ★ Average  $\kappa \sim 0.238$
- ★ 2 OOM change in hygroscopicity

Why the Shift?

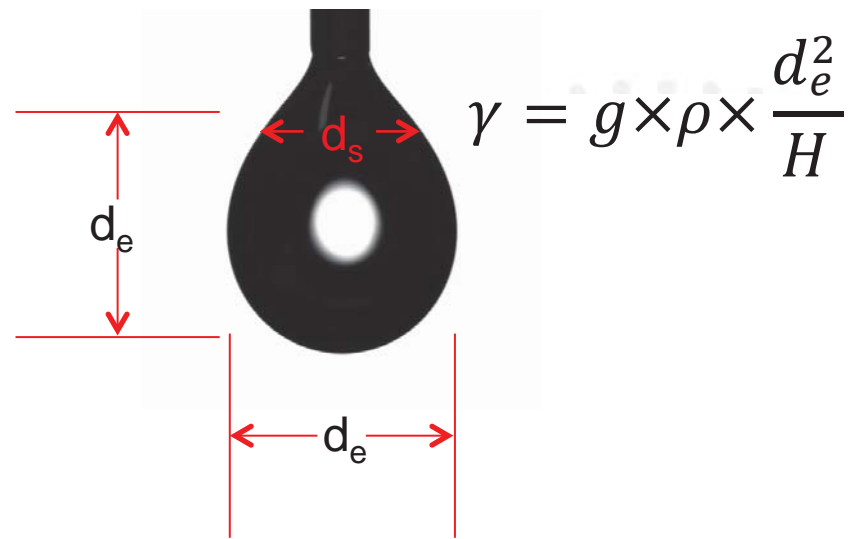
# Surface Tension Measurement

Aerosols are deposited onto a Teflon filter

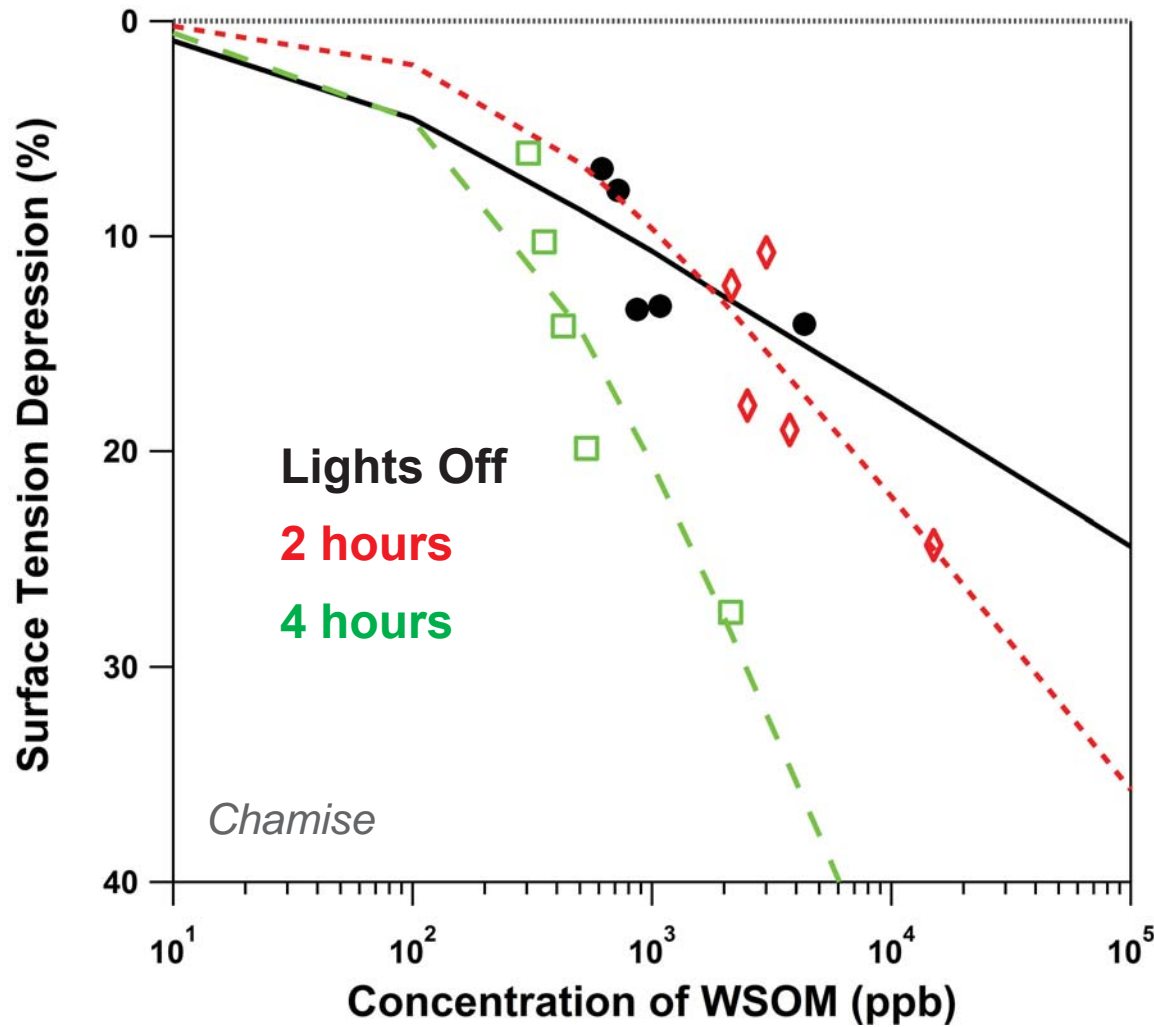


Filters are sonicated in MilliQ water

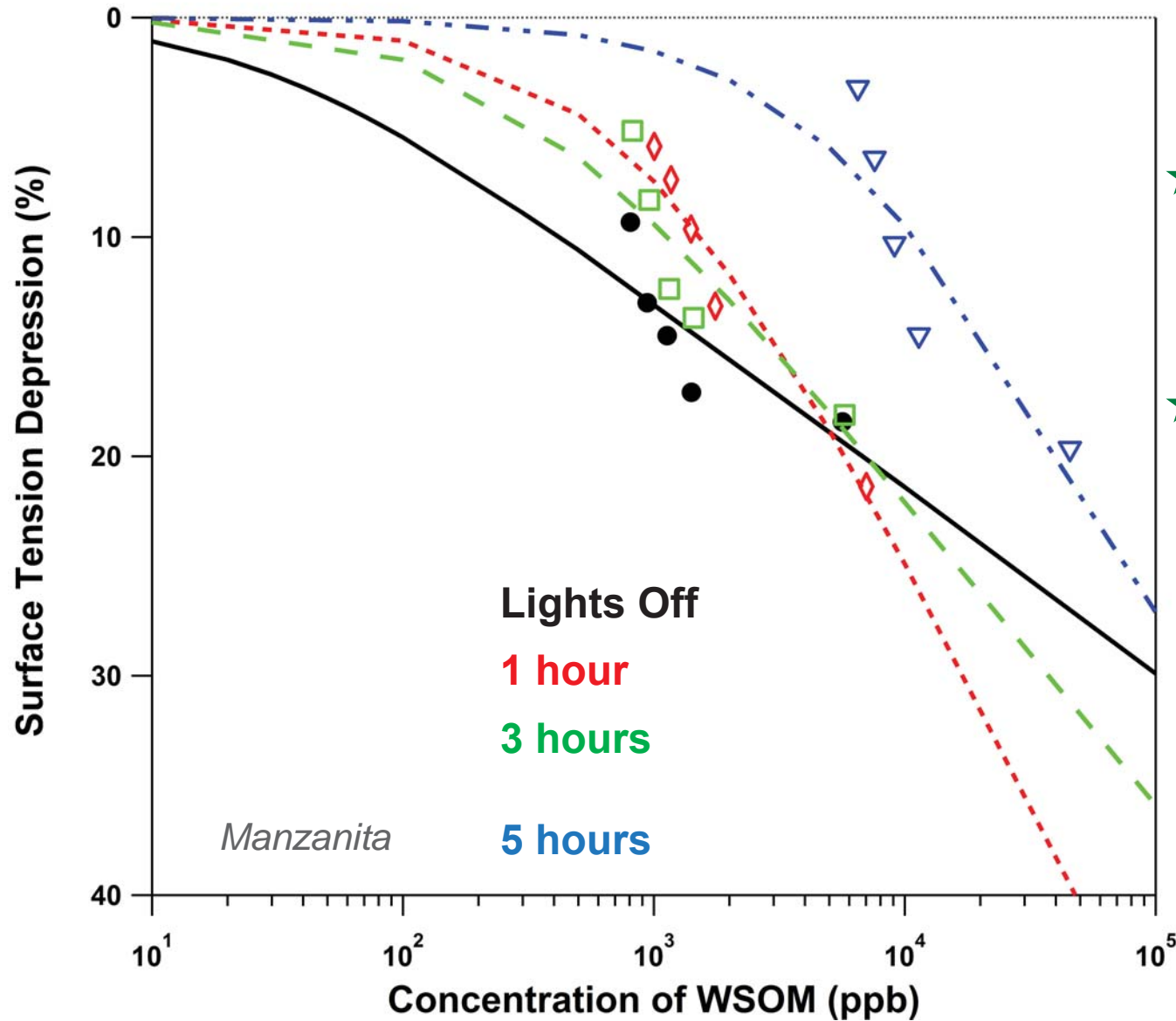
Samples are photographed with a Pendant Drop Tensiometer (PDT) and the Young-Laplace Equation



$H = \text{correction factor based on } d_e/d_s$



**More surfactants  
with time**

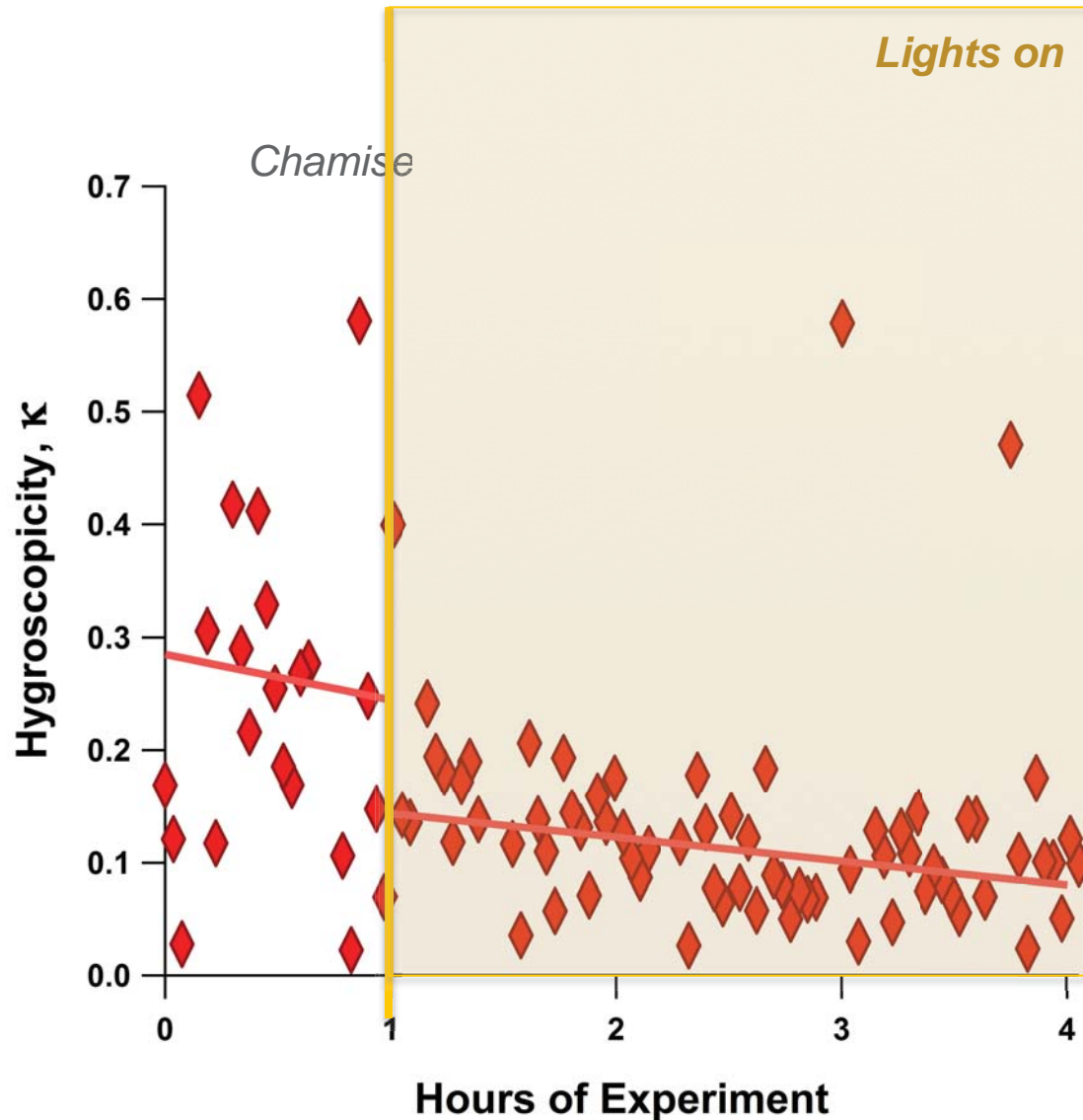


★ Reverse for Manzanita.

★ Ageing can reduce the amount of surface active materials in the aerosol



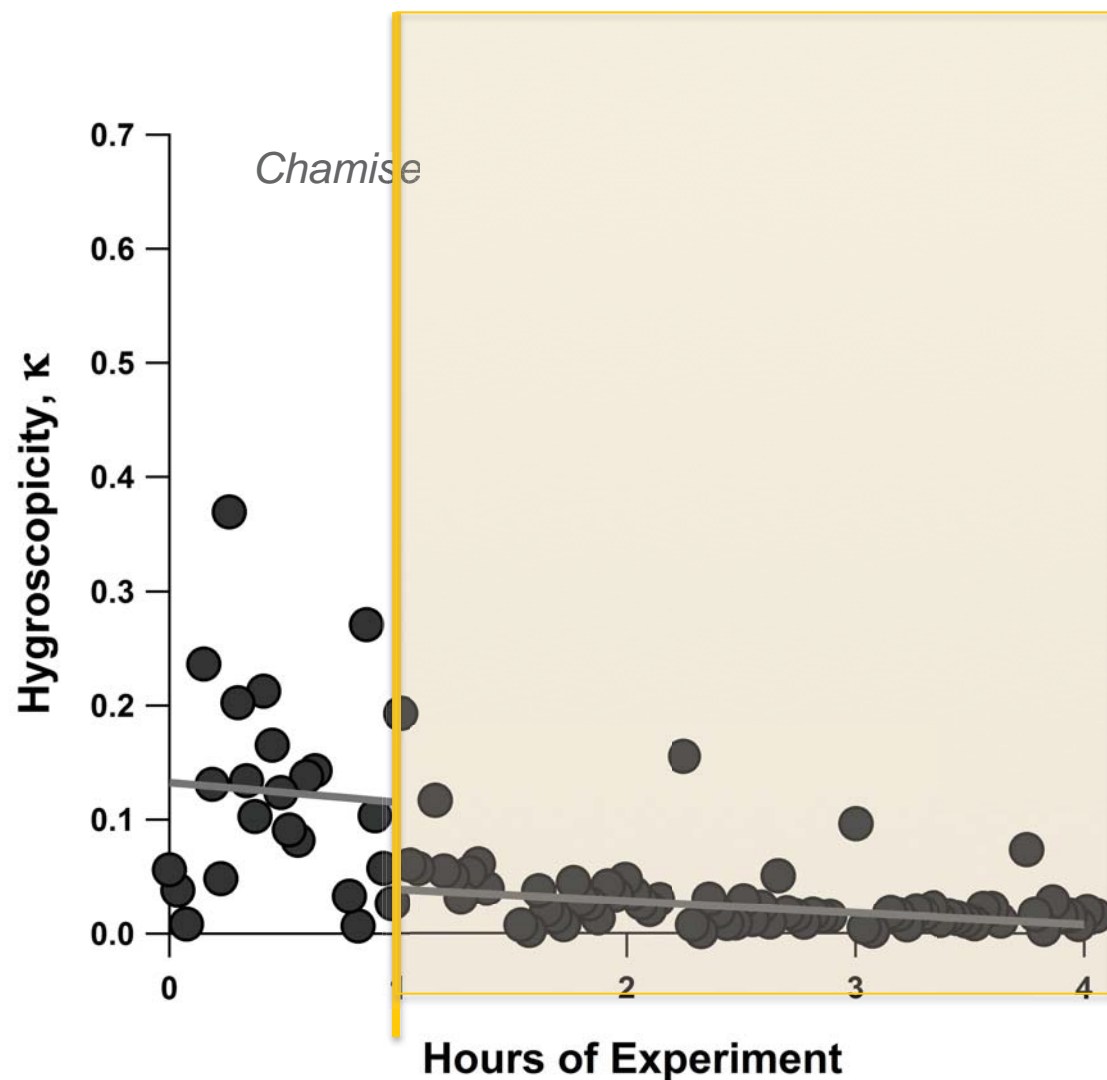
# Correcting for Surfactants



★ The apparent  $\kappa$  shows the material is hygroscopic

★ solute  $\kappa$  must be corrected for  $\sigma$

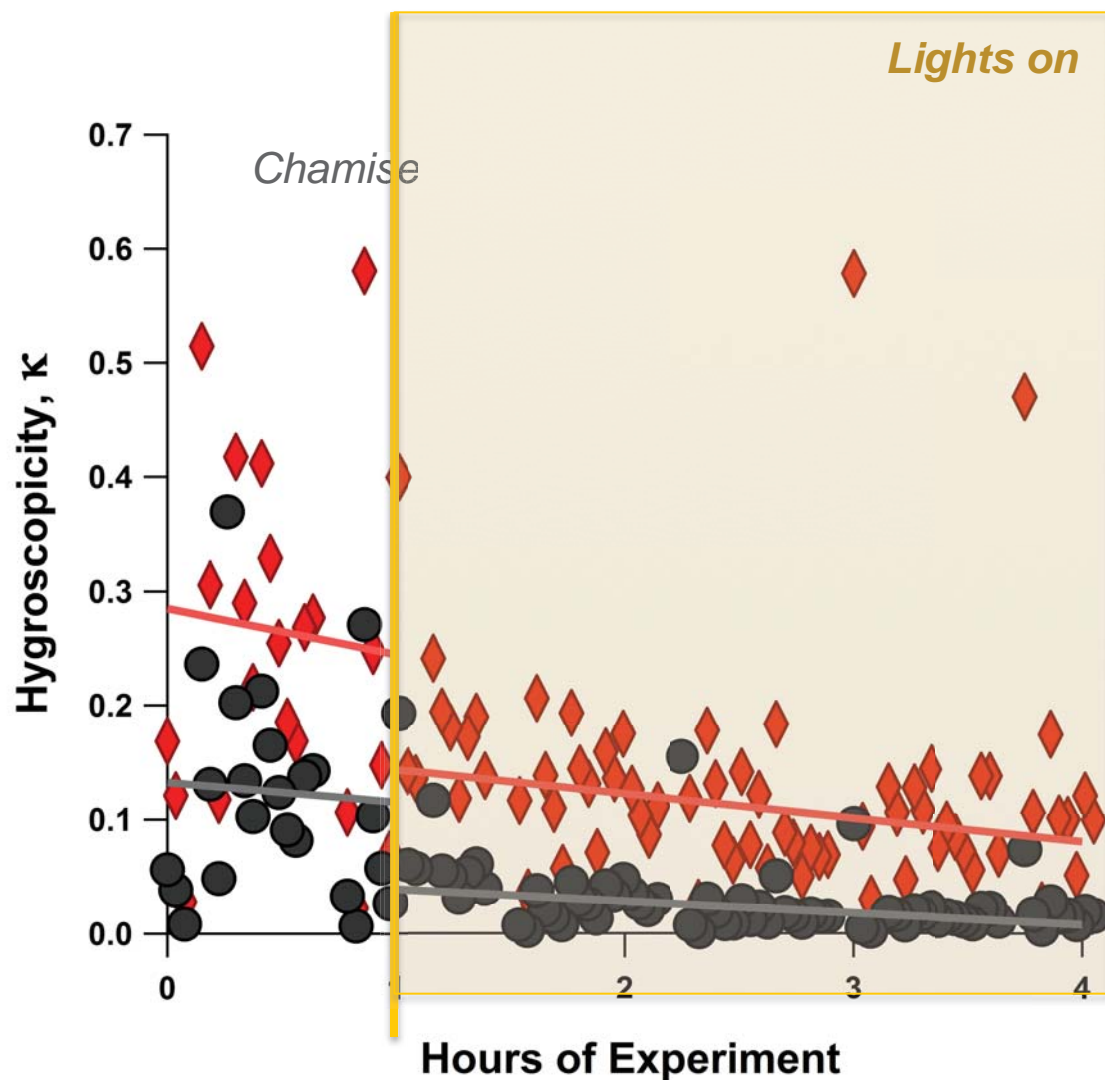
# Correcting for Surfactants



★ The corrected CCN  $\kappa$  derived values are much lower

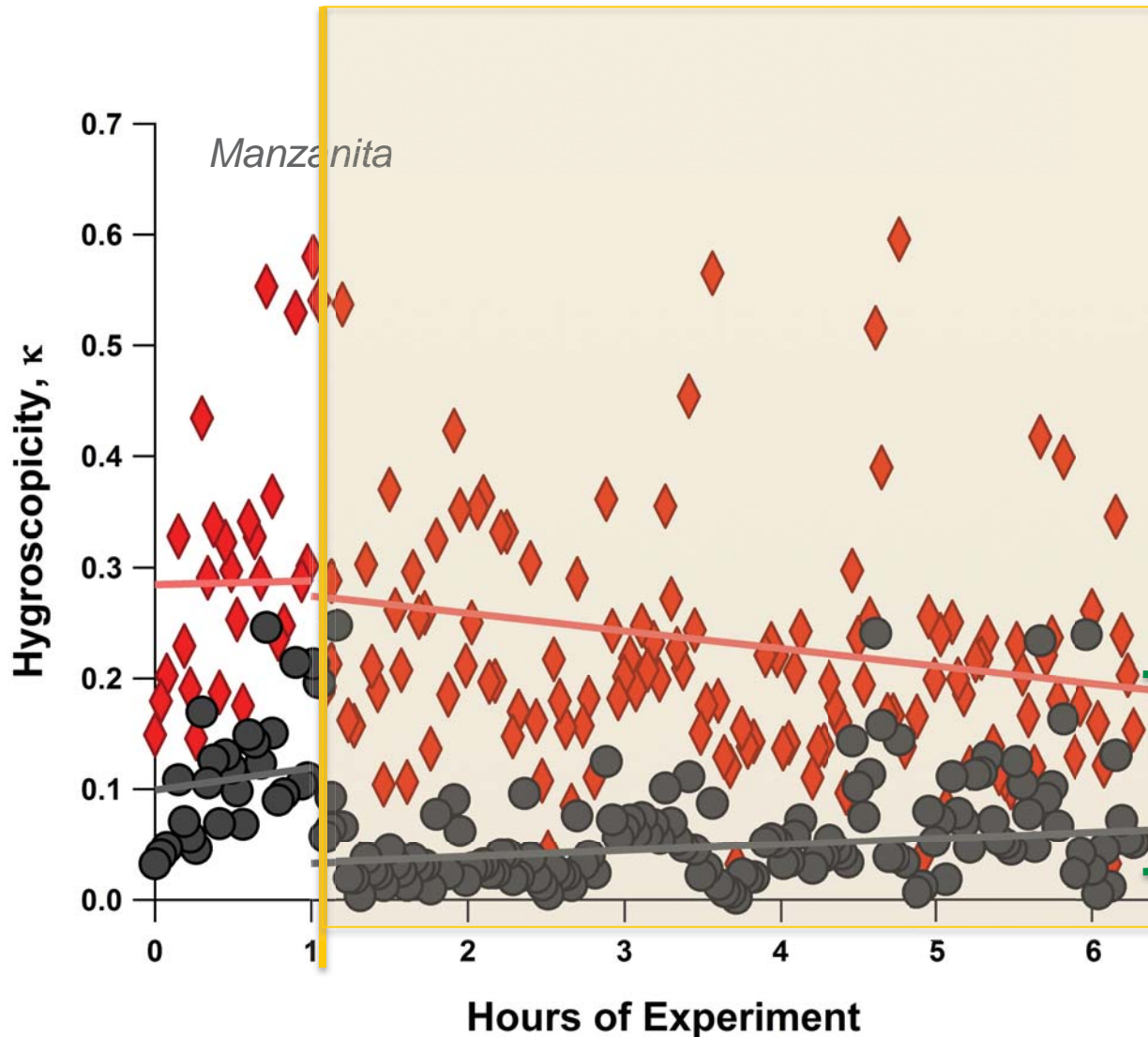
★ Lower values Consistent with values observed with HTDMA data sets

# Correcting for Surfactants



★ SURFACTANTS  
ARE REAL!

# Correcting for Surfactants



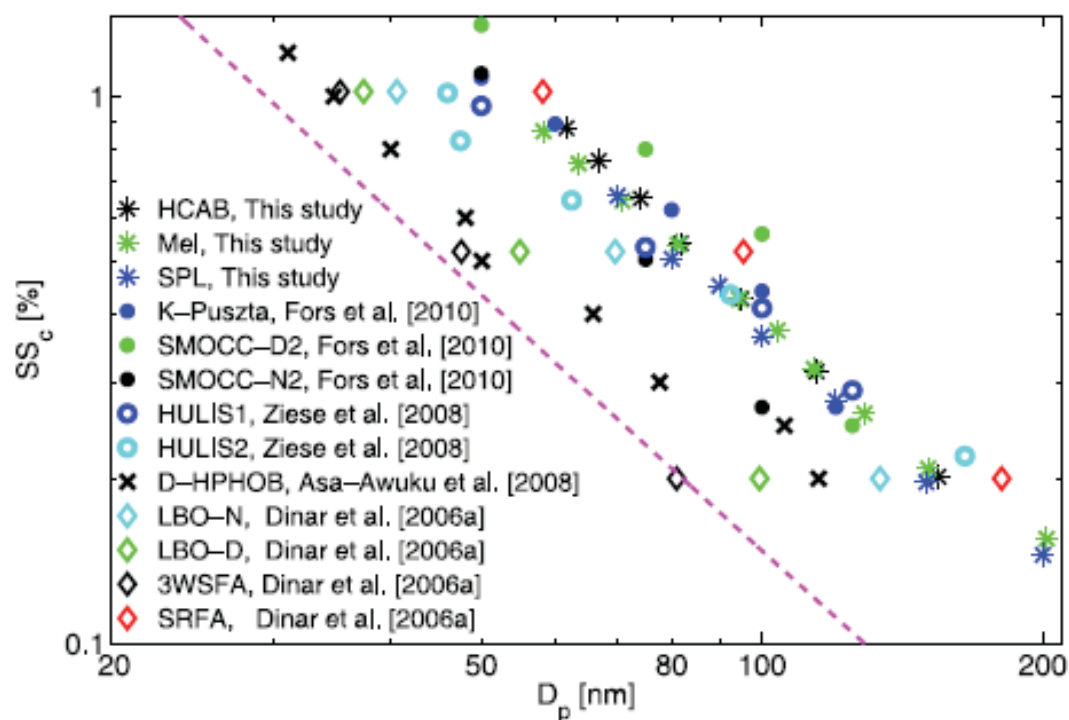
★ SURFACTANTS  
ARE REAL!

★ And their  
effects can be  
significant!

## Hygroscopic growth and CCN activity of HULIS from different environments

Thomas B. Kristensen,<sup>1</sup> Heike Wex,<sup>2</sup> Bettina Nekat,<sup>2</sup> Jacob K. Nøjgaard,<sup>3</sup>  
Dominik van Pinxteren,<sup>2</sup> Douglas H. Lowenthal,<sup>4</sup> Lynn R. Mazzoleni,<sup>5</sup>  
Katrin Dieckmann,<sup>2</sup> Christian Bender Koch,<sup>1</sup> Thomas F. Mentel,<sup>6</sup>  
Hartmut Herrmann,<sup>2</sup> A. Gannet Hallar,<sup>7</sup> Frank Stratmann,<sup>2</sup> and Merete Bilde<sup>1</sup>

Received 21 June 2012; revised 21 September 2012; accepted 29 September 2012; published 28 November 2012.



**(3) Time changes everything**

**(2) Chemistry is Important**

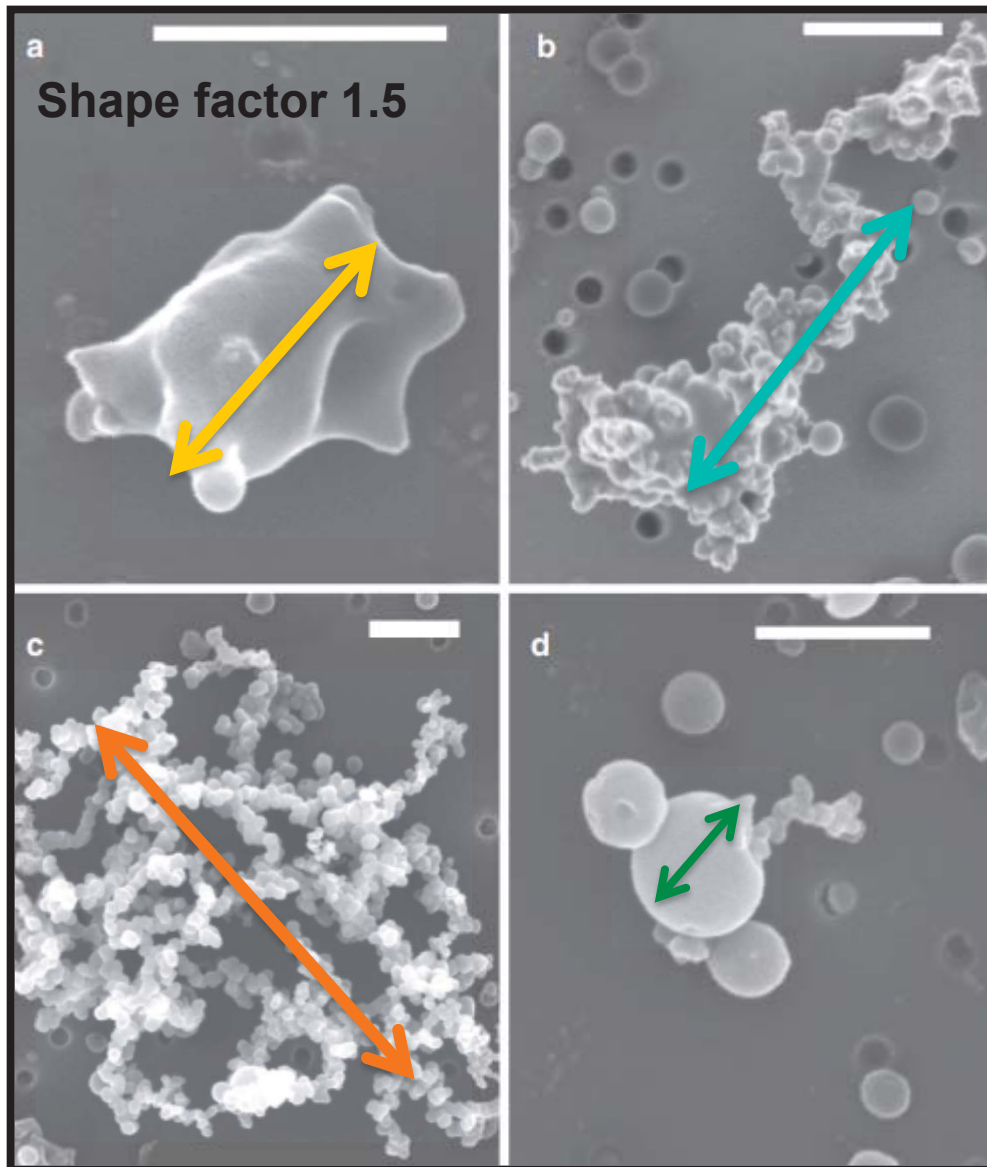
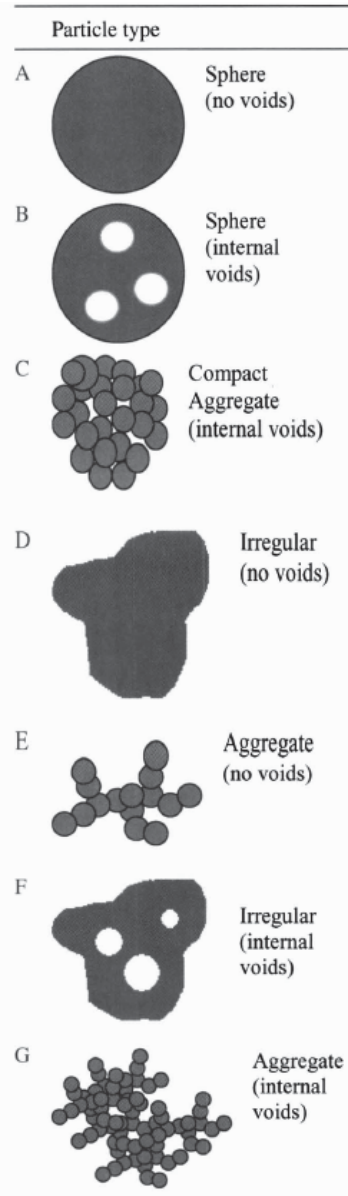
Figure 1. CCN activities of atmospheric HULIS samples as reported in the literature, together with values obtained in this study. For comparison SRFA is included, and the dashed line gives the theoretical values for ammonium sulfate. For details about the studies and samples see Table 1.



# Size Does Matter!

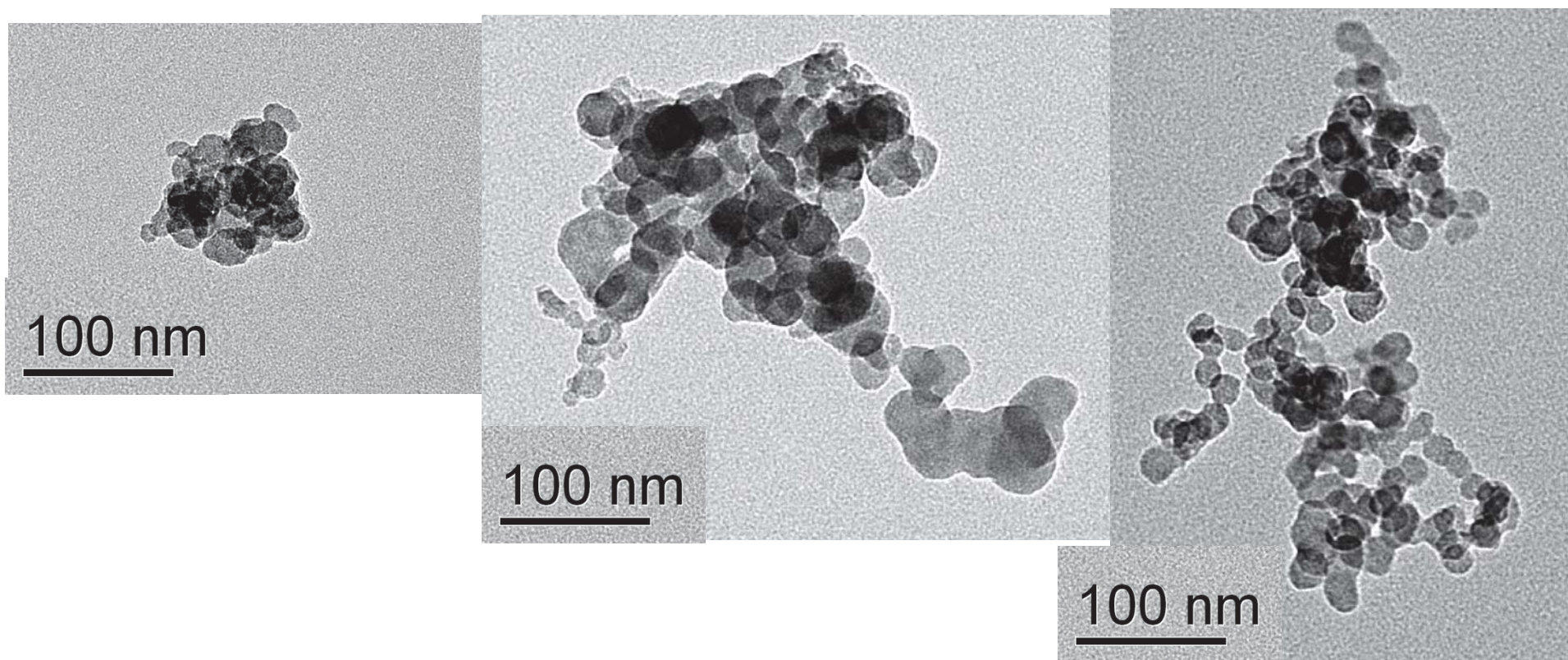
*DeCarlo et al., 2010 ACP*

*China et al., 2013; Nature*



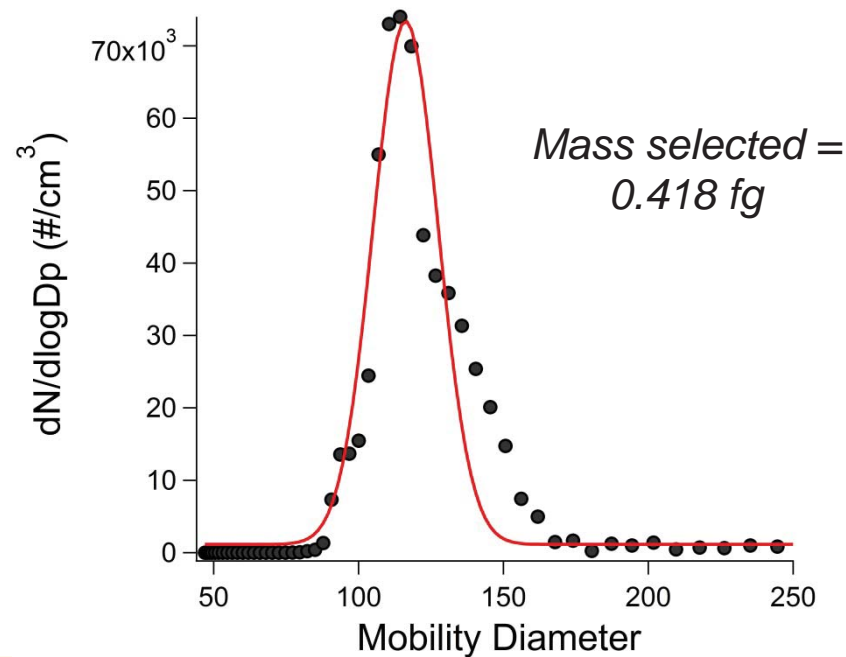
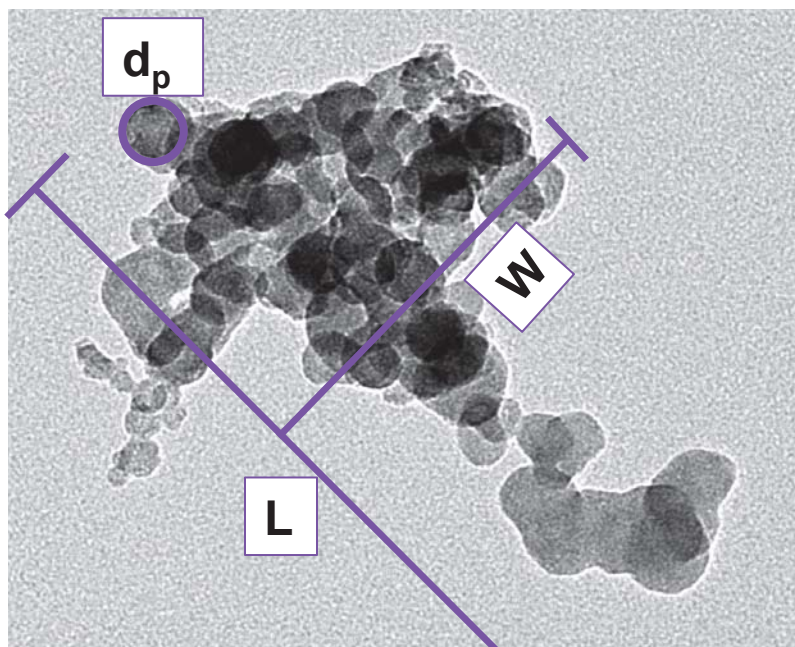
# Shape Factor ( $\chi$ )

- ▶ Use APM to select a single particle mass
  - ▶ Electrostatically precipitate onto a TEM grid



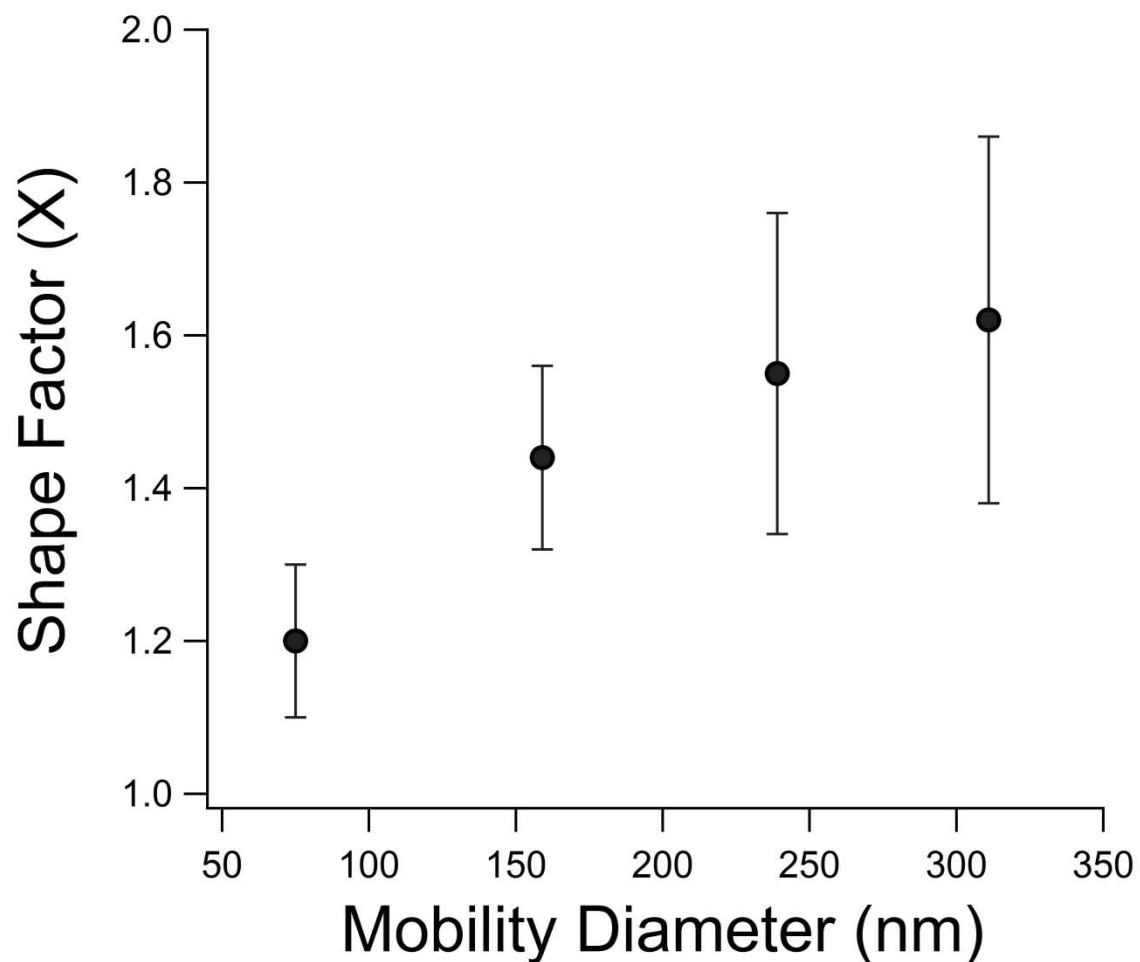


# Shape Factor ( $\chi$ )



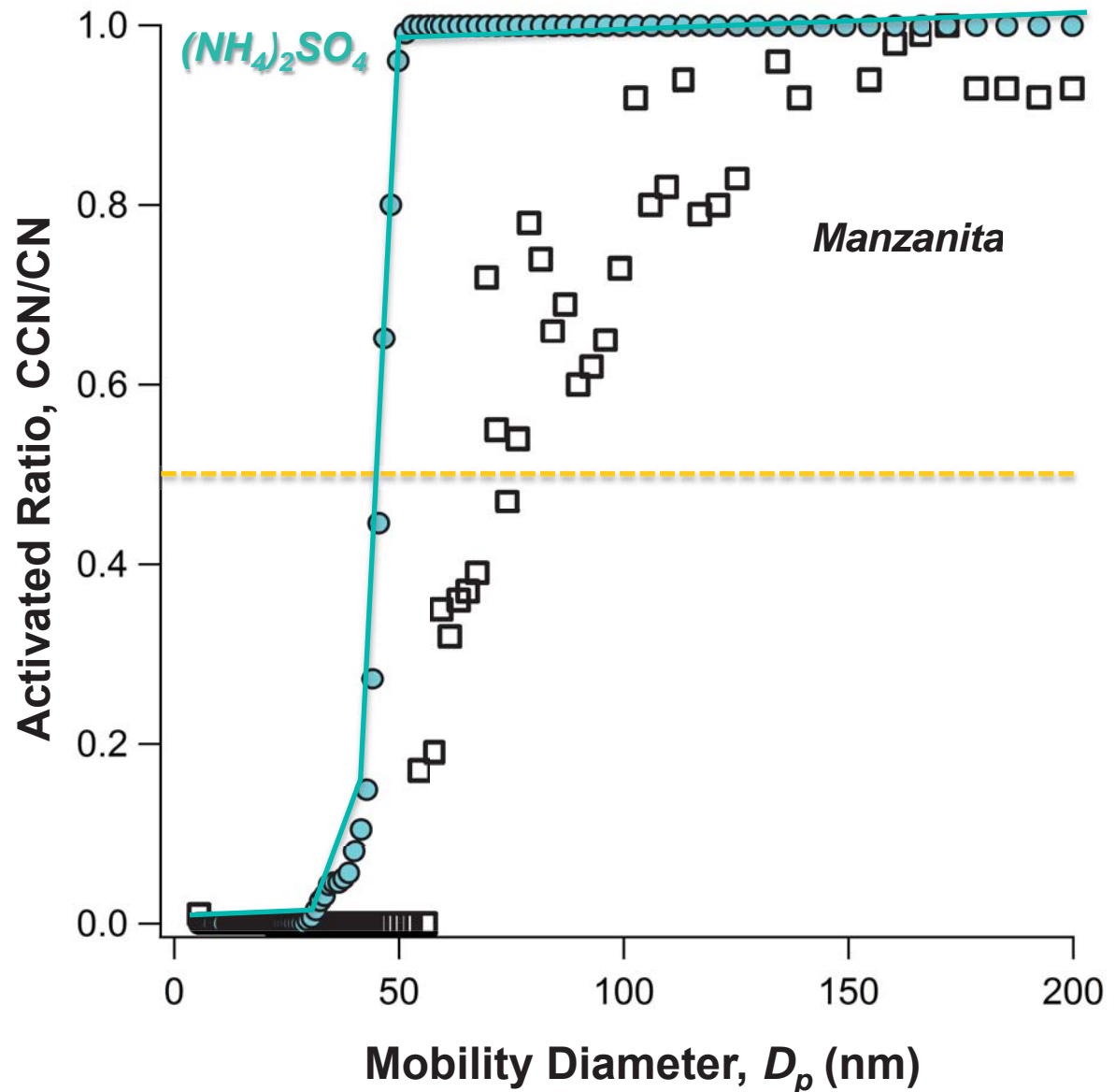
Mass selected (fg)	$n$	$L$ (nm)	$W$ (nm)	$N$	$d_p$ (nm)	$V_{\text{calc}}$ (nm <sup>3</sup> )	$d_{\text{calc}}$ (nm)	Mobility Diameter	Shape Factor ( $\chi$ )
0.177	8	157 ± 42	120 ± 27	60 ± 15	16 ± 4	1.29E+05	<b>62 ± 4</b>	<b>75</b>	<b>1.20 ± 0.1</b>
0.418	13	238 ± 90	139 ± 45	167 ± 34	20 ± 3	7.00E+05	<b>110 ± 9</b>	<b>159</b>	<b>1.44 ± 0.12</b>
0.82	14	403 ± 98	266 ± 90	299 ± 101	23 ± 4	1.90E+06	<b>153 ± 15</b>	<b>239</b>	<b>1.55 ± 0.21</b>
1.41	19	570 ± 199	322 ± 104	510 ± 199	24 ± 5	3.69E+06	<b>191 ± 22</b>	<b>311</b>	<b>1.62 ± 0.24</b>

# Shape Factor ( $\chi$ )



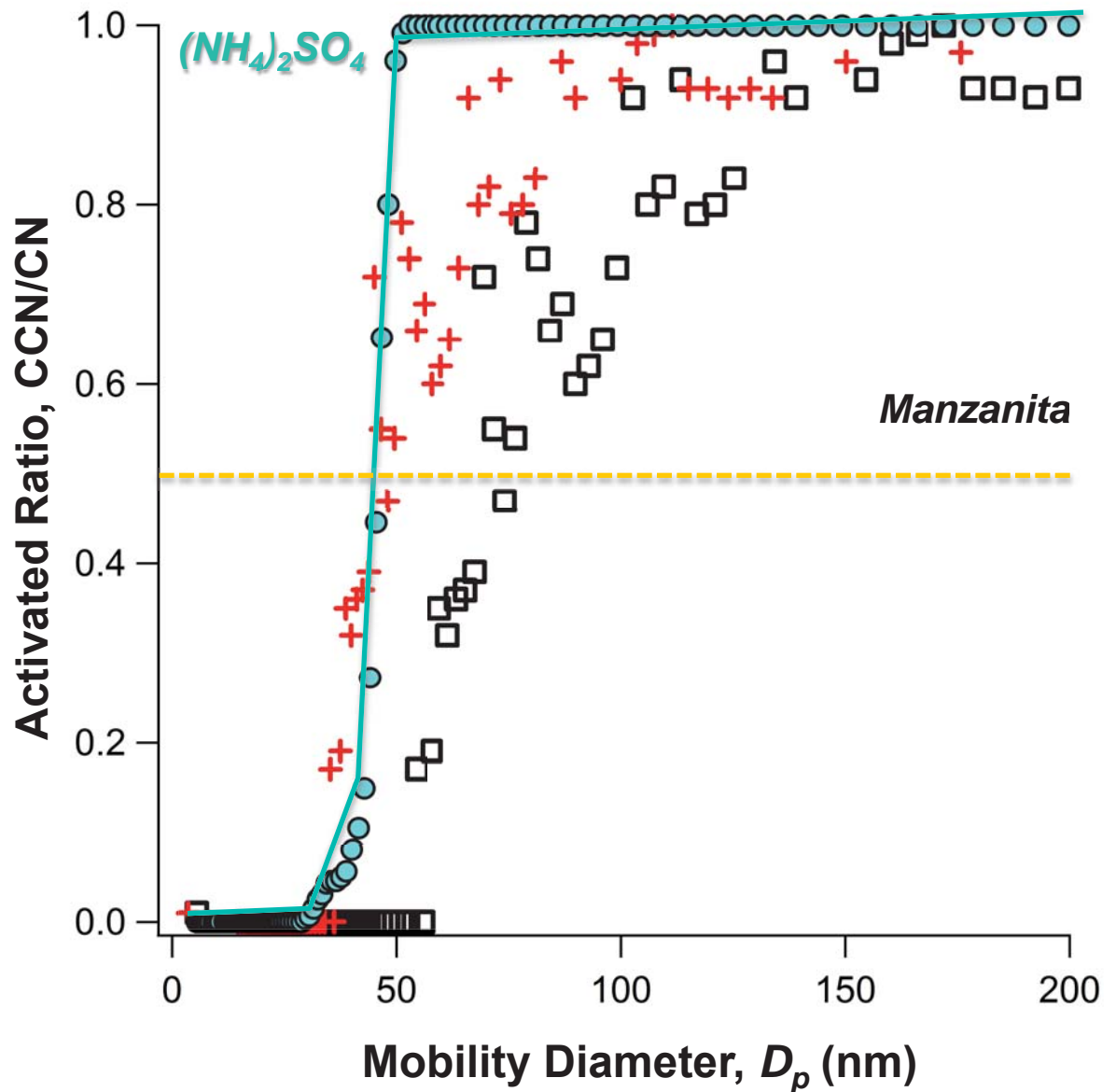
How does this affect CCN calculations?

- ★ For CCN, mobility diameter alone is inadequate
- ★ We need effective density/fractal dimension and shape factor information to correct data points

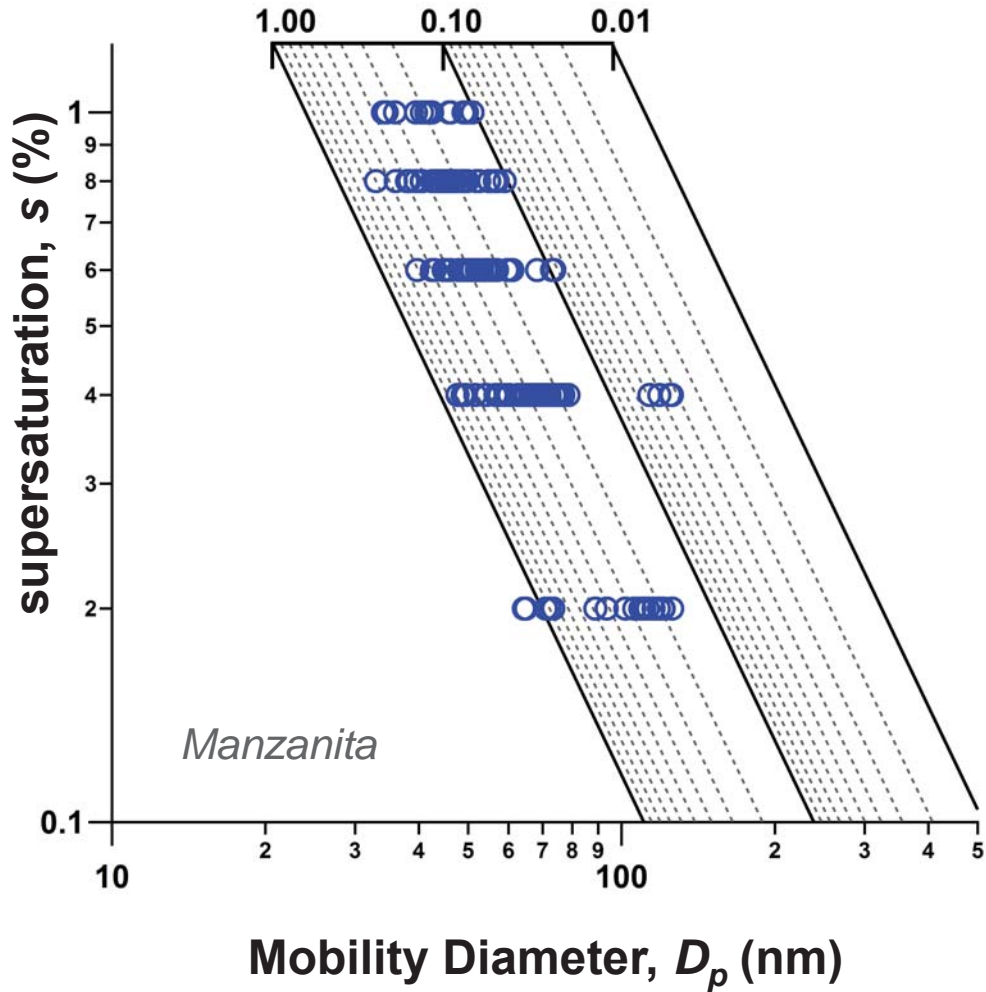


*Volume  
Equivalent  
Diameter -  
Corrected data  
points*

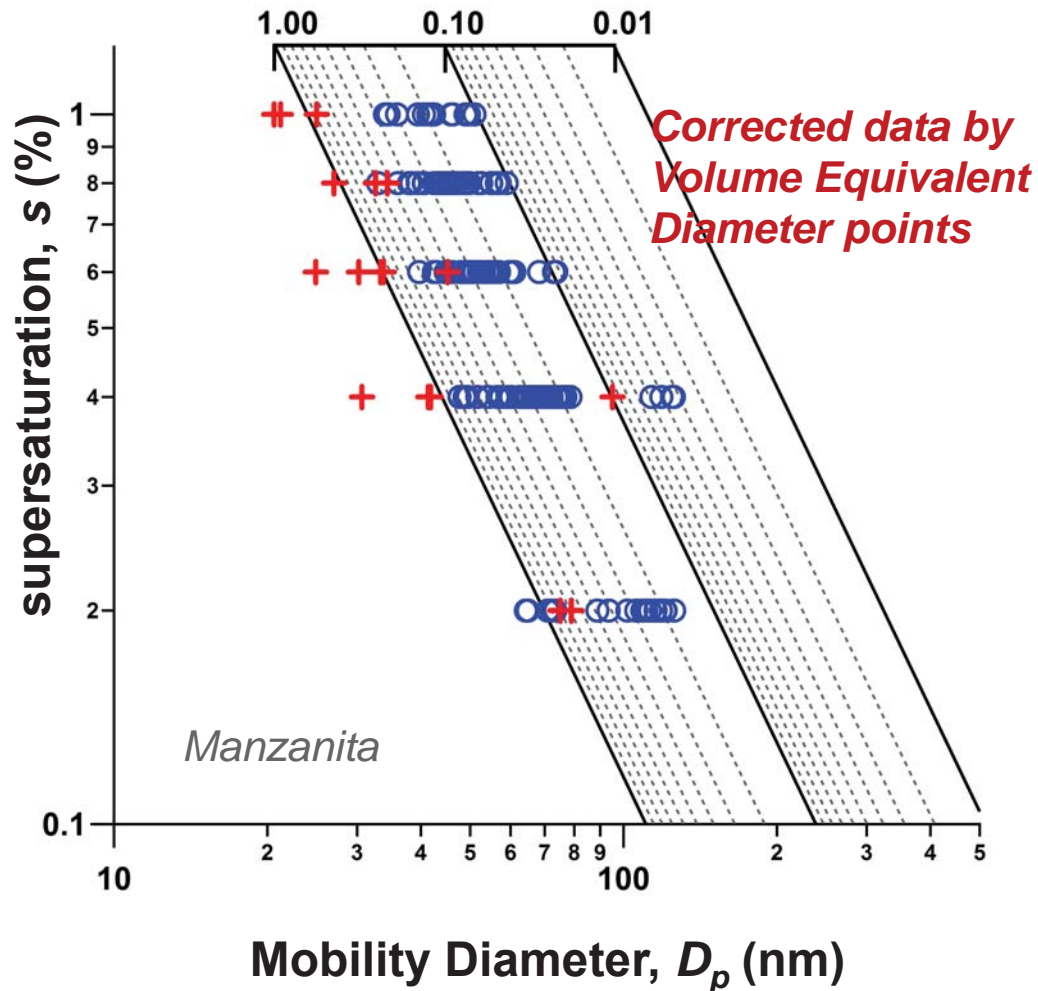
**Size Matters!**



$\kappa$ , hygroscopicity



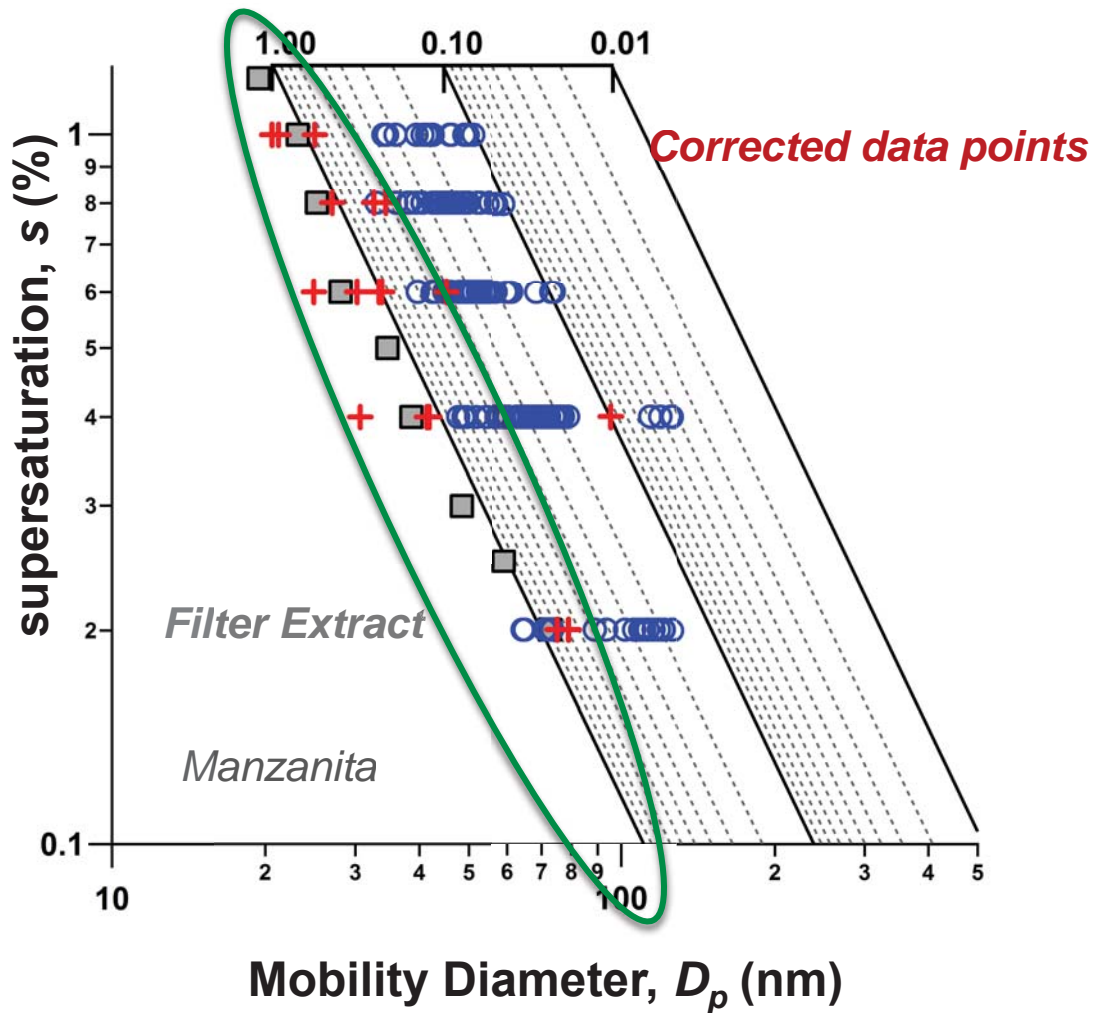
$\kappa$ , hygroscopicity



- Correcting for available solute mass shifts activity to the left



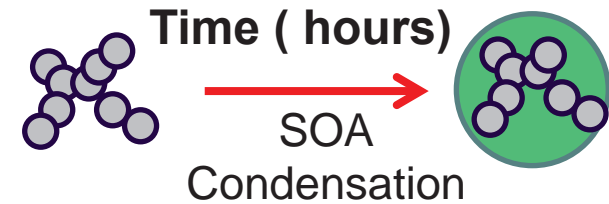
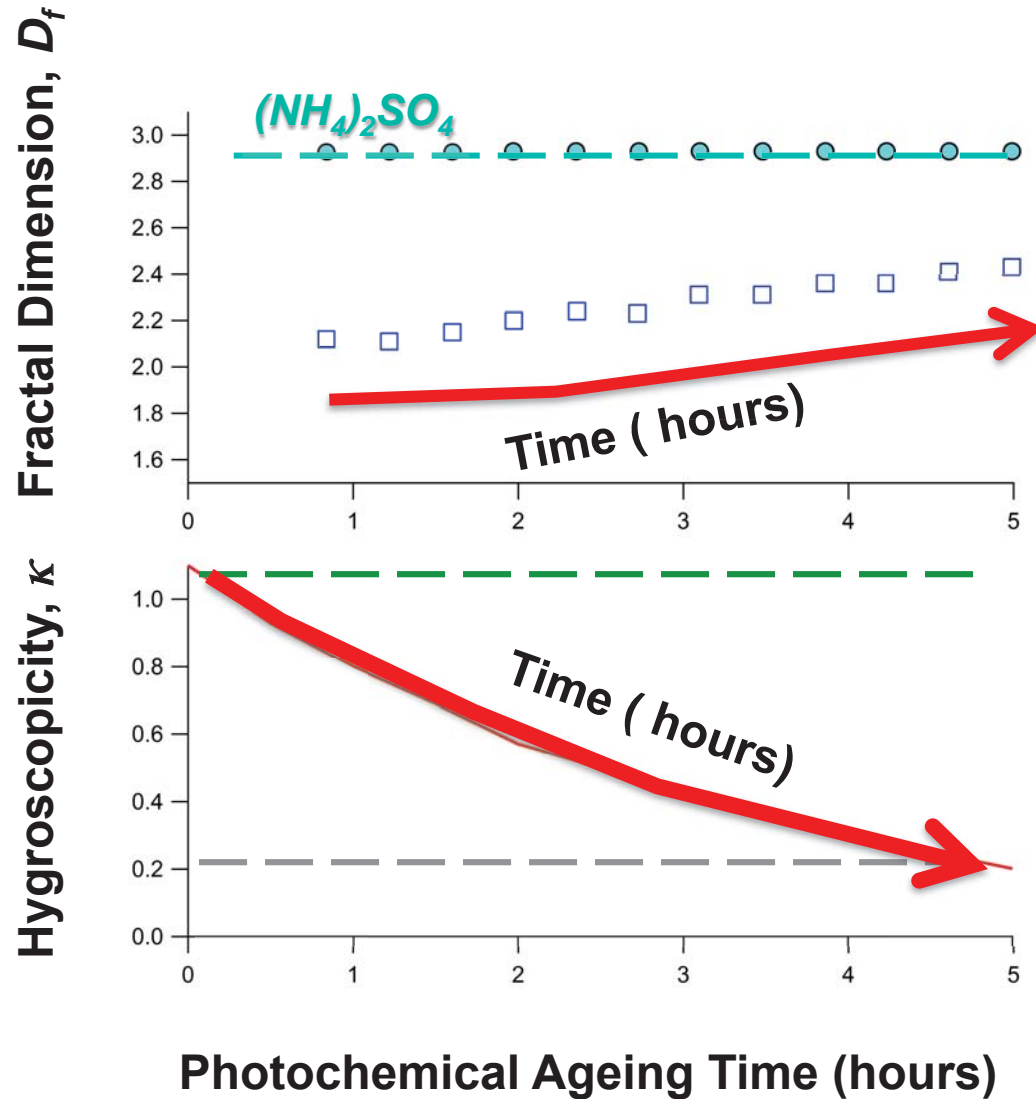
$\kappa$ , hygroscopicity



- Correcting for available solute mass shifts activity to the left



# Shifting from non-spherical to spherical



- Secondary Ageing, reduces fractal nature and hygroscopicity also decreases

**Photochemical ageing will change sphericity.**

*Giordano et al., 2014, ACP*

## › **Surfactants are Real**

- › Surfactants are indeed present in aerosol systems, can be generated under controlled conditions, and may alter observed hygroscopicity and droplet formation ability by twofold.
- › Surfactant properties depend on aerosol aging and can be ephemeral thus explaining the lack of consensus in the current body of literature, .

## › **The changing fractal/sphericity of fresh and aged biomass burning aerosol can be accounted for in CCN Analysis**

## › **Size, Chemistry and Time are critical and relevant properties for CCN Biomass Burning Analysis.**

## Changes in Droplet Surface Tension Affect the Observed Hygroscopicity of Photochemically Aged Biomass Burning Aerosol

Michael R. Giordano,<sup>†,‡</sup> Daniel Z. Short,<sup>†,‡</sup> Seyedehs and Akua A. Asa-Awuku<sup>\*,†,‡</sup>

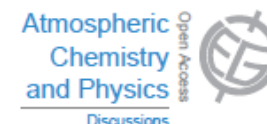
<sup>†</sup>Department of Chemical and Environmental Engineering, Univer

<sup>‡</sup>College of Engineering—Center for Environmental Research and

<sup>§</sup>Department of Mechanical Engineering, University of California—

**S** Supporting Information

Atmos. Chem. Phys. Discuss., 14, 12555–12589, 2014  
www.atmos-chem-phys-discuss.net/14/12555/2014/  
doi:10.5194/acpd-14-12555-2014  
© Author(s) 2014. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

## Experimentally measured morphology of biomass burning aerosol and its impacts on CCN ability

M. Giordano<sup>1,2</sup>, C. Espinoza<sup>1,2</sup>, and A. Asa-Awuku<sup>1,2</sup>

<sup>1</sup>Department of Chemical and Environmental Engineering, University of California – Riverside, Riverside, California, USA

<sup>2</sup>College of Engineering – Center for Environmental Research and Technology (CE-CERT), Riverside, CA, USA

Received: 10 April 2014 – Accepted: 17 April 2014 – Published: 16 May 2014

Correspondence to: A. Asa-Awuku (akua@engr.ucr.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

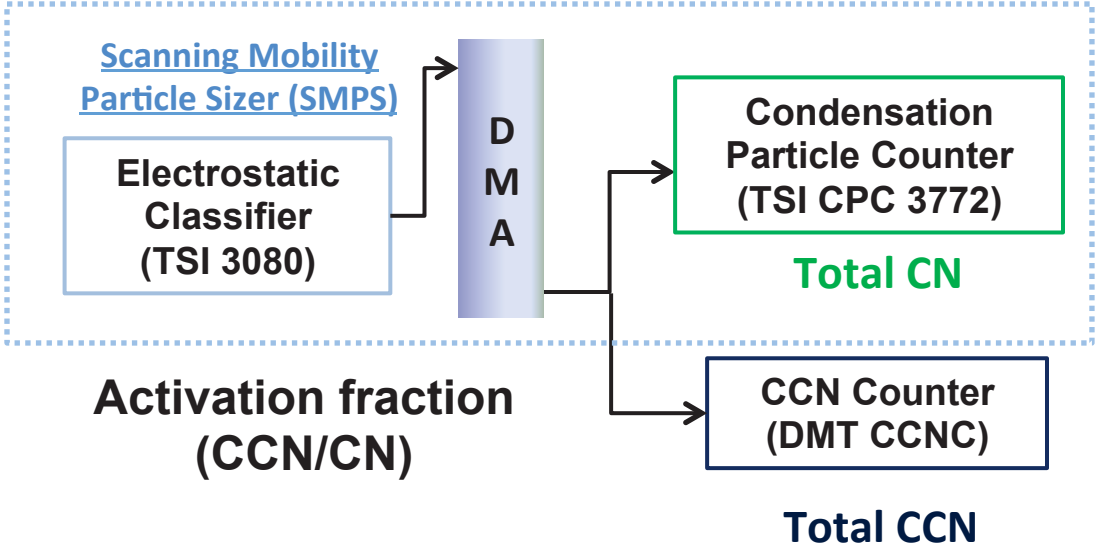
*Giordano et al., 2014, in press*



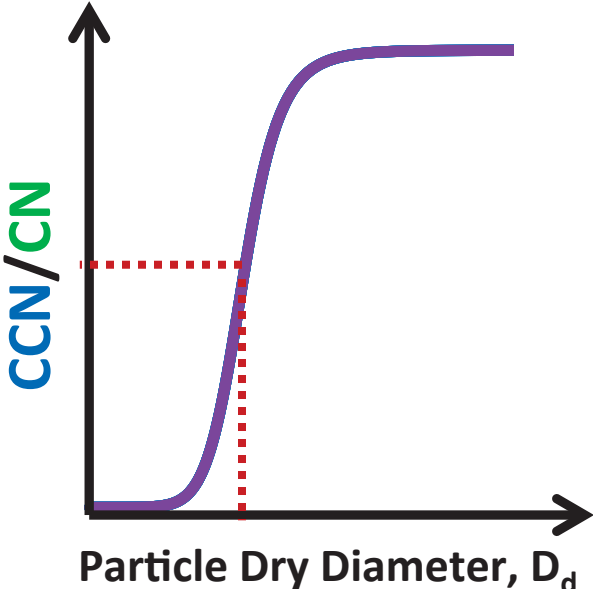
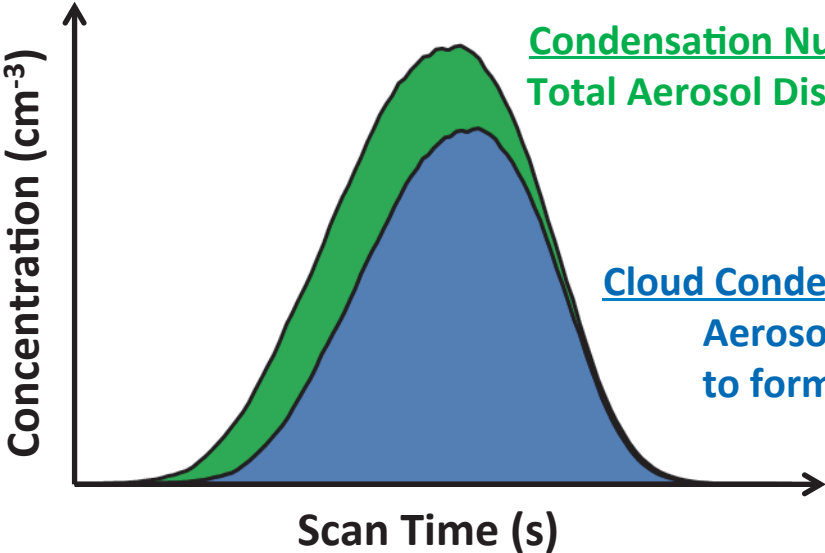
**MIXING STATE FLOW TUBE**

# **Part 3: BC/OC Mixing State CCN**

# Measuring CCN Activity



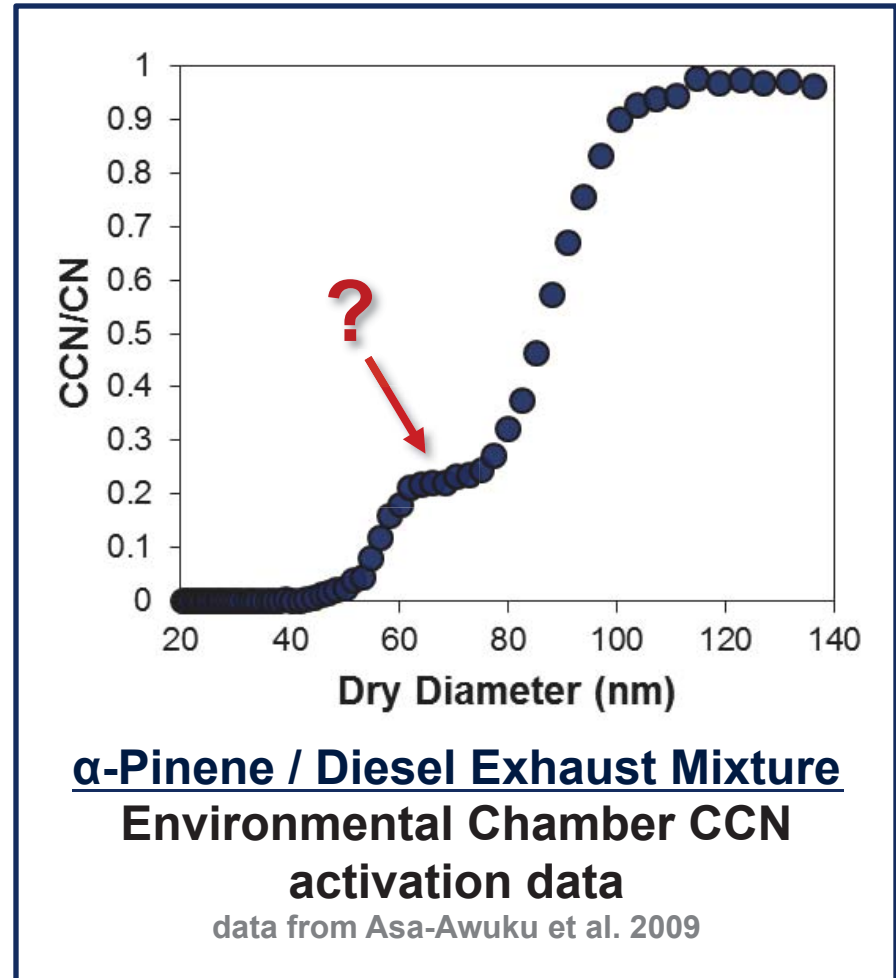
**Scanning Mobility CCN Analysis:**  
(Moore et al. 2010)  
**Determines  $D_d$  for various supersaturations**



*Vu et al., in prep*

# Real Data Sets

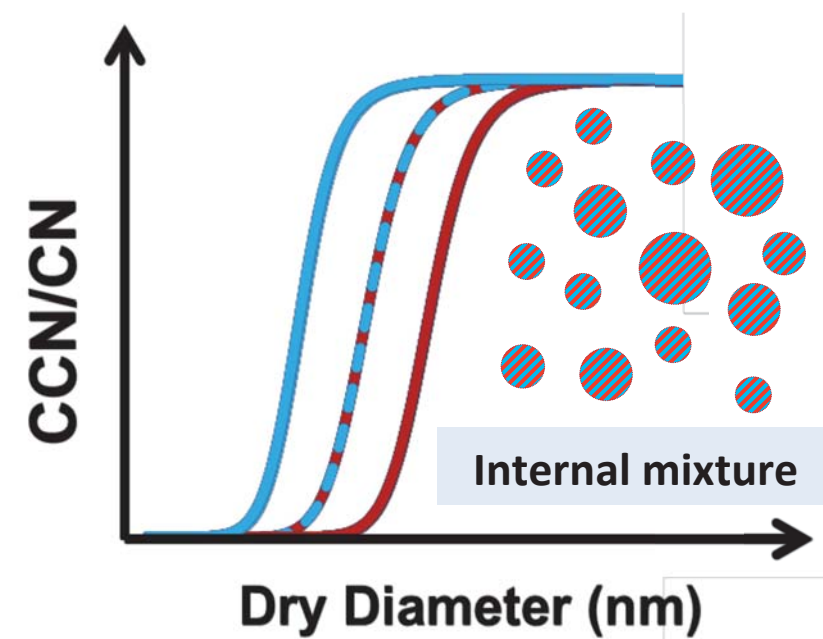
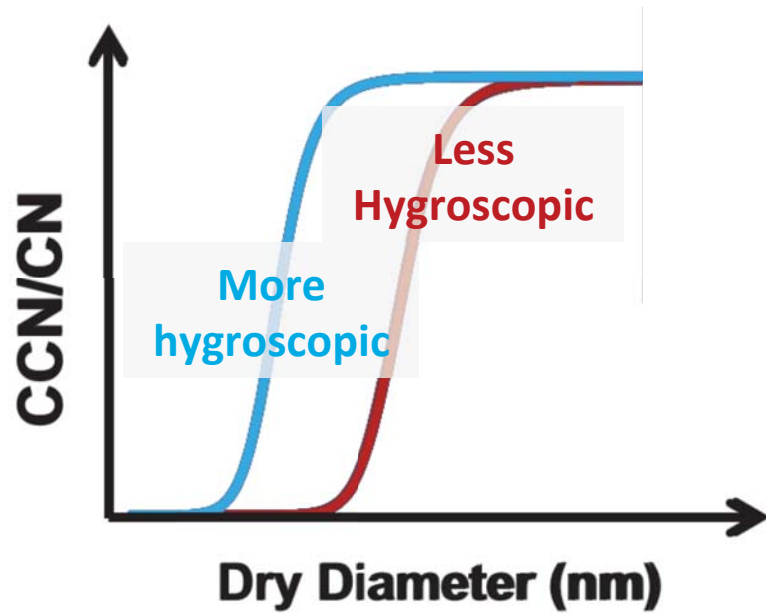
- **CCN** data sets from ambient and environmental chamber studies can consist of **complex mixtures** of organic and inorganic aerosols
- **Common assumptions**
  - Doubly charged aerosols
  - Uniform composition
  - Single fit
- **Multiple activation curves...?**
  - Different components?
  - Mixing state? Type / Extent?
  - Complex mixtures?



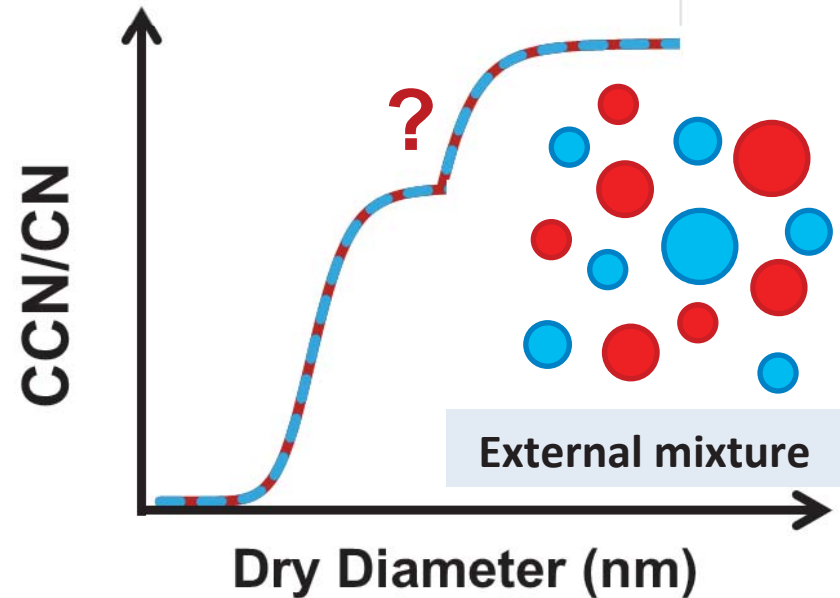
**GOAL: Improve experimental analysis techniques of CCN of complex mixtures**



# Mixing States: Internal / External Mixtures

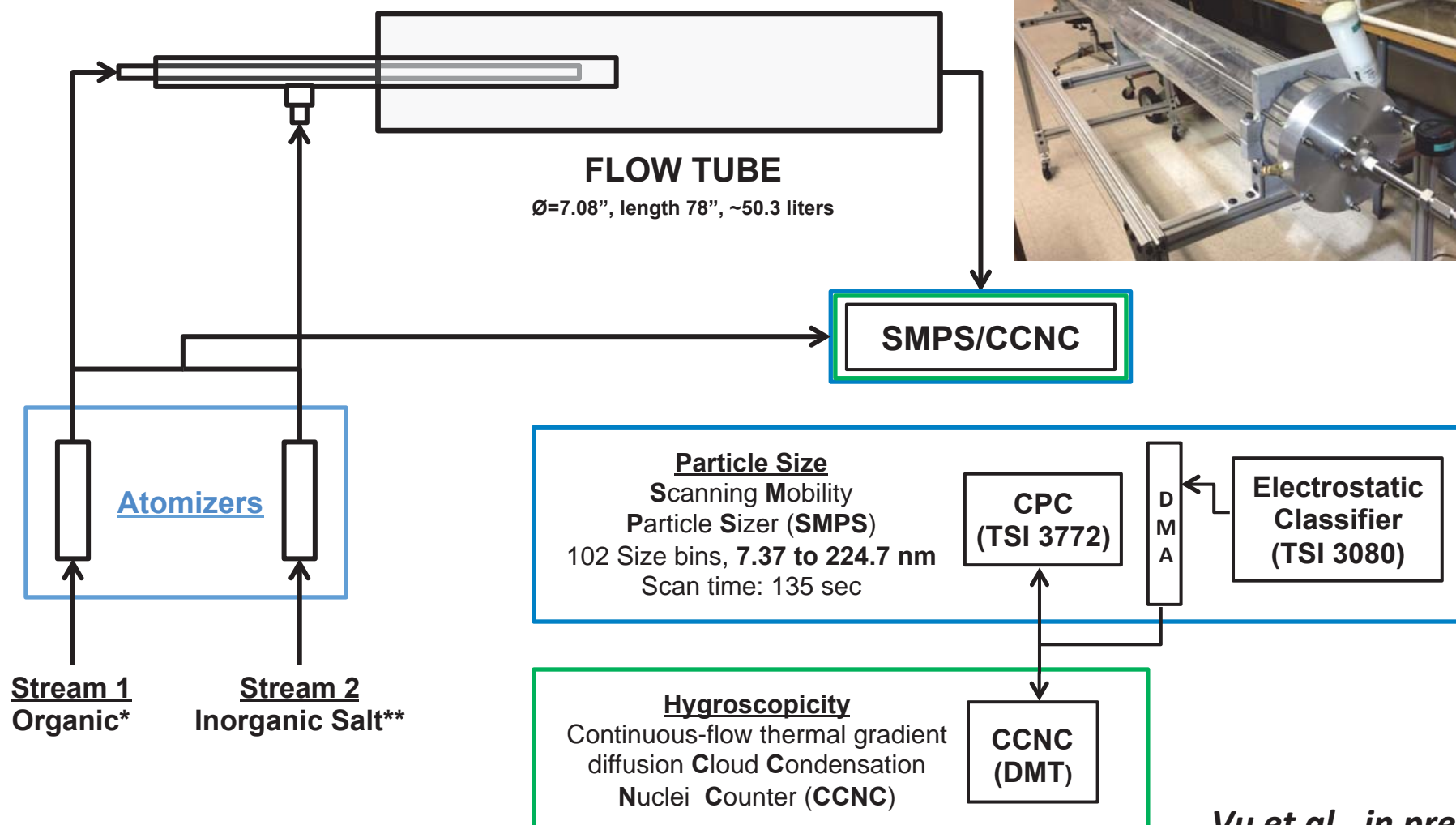


Atmospheric aerosols are often **mixed** and comprised of **multiple components**



# Recreating Activation Curves: Known Mixtures

CCNC was operated between 0.2 and 1.1 SS%



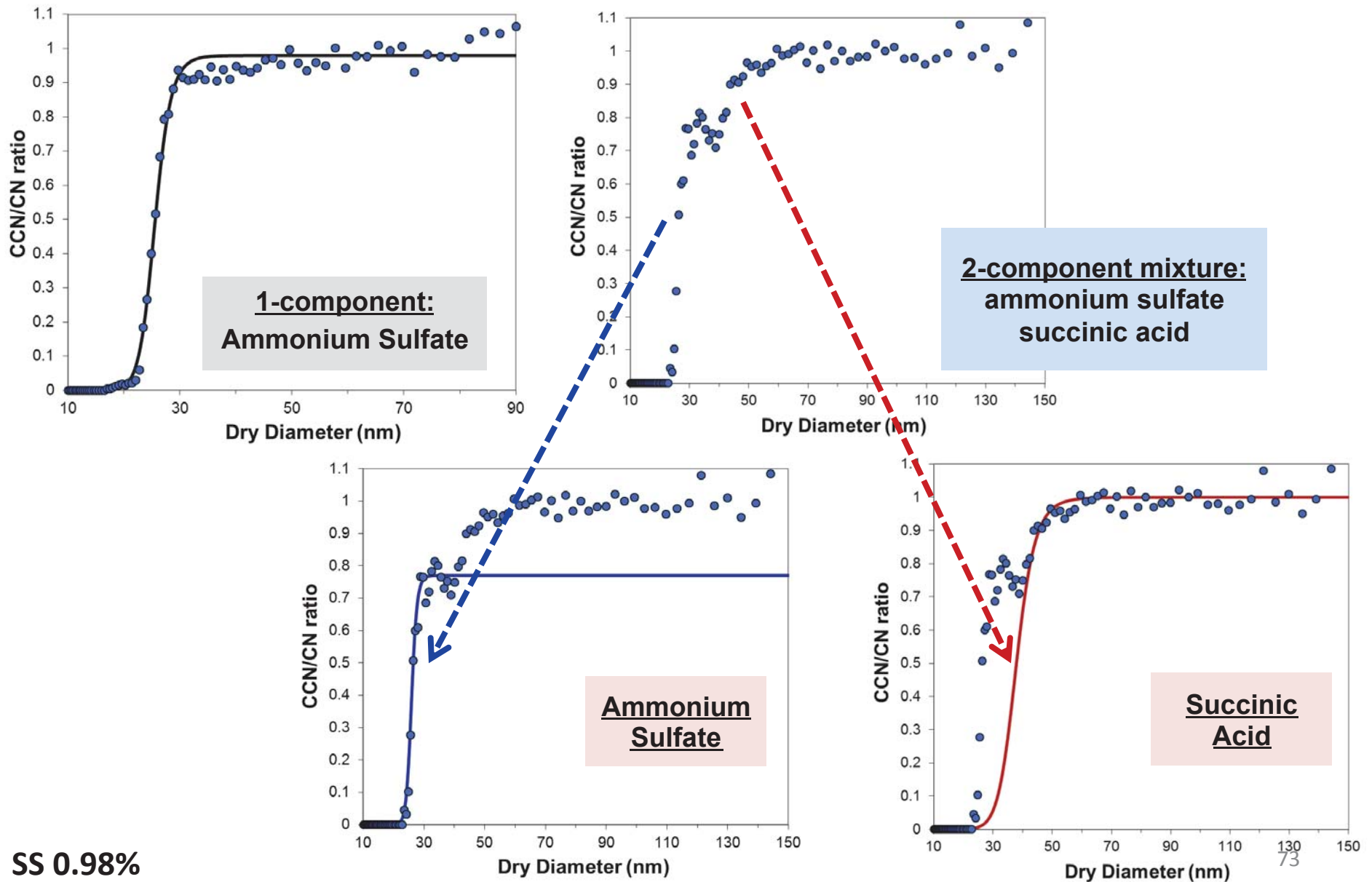
\*Organic: Succinic Acid,  $C_4H_6O_4$

\*\*Inorganic Salt: Ammonium Sulfate,  $(NH_4)_2SO_4$ , Sodium Chloride, NaCl

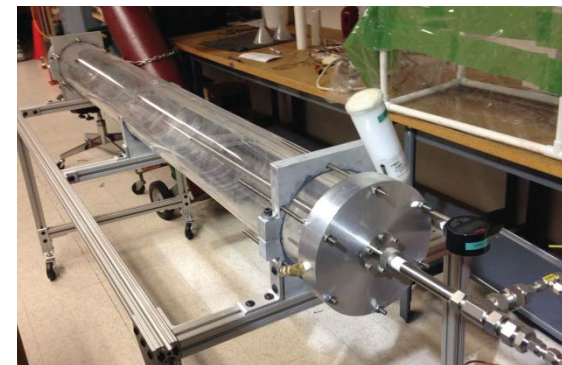
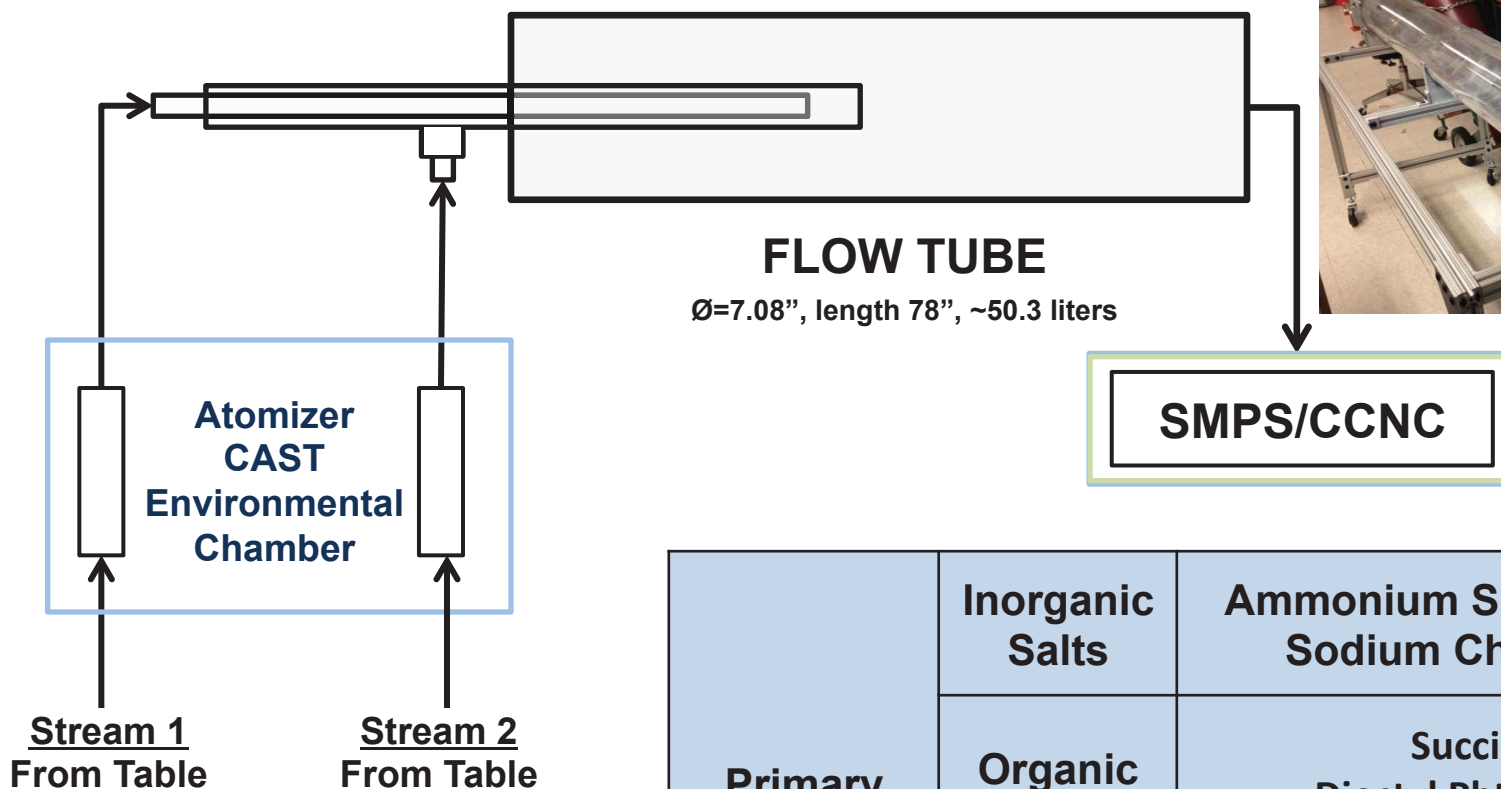
*Vu et al., in prep*

# Multiple Activation Curves: External Mixtures

Data sets yielding multiple activation curves were recreated by mixing two well characterized compounds



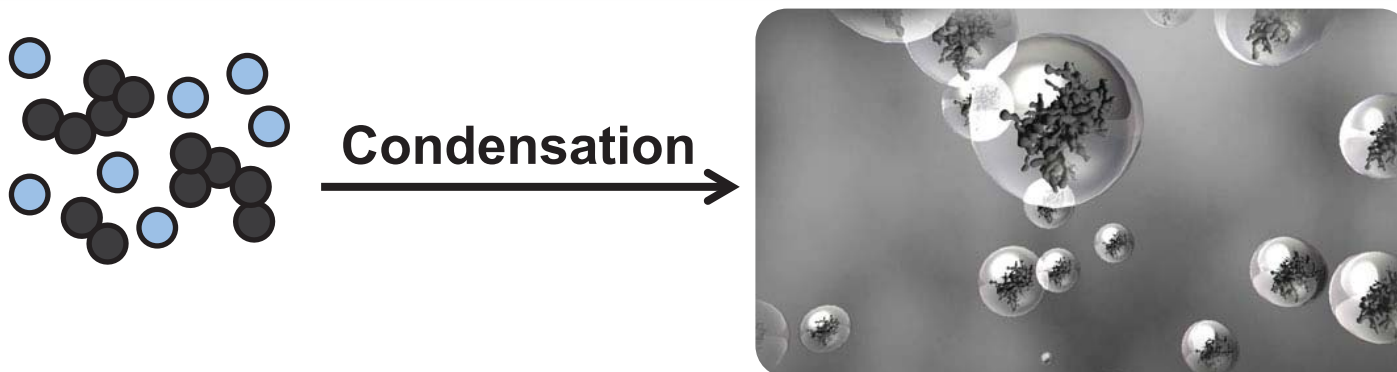
# Future Work



Extend data analysis to include more complex mixed systems from both primary and secondary sources

<b><u>Primary</u></b>	<b>Inorganic Salts</b>	<b>Ammonium Sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> Sodium Chloride (NaCl)</b>
	<b>Organic</b>	<b>Succinic Acid Diethyl Phthalate (DOP)</b>
	<b>Black Carbon</b>	<b>Combustion Aerosol Standard (CAST): soot particles generated similar to soot derived diesel engines</b>
<b><u>Secondary</u></b>	<b>Biogenic SOA</b>	<b>Isoprene -pinene</b>

## OUR APPROACH TO COMPLEX HYGROSCOPIC PARTICLES



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

**(1) Provide Fast Measurement Techniques for Real-World BC Sources**

**(2) Characterize changes in Physical and Chemical Properties that can alter perceived Hygroscopicity of BC sources**

**(3) Refine Analysis Methods for complex CCN Mixing States**

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## Published

Short, D., Giordano, M., Zhu, Y., Fine, P., Polidori, A., Asa-Awuku, A. A Unique On-line Method to Infer Water-Insoluble Particle Contributions. *Aerosol Science and Technology*. Vol. 48: 7 p. 706-714. 9p. 2014

Karavalakis, G., Short, D., Vu, D., Villela, M., Asa-Awuku, A., Durbin, T. Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and SI-DI vehicles operating on different ethanol and iso-butanol blends. *Fuel*. Vol. 128: p.410-421., 2014

Giordano, M., Espinoza, C., Asa-Awuku, A. 2014. Experimentally measured morphology of biomass burning aerosol and its impacts on CCN ability. *Atmospheric Chemistry and Physics*. Vol. 14: p. 12555-12589.

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Giordano, M. R., D. Z. Short, E. Hosseini, W. Lichtenberg, and A. Asa-Awuku. Changes in Droplet Surface Tension Affect the Observed Hygroscopicity of Photochemically Aged Biomass Burning Aerosol. *Env. Sci. & Tech.* doi:10.1021/es401867j, 2013

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Short, D., Vu, D., Durbin, T., Karavalakis, G., Asa-Awuku, A. Particle Speciation of Emissions from Iso-Butanol and Ethanol Blended Gasoline in Light-Duty Spark-Ignition Vehicles. *Journal of Aerosol Science*. (Submitted 06/24/2014. 38 manuscript pages.)

Karavalakis, G., Short, D., Russell, R., Jung, H., Johnson, K.C., Asa-Awuku, A., Durbin, T. Assessing the Impacts of Ethanol and Iso-Butanol Impacts on Gaseous and Particulate Emissions from Flexible Fuel Vehicles. *Environmental Science and Technology*. (Submitted 07/17/2014. 25 manuscript pages.)

Short, D., Vu, D., Durbin, T., Asa-Awuku, A. Components of Particle Emissions from Light- Duty Spark-Ignition Vehicles with Varying Aromatic Content and Octane Rating in Gasoline. *Environmental Science and Technology*. (Submitted to *ES&T* Prepared 08/10/2014.)

## Conference Papers

Karavalakis, G., Short, D., Hajabeibi, M., Vu, D., Villela, M., Russell, R., Durbin, T., Asa-Awuku, A. 2013. Criteria Emissions, Particle Number Emissions, Size Distributions, and Black Carbon Measurements from PFI Gasoline Vehicles Fuelled with Different Ethanol and Butanol Blends . SAE, doi:10.4271/2013-01-1147. 10p. Detroit, Michigan. 04/08/2013.

Karavalakis, G., Short, D., Vu, D., Villela, M., Russell, R., Jung, H., Asa-Awuku, A., and Durbin, T. “Regulated Emissions, Air Toxics, and Particle Emissions from SI-DI Light-Duty Vehicles Operating on Different Iso-Butanol and Ethanol Blends”, SAE Technical Paper,, 2014

Karavalakis, G., Short, D., Chen, V., Espinoza, C., Berte, T., Durbin, T., Asa-Awuku, A., Jung, H. 2014. “Regulated Emissions, Air Toxics, and Particle Emissions from SI-DI Light-Duty Vehicles Operating on Different Iso-Butanol and Ethanol Blends”, SAE Technical Paper, 2014



# UCR

Correspondence: [akua@engr.ucr.edu](mailto:akua@engr.ucr.edu)

## Aerosol-Climate Effects Group



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# UCR



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

*Akua Asa-Awuku*

**<sup>1</sup> University of California-Riverside**  
Dept of Chemical and Environmental Engineering  
Bourns College of Engineering  
Center of Environmental Research and Technology  
EPA Black Carbon STAR Meeting  
November 13<sup>th</sup>, 2014

UNIVERSITY OF CALIFORNIA, RIVERSIDE

