Using Size-Resolved CCN Measurements to Obtain Aerosol Composition, Mixing State and Droplet Growth Kinetics

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photo: S.Lance

Objectives of this work

- measure aerosol-water interactions in two regimes
  - **concentrated** aqueous solutions

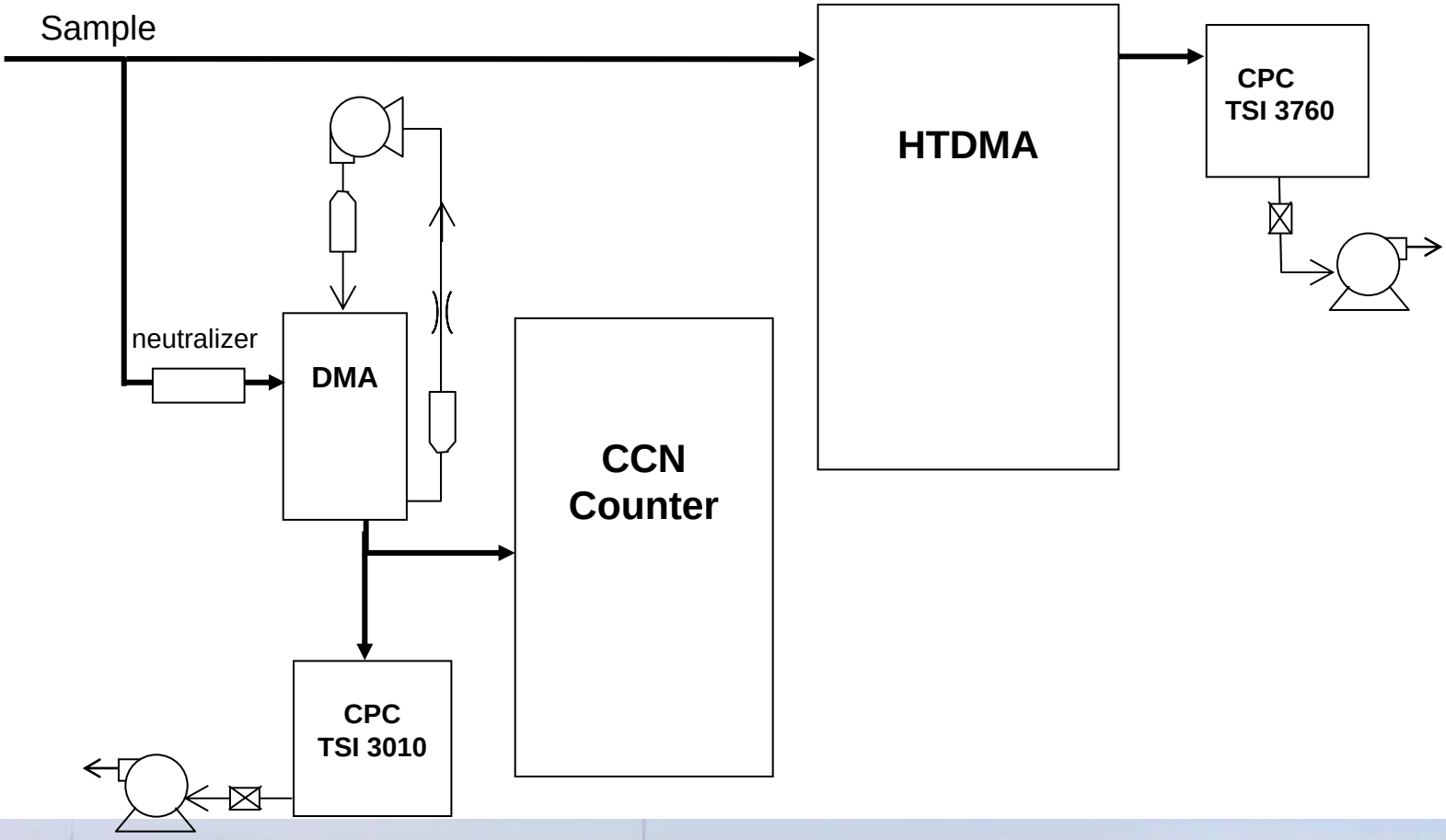
    aerosol hygroscopic growth (uptake of water at controlled humidity <100% RH) – we use a hygroscopicity TDMA

  - **dilute** aqueous solutions

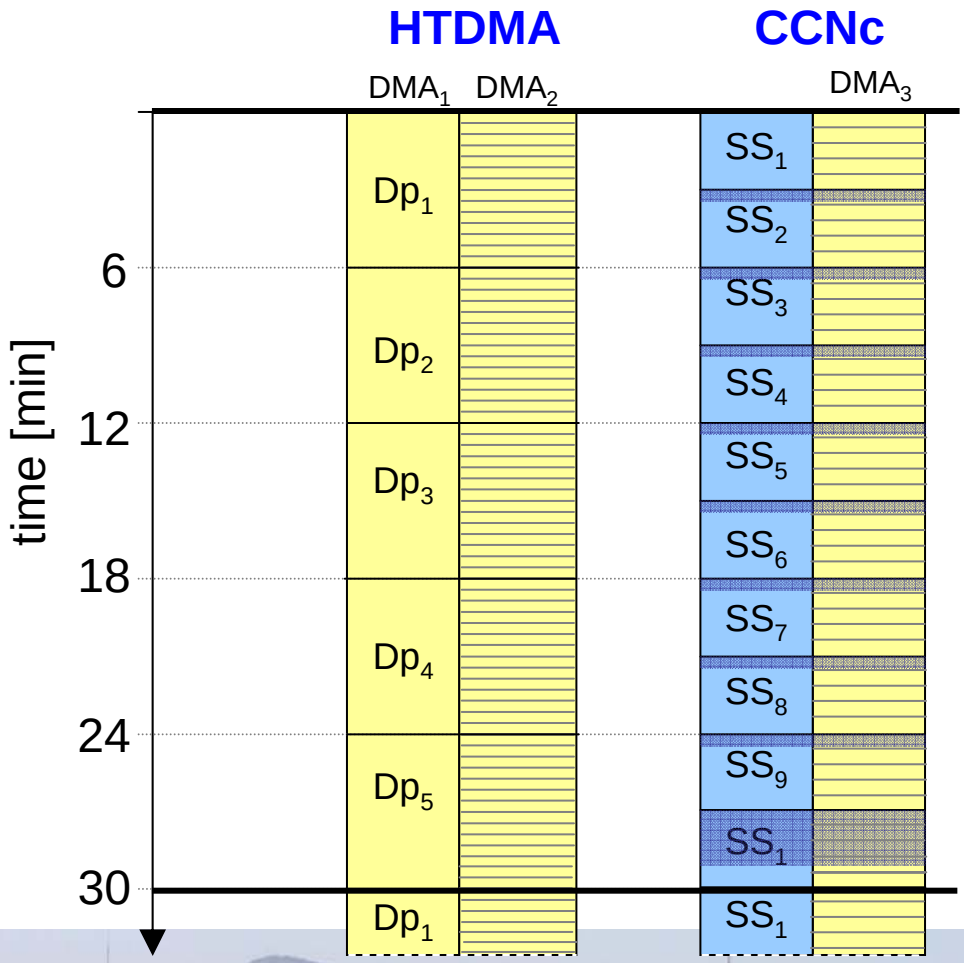
    CCN activity (water vapor supersaturation required to become a cloud droplet) – we use a CCN counter

- “aggregate” properties are needed as constraints for global climate model parameterizations of aerosol-cloud interactions.

Parallel Aerosol-Water Interactions Measurements



Instrument operation schedule



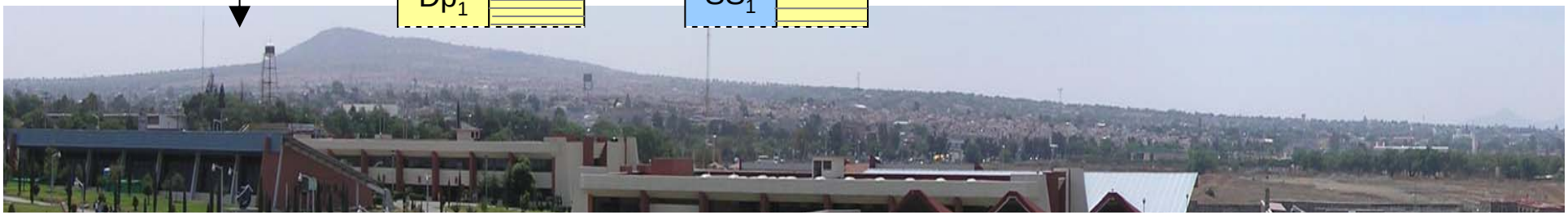
D_{p1}, D_{p3} = 20, 40, 60, 80, 100 nm

D_{p2} = 30 values, growth factors from 0.7 to 3.0

SS = 9 values between 0.15% and 1.0%

complete characterization every 30 min

We can cycle faster.



What information can we get from these measurements?

Directly measured:

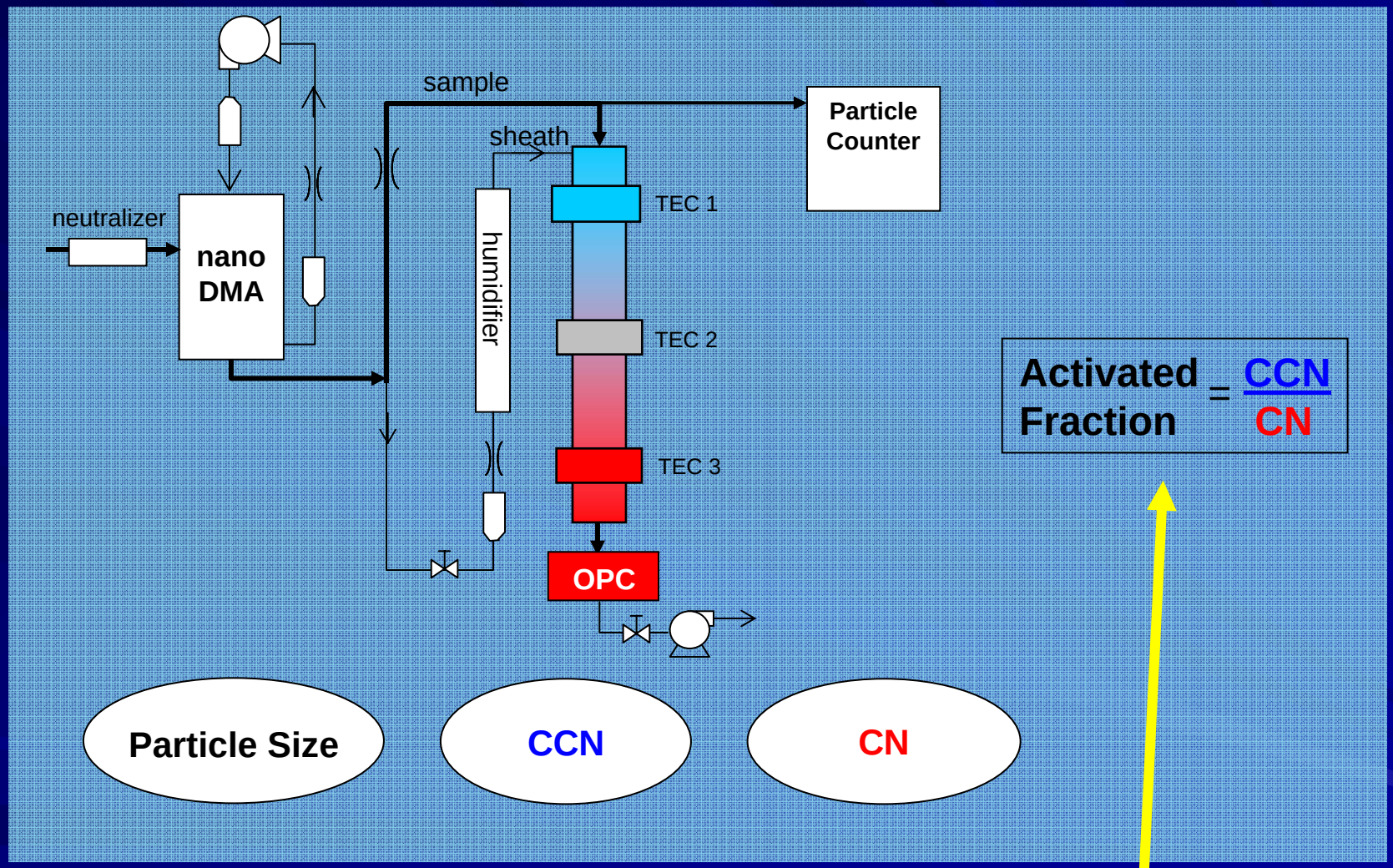
- CCN properties and hygroscopic growth
- mixing state
- droplet growth kinetics

Inferred properties:

- Characterization of the aerosols chemical composition (soluble fraction, organic molecular weight and solubility).
- Water vapor uptake coefficient
- Chemical aging of the aerosol

These properties are in an ideal "format" for GCM assessments, and for constraining/developing parameterizations of aerosol-cloud interactions.

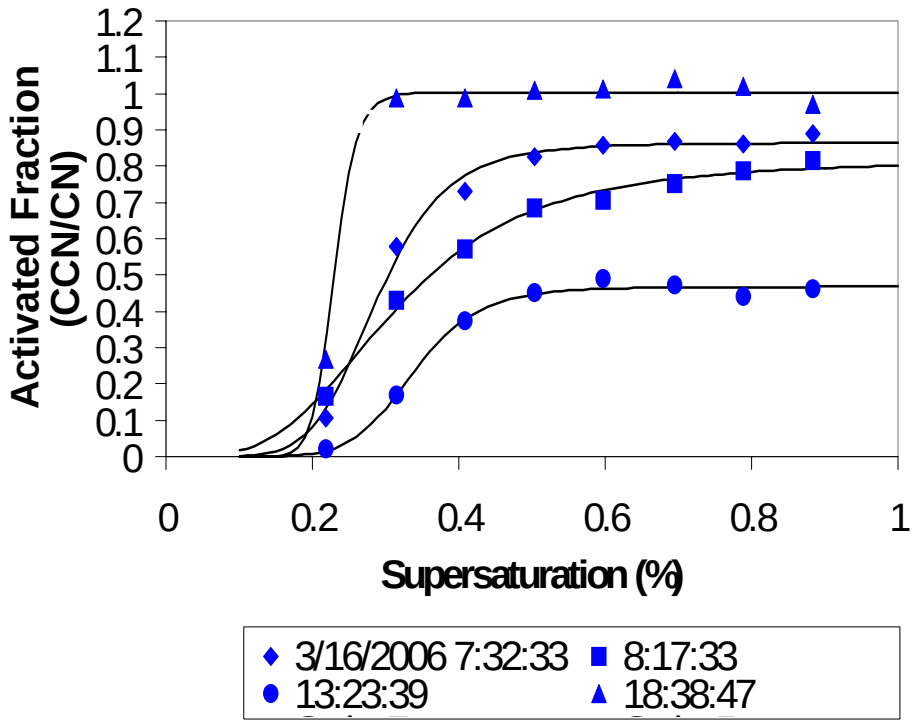
Focus on size-resolved CCN measurements

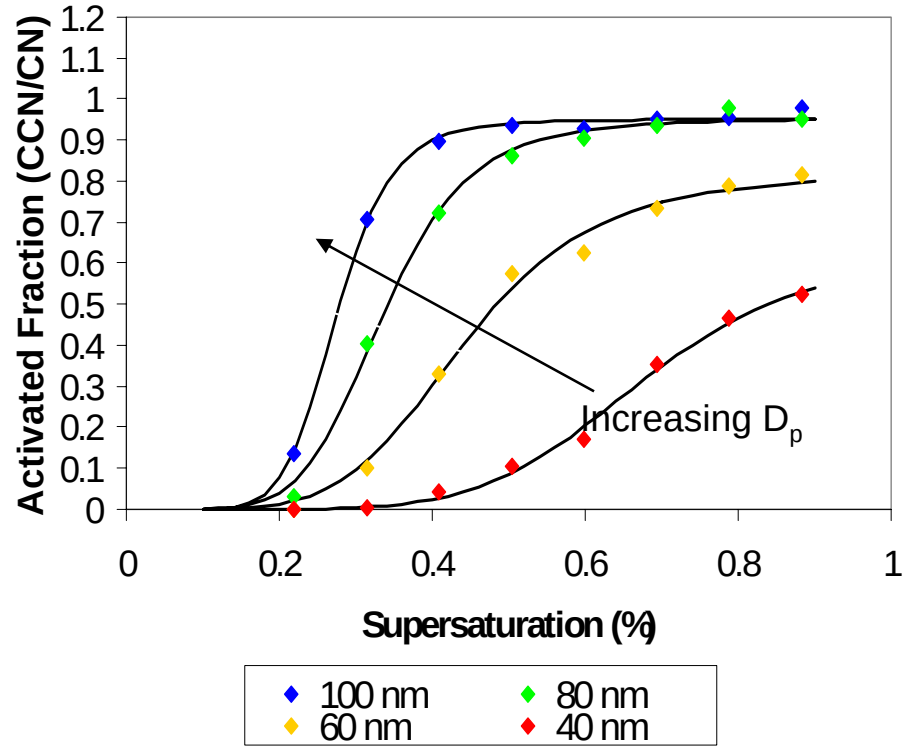


$$\text{Activated Fraction} = \frac{\text{CCN}}{\text{CN}}$$

Express measurements in terms of an “activated fraction”

CCN Activation Curves



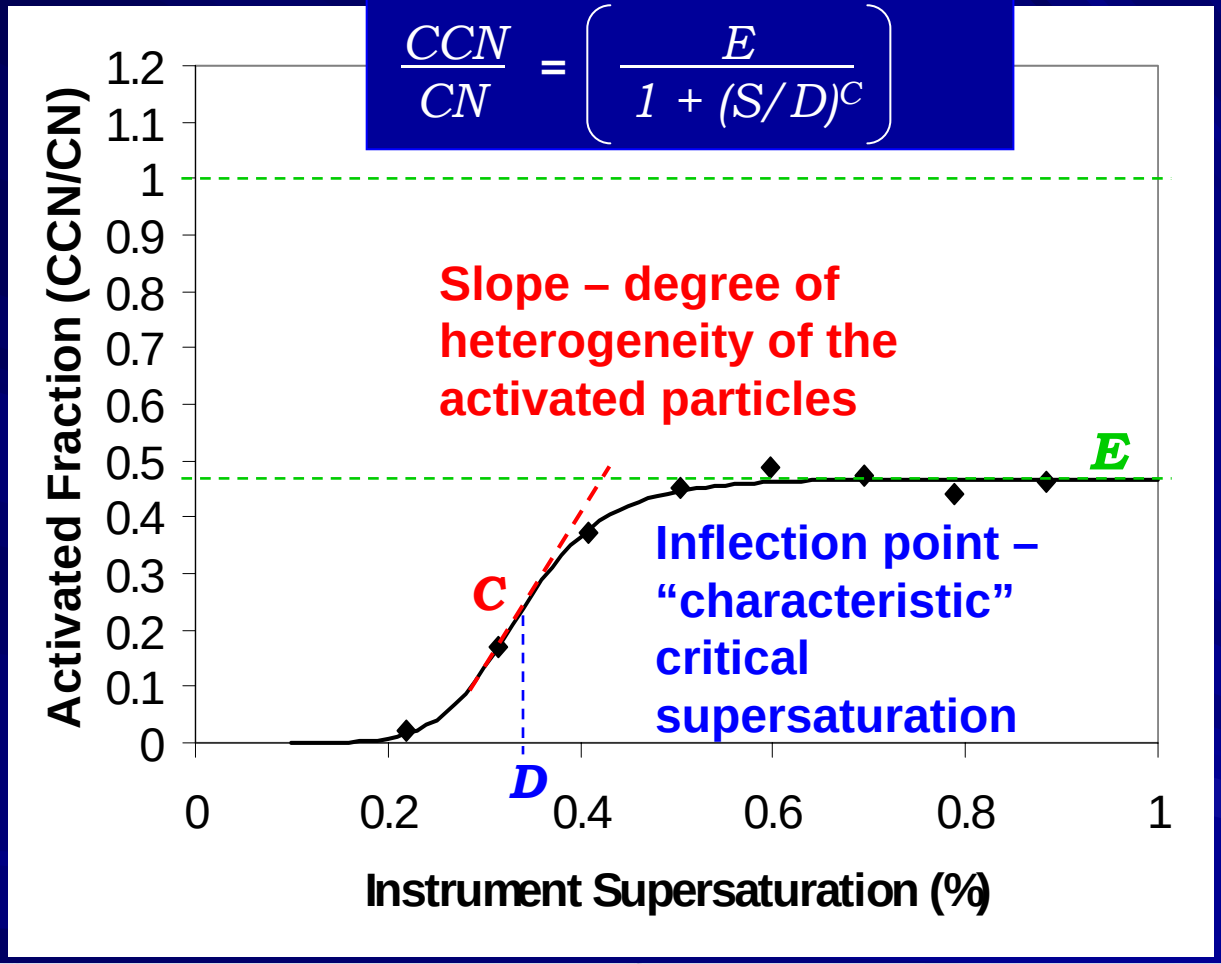


Activation curves can vary significantly throughout a day

Activation curves change also with dry particle size

What the Activation Curves tell us

$$\frac{CCN}{CN} = \left(\frac{E}{1 + (S/D)^C} \right)$$



Fraction of non-hygroscopic externally mixed particles

What Activation Curves tell us

They can quantify the chemical heterogeneity of the CCN

$$\left(\frac{CCN}{CN}\right)^{*} = \left(\frac{1}{1+(S/D)^{C}}\right)$$

Normalized to remove the unactivated particles from the calculation

Assume the particles are composed of a soluble and insoluble mixture.

From Köhler Theory:

$$S_c = 100\left[\exp\left(\frac{4A^3}{27B}\right)^{1/2} - 1\right]$$

$$A = \frac{4M_w\sigma}{RT\rho_w}$$

$$B = \frac{M_w\rho_s\nu}{M_s\rho_w}D_p^3\varepsilon_s$$

D_p is constant, the sigmoid describes the distribution of critical supersaturations for that size

What the Activation Curves tell us

The sigmoid then becomes:

$$\left(\frac{CCN}{CN}\right)^{*} = \frac{1}{1+\left(\frac{\omega\varepsilon_s^{-1/2}}{D}\right)^{C}}$$

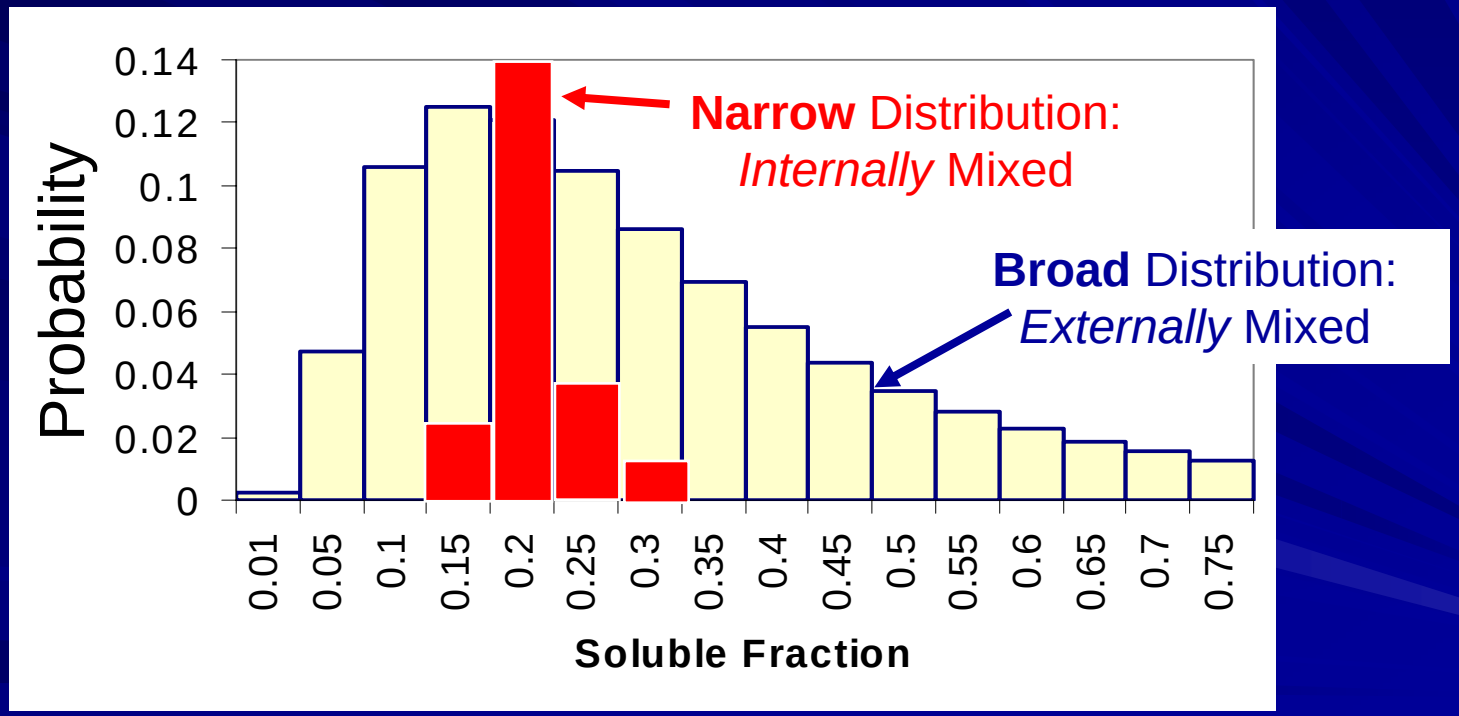
$$\omega \approx 100\left[\frac{4A^3}{27}\frac{M_s\rho_w}{M_w\rho_s\nu D_p^3}\right]^{1/2}$$

From which we can derive a volume fraction distribution:

$$\frac{d}{d\varepsilon_s}\left(\frac{CCN}{CN}\right)^{*} = \frac{C\left(\frac{\omega\varepsilon_s^{-1/2}}{D}\right)^{C-1}\omega\varepsilon_s^{-1/2}}{2D\left[1+\left(\frac{\omega\varepsilon_s^{-1/2}}{D}\right)^{C}\right]^{2}}$$

Result: Soluble Fraction Distribution for each particle size

The sigmoid describes a distribution of soluble fractions for the CCN active compounds. This is a direct measure of mixing state and aging

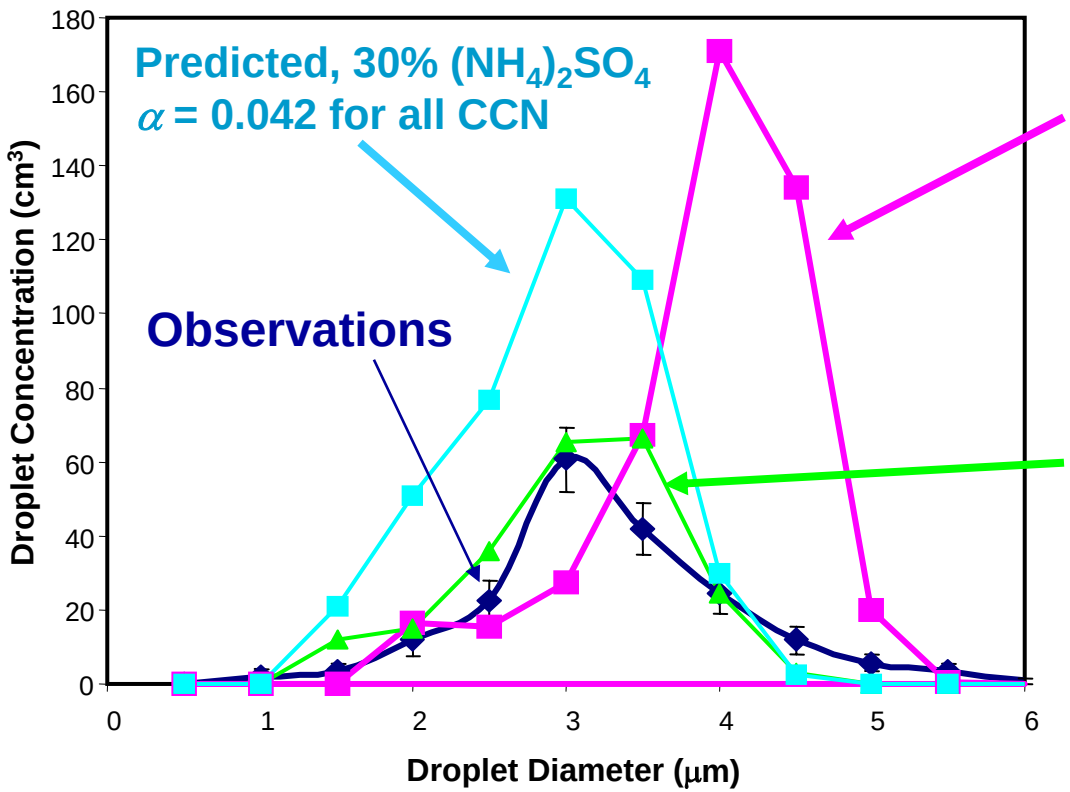


Lance et al., *in preparation*

Activation curves give us AMAZING insight into the aerosol!

Characterizing Growth Kinetics

- Instrument sizes the droplets that form in the instrument.
- This can be used to obtain kinetic growth information.
- Droplet size sensitive to composition, mixing state and other processes that affect growth kinetics (water vapor uptake).
- Modeling aerosol growth gives POWERFUL information



Predicted, 30% $(NH_4)_2SO_4$ α = 1.0 for all CCN

Predicted, 30% $(NH_4)_2SO_4$ α= 1.0 for submicron CCN; α = 0.042 for coarse particles. Aerosol 30% mixed.

Growth Kinetics: CCN Instrument Model

Gas phase (Eulerian):

$$\frac{\partial}{\partial t}(\rho\phi) + div(\rho\vec{u}\phi) + div\left(-\Gamma_\phi \vec{\nabla}\phi\right) = S_\phi$$

transient *advection* *diffusion* *source*

Conservation Law	ϕ	Γ_ϕ	S_ϕ
Continuity	1	0	0
x_1 -momentum	u	μ	$-x_2^a \frac{\partial P}{\partial x_1} + x_2^a \frac{\partial}{\partial x_1}\left(\mu \frac{\partial u}{\partial x_1}\right) + \frac{\partial}{\partial x_2}\left(x_2^a \mu \frac{\partial v}{\partial x_1}\right) + J_{buoy}$
x_2 -momentum	v	μ	$-x_2^a \frac{\partial P}{\partial x_2} + x_2^a \frac{\partial}{\partial x_1}\left(\mu \frac{\partial u}{\partial x_2}\right) + \frac{\partial}{\partial x_2}\left(x_2^a \mu \frac{\partial v}{\partial x_2}\right) - \frac{a\mu v}{x_2}$
Heat	T	$\frac{k_a}{c_p}$	$\frac{\Delta H_{vap}}{c_p} J_{cond}$
Water vapor	C	ρD_v	$-\rho J_{cond}$

Calculated from instrument model

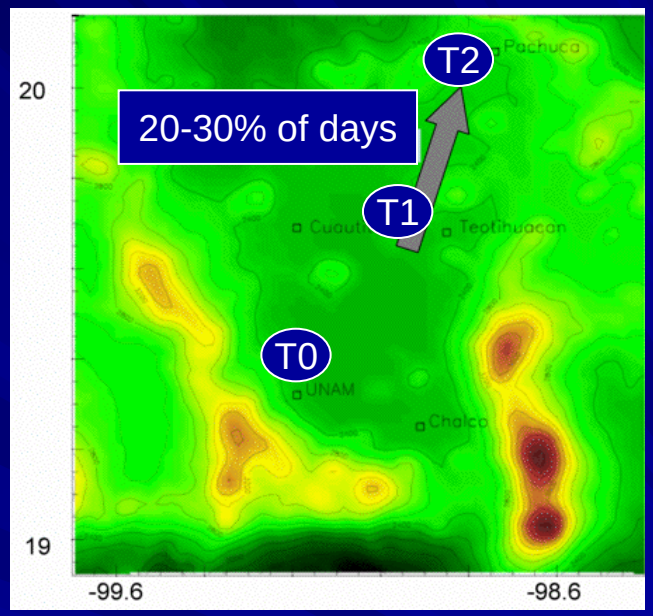
from Kohler theory

Particle phase (Lagrangian):

$$\frac{dD_p}{dt} \propto \frac{S(r,z) - S_{eq}(r,z)}{D_p}$$

Roberts and Nenes (2005); Lance et al. (2006)

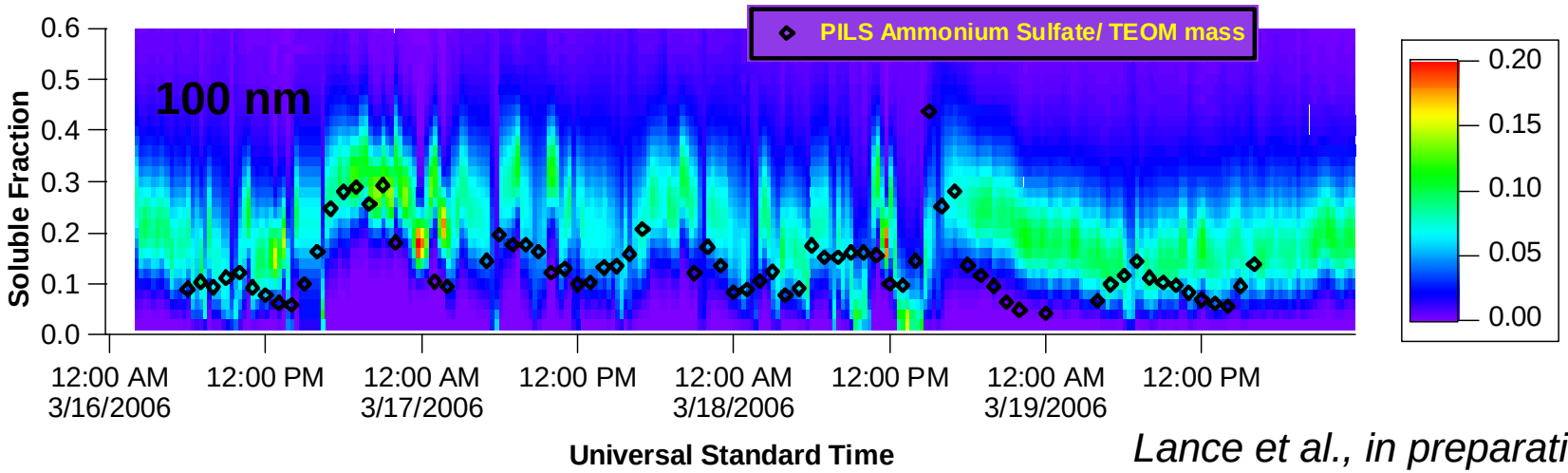
Application: Megacities Impacts on Regional and Global Environments (MIRAGE)



- T1 Ground Site, University of Tecamac
- Our data: March 16th-31st
- Measuring the pollution outflow from Mexico City

Biomass burning, dust, vehicle exhaust, sheep, pollution…“the works”

Derived vs. measured mass fractions



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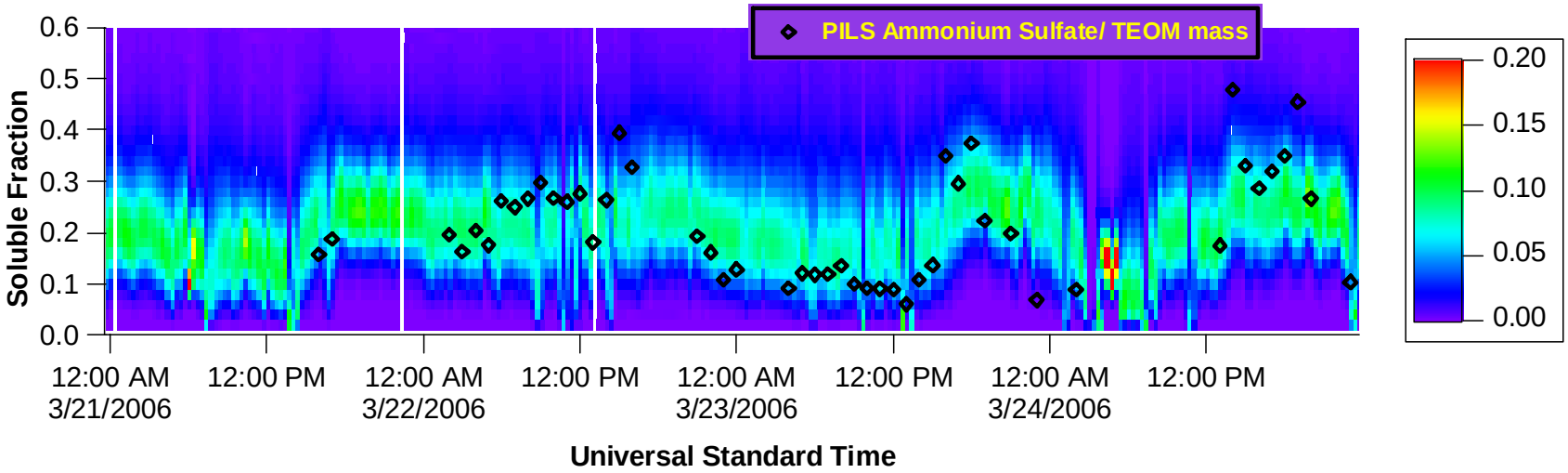
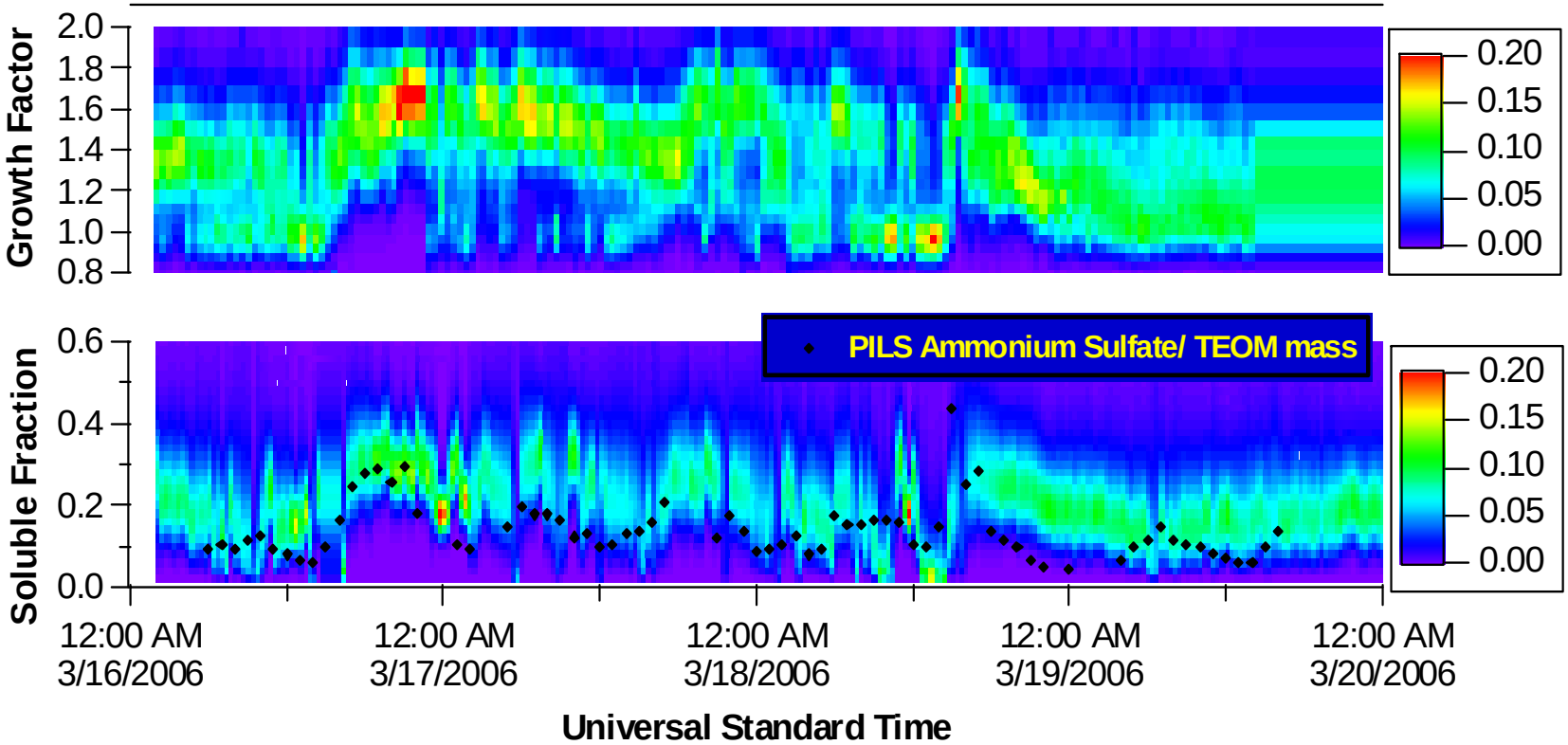


The idea works! We can get PDF's of composition vs. size…. Very powerful characterization of chemical ageing and heterogeneity.

Comparison of measurements



- **Hygroscopic growth factor (GF) is consistent with inferred soluble fraction.**
- **CCN mixing state (width of the soluble fraction PDF) is correlated with the GF distributions.**

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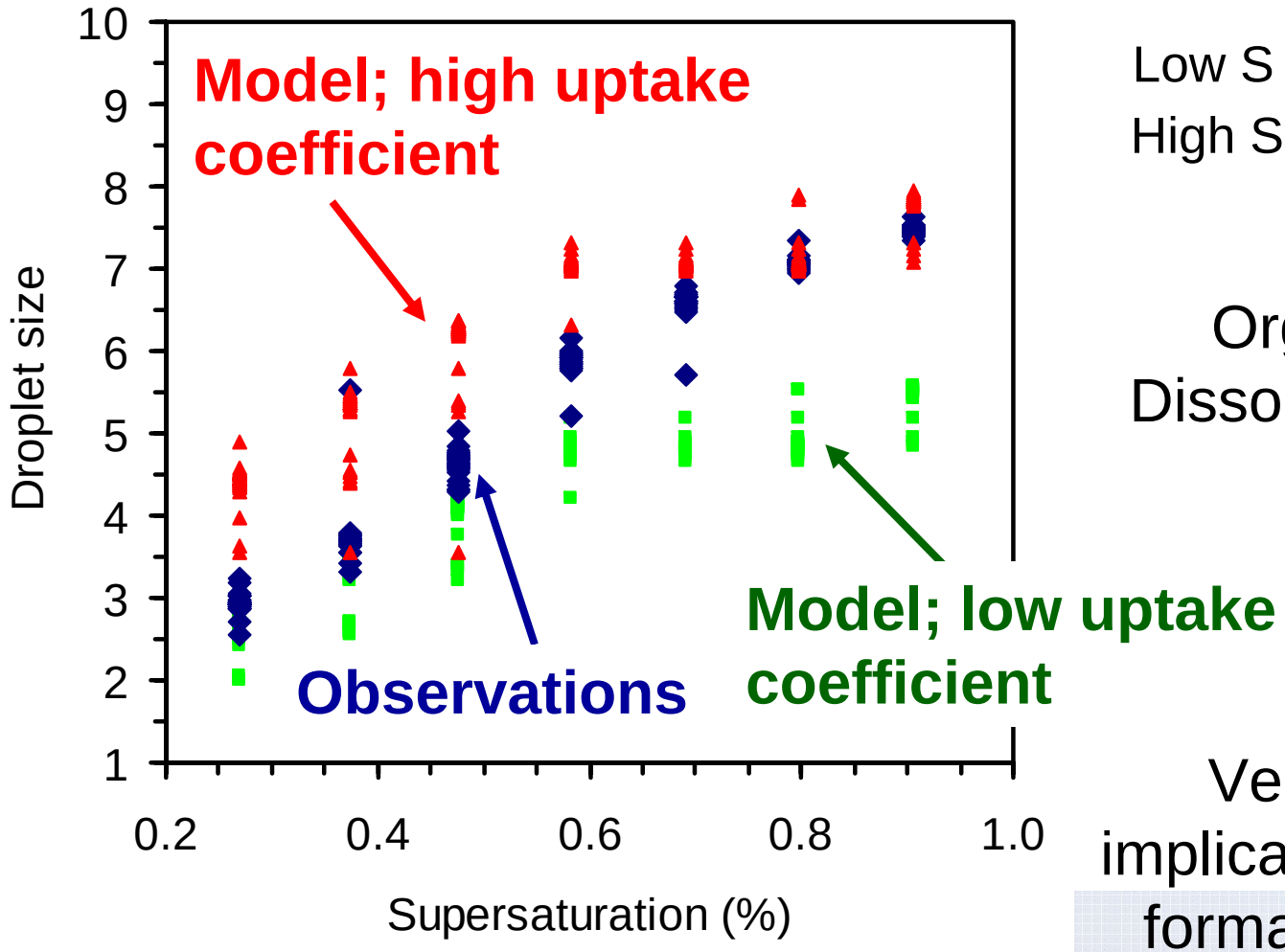
Droplet Growth Kinetics



Low S → slower uptake.
High S → faster uptake.

Organic films?
Dissolution kinetics?

Very important implications for droplet formation & indirect forcing estimates

Lance et al., in preparation

Take-home messages

Size resolved CCN and hygroscopicity measurements provide very powerful and unique information on

- Mixing state - I (completely hygroscopic/hydrophobic)
- Mixing state - II (soluble fraction distributions)
- Aging of the CCN
- Characterization of growth kinetics
- Unique insights on impacts of organics on CCN
- Very fast time resolution

This analysis and measurement strategy needs to be done for all sites that have CCN and/or hygroscopicity measurements.

DOE-ARM with its infrastructure and external collaborations (GaTech?) can accomplish these goals.

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