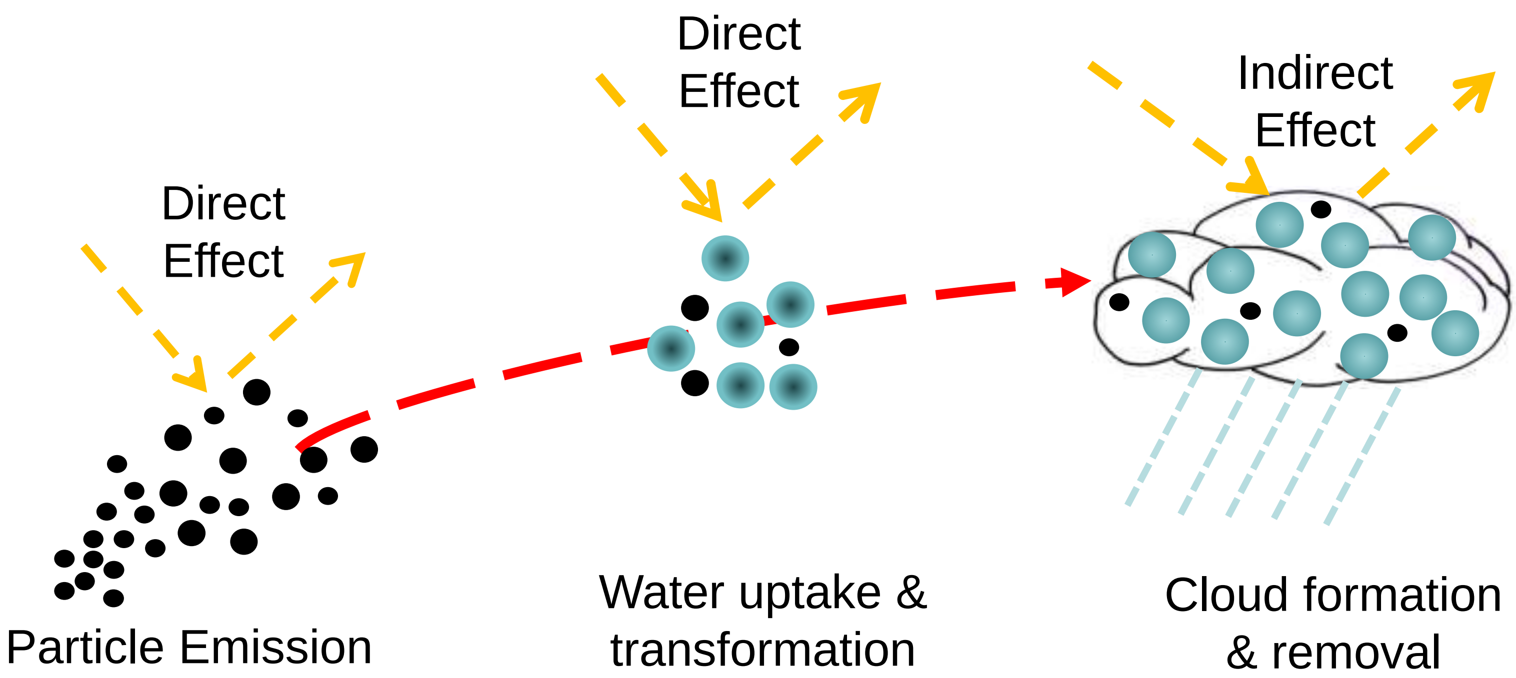
Cloud Condensation Nuclei Measurements During the SENEX Campaign: Observations, Analysis and Impacts

A.Nenes[1,2], J. J.Lin[1], A.Bougiatioti[1,3], K.M.Cerully[2], R.Morales[1], C.A.Brock[4,5], N.L.Wagner[4,5], D.A.Lack[4,5], D.Law[4], T.Gordon[4,5], M.S.Richardson[4,5], M.Markovic[4,5], J.P.Schwarz[4,5], A.M.Middlebrook[4], J.Liao[4,5], A.Welti[4,5†], J.deGouw[4,5], L.Xu[2], N.L.Ng.[1,2], H.Guo[1], R.Weber[1]

[1]School of Earth and Atmospheric Sciences, Georgia Tech, Atlanta, GA; [2]School of Chemical and Biomolecular Engineering, Georgia Tech, Atlanta, GA; [3]National Technical University of Athens, Zografou Campus, Athens, Greece; [4]NOAA Earth System Research Laboratory, Boulder, CO; [5]CIRES, University of Colorado Boulder, Boulder, CO; [*]Now at Departamento de Ingeniería Civil y Ambiental, Universidad de los Andes, Colombia; [†]Now at Institute for Atmosphere and Climate, ETH Zürich, Switzerland

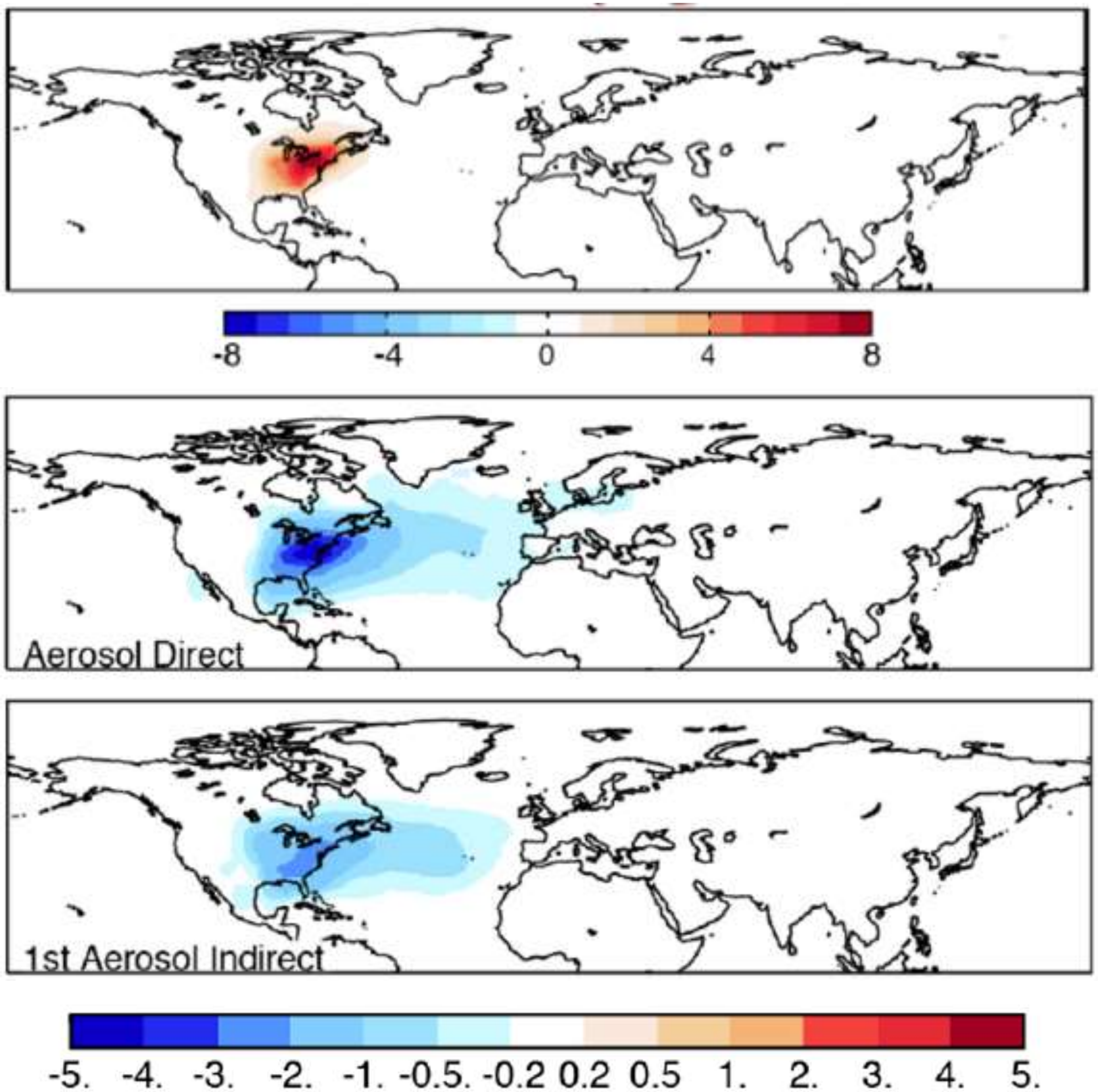
Acknowledgments: EPA, NSF, NOAA, NASA

Climate-relevant impacts of Aerosol



Relevant properties : Water uptake (hygroscopicity), CCN number, optical properties.

Climate impacts from US anthropogenic aerosol



Change in droplet number (%)

Direct radiative forcing ($W\ m^{-2}$)

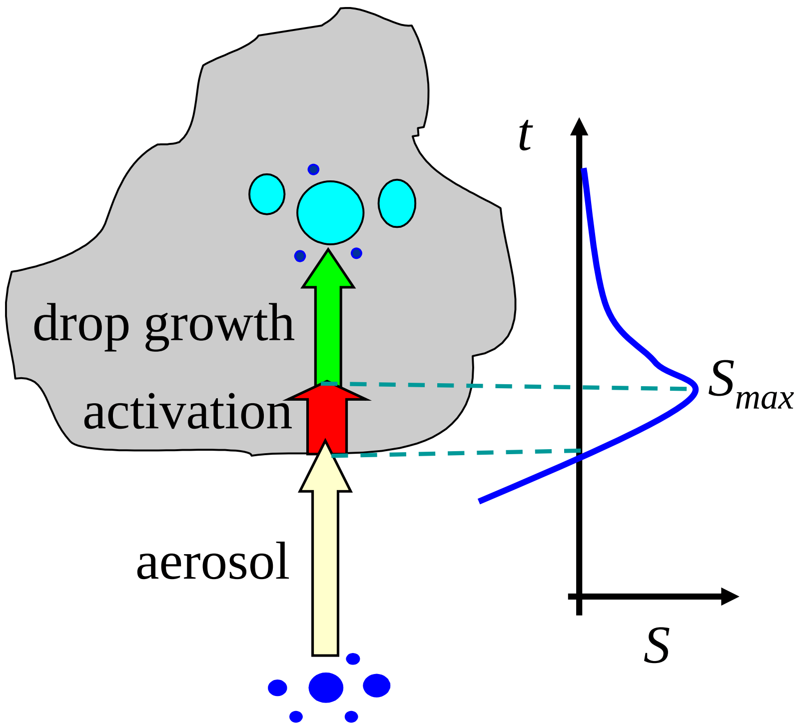
Indirect radiative forcing ($W\ m^{-2}$)

Liebensperger et al., ACP, 2012a

Warm (Liquid) Cloud Formation

The "simple story" (1D parcel theory)

Consider conservation of energy and water vapor condensing on aerosol particles in cloudy updrafts.



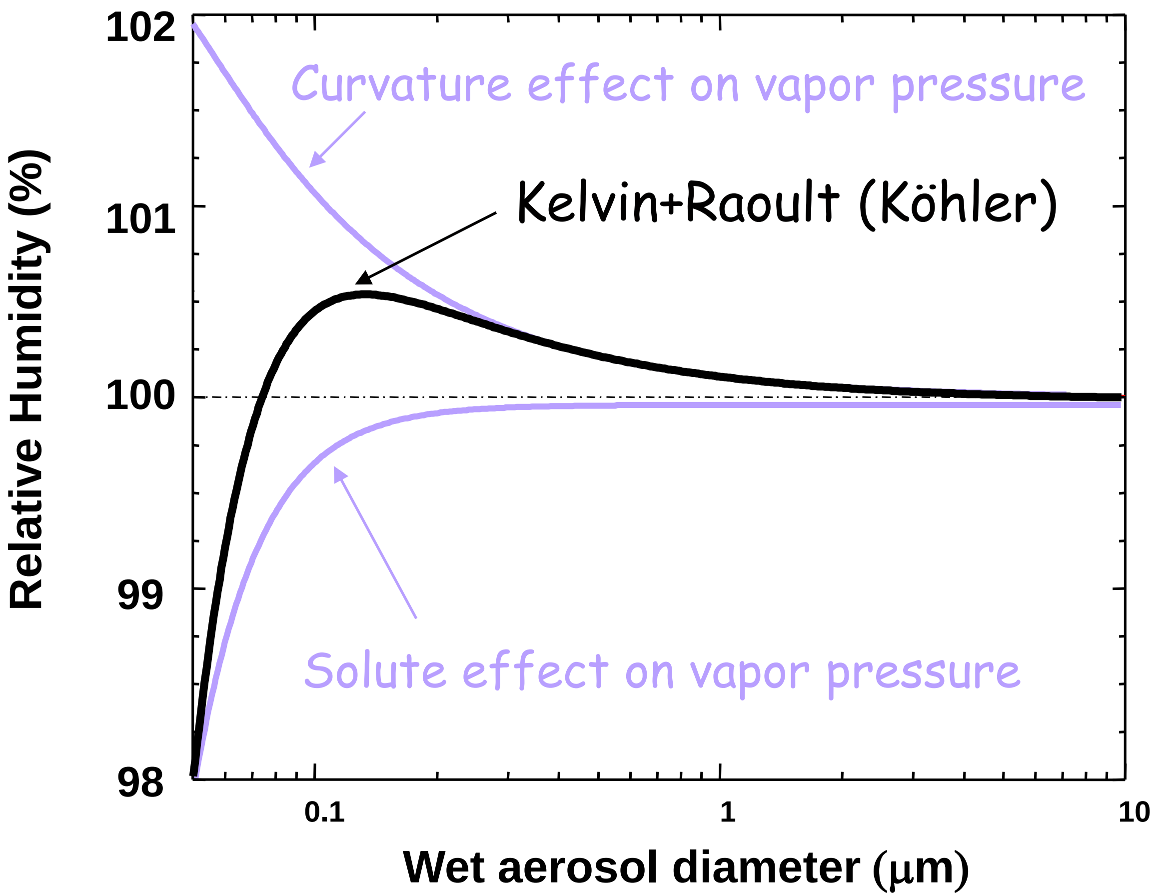
Conceptual steps are:

- Air parcel cools, exceeds dew point
- Water vapor is **supersaturated**
- Droplets start forming on existing CCN.
- Condensation of water on droplets becomes intense.
- Humidity reaches a **maximum**
- No more additional drops form

A "classical" nucleation/growth problem

When does an aerosol act as a CCN ?

Examine the equilibrium vapor pressure of a wet aerosol particle.
Consider the effects of *solute* and *droplet curvature*



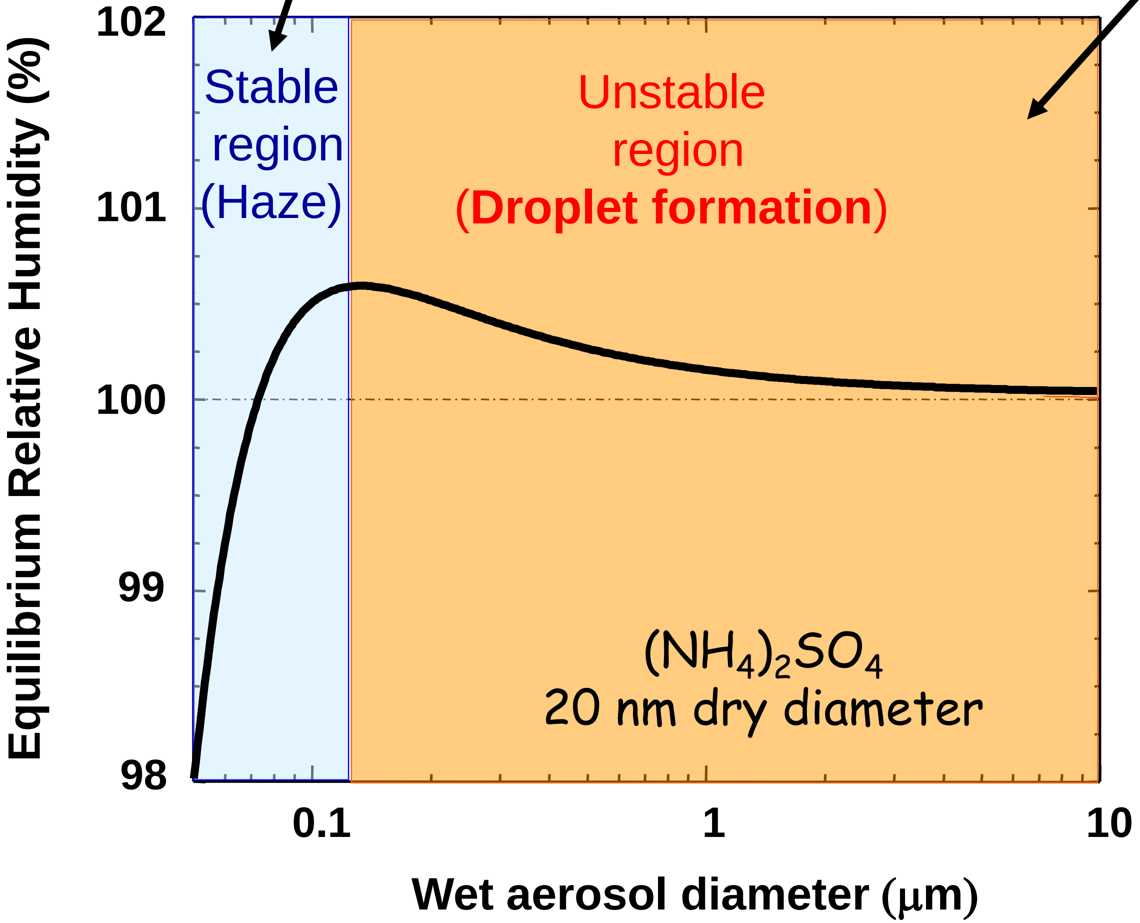
The combined Kelvin and Raoult effects is known as the **Köhler equation (1922)**.

You can be in equilibrium even if you are above saturation.

When does an aerosol particle act as a CCN ?

Ambient RH **less** than S_c -> *stable* equilibrium.

Ambient RH **above** S_c -> unstable equilibrium.



Köhler theory:

$$s_c = \left(\frac{4A^3}{27B} \right)^{1/2}$$

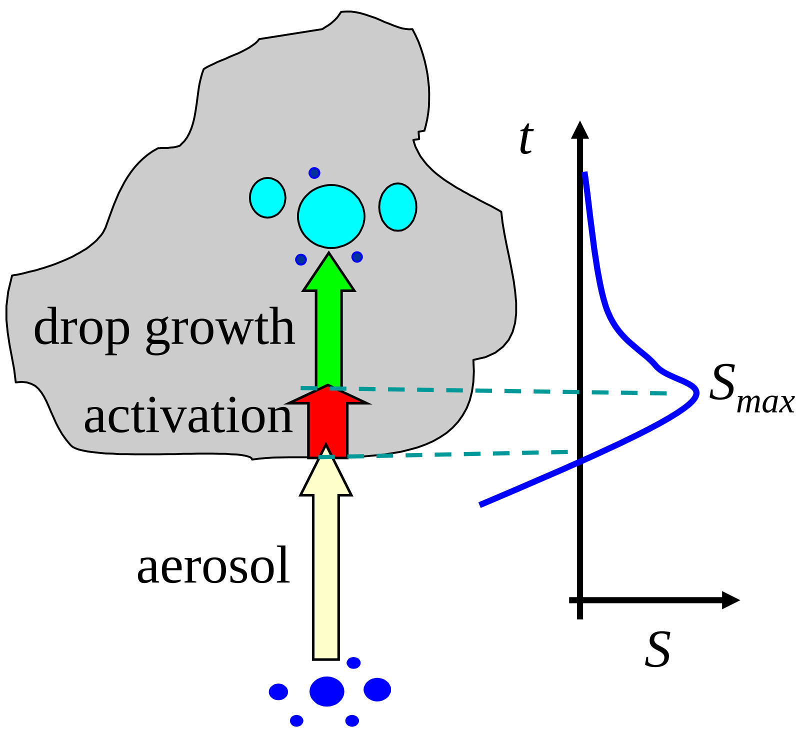
$$s_c \sim d_{dry}^{-3/2},\ \varepsilon_{\mathbf{soluble}}^{-1/2}$$

Size is more important than composition

Droplet number needs CCN and max.cloud RH…

Algorithm for calculating N_d (Mechanistic parameterization):

1. Calculate s_{max} (approach-dependent)
2. N_d is equal to the CCN with $s_c \leq s_{max}$



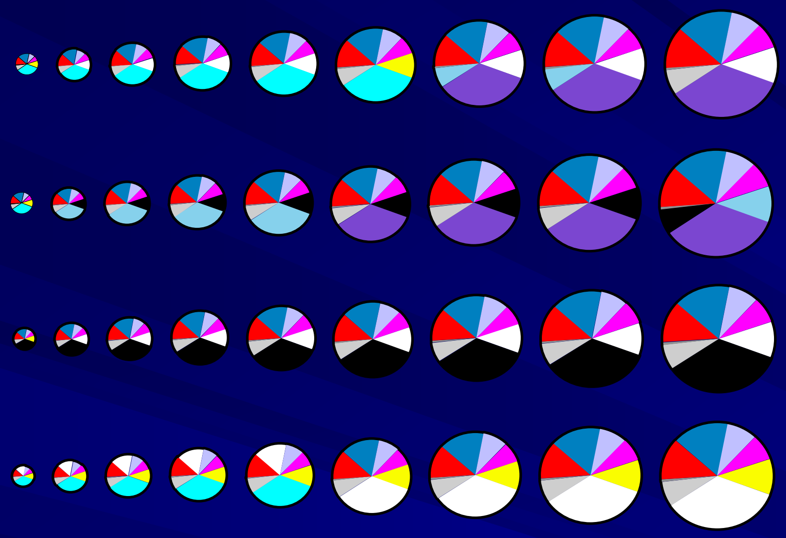
Mechanistic Parameterizations: Twomey (1959); Abdul-Razzak et al., (1998); Nenes and Seinfeld, (2003); Fountoukis and Nenes, (2005); Kumar et al. (2009), Morales and Nenes (2014), and others.

Input: P,T, vertical wind, particle size distribution,composition.

Output: Cloud properties (droplet number, size distribution).

Comprehensive review & intercomparison:
Ghan, et al., *JAMES* (2011); Morales and Nenes (2014)

Aerosol Problem: Complexity



An integrated "soup" of

- Inorganics, organics (1000's)
- Particles can have uniform composition with size…
- … or not
- Can vary vastly with space and time (esp. near sources)

Organic species have been a headache

- They can facilitate cloud formation by acting as surfactants and adding solute (hygroscopicity)
- Oily films can form and delay cloud growth kinetics

In-situ data to study the aerosol-CCN link:

Usage of CCN activity measurements to "constrain" the above "chemical effects" on cloud droplet formation.

Parameterizing "characteristic" CCN activity…

Petters and Kreidenweis (2007) expressed the solute parameter in terms of a "hygroscopicity parameter", κ

$$s_c = \left(\frac{4A^3}{27B}\right)^{1/2} \Rightarrow s_c = \left(\frac{4A^3}{27\kappa}\right)^{1/2} d^{-3/2}$$

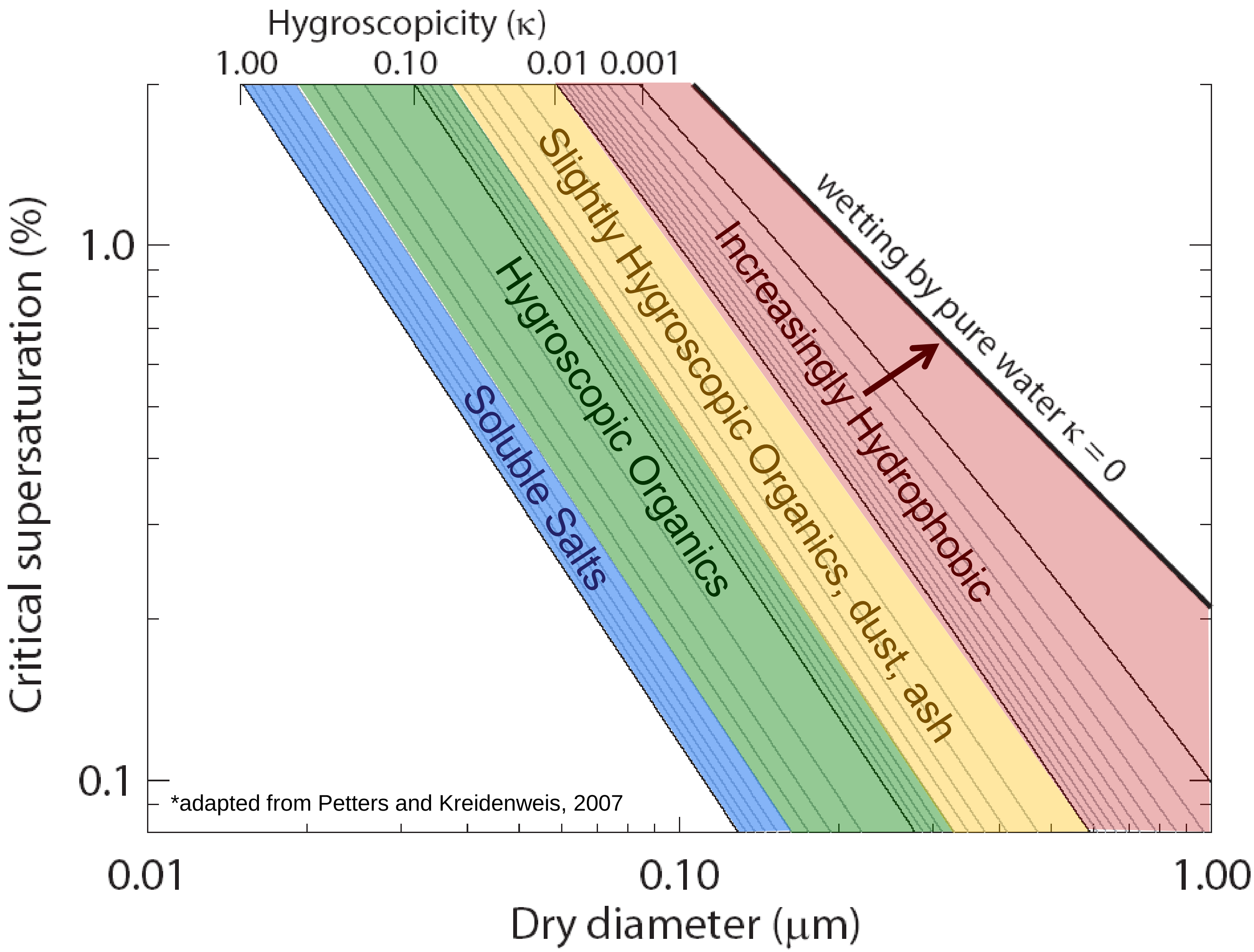
$\kappa \sim 1$ for NaCl, ~ 0.6 for $(NH_4)_2SO_4$, $\sim$ 0-0.3 for organics

κ rarely exceeds 1 in atmospheric aerosol

Simple way to think of κ: the "equivalent" volume fraction of NaCl in the aerosol (the rest being insoluble).

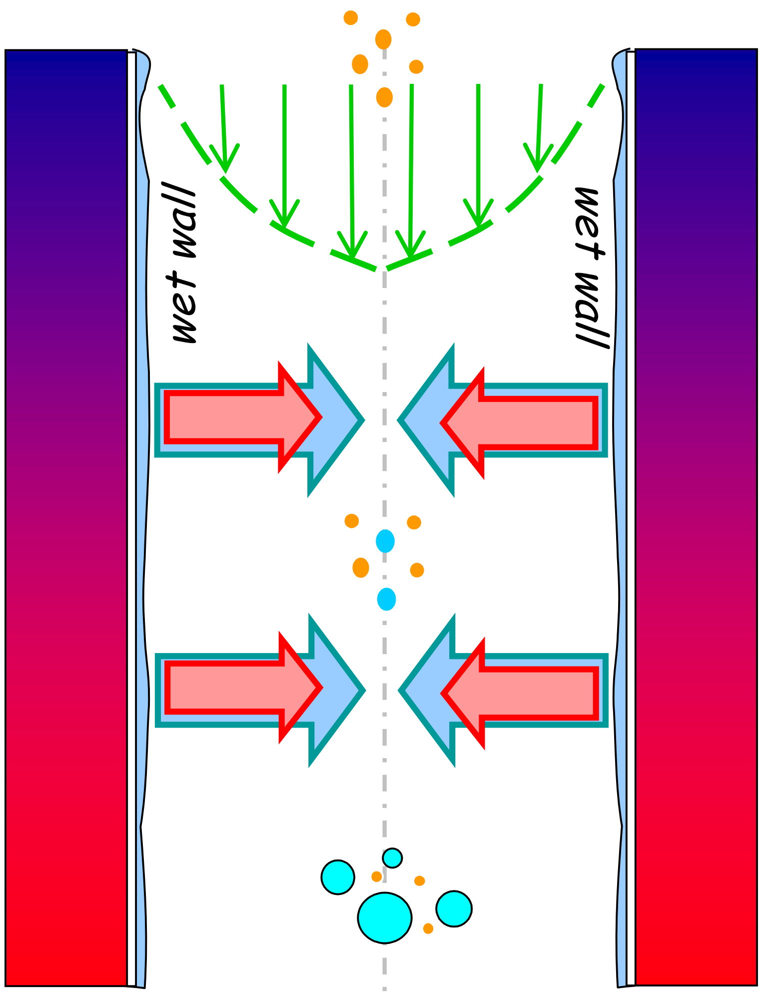
$\kappa \sim 0.6$ ⇨ particle behaves like 60% NaCl, 40% insoluble

Hygroscopicity Space



- κ is used to parameterize the activation of particles in the atmosphere

Source of CCN measurements: DMT CFSTGC



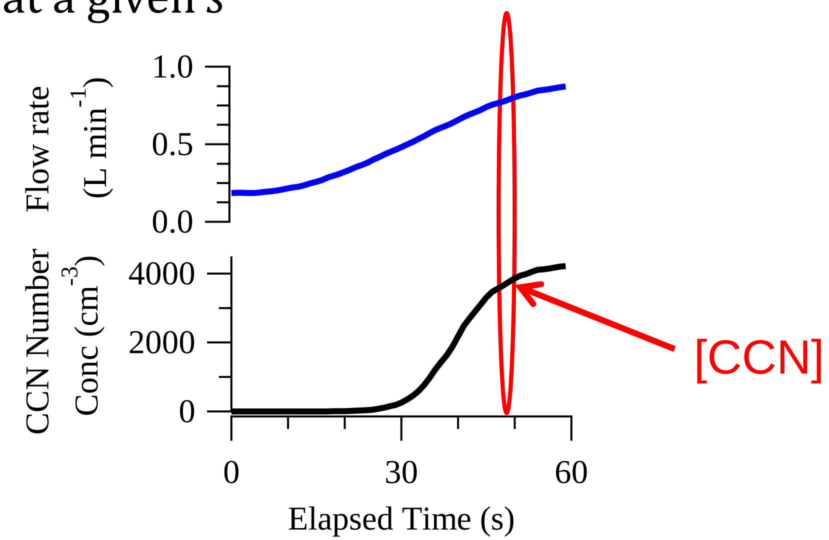
- Standard CCN measurement (>100 instruments in operation).
- Metal cylinder with wetted walls
- Streamwise Temp. Gradient
- Water diffuses faster than heat
- Supersaturation, S, generated at the centerline = *f* (Flowrate, Pressure, and Temp. Gradient)
- Operated as a *spectrometer* using Scanning Flow CCN Analysis (Moore and Nenes, 2009)

Roberts and Nenes (2005), US Patent 7,656,510

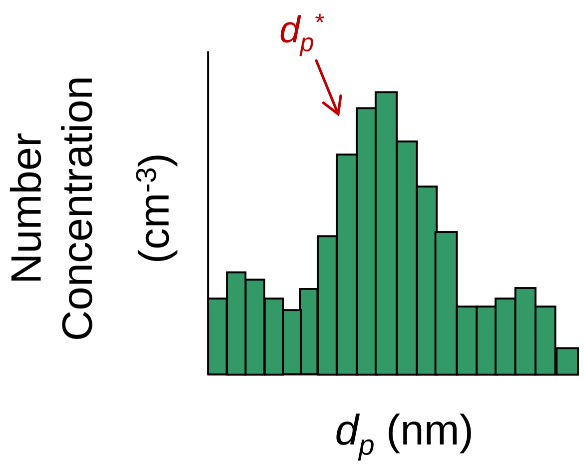
Lance et al., (2006), Lathem and Nenes (2011), Raatikainen et al. (2012, 2013)

Obtaining κ from CCN Measurements

1. Using Scanning Flow CCN Analysis, determine CCN concentration, [CCN], at a given s^*



2. Find where backwards integrated size distribution = [CCN] to obtain the critical diameter, d_p^*



3. Calculate κ

$$\kappa \approx \frac{4A^3}{27 d_p^3 s^{*2}} = \frac{M_w \rho_s}{\rho_w M_s} \upsilon \varepsilon_s$$

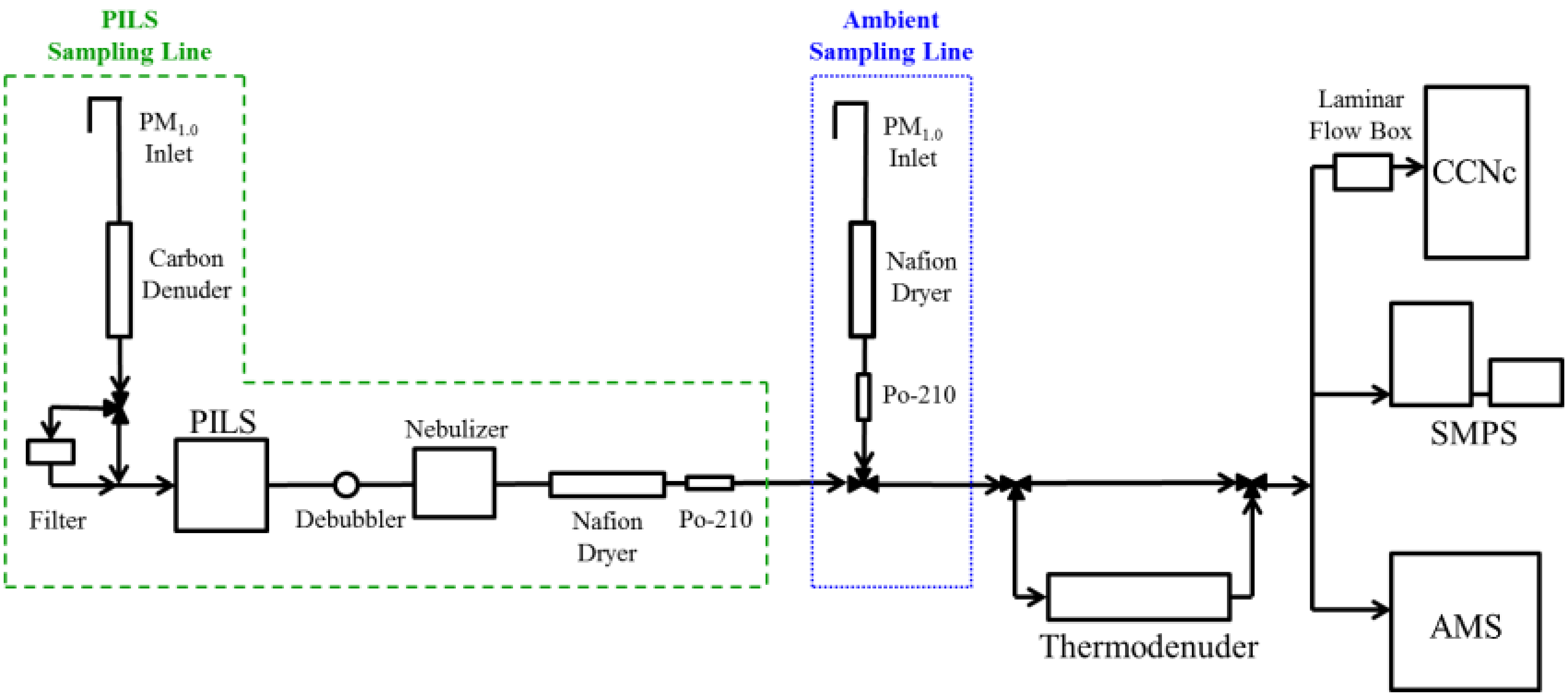
Moore and Nenes (2009)

Our goals for **SOAS** and SENEX

Photo credit: Jon Mak's Long-EZ

- ***Study*** *links between volatility, hygroscopicity & oxidation state of the Organic Aerosol (OA).*
- ***Investigate*** *which fractions of the OA are responsible for the observed hygroscopicity and volatility.*
- ***Quantify*** *the major contributors of LWC variability, particularly the relative role of organic vs. inorganic species.*
- ***Estimate*** *the impact of aerosol properties on cloud droplet number and cloud supersaturation*

SOAS: Measurement Setup



- Measured ambient and water-soluble (PILS) aerosol at 3 different supersaturations and 4 temperature conditions (non-denuded, 60°C, 80°C, and 100°C)

SOAS: κ_{org}, Volatility, and O:C

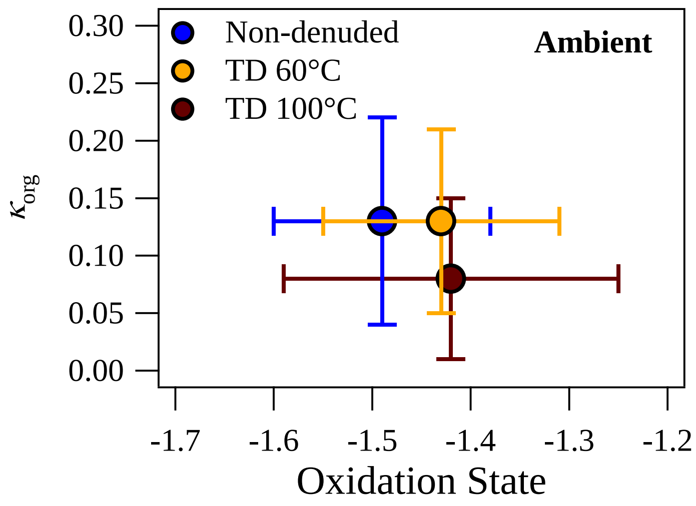
- κ_{org} calculated from AMS composition measurements: $\kappa = \kappa_{org}\varepsilon_{org} + \kappa_{inorg}\varepsilon_{inorg}$

κ_{org} with volatility

	Ambient	PILS
Non-denuded	0.14±0.09	0.14±0.06
TD at 60°C	0.12±0.08	0.12±0.06
TD at 80°C	0.12±0.11	0.09±0.04
TD at 100°C	0.08±0.07	0.08±0.06

Most volatile fraction is also the most hygroscopic (contradictory to expected link) … but why?

- Investigate κ_{org} and oxidation state… Looking at ambient data



Organic fraction hygroscopicity actually seems to go down a little when you heat the aerosol a lot..

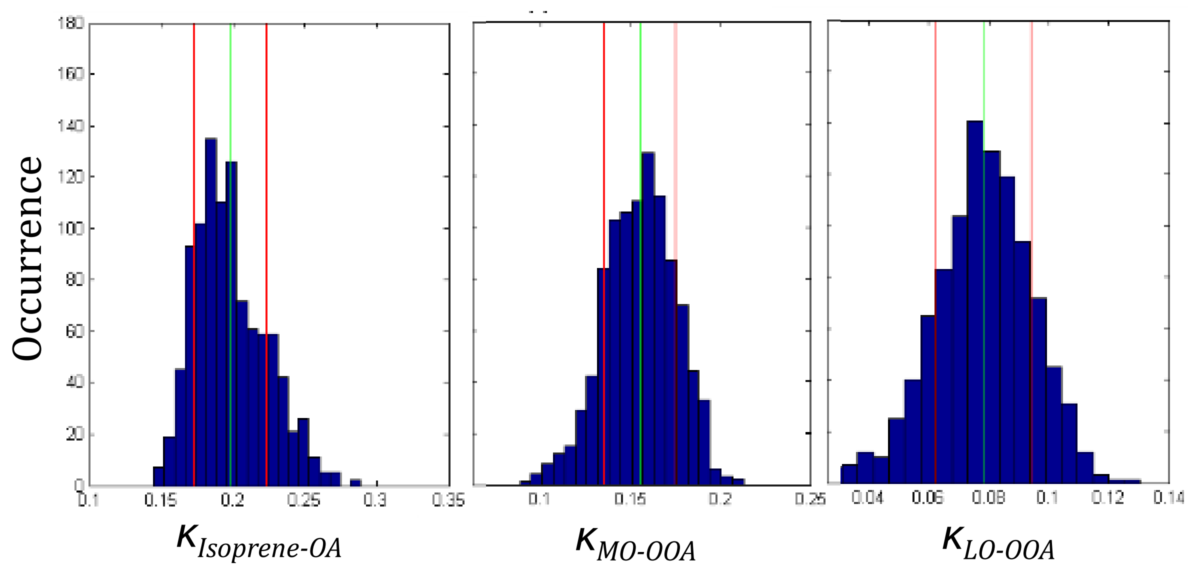
Cerully et al., ACP, (2015)

SOAS: κ_{org} and O:C of PMF Factors

- AMS Positive Matrix Factorization (PMF) determined 3 factors describing the PILS aerosol (Xu et al., PNAS, 2015)
  - Less oxidized oxygenated organic aerosol (LO-OOA)
  - More oxidized oxygenated organic aerosol (MO-OOA)
  - Isoprene-derived organic aerosol (Isoprene-OA)

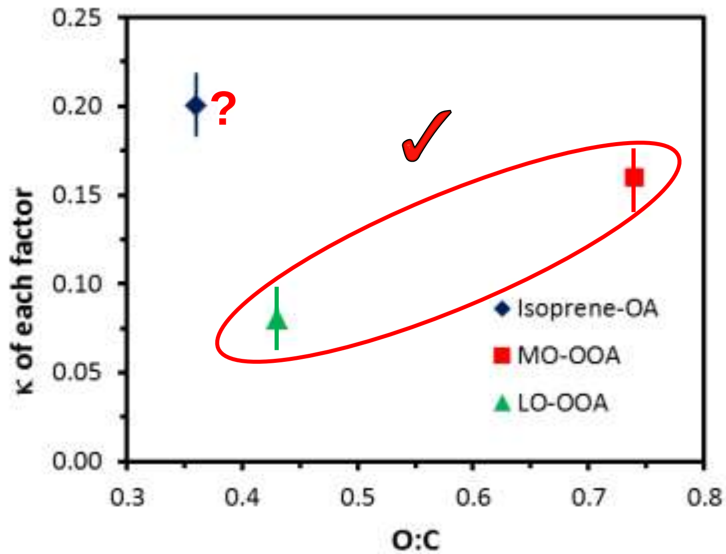
- The κ_{org} of each respective factor was found by bootstrapped resampling of the linear regression of the three factors:

$$\kappa_{org} = \varepsilon_{LO-OOA}\kappa_{LO-OOA} + \varepsilon_{MO-OOA}\kappa_{MO-OOA} + \varepsilon_{Isoprene-OA}\kappa_{Isoprene-OA}$$



Cerully et al., ACP, (2015)

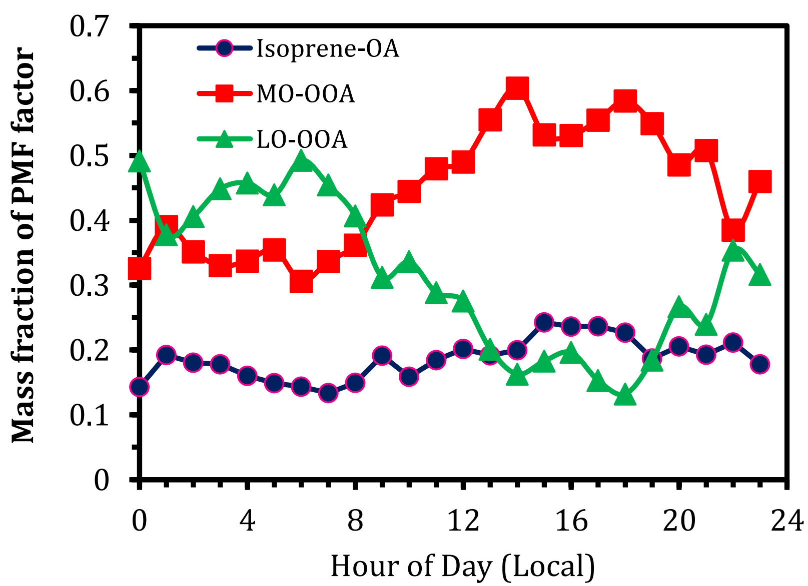
SOAS: κ_{org} and O:C of PMF Factors

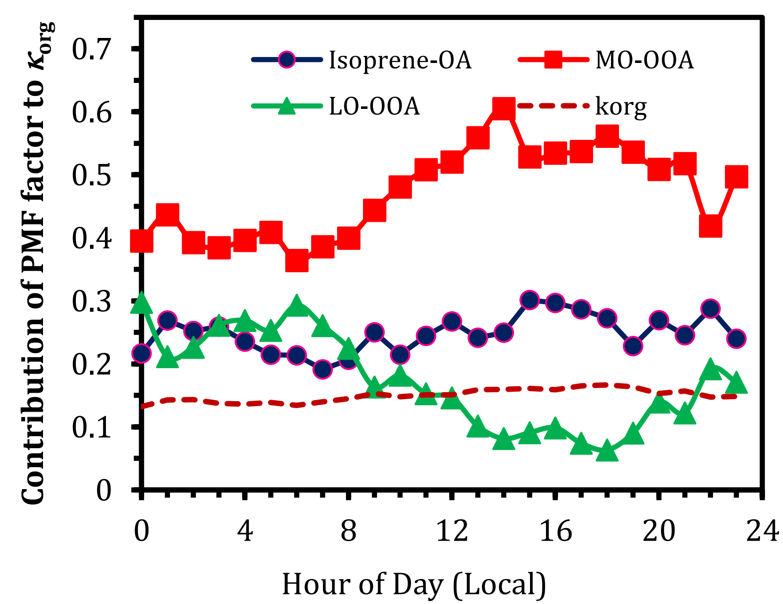


- MO-OOA displayed a higher κ_{org} and O:C compared to LO-OOA

- In general, no clear correlation between κ_{org} and O:C (or oxidation state)

Cerully et al., ACP, (2015); Xu et al., PNAS, (2015)

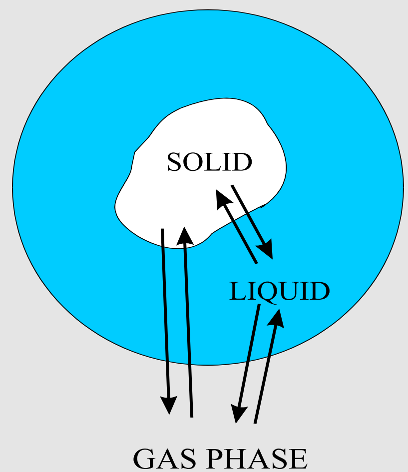




Using hygroscopicity for LWC calculations

Inorganic species: ISORROPIA-II (Fountoukis and Nenes, 2007)

Liquid: Na^+, NH_4^+, H^+, OH^-, HSO_4^-, SO_4^{2-}, NO_3^-, Cl^-, H_2O, $HNO_{3(aq)}$, $HCl_{(aq)}$, $NH_{3(aq)}$, $\mathbf{Ca^{2+}}$, $\mathbf{K^+}$, $\mathbf{Mg^{2+}}$



T, RH

Solids: $NaHSO_4$, NH_4HSO_4, Na_2SO_4, $NaCl$, $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaNO_3$, $\mathbf{K_2SO_4}$, $\mathbf{KHSO_4}$, $\mathbf{KNO_3}$, $\mathbf{KCl}$, $\mathbf{CaSO_4}$, $\mathbf{Ca(NO_3)_2}$, $\mathbf{CaCl_2}$, $\mathbf{MgSO_4}$, $\mathbf{MgCl_2}$, $\mathbf{Mg(NO_3)_2}$

Gas: HNO_3, HCl, NH_3, H_2O

Organic species: κ-Köhler theory (Petters and Kreidenweis, 2007)

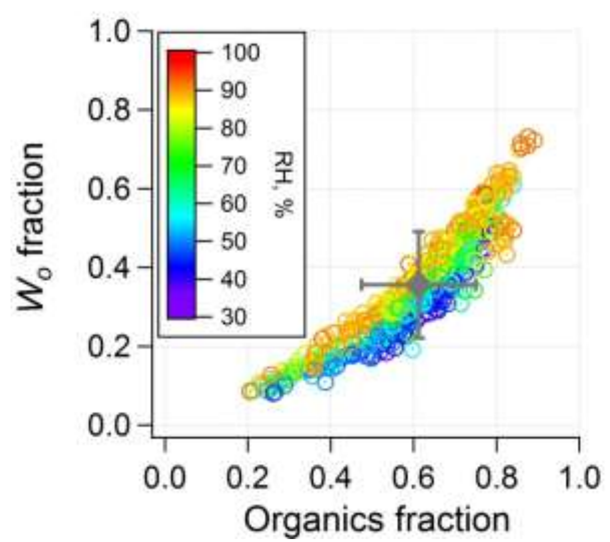
$$W_o = \frac{m_o}{\rho_p}\frac{\kappa_o}{(1-\mathrm{RH})}$$

m_o: aerosol mass
ρ_p: aerosol density
k_o: hygroscopicity parameter

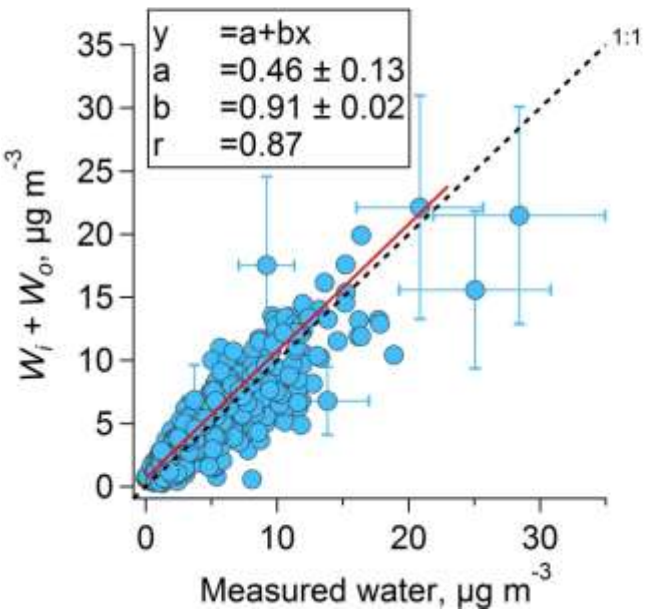
Predicted LWC vs measured LWC (SOAS)

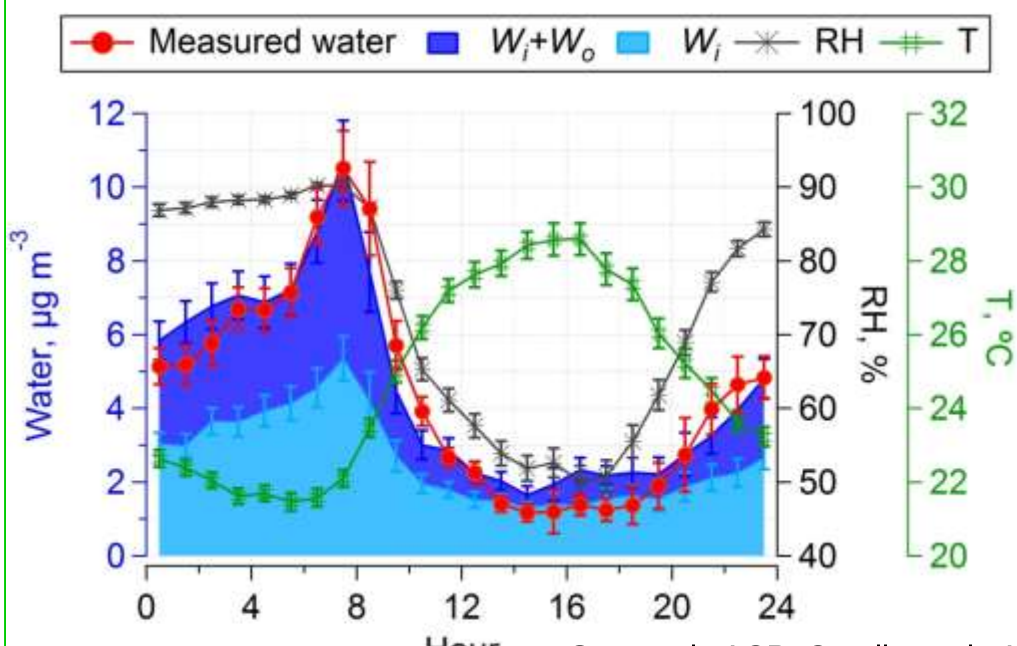
- W_i: LWC associated with inorganics
  W_o: LWC associated with organics
- Total predicted water (W_i + W_o) matches nephelometer-derived water very well.
- LWC diurnal ratio (max/min) is **5**.
- W_o was significant, **29-39%** of total LWC at all sites.

Fraction of organic water



Liquid Water: Predicted vs Measured





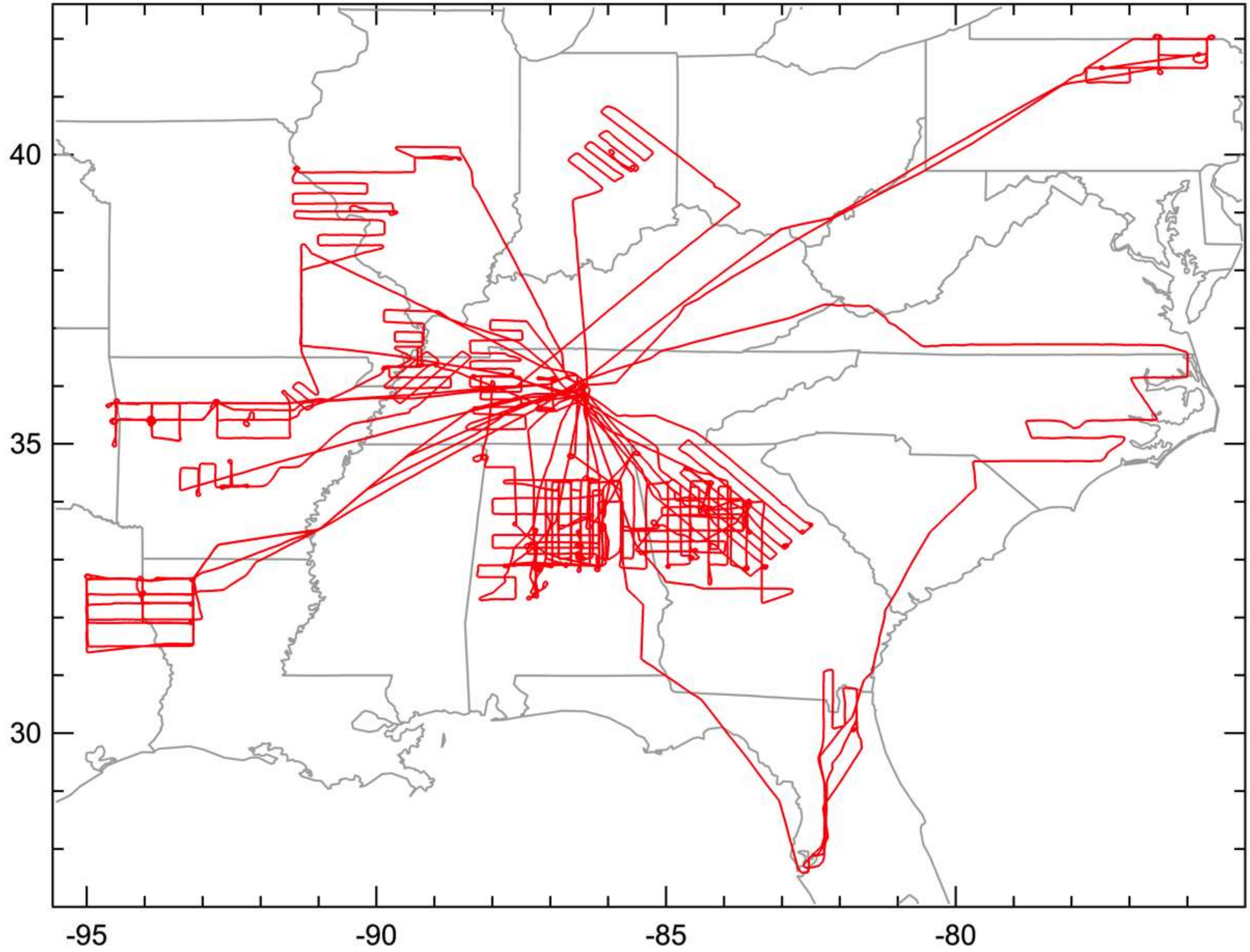
Guo et al., ACP; Cerully et al., ACP

Our goals for SOAS and **SENEX**

Photo credit: Jon Mak's Long-EZ

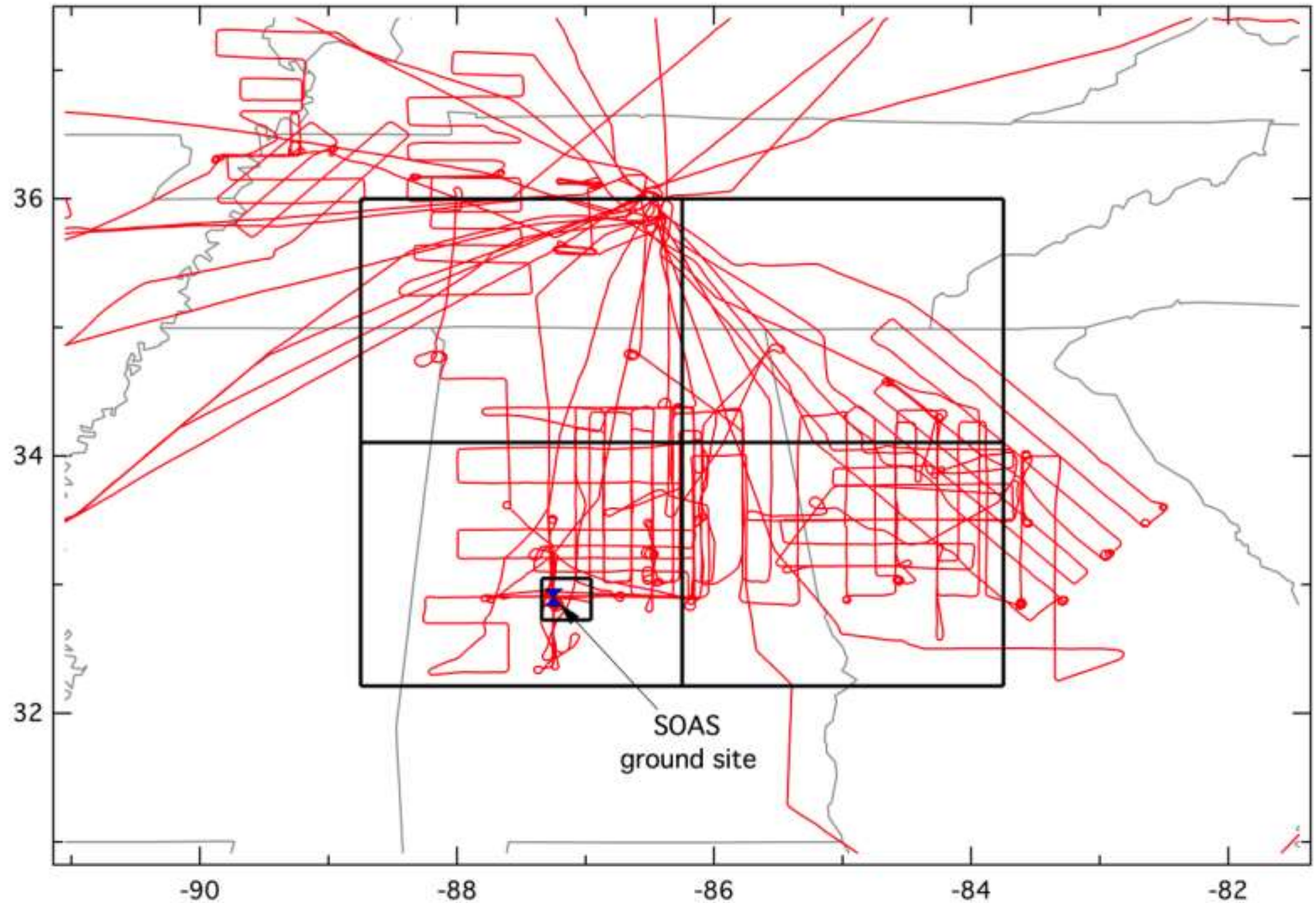
- ***Study*** *links between volatility, hygroscopicity & oxidation state of the Organic Aerosol (OA).*
- ***Investigate*** *which fractions of the OA are responsible for the observed hygroscopicity and volatility.*
- ***Quantify*** *the major contributors of LWC variability, particularly the relative role of organic vs. inorganic species.*
- ***Estimate*** *the impact of aerosol properties on cloud droplet number and cloud supersaturation*

SENEX: flight overview (June-July 2013)



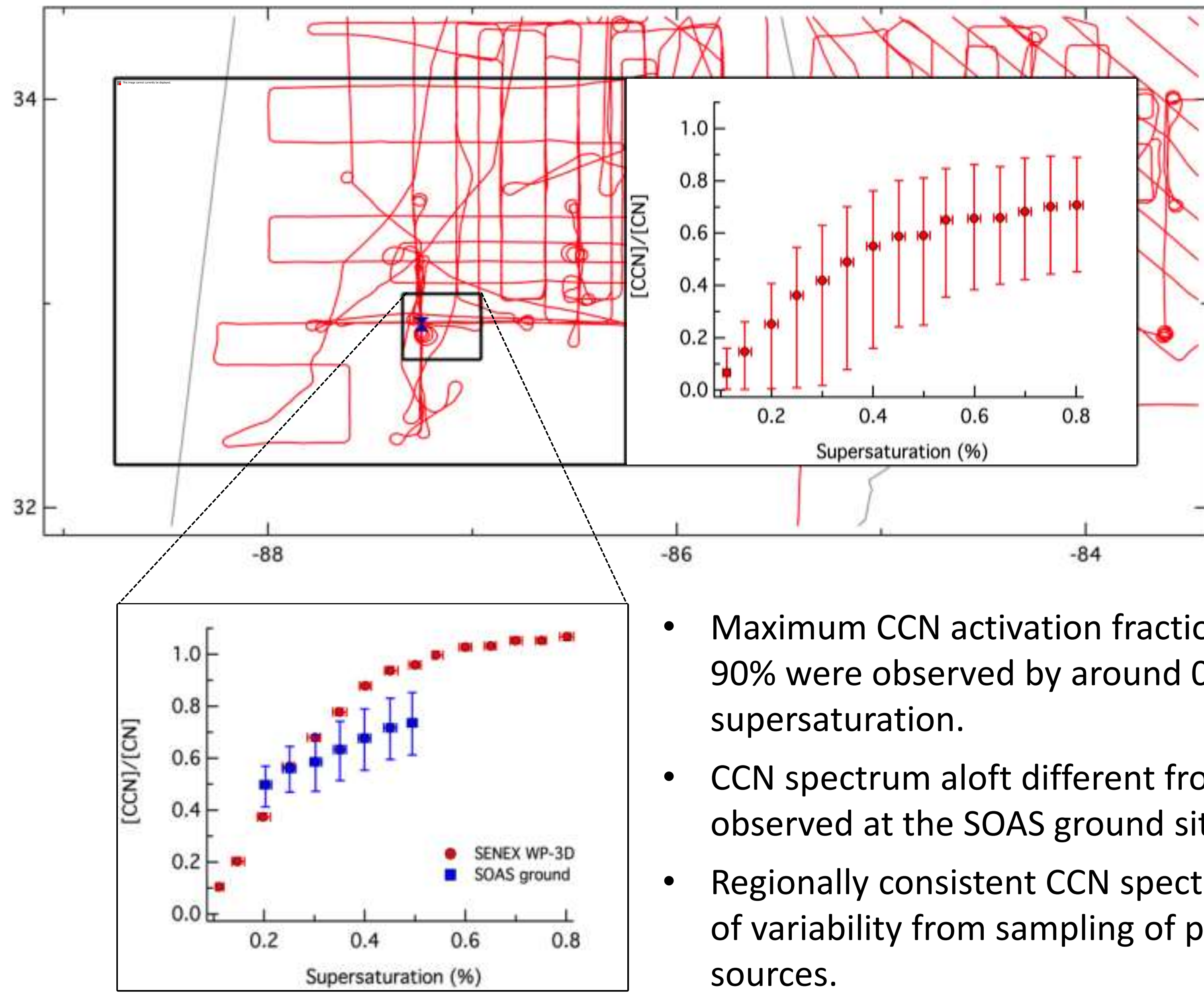
Lin et al., in prep; Bougiatioti et al., in prep

Area of interest: SE US around Centerville



Lin et al., in prep; Bougiatioti et al., in prep

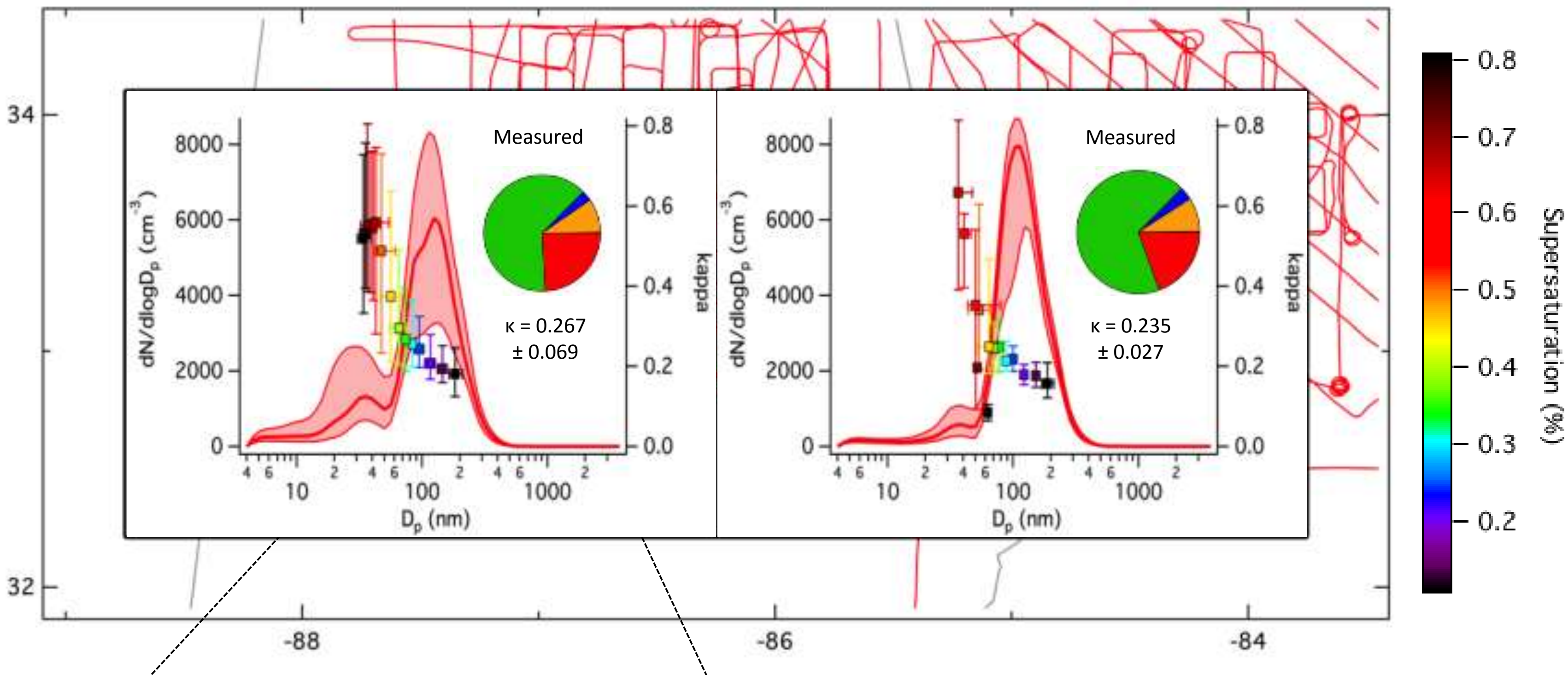
CCN spectra: SE US around Centerville

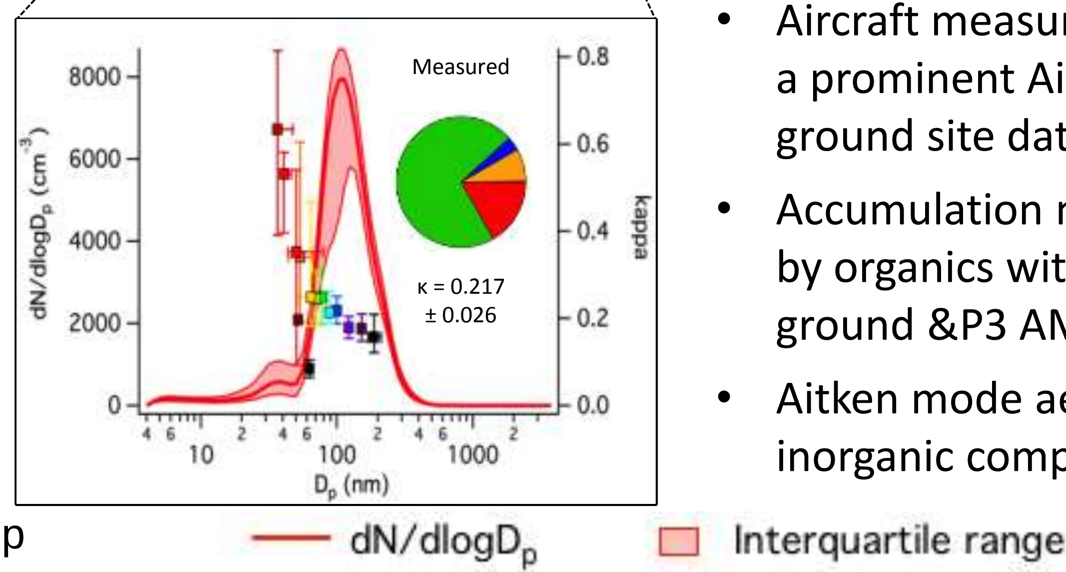


- Maximum CCN activation fractions of 90% were observed by around 0.6% supersaturation.
- CCN spectrum aloft different from that observed at the SOAS ground site.
- Regionally consistent CCN spectra. A lot of variability from sampling of point sources.

Lin et al., in prep

Aerosol hygroscopicity: SE US around Centerville

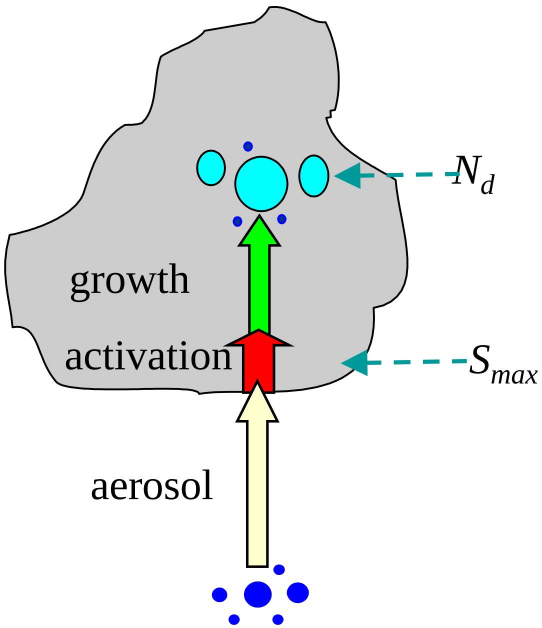




- Aircraft measured size distributions have a prominent Aitken mode – not seen in ground site data.
- Accumulation mode aerosol dominated by organics with κ ~ 0.2 – consistent with ground &P3 AMS data (bulk).
- Aitken mode aerosol is dominated by inorganic compounds, with κ ~ 0.6.

Lin et al., in prep

From SENEX data to cloud drops and s_{max}

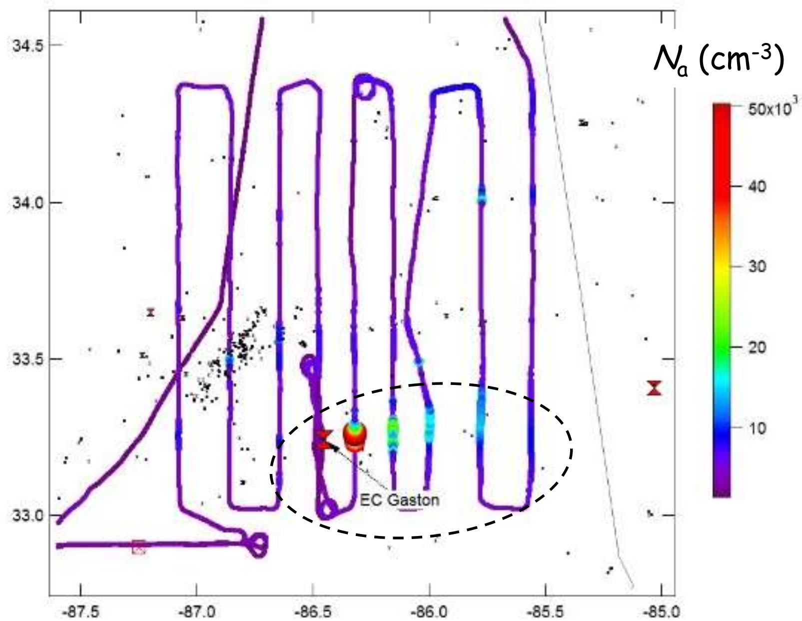


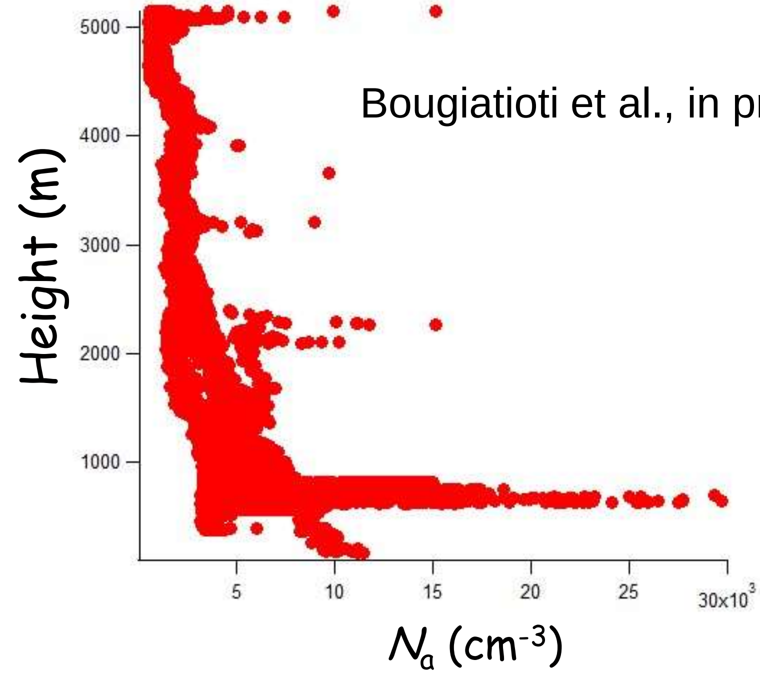
Input: P,T, vertical wind, particle size distribution & κ **or** CCN spectra.

Output: N_d, s_{max}

- CCN at fixed give an **incomplete** picture of cloud droplet responses to aerosol.
- You need to know s_{max} in clouds and how it **responds** to aerosol changes because of water vapor competition.
- Droplet parameterizations for climate models solve this effectively.
- **We use** Nenes and Seinfeld, (2003) with modifications by Fountoukis and Nenes, (2005), Barahona et al., (2010) and Morales and Nenes (2014).
- **Input velocity:** Integrated droplet number over a PDF of vertical velocities characteristic of BL clouds
  - ✓ σ_w=0.3 ms^{-1}, 0.6 ms^{-1}
- **Attribution** of N_d variability with sensitivities

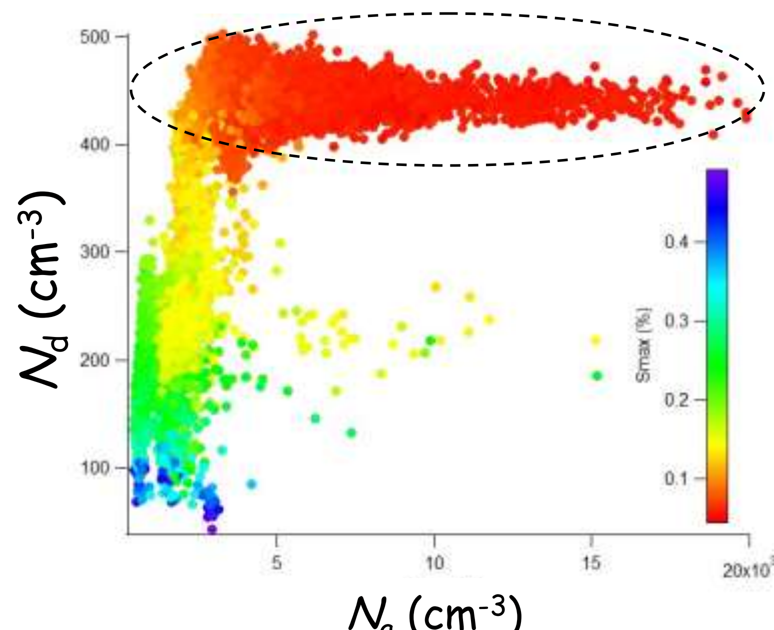
SENEX: Birmingham and Alabama (Flight 5)



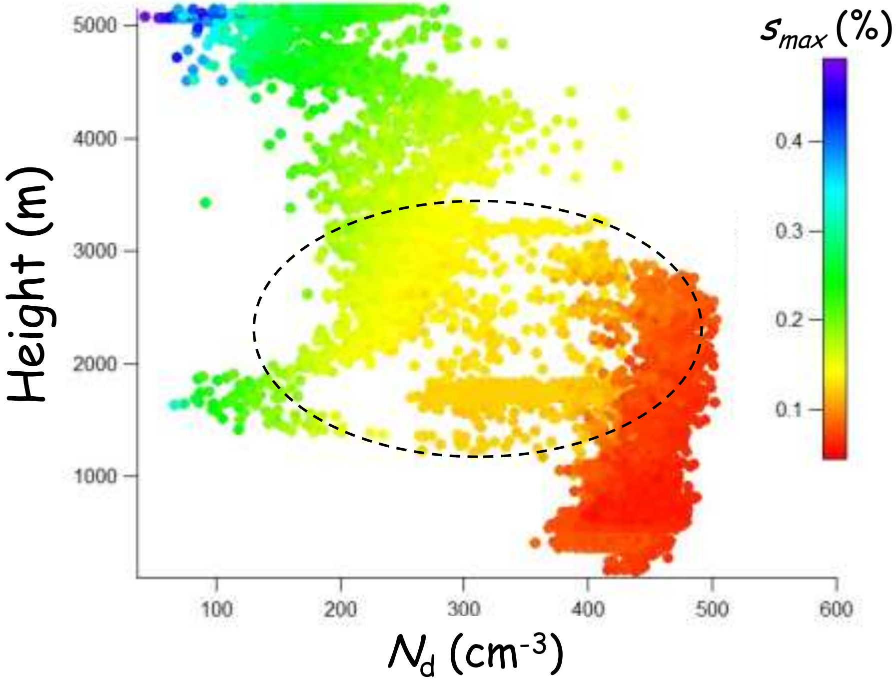


Bougiatioti et al., in prep

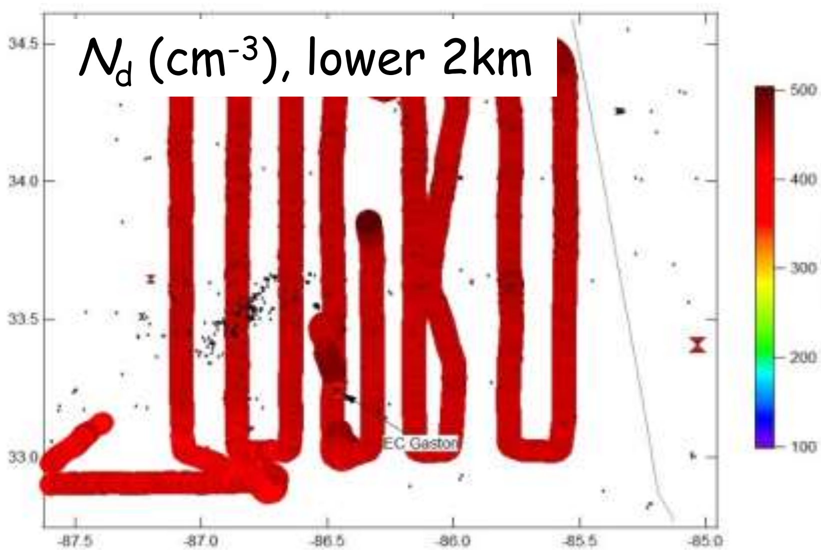
- Much less variability in CCN – except in the Gaston EC plume.
- Maximum supersaturation drops with increasing aerosol – and most often is below 0.1% in the BL.
- Droplet number concentrations exhibit low variability, in the BL.
- We see indications of a negative response of N_d to N_a (overseeding).

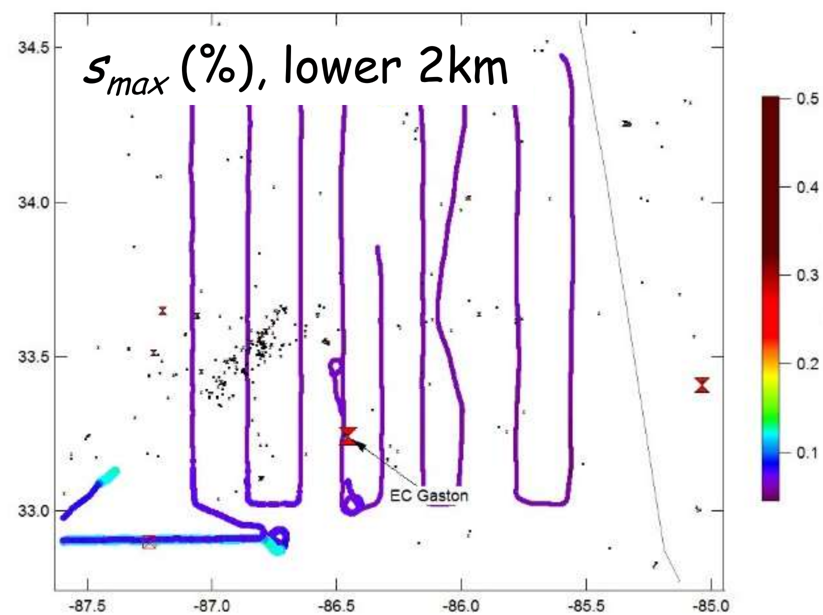


SENEX: Birmingham and Alabama (Flight 5)



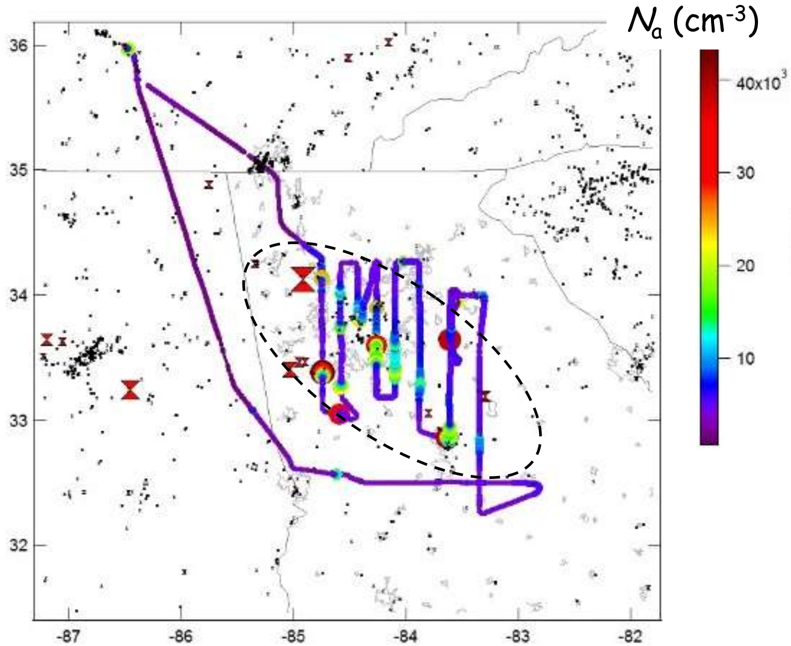
- Above 2-3km, concentrations drop considerably, and s_{max} increases
- Between 1-2km, there is mixing of airmasses, so s is between 0.1-0.2%.
- In the boundary layer, s much less than 0.1% *again* (its ~ 0.06%).
- Droplet number shows very little sensitivity to aerosol changes *even when flying through the EC plume.*

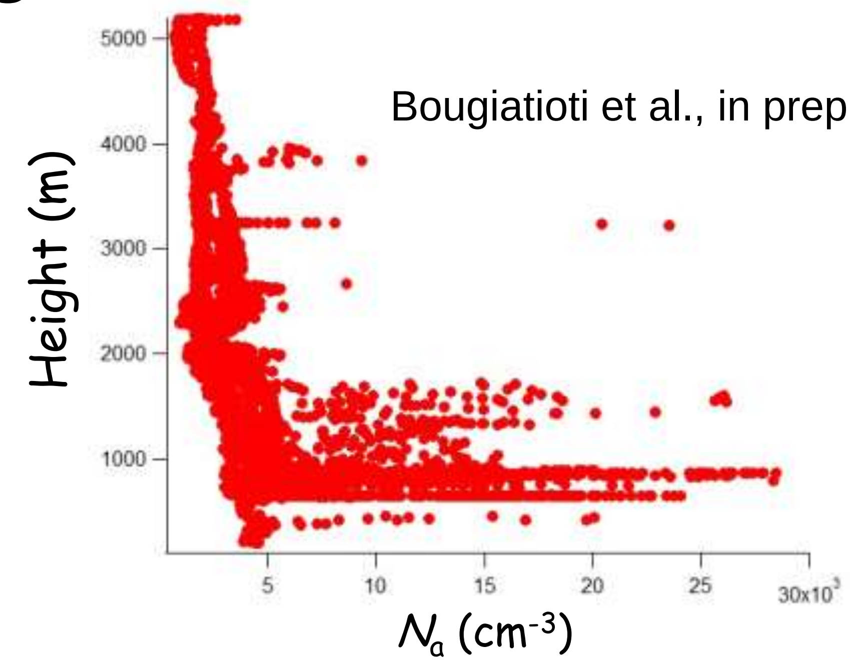




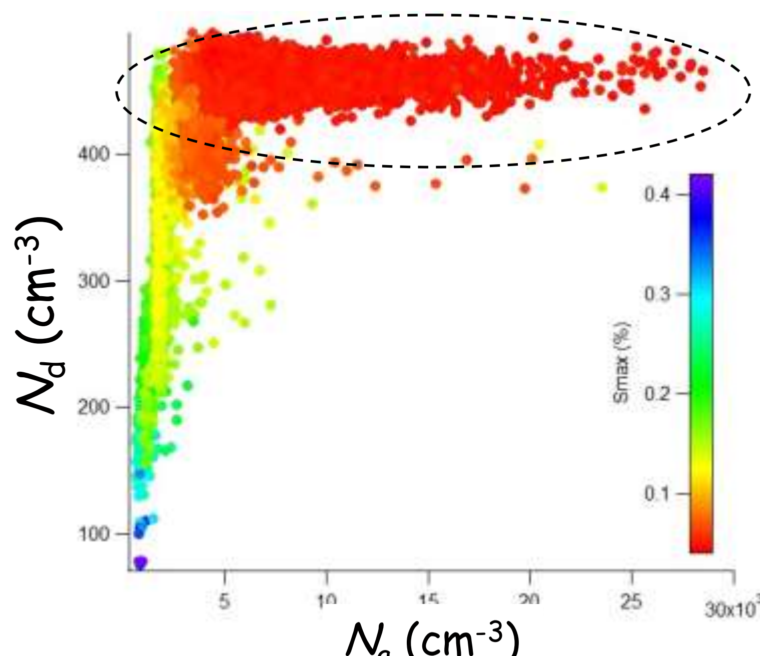
Bougiatioti et al., in prep

SENEX: Atlanta PM flight (Flight 6)

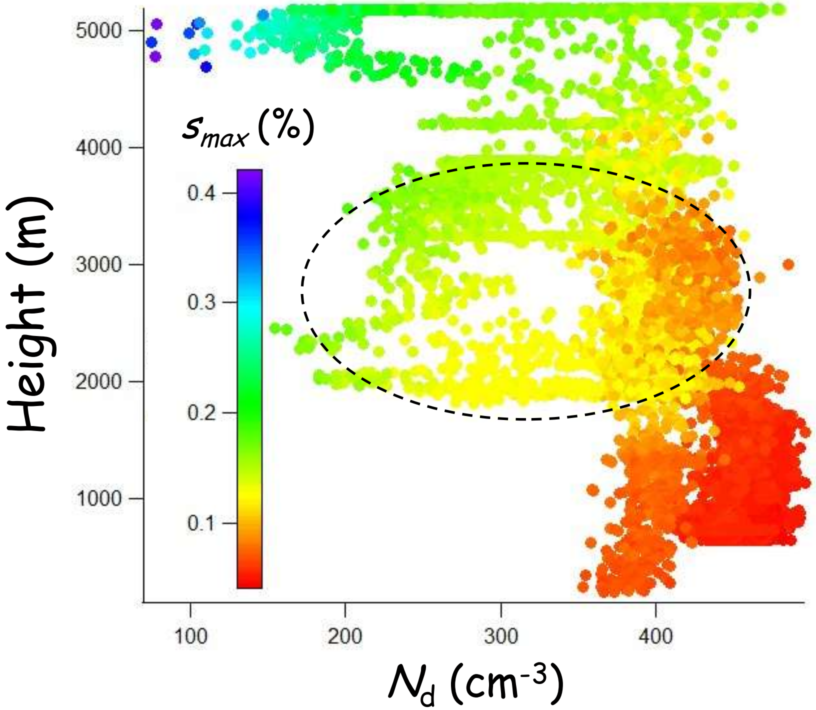




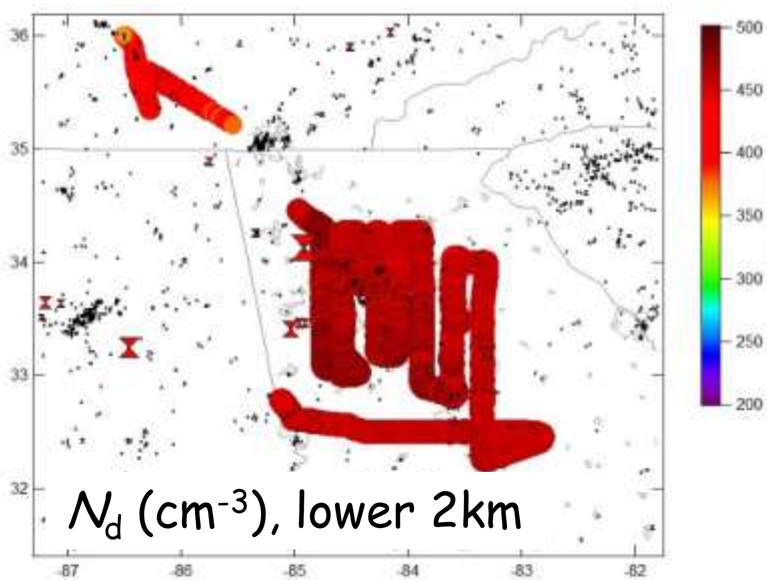
- A lot of variability in CCN in the Atlanta plume.
- Droplet number concentrations exhibit low variability in the boundary layer, only when you go out it changes.
- Maximum supersaturation drops with increasing aerosol – and almost always is below 0.1% in the BL.

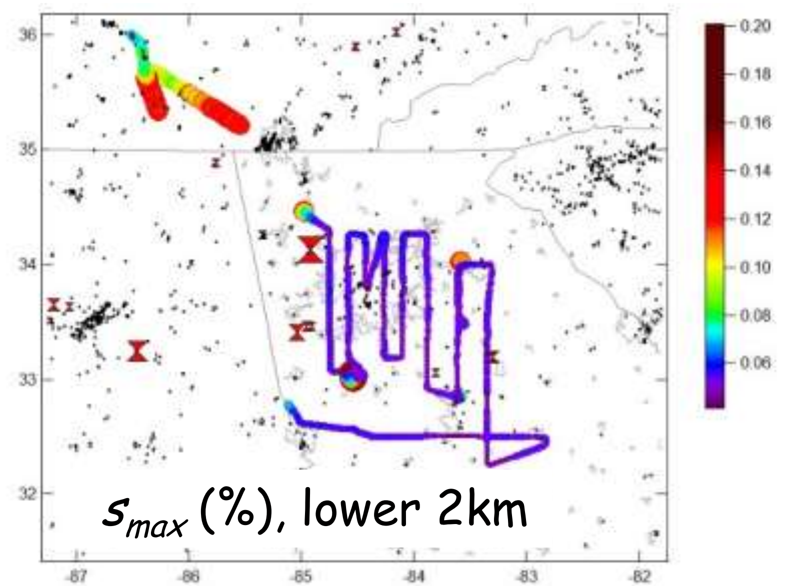


SENEX: Atlanta PM flight (Flight 6)



- Above 2-3km, concentrations drop considerably, and s_{max} increases
- Between 1-2km, there is mixing of airmasses, so s is between 0.1-0.2%.
- In the boundary layer, s much less than 0.1% *again* (its < 0.06%).
- Droplet number shows very little sensitivity to aerosol changes *even when flying through Atlanta.*





Bougiatioti et al., in prep

Summary of Results: SOAS

- Changes in total κ from thermally-denuding are small (relative change<12%) even with mass losses of ~ 35%.
- κ_{org} appears to decrease with increased heating regardless of O:C or oxidation state, opposing the conventional view of the most volatile compounds being the least hygroscopic.
- No clear correlation between κ_{org} and O:C for all PILS non-denuded PMF factors, but MO-OOA and LO-OOA factors show the expected property relationships.
- MO-OOA is responsible for 50% of the mass and up to 60% of the water uptake of all the organic aerosol.
- Organic contribution to aerosol LWC is maximum early morning and can be up to 70% of the total aerosol water (diurnal average: 30%).

Summary of Results: SENEX

- Aircraft measured size distributions have a prominent Aitken mode – not seen in ground site data.
- Accumulation mode aerosol dominated by organics with overall $\kappa \sim 0.2$ – consistent with ground & P3 AMS data (bulk).
- Aitken mode aerosol is much more $(NH_4)_2SO_4$-like, with $\kappa \sim 0.6$.
- Cloud droplet calculations driven by the aircraft data show that:
  - ✓ Much of the variability of CCN observed in the CCN is *not* reflected in the droplet calculations. Supersaturation fluctuates in response to aerosol fluctuations.
  - ✓ Strong insensitivity of N_d to aerosol levels in BL clouds. We actually see at times evidence of a *negative* impact of aerosol increases on N_d (from overseeding)
  - ✓ Very low s_{max} is predicted for those clouds (0.05-0.1%).
  - ✓ Any impacts of aerosol can only be seen in the "buffer" zone and detrainment in the free troposphere.

Acknowledgements

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R83541001

EPA Grant R83541001*

National Science Foundation

SOAS
Southern Oxidant & Aerosol Study

SOAS/SENEX participants

THANK YOU!

*A portion of this work was made possible by US EPA grant R8341001. The contents are solely the responsibility of the grantee and do not necessarily represent the official views of the US EPA. Further, US EPA does not endorse the purchase of any commercial products or services mentioned in the work.