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

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Climate-relevant impacts of Aerosol

Haze and Air Quality

Direct Effect

Indirect Effect

Particle Emission

Water uptake & transformation

Cloud formation & removal

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

When does an aerosol act as a CCN?

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 $S_c \rightarrow$ **stable equilibrium.**

Ambient RH **above** $S_c \rightarrow$ **unstable equilibrium.**

**Köhler theory:**

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

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

**Size is more important than composition**

**Equilibrium Relative Humidity (%)**

**Wet aerosol diameter (µm)**

- **Stable region (Haze)**
- **Unstable region (Droplet formation)**

$\text{(NH}_4\text{)}_2\text{SO}_4$

20 nm dry diameter
Droplet number needs CCN and max. cloud RH...

Algorithm for calculating $N_d$ (Mechanistic parameterization):

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

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.

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”, $\kappa$

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

$\kappa \sim 1$ for NaCl, $\sim 0.6$ for $(\text{NH}_4)_2\text{SO}_4$, $\sim 0-0.3$ for organics

$\kappa$ rarely exceeds 1 in atmospheric aerosol

Simple way to think of $\kappa$: the “equivalent” volume fraction of NaCl in the aerosol (the rest being insoluble).

$\kappa \sim 0.6 \Rightarrow$ particle behaves like 60% NaCl, 40% insoluble
Hygroscopicity Space

$k$ is used to parameterize the activation of particles in the atmosphere

*adapted from Petters and Kreidenweis, 2007*
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
Obtaining $\kappa$ from CCN Measurements

1. Using Scanning Flow CCN Analysis, determine CCN concentration, $[\text{CCN}]$, at a given $s^*$

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

3. Calculate $\kappa$

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

*Moore and Nenes (2009)*
Our goals for **SOAS** and **SENEX**

- **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.

*Photo credit: Jon Mak’s Long-EZ*
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: $\kappa_{\text{org}}$, Volatility, and O:C

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

<table>
<thead>
<tr>
<th>$\kappa_{\text{org}}$ with volatility</th>
<th>Ambient</th>
<th>PILS</th>
<th>Most volatile fraction is also the most hygroscopic (contradictory to expected link) ... but why?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-denuded</td>
<td>0.14±0.09</td>
<td>0.14±0.06</td>
<td></td>
</tr>
<tr>
<td>TD at 60°C</td>
<td>0.12±0.08</td>
<td>0.12±0.06</td>
<td></td>
</tr>
<tr>
<td>TD at 80°C</td>
<td>0.12±0.11</td>
<td>0.09±0.04</td>
<td></td>
</tr>
<tr>
<td>TD at 100°C</td>
<td>0.08±0.07</td>
<td>0.08±0.06</td>
<td></td>
</tr>
</tbody>
</table>

- Investigate $\kappa_{\text{org}}$ 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: $\kappa_{\text{org}}$ 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 $\kappa_{\text{org}}$ of each respective factor was found by bootstrapped resampling of the linear regression of the three factors:

\[
\kappa_{\text{org}} = \varepsilon_{\text{LO-OOA}} \kappa_{\text{LO-OOA}} + \varepsilon_{\text{MO-OOA}} \kappa_{\text{MO-OOA}} + \varepsilon_{\text{Isoprene-OA}} \kappa_{\text{Isoprene-OA}}
\]

Cerully et al., ACP, (2015)
SOAS: $\kappa_{\text{org}}$ and O:C of PMF Factors

- MO-OOA displayed a higher $\kappa_{\text{org}}$ and O:C compared to LO-OOA
- In general, no clear correlation between $\kappa_{\text{org}}$ 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⁺, NH₄⁺, H⁺, OH⁻, HSO₄⁻, SO₄²⁻, NO₃⁻, Cl⁻, H₂O, HNO₃(aq), HCl(aq), NH₃(aq), Ca²⁺, K⁺, Mg²⁺

**Solid:** NaHSO₄, NH₄HSO₄, Na₂SO₄, NaCl, (NH₄)₂SO₄, (NH₄)₃H(SO₄)₂, NH₄NO₃, NH₄Cl, NaNO₃, K₂SO₄, KHSO₄, KNO₃, KCl, CaSO₄, Ca(NO₃)₂, CaCl₂, MgSO₄, MgCl₂, Mg(NO₃)₂

**Gas:** HNO₃, HCl, NH₃, H₂O

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

\[ W_o = \frac{m_o}{\rho_p (1 - RH)} \]

- \( m_o \): aerosol mass
- \( \rho_p \): 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**

- **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 $\kappa \sim 0.2$ – consistent with ground &P3 AMS data (bulk).
• Aitken mode aerosol is dominated by inorganic compounds, with $\kappa \sim 0.6$.

Lin et al., in prep
From SENEX data to cloud drops and $s_{\text{max}}$

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

**Output:** $N_d, s_{\text{max}}$

- CCN at fixed give an **incomplete** picture of cloud droplet responses to aerosol.
- You need to know $s_{\text{max}}$ in clouds and how it **responds** to aerosol changes because of water vapor competition.
- Droplet parameterizations for climate models solve this effectively.
- **Input velocity:** Integrated droplet number over a PDF of vertical velocities characteristic of BL clouds
  - $\sigma_w=0.3 \text{ ms}^{-1}, 0.6 \text{ ms}^{-1}$
- **Attribution** of $N_d$ variability with sensitivities
SENEX: Birmingham and Alabama (Flight 5)

- 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 $s_{\text{max}}$ 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.

Bougiatioti et al., in prep
SENEX: Atlanta PM flight (Flight 6)

- Above 2-3km, concentrations drop considerably, and $s_{\text{max}}$ 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 ($s < 0.06\%$).
- 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 $\kappa$ from thermally-denuding are small (relative change $<12\%$) even with mass losses of $\sim 35\%$.

- $\kappa_{org}$ 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 $\kappa_{org}$ 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 $(\text{NH}_4)_2\text{SO}_4$-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 $s_{\text{max}}$ 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.
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