Vertical profiles of cloud condensation nuclei, aerosol hygroscopicity, water uptake, and scattering across the United States

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Introduction

Motivation:
• Near surface pollution is difficult to diagnose from satellite-borne observations.
• Evolution of vertical distributions of aerosol properties are important for air quality and radiative transfer.
• Water uptake has a critical impact on aerosol optical depth and its radiative impacts (2-3 times the aerosol dry mass globally; Liao and Seinfeld, 2005).

Objectives:
• Vertical profiles of cloud condensation nuclei (CCN) and water uptake properties.
• Evaluate measurements of water uptake against predictions.
• Quantify the major contributors of LWC variability, particularly the relative role of organic vs. inorganic species.
DISCOVER-AQ Datasets

**Baltimore-Washington (July 2011)**

**San Joaquin Valley (Jan-Feb 2013)**

**Denver, Colorado (July-August 2014)**

**Houston, Texas (September 2013)**
Experimental methods: Data from DISCOVER-AQ

Aerosol Concentrations:
- Total and Non-Volatile Particles
- CCN counter (activation efficiency)

Aerosol Sizes (10 nm - 5 μm):
- SMPS, UHSAS, OPC & APS

Optical Properties:
- Scattering & Absorption Coefficients
- Single Scattering Albedo
- Angstrom Exponent
- f(RH)_{80/20} (effects of humidity on scattering)

Composition:
- Black Carbon Mass (SP2)
- Particle-Into Liquid Sampler (PILS, 4 min. resolution)
Focus on DISCOVER-AQ Houston Flights

• Unlike in other phases, Houston displayed a complex and heterogeneous vertical structure.

• Above boundary layer you had layers of smoke transported from east; sometimes aerosol in BL less concentrated than aloft.
Data used for analysis

**PILS-IC** (Particle-Into-Liquid-Sampler coupled with Ion Chromatograph) → water soluble ions in particles (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Br$^-$, NO$_2^-$, PO$_4^{3-}$, NH$_4^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, K$^+$, etc.).

**PILS-TOC** (Particle-Into-Liquid-Sampler, Total Organic Carbon) → water soluble organic carbon.

**AMS** (HR-ToF-AMS) → non-refractory components of submicron aerosols (primarily organic aerosol mass).

**SMPS, UHSAS** → aerosol size distribution

**CCNc** → particle hygroscopic parameter ($\kappa$).

**Nephelometers** → ambient and dry aerosol light scattering coefficients ($\sigma_{sp}$), used to infer LWC.

$$ f(RH) = \frac{\sigma_{sp}(wet)}{\sigma_{sp}(dry)} \quad \text{LWC} = [f(RH)^{1.5} - 1]m_{dry}/\rho_p $$
Analysis methods - 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⁺

Solids: 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: \(\kappa\)-Köhler theory (Petters and Kreidenweis, 2007)

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

- \( m_o \): aerosol mass
- \( \rho_p \): aerosol density
- \( k_o \): hygroscopicity parameter
Analysis method: LWC/hygroscopicity closure

Input data includes:

- **Particle ions** ($SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^2$);
- **Total organics, $\kappa_{org}$ and $f(RH)$**;
- **Nephelometer RH and T**

### Input

- Ions
- Neph. RH, T
- Organics
- $\kappa_{org}$
- $\sigma_{sp}$

### Calculations

- $W_i$, particle water associated with inorganics (ISORROPIA)
- $W_o$, particle water associated with organics

$\frac{m_{dry}}{\rho_p}$

$W_i$ vs $W_o$

**Predicted LWC** vs **Measured LWC**
Analysis method: LWC/hygroscopicity closure
Analysis method: LWC/hygroscopicity closure
Analysis method: LWC attribution for ambient RH

Input data includes:

- *Particle ions* ($SO_4^{2-}, NH_4^+, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^2$);
- *Total organics*, $k_{org}$ and $f(RH)$
- *Ambient RH* and *$T$*

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**Input**

- Ions
- Amb. RH, $T$
- Organics
- $k_{org}$

**Attribution of LWC, and optical properties**

$W_i$, particle water associated with inorganics (ISORROPIA)

$W_o$, particle water associated with organics

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[Graph showing the relationship between RH, Organics fraction, and $W_o$ fraction]
Organics contribute comparable (or more) water than inorganics.
Most of the dry (and wet) aerosol mass in the boundary layer.
LWC attribution: Galveston

- Organics contribute comparable (or more) water than inorganics
- Smoke above boundary layer that dominates the aerosol (+water) mass in the column.
Sept. 13th, Circuit #1
Highest aerosol loadings at 2 km in the northern portion of the circuit
- Northeastern back-trajectories
- Acetonitrile ~ 300 pptv
  - Possible indication of smoke
Comparison against SOAS (Jun-Jul 2013)

- \( W_i \): LWC associated with inorganics
- \( W_o \): LWC associated with organics
- Total predicted water \( (W_i + W_o) \) matches measured water very well (at ambient RH)
- LWC diurnal ratio (max/min) is 5.
- \( W_o \) was significant, 29-39% of total LWC at all sites. (See Guo et al., 2014, ACPD)

Liquid Water: Predicted vs Measured

\[
y = a + bx
\]
\[
a = 0.46 \pm 0.13
\]
\[
b = 0.91 \pm 0.02
\]
\[
r = 0.87
\]
Take home messages

• Thermodynamic prediction of LWC verified by f(RH) and hygroscopicity measurements.

• Organics (mostly water-soluble) dominated the aerosol composition.

• Water associated with organic species is significant: 20-90%.

• The effect of organic water is higher in the BL but still significant above. Sometimes even more important (BB).

• The importance of organic water is not episodic but seems to be regional (SE US).

• This has important implications for aerosol chemistry.

• Aerosol loadings at ground-level (Houston) were low but high altitude aerosol layers contributed significantly (hence AOD).
THANK YOU!