How Physical and Chemical Properties Data Reflects Aerosol Formation Processes and their Evolution

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Outline:
1. Instrumentation based on analysis of water-soluble gas/particle components.
2. Example application: Secondary organic aerosol (SOA) formation in LA vs Atlanta.

Funded by NSF and EPA
Instruments to Quantify Particle/Gas Components

**Particle Phase Species**

Filter Collection with Off-line Water-Extraction and Analysis

**Automated On-line Analysis**

![Diagram of automated on-line analysis](image)

**Gas Phase Species**

Mist Chamber: gas scrubber (or use; continuous flow wet denuders)
ANALYTICAL METHOD: Approaches to Measure a Range of Gas and Aerosol Phase Properties

**Inorganic and Organic Ions**

- Soluble gases
- PM2.5 (?)
- Mist Chamber
- Particle Into Liquid Sampler (PILS)
- Ion Chromatograph
- Cations: Na\(^+\), NH\(_4\)^+, K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Amines...
- Anions: Cl\(^-\), NO\(_2\)^-, NO\(_3\)^-, SO\(_4^{2-}\), Organic Acids...

**WSOC\(_g\) and WSOC\(_p\)**

- Soluble gases
- PM2.5 (?)
- Mist Chamber
- Particle Into Liquid Sampler (PILS)
- Total Organic Carbon Analyzer
- WSOC\(_g\), WSOC\(_p\)
- Cations: NH\(_3\)
- Anions: Cl, HONO, HNO\(_3\), SO\(_2\), Organic Acids...

*(Weber et al AS&T 2001; Orsini et al, Atm Env. 2003)*

*(Sullivan et al; GRL 2004, JGR 2006)*
WSOC\textsubscript{p} & Hydrophilic/phobic fractions

(Sullivan et al JGR 2006)

PM2.5 (?)

Particle Into Liquid Sampler (PILS)

Actuated Valve

XAD-8 Column

Hydrophobic WSOC Retained
(high MW, aromatics, HULIS, less soluble ...)

Total Organic Carbon Analyzer

Penetrates Hydrophilic WSOC
(lower MW..., highly soluble)

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WSOC\textsubscript{p} & Soluble Light Absorption Spectra

(Hecobian et al, ACP 2010)

PM2.5 (?)

Particle Into Liquid Sampler (PILS)

Compact UV-VIS Spectrophotometer
(200 to 800nm)

1-m path length
LWCC (0.25 mL)

Total Organic Carbon Analyzer

“Brown Carbon”

Abs’n Å ~ 2 to 7 (\(\lambda\) Å)

Mass Abs’n Eff: \(\text{Abs}/\text{WSOC}\textsubscript{p}\)

Abs\textsubscript{365}
South and Southeastern US are Interesting Aerosol Regions

Aerosol Optical Thickness (AOT): JJA - DJF

Predicted Biogenic-VOC Emissions

(Goldstein et al., PNAS, 2009)

Annual Temperature anomalies 1901-2005

Large role played by BVOCs in Eastern US

http://www.epa.gov/climatechange/science/recenttc_tempanom.html
2007 FRM Filter Data: WSOC High In Summer When Hot

24h-filters from 15 FRM sites throughout SE, 60 filters/site, 900 filters:
Measured: non-volatile WSOC$_p$, Light Abs, Carbohydrates, sulfate...

WSOC$_p$ Highest in Summer: highly correlated with PM$_{2.5}$ mass ($r^2 = 0.70$) and highly correlated with T (biogenic VOCs?)

(Zhang et al, ACP 2010)
How Secondary Organic Aerosol Mass is Created - Conceptual Ideas -

“Classic” (Pankow) Partitioning

\[
K_P = \frac{C_P / M_O}{C_g} = \frac{760 \, R \, T \, f_{OM}}{10^6 \, MW_{OM} \, \xi \, p_i^o}
\]

Partitions to aerosol organic mass \((M_O)\) and depends on SVOC vapor pressure

Possible aqSOA Route (important?)

Partitions to liquid water (LWC) and depends on SVOC solubility (Henry’s Law Constant, \(K_H\)), then undergoes heterogeneous oxidation to lower \(p_i^o\)

Water (haze, cloud)
Estimated VOC Emissions in LA and Atlanta

Biogenic VOCs are much higher in the SE and within Atlanta, does that impact SOA formation within Atlanta? Compare Atlanta to LA.
SOA Formation in the SE is Subtle

In Atlanta (and other sites in eastern US) no clear diurnal trend to SOA
Jst and Yrk generally track on times scales of synoptic meteorological processes. Jst consistently higher on a higher frequency scale due to anthrop. Influence.
Urban/Rural WSOC$_p$ Diurnal Tends

Summer 2008

WSOC$_p$, $\mu$gC/m$^3$

- Atlanta signal riding on large regional background
- Some evidence for a daytime increase (photochemical SOA)

~ 70 km apart

Atlanta

Yorkville (NW of Atl)
Comparison of Diurnal Trends: Daytime Increases

Changes relative to background → Secondary process that day

LA: CalTech

\(\Delta WSO\text{C}g\) tracks other \(\Delta (\text{Oxyg-VOCs})\)
\(\Delta WSO\text{C}p\) tracks other \(\Delta \text{SOA}\)
(eg, gas and particle organic acids)

Atl: GaTech

\(\Delta WSO\text{C}g\) and \(\Delta WSO\text{C}p\) completely different trends wrt each other and LA.
Comparison of Diurnal Trends: $\text{Abs}_{365}$

LA-CalTech

$$\frac{\Delta \text{Abs}}{\Delta \text{WSOC}_p} = 0.77 \times 10^{-6}$$

LA 5 to 6x higher

Atl-GaTech

$$\frac{\Delta \text{Abs}}{\Delta \text{WSOC}_p} = 0.14 \times 10^{-6}$$

LA: Colored SOA
Atl (fresh) SOA is not.
Comparison of Diurnal Trends: $\text{Abs}_{365}$

**LA-CalTech**

\[
\frac{\Delta \text{Abs}}{\Delta \text{WSOCp}} = 0.77 \times 10^{-6}
\]

**FRM Data From One Site**

- $6x$ higher

But over time in Southeast, $\text{Abs}$ and WSOCp are related.
Comparison of Diurnal Trends: Oxalic Acid

LA: CalTech
Oxalic acid and WSOCp (SOA) track

Atl: GaTech
Oxalic acid formed later in day

But over time (FRM Data) WSOCp, Abs365, Oxalate become correlated (PMF analysis)

Many more differences... $\rightarrow$ differences in the SOA formation process??
Different Process?
Partitioning to Organic Mass?

**Organic Aerosol**
- VOC
- SVOC \((WSOC_g)\)
- Oxidant \((OH, O_3...)\)
- \((WSOC_p) \sim \text{SOA}\)

**OC**

“Classic” (Pankow) Partitioning Theory

\[
K_P = \frac{C_P / M_O}{C_g} = \frac{760 R T f_{OM}}{10^6 \frac{MW_{OM}}{\xi p_i^o}}
\]

\[
F_p = \frac{WSOC_p}{WSOC_p + WSOC_g}
\]

**Partitioning related to OC?**

**Not Partitioning to OC**

LA-CalTech

Atl-GaTech
Different Process?
Partitioning to Aerosol Water?

Atlanta SOA formation process very different from LA and generally consistent with aqSOA formation route
Aircraft Measurements also Indicate AqSOA Occurs Aloft

Sorooshian et al, GRL 2010
Ensemble of Caltech aircraft data

Peltier et al., ACP 2008; NSF C-130 INTEX-B

Convective Clouds

WSOCp formed in (associated w/) clouds

Organic acids produced in haze/clouds
Size Distributions of Organic Aerosol and Correlations with $SO_4^{2-}$ also Provide Evidence For Prevalence of aqSOA

Pasadena Aerosol Characterization Observatory (PACO) 5/21 to 8/6 2009 CalTech

5/21 - 6/14
High RH Rainy

6/19 - 7/19
Marine layers am Sunny Photochem pm

7/13 - 8/6
Hot Dry

Other studies show organic acids & WSOC correlated with droplet mode and sulfate
- Huang et al, *JGR* 2006 (S. China)
- Lin et al, *JAS* 2010 (Rural S. China)
- Sorooshian et al, *JGR*, 2006 (midwest)
- Yao et al, *Atm Env* 2003 (Beijing)
Summary Thoughts

1. Understand processes to assess responses to changing climate
   - Eg, role of T on BVOCs and their link to SOA: BVOC ≠ “natural” BSOA.
2. Current models predicting SOA ignore aqSOA route, most interested in getting SOA mass, yet process affects size distribution → CCN, Scattering
3. aqSOA has interesting cloud-SOA-cloud interactions
   - WSOCp mass fraction affects water uptake; haze and CCN activation
   - WSOCp, to some extent, is produced in haze and clouds
   - WSOCp aqueous chemical aging affects MW, light abs, surfactant properties ...
     (aerosol undergoes many cycles of wet/dry..., day/nite and cloud cycling)

Measurement Opportunities/Needs

1. Utilize existing network sites by developing novel analysis techniques (use FRM-filters for: BC by filter darkness, WSOCp, Absn Spectra, levog ... from teflon filters)
2. To understand partitioning process, measure gas and particle.
3. Size-resolved composition informs process: condensation/droplet modes
4. Aerosol phase oxidants critical for aqSOA (interest in health studies)