Measurements of Ambient Carbonaceous Particles That Are Soluble in Water

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Outline

- Collecting particles into water
- The organic aerosol
  - Water-Soluble Organic Carbon (WSOC)
- On-line measurements of WSOC
- OC and WSOC in St Louis
- Airborne measurements of WSOC
- Method to group speciate WSOC involving XAD-8 resin
- Ambient results from urban sites
- Summary/Issues/Future Work
Particle-Into-Liquid-Sampler Schematic
A method to continuously collect particles into a flowing liquid

1. Continuous liquid flow at selectable rate; 30 nl/min to 2 ml/min.
2. Concentrated liquid sample.
3. Fast response time (small wetted surface).
PILS For Inorganic Particle Composition

Particle Size Selector (PM$_{1}$)

Na$_2$CO$_3$, Citric Acid

Denuders (Gas Removal)

Multi-channel activated Carbon (MAST)

Scrubs NO$_x$ to eliminate NO$_2^-$ artifact

OD: 20 ng/m$^3$ anions, 0.1 µg/m$^3$ cations
Sampling Rate: 2.5 to 15 minutes
Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, Organic Acids
Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$
Liquid-Based System Can Measure Many of the Ambient Aerosol Compounds, What about the Organic Fraction

OC - Much Remains Unidentified

Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds were identified and quantified they represented only 15 percent or so of the total organic mass.
Organics: Complexity Makes Complete Speciation Difficult

- Group speciate
- Grouping may be driven by question of interest
  - What are the sources?
  - What are their effects?
    - Adverse health
    - Visibility and Radiative forcing
      - Water uptake $f(\text{RH})$

Broadly separate OC into WSOC vs WIOC
Water-Soluble Organic Carbon: Why measure it?

- Water is a natural solvent relevant to atmospheric processes.
  - Particle water uptake (RH<1, RH>1)
  - Depositional loss (dry vs wet).
  - Secondary aerosol is water-soluble (major source of WSOC ?).

- Much of the organic aerosol is soluble in water (esp. aged).
  - Unlike organic solvents, much of the organic aerosol can be extracted in water.
  - First step in development of comprehensive OC measurement method.

- Little is known about its chemical nature and abundance
  - Focus has been on organic solvent extraction and GCMS
PILS-TOC: An on-line method to measure WSOC

- Ammonium persulfate and UV convert carbonaceous material to CO$_2$
- CO$_2$ measured by conductivity
- Two channels: OC = TC - IC
- Background due to OC in water, no evidence for gas absorption
- Why: minimal wetted collection area?
• June: WSOC/OC low at night (40%), high during day (80%).
• “Fresh” plumes are mainly water-insoluble OC.
June Tend: buildup - rain - buildup - rain

June
- Concentrations building over time; regional build-up?
Regional Pollution Buildup June 20 to 25

Slope of: \( OC > WSOC > EC \)
\( OC = OC_{sec} + Oc_{prim} \)
WSOC mostly SOA?

During regional buildup fraction of OC that is water-soluble is correlated with \( O_3 \).
### Mean Concentrations

<table>
<thead>
<tr>
<th>Month</th>
<th>EC</th>
<th>OC</th>
<th>WSOC</th>
<th>WSOC/OC</th>
</tr>
</thead>
<tbody>
<tr>
<td>June</td>
<td>0.8</td>
<td>4.76</td>
<td>2.87</td>
<td>0.64</td>
</tr>
<tr>
<td>August*</td>
<td>0.62</td>
<td>4.04</td>
<td>2.40</td>
<td>0.61</td>
</tr>
<tr>
<td>October</td>
<td>1.11</td>
<td>4.55</td>
<td>1.33</td>
<td>0.31</td>
</tr>
</tbody>
</table>

* Mean over Aug 1 through 17

WSOC/OC higher in summer, greater photochemical processing?
Airborne Measurements of WSOC and Ions: INTEX July/Aug. 2004
Close-up of Quebec Biomass Plume

WSOC tracks plume fine structure
PM1: Ions + WSOC vs Volume

[Graph showing concentrations of various pollutants over time, with labels for Altitude, Ammonium, Nitrate, Water-Soluble OC (g C m\(^{-3}\)), Sulfate, Ions + WSOC, and PM1 Vol (density 1.0 g cm\(^{-3}\)).]
In NE US: Most Variability in PM1 due to SO$_4^{2-}$

Highest concentrations near the surface
Can Liquid Systems Be Developed to Measure OC?

PILS-TOC:
- Capable of fast, quantitative, highly sensitive measurement (0.1 $\mu$gC/m$^3$ at < 1 min).

But:
- Must efficiently capture and transport insoluble particles to TOC analyzer.
- TOC analyzer must be capable of oxidizing insoluble carbonaceous particles (size dependence).
- Assess loss of semi-volatile compounds.
- Must develop method to delineate EC.
Group classify organic compounds by property of interest

Qualitative observations: natural surfactant likely associated with the ambient aerosol.

Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds were identified and quantified they represented only 15 percent or so of the total organic mass.
Surfactants, Cloud Microphysics, and Indirect Forcing

Köhler Theory
- $S_c$, critical super-saturation for cloud droplet growth
- $S_c$ is a function of droplet surface tension, $\nu$.

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

Facchini et al, (Atm Env. 2000)
- WSOC fraction has lower $\nu$ wrt pure H$_2$O
- polyacids (HULIS) most $\nu$ reduction.

Finlayson-Pitts & Pitts; Gill et al., 1983
HULIS = Humic Like Substances

A component of the ambient aerosol appears to have some properties similar to natural aquatic humic and fulvic acids, (spectroscopic, chromatographic, etc).

Humic/fulvic acid: high MW acids associated with brown colored waters.
Formation Routes for HULIS

- **Heterogeneous**
  - Terpenes, Isoprene
  - Marine Emissions
  - Lignin pyrolysis products
  - Decomposition products

- **Direct Emission**
  - ODowd et al., 2004
  - Zappoli et al., 1999
  - Mayol-Bracero et al., 2002
  - Iinuma et al., 2004

- **Multiphase**
  - Limbeck et al., 2003
  - Gelencsér et al., 2002
  - Hoffer et al., 2004
  - Gelencsér et al., 2003

- **OH, H_2O_2**
  - OH, H_2O_2

- **Droplet**
  - Aerosol

Adopted From Andreas Gelencser presentation, Organic Speciation Workshop
XAD-8 for Water-Soluble Aerosols

- XAD-8 resin used by geochemists to isolate humic/fulvic acid (hydrophobic material) from natural waters
  - Method to produce humic and fulvic acid standards.
  - Delineation between hydrophobic-hydrophilic (not sharp, but is reproducible).
Broad Classification of Fine Particle Organic Carbon

Aerosol Organic Carbon

- Water Insoluble OC
  - Sunset OCEC

- Water Soluble OC
  - PILS-TOC

  - Hydrophilic
    - Penetrates XAD-8
  
  - Hydrophobic
    - Retained On XAD-8
      - Surface-active properties?

"Neutral"

Acidic

- Off-line Analysis
  - Some fraction is HULIS
Group Speciation of WSOC with PILS-TOC and XAD-8 resin into Hydrophilic vs Hydrophobic

-6mm ID x 100 cm length handpacked glass column with XAD-8 resin
-column selectively removes hydrophobic fraction, we measure hydrophilic fraction
XAD-8 Column Sampling On-line

Filtered Liquid Sample from PILS-TOC

0.1 M HCl
Adjust pH~2

-XAD-8 resin adsorbs hydrophobic compounds, Except all basic compounds.

Measures hydrophilic fraction
(all bases and hydrophilic acids, hydrophilic neutrals)

Sievers TOC analyzer

Penetrates

No Organic Solvents!
### XAD-8 Penetration Tests

<table>
<thead>
<tr>
<th>Mono-Acids</th>
<th>Di-Acids</th>
<th>Aldehydes</th>
<th>Phenols</th>
<th>Humic Substances</th>
</tr>
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<tr>
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<td></td>
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<td>Formic (1)</td>
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Also Hydrophilic: Organic bases, hydrophilic neutrals.
Color of XAD-8 Retained Compounds of the Ambient PM2.5 Organic Aerosol

Biomass Burning Smoke (Ft. Benning Columbus, GA)

Urban Atlanta, GA, July 2004

Humic/Fulvic acid is only compound tested that produces this color

/loading of large particulate mass needed to see color
On-line Hydrophilic/Hydrophobic Fractions: Typical Winter in St. Louis

Frequent evening events with hydrophobic > hydrophilic
On-line Hydrophilic/Hydrophobic Fractions:
Typical Summer in Atlanta

Typically 50:50 hydrophilic and hydrophobic
On-line Hydrophilic/Hydrophobic Fractions: Summer Event in Atlanta

- Highest PM2.5, Ozone, Temperature of Atlanta 2004 summer
- General increase in all species; hydrophilic > hydrophobic

E.g.
- O-nitrates,
- Acids & Aldehydes \( C_{>5} \),
- Neutral-philic, ...

E.g.,
- Acids & Aldehydes \( C_{>5} \),
- Phenols, humic acids (HULIS), ...

Concentration, \( \mu gC \ m^{-3} \)

Month/Day of 2004

OC  WSOC
Hydrophilic  Hydrophobic

Atlanta
Regional Buildup in Atlanta During Smog Event

Hydrophilics:
- O-nitrates,
- Acids & Aldehydes $C_{<5}$,
- Neutral-philic

Hydrophobics:
- Acids & Aldehydes $C_{>5}$,
- Phenols, humic acid (HULIS),
- Neutral-phobics,

Average Concentration, $\mu$gC/m$^3$

Day of July

- $y = -27.528 + 1.686x$ $R = 0.99023$
- $y = -7.464 + 0.453x$ $R = 0.87372$
- $y = -23.153 + 1.381x$ $R = 0.9974$
- $y = -15.043 + 0.876x$ $R = 0.99647$
- $y = -8.21 + 0.5x$ $R = 0.98898$

$S = 1.69$

$S = 1.38$

$S = 0.88$

$S = 0.50$

$S = 0.45$
Hydrophilic fraction of WSOC dominates in summer, hydrophobic in winter.

- **Summer:**
  - hydrophilic/OC ~ 30 - 40%
  - hydrophobic/OC ~ 25 - 30%

- **Winter:**
  - hydrophilic/OC ~ 15 - 20%
  - hydrophobic/OC ~ 25 - 30%
Division of Hydrophobic Fraction

- Collected 24-hr integrated Hi-Vol Quartz Filter Samples during June and August 2004 – Atlanta
- Extracted filter in 125 ml Deionized Water (WSOC)
- Adjust pH to 2, pass through XAD-8 column
- Extract XAD-8 column
  - Collect and analyze NaOH column wash
0.1 M NaOH

- some fraction remains adsorbed to XAD-8

Penetrates

Measure desorbed fraction

Sievers TOC analyzer

No Organic Solvents!
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<td><strong>20% rec.</strong></td>
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<td><strong>20% rec.</strong></td>
<td><strong>100% rec.</strong></td>
<td></td>
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Hydrophilic compounds were found to be more easily adsorbed on XAD-8 resin compared to hydrophobic compounds.
Color of XAD-8 Retained Compounds of the Ambient PM2.5 Organic Aerosol

Biomass Burning Smoke (Ft. Benning Columbus, GA)

Urban Atlanta, GA

Color is removed when column extracted with NaOH
- color due to aromatic compounds (\(^1\)H-NMR)?
Hydrophobic Acids correlated with:

- OC ($R^2 = 0.80$)
- WSOC ($R^2 = 0.86$)
- Hydrophilic ($R^2 = 0.82$)

(24 hr integrated data)

(Hydrophobic Acid)/OC = 17% $\mu g$ C/$\mu g$ C

Hydrophobic Acids: phenols and Humic Acids, ...
Ultra-Filtration of Urban Atlanta WSOC and Hydrophobic Hydrophilic Fractions

Ultrafiltration with a 500 Da (MW) membrane.

WSOC: 80% penetrated (MW < 500)
Hydrophobic WSOC: 80% penetrated
Hydrophilic WSOC: 80% penetrated

Missing 20% thought to be due to hangup on membrane and not result of separation

Conclusions; WSOC and all fractions have MW's less than 500 Da. (similar to Kiss et al)
Summary

Coupling PILS-TOC

- Fast quantitative measurements of WSOC (0.1 µgC/m³, < 1 min)
- Has potential as a method to measure OC.
- XAD-8 resin, on-line separation of hydrophilic/hydrophobic WSOC fractions.

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<th>phobic</th>
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<td>neutrals, ...</td>
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Winter: hydrophobic > hydrophilic (biomass burning?)
Summer: Generally 50:50 hydrophilic/hydrophobic
Atlanta PM2.5 event: hydrophilic > hydrophobic

-(hydrophilic WSOC)/OC ~ 40% µg C/ µg C
Extraction of XAD-8 provides further broad group separation. Hydrophobic fractionated into:

Recovered
Phonels, humic/fulvic acid
(HULIS) ... VS

Not Recovered
C>5 Carboxylic Acids Aldehydes, Neutrals...
Atlanta Summer 2004

(XAD-8-Recovered WSOC)/OC ~ 17% μgC/μgC
Unresolved Issues

• Loss of SVOC's in steam system
  - use a scrubber instead; problems with gas adsorption.

• Artifacts due to low/high pH in XAD system. Acid-catalyzed reactions in the liquid phase leading to polymerization?
  - Compare MW distributions of WSOC to hydrophobic and hydrophilic fractions.
Ongoing and Future Work

• Compare and Contrast WSOC-Hydrophobic-Hydrophilic Fractions
  – Measurement of surface tension.
  – Activation in CCN counter (RH>1)
  – Water-uptake at RH<1 (TDMA experiments)
  – Molecular Weight Distributions
    • Size exclusion chromatography
    • Electrospray Ionization MS
    – $^1$H-NMR, $^{13}$C-NMR

• Compare contrast characteristics of different locations (rural/urban, Atlanta/LA, etc)