Investigation of the Physical Properties of Fine Particle Water-Soluble Organic Carbon Aerosols

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Outline

• Water-Soluble Organic Carbon (WSOC)

• Brief overview of method to group speciate WSOC involving XAD-8 resin and Size-Exclusion Chromatography (SEC)

• Solid State $^{13}$Carbon-Nuclear Magnetic Resonance ($^{13}$C-NMR) on WSOC, hydrophilic, and recovered hydrophobic fractions from an urban site and biomass burning

• Light Absorption

• Summary
Why is WSOC of interest?

- A large fraction of total organic carbon (OC)
- Secondary Organic Aerosol (SOA) formation leads to WSOC
- WSOC has unique and important physical properties

But:

- Only small fraction of WSOC identified because polar oxygenated organic compounds not analyzable by GC-MS

Solution:

- Use methods to comprehensively group speciate WSOC (e.g. Decesari et al., *JGR*, 2000)
- Isolated fractions of WSOC can be analyzed
  - Droplet surface tension (Asa-Awuku et al., *AAAR*, 2005)
  - $^{13}$C-NMR
  - Visible Light Absorption
Overview of Method to Chemically Fractionate WSOC

Aerosol Organic Carbon

Water-Soluble OC

- Water-Insoluble OC
  - Hydrophilic
    - Recovered
    - Unrecovered
  - Hydrophobic
    - Recovered
    - Unrecovered

Step 1
XAD-8

Step 2
SEC

- Aliphatic Acids
- Neutrals
- Bases
- Aromatic Acids
- Phenols
## XAD-8 Calibration (based on 36 standards)

<table>
<thead>
<tr>
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Solid State $^{13}$C-NMR of Organic Fine Aerosol Particles

Investigate Urban and Biomass Burning Particles:
1. WSOC
2. Hydrophilic WSOC
3. Recovered Hydrophobic WSOC

Solid State $^{13}$C-NMR

• Provides independent measure of XAD-8 isolated sample composition

• Provides a comprehensive and semi-quantitative measure of types of carbon bonds in sample

• Disadvantage:
  – Low sensitivity, required 8 24-hour integrated Hi-Volume filter samples from urban Atlanta
Solid State $^{13}$C-NMR

- 25-30 mg C (40-70 mg total sample) obtained by freeze drying XAD-8 liquid extracts

- Spectra split into 7 spectral regions on ppm scale and integrated using a commercial software package

- From peak areas able to understand major overall trends in organic C composition
Atlanta Summer

Carboxyl/Amide: O=C-(OH/NH₂)

Aromatic: C=C-(C,H)

Aromatic: C=C-(O,N)

Acetal: O-C-O

O-alkyl: C-O

N-alkyl: R₂NCH₃

WSOC

hydrophilic

recovered
hydrophobic

ppm

-50 -25 0 25 50 75 100 125 150 175 200 225 200 175 150 125 100 75 50 25 0 -25 -50
- Aliphatic and aromatic C in carboxylic acids, amides, and alcohols
-10:1 ratio of O-alkyl to anomeric peak suggesting not associated with ring polysaccharides
-10% of carbon associated with carboxylic acids, likely aliphatic
- Only detected in WSOC and recovered hydrophobic fraction
- Unsubstituted or substituted by C-alkyl, carboxylic acid, or O-alkyl
Comparison to Suwannee River Humic Acid

- Only qualitatively similar, Suwannee River humic acid higher carboxylic acid/aromatic and lower C/O-alkyl
Biomass Burning

- Carboxyl/Amide: O=C-(OH/NH₂)
- Aromatic: C=C-(O,N)
- Acetal: O-C-O
- O-alkyl: C=O
- N-alkyl: R₂NCH₃
- Alkyl: C-C

WSOC

Recovered hydrophobic

Hydrophilic
-Peak at ~145 ppm in WSOC and recovered hydrophobic fraction
- Larger N-alkyl peak, can be present in aliphatic amines
-5:1 ratio of O-alkyl to anomeric peak suggesting associated with ring polysaccharides
Use SEC to determine the % of each functional group in hydrophilic and recovered hydrophobic fractions.

Compare SEC to % peak area from $^{13}$C-NMR.
## Hydrophilic Comparison

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Summer SEC</th>
<th>Summer $^{13}$C-NMR</th>
<th>Biomass Burning SEC</th>
<th>Biomass Burning $^{13}$C-NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic acids</td>
<td>58%</td>
<td>60% C-alkyl</td>
<td>67% neutrals</td>
<td>76% O-alkyl</td>
</tr>
<tr>
<td>Neutrals</td>
<td>23%</td>
<td>24% O-alkyl</td>
<td>28% unrecovered</td>
<td>24% N-alkyl</td>
</tr>
<tr>
<td>Unrecovered</td>
<td>16%</td>
<td>10% carboxylic</td>
<td>5% aliphatic acids</td>
<td>All others 0</td>
</tr>
<tr>
<td>Bases</td>
<td>2%</td>
<td>7% N-alkyl</td>
<td>0% bases</td>
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*XAD-8/SEC is by functional group vs. $^{13}$C-NMR is by C bond*

- SEC and $^{13}$C-NMR qualitatively agree
- No aromatic peaks found in $^{13}$C-NMR spectra of hydrophilic fraction, agrees with XAD-8 calibration results
# Recovered Hydrophobic Comparison

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<thead>
<tr>
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<th>$^{13}$C-NMR</th>
<th>Biomass Burning SEC</th>
<th>$^{13}$C-NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic acids</td>
<td>34%</td>
<td>60% C-alkyl</td>
<td>47% phenols</td>
<td>36% C-alkyl</td>
</tr>
<tr>
<td>Phenols</td>
<td>11%</td>
<td>18% O-alkyl</td>
<td>0% aromatic acids</td>
<td>22% alkyl aromatics</td>
</tr>
<tr>
<td>Unrecovered</td>
<td>54%</td>
<td>9% carboxylic</td>
<td>53% unrecovered</td>
<td>12% anomeric/ acetal C</td>
</tr>
<tr>
<td>Alkyl aromatic</td>
<td>8%</td>
<td></td>
<td>9% O-alkyl, N/O aromatics</td>
<td></td>
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</table>

- Based on calibration results would expect $^{13}$C-NMR to be mostly aromatics, not C-alkyls
- Aromatics may be highly substituted?
Light Absorption by Organic Fine Aerosol Particles
-Preliminary Results-

• Many studies report HULIS (polyacids, high molecular weight compounds) is brown
• Ambient studies suggest OC is light absorbing (e.g. Malm et al., JGR, 1996)
• Of our isolated compounds, which absorb light?
Color of XAD-8 Retained Compounds of the Ambient PM$_{2.5}$ Organic Aerosol

Biomass Burning Smoke from Ft. Benning in Columbus, GA

Urban Atlanta, GA

- Significant color is removed when column extracted with sodium hydroxide (NaOH), implying the color is due in part to recovered hydrophobic compounds
- No color observed in hydrophilic species
Light Absorption Method

• Integrated filter samples included Atlanta Summer, Atlanta Winter, and Biomass Burning

• Collected aromatic acids (<34 minutes) and phenols (>34 minutes) from SEC of recovered hydrophobic XAD-8 fraction

• Blank (or Reference Cell) was deionized water passed through XAD-8/SEC

• Measured carbon concentration for all fractions with TOC Analyzer

• Absorption Detector = Hewlett Packard 8451a diode array spectrophotometer scanning from 400-800 nm
Visible Light Absorption Results
(Absorbance per Carbon Mass)

- Phenols more effective light absorbers than the aromatic acids, especially in Winter followed by Biomass Burning
- Winter aromatics differ from summer aromatic composition?
Summary

• $^{13}$C-NMR useful for investigating WSOC composition
  – Provides information on carbon bonds
  – Spectra simplified by first separating WSOC into fractions

• General agreement of $^{13}$C-NMR and XAD-8 calibration results
  ✓ Aromatics found only in recovered hydrophobic fraction

• Atlanta summer mainly C/O-alkyl and carboxylic acids, whereas biomass burning additionally had phenolic compounds and N-alkyl
• Ambient samples only qualitatively similar to Suwannee River Humic Acid

• Light Absorption by WSOC compounds
  – Urban Atlanta Winter, Biomass Burning, and then Atlanta Summer are most effective absorbing compounds per carbon mass
  • In each group, phenolic absorbance > aromatic acids absorbance
    – Evidence for conjugated bonds
    – $^{13}$C-NMR suggests aromatics highly substituted
  – Hydrophilic compounds (C < 4 or 5 aliphatic acids and neutrals) don’t effectively absorb light