A Method for Airborne Measurements of Water-Soluble Organic Carbon: PILS-TOC results from the NOAA WP-3D during ICARTT

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Outline

• Water-Soluble Organic Carbon (WSOC)

• Components of PILS-TOC

• Results from ITCT 2K4 with emphasis on understanding the sources of WSOC
  – Biomass versus non-Biomass WSOC
  – Plume Evolution

• Summary
Why measure WSOC?

- WSOC can be a large fraction of the total organic carbon (OC)

- WSOC not well understood since most previous analyses involve GC-MS, which is not amendable to polar compounds

- Secondary Organic Aerosol (SOA) formation is thought to be one of its major sources

- Chemical nature may have important physical properties
  - Aerosol water uptake (light scattering, CCN, precipitation scavenging)

- Airborne measurements can provide unique information
  - Requires quantitative, rapid measurements
Schematic of PILS-TOC

- Particle Size Selector (PM₁)
- Teflon Filter (Background)
- Valve
- Activated Carbon Denuder
- Vacuum Pump
- Debubbler
- Liquid Sample via syringe pumps
- Liquid Filter
- Sievers TOC
- Drain
- Steam

Transport Liquid Flow via syringe pumps
Picture of PILS-TOC in WP-3B

Completely automated system

TOC Analyzer

“tee”

Syringe Pumps

Liquid Filter

PILS

Debubbler
PILS-TOC Calibration

Calibration with Oxalic Acid

Actual Concentration (ppb C)

$y = 0.94x \pm 0.05 - 51 \pm 20$

$R^2 = 0.98$
Sample Background Measurements

- Background low and fairly steady within a flight regardless of altitude
- Limit of detection of 1 µg C/m³ for 3 s measurement (based on 3x signal to noise)
- Response time = time per unit change in concentration from 10% to 90% of difference from A to B
- Doubling liquid flowrate, increased response time to \( \sim 2.4 \text{ s/(µg C/m}^3\text{)} \)
Definition of WSOC

- WSOC defined as fraction of organic carbon collected by PILS, passed through liquid filter (0.5 μm pore size) and transport tubing, and detected by TOC analyzer

- Positive artifacts minimized by denuder and background measurement

- Negative artifacts due to evaporative losses of semi-volatile organics have not been assessed
New England Air Quality Study: ITCT 2004
WSOC as a Function of Altitude

Biomass Burning (acetonitrile > 200 pptv)

- Largest biomass plumes between 3 and 4 km and observed near surface

Non-Biomass Burning (acetonitrile < 200 pptv)

- Highest concentrations observed near surface, similar to sulfate
Characteristics of the Biomass Burning Plumes

• Intercepted four major biomass plumes, typically between 3 and 4 km altitude

• Based on Flexpart all from fires in Alaska/Yukon region

• All high WSOC-Acetonitrile correlations ($R^2 = 0.84$ to $0.95$)

• Three out of four WSOC-CO correlations greater than $0.90$

• Highest concentrations of WSOC and PM$_{2.5}$ volume for the entire study
Example of Biomass Burning Plume: Time Series

- Adveected to northern Quebec after a period of 6 to 8 days from a fire in the Alaska/Yukon region
- WSOC/Volume = 12% (µg C/m³)/(µm³/cm³)
Example of Biomass Burning Plume: WSOC vs. Acetonitrile and CO

- High correlation between WSOC-Acetonitrile and WSOC-CO
Example of Biomass Burning Plume: Closer Look

-3 s WSOC and acetonitrile track even on finer scale
Non-Biomass Burning WSOC

- Possible sources include primary and secondary organic compounds from biogenic emissions, mobile sources, and industrial emissions.

- To investigate non-biomass burning surface sources only considering data with:
  - Acetonitrile < 200 pptv (i.e. removed biomass burning events)
  - Measurements at less than 2 km altitude
Non-Biomass WSOC vs. CO

All Data

$y = -2.2 \pm 0.08 + 0.03x \pm 0.01 \quad R^2 = 0.53$

-WSOC-CO $R^2 = 0.53$, fairly well correlated
Non-Biomass WSOC vs. CO

New York City Plume

- WSOC-CO $R^2 = 0.82$, highly correlated in specific urban plumes
- Background WSOC $\sim 1-2 \mu g C/m^3$, similar concentrations in rural plumes
Based on Flexpart, A and B from New York City and its surrounding region
### Comparison of Two Locations in the New York City Plume

<table>
<thead>
<tr>
<th>Advection time from New York City</th>
<th>A</th>
<th>B</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 day</td>
<td>2 to 3 days</td>
<td></td>
</tr>
<tr>
<td>WSOC (µg C/m³)</td>
<td>5.1</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>268</td>
<td>229</td>
<td></td>
</tr>
<tr>
<td>WSOC/CO (µg C/m³ per ppmv)</td>
<td>19</td>
<td>18</td>
<td>-4%</td>
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<tr>
<td>SO₄⁻²/CO (µg/m³ per ppmv)</td>
<td>49</td>
<td>53</td>
<td>7%</td>
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<tr>
<td>SO₂/CO (ppbv per ppmv)</td>
<td>22</td>
<td>9</td>
<td>-57%</td>
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<tr>
<td>SO₄⁻²/(SO₄⁻²+SO₂)</td>
<td>0.38</td>
<td>0.61</td>
<td></td>
</tr>
</tbody>
</table>
Summary

• PILS-TOC provides a rapid method for airborne measurement of WSOC

• Two major sources of WSOC during ITCT 2K4: biomass burning and urban emissions

• Biomass Burning:
  – Based on Flexpart from fires in Alaska/Yukon region
  – WSOC correlated well with acetonitrile and CO
  – Highest mission WSOC and fine particle volume concentrations
    • Biomass WSOC 3 to 4 times higher than in urban plumes
• Non-Biomass Burning:
  – WSOC mainly associated with CO from urban centers highest, much lower in rural regions
    • WSOC-CO correlations suggest mobile sources
    • Experiments in Atlanta show little evidence for primary WSOC from mobile sources, appears to be secondary
    • Similar WSOC/CO ratios 1 day and 2-3 days downwind of New York City suggests fairly rapid WSOC formation