Investigation into Secondary Organic Aerosol Formation in Metro Atlanta

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Outline

• Motivation

• Overview of methods
  – Components of PILS-TOC (On-line)
  – Group speciation of WSOC involving XAD-8 resin and Size-Exclusion Chromatography (SEC) (Off-line)

• Ambient results from urban Atlanta and its surrounding regions during summer
  – Airborne on-line WSOC measurements
  – Off-line WSOC group speciation at various locations

• Summary
Motivation

• Sources of organic carbon (OC) not fully known, esp. secondary products.

• EC tracer method suggests 50% of Atlanta OC secondary, can be near 90% on short time scales [Lim and Turpin, *ES&T*, 2002].

• Chamber studies show biogenic emissions (e.g., terpenes) are readily oxidized to form Secondary Organic Aerosol (SOA).

• Southeastern urban centers densely forested with coniferous trees implying that biogenic precursors are major contributor to SOA.
How can WSOC Measurements Help?

- SOA formation is thought to be one of the major sources of WSOC
  
  Maybe:
  
  WSOC = SOA (to 1st approx. when no biomass burning)

- Chemical analysis of WSOC could be used to investigate SOA products.
Method 1: On-line Measurement of WSOC

Schematic of PILS-TOC

- Limit of Detection = 0.1 µg C/m³
- Sampling rate = 3 s
Method 2: Off-line Group Speciation of WSOC

-Analysis performed on Hi-Volume integrated filters
Step A: XAD-8 Separation
(Calibration based on 36 "standards")

WSOC Extracted From Filter

XAD-8 Column

Un-Recovered Hydrophobic
> C₄ acids
> C₄ carbonyls
Cyclic Acids
Organic Nitrates

Recovered Hydrophobic
Aromatics (aromatic-like)

Hydrophilic
C₁-C₄ acids
C₁-C₄ carbonyls
Saccharides

Measured directly with TOC
Step 2B: Modified SEC Method

WSOC, Hydrophilic, or Recovered Hydrophobic Sample

By not adjusting ionic strength and buffering sample (pH 6.8) obtain separation by functional groups

Hydrophilic Calibration
**Ambient Results**

XAD-8 & SEC on 24-hr integrated Hi Vol Filters

Urban Atlanta Summer 2004

Atlanta Winter 2004

Biomass Burning Fort Benning

**Most of Summer WSOC is acidic**

- Aliphatic acids
- Neutrals
- Aromatic acids
- Phenols
- Bases

**Most of Biomass Burning is neutral**

- Aliphatic acids
- Neutrals
- Aromatic acids
- Phenols
- Bases

**Ambient Results**

Most of Summer WSOC is acidic

**Ambient Results**

Most of Biomass Burning is neutral
ICARTT: ITCT 2004

Online WSOC
Non-Biomass Near-Surface Data: WSOC versus CO
(acetonitrile < 200 pptv and altitude < 2 km)

All Data: WSOC-CO $R^2 = 0.53$, fairly well correlated

WSOC-CO $R^2 = 0.82$, highly correlated in specific urban plumes

All Data: WSOC-CO $R^2 = 0.53$, fairly well correlated
WSOC Evolution in Urban Plumes

Back trajectories of WSOC plumes that intercepted NYC.

$\Delta$WSOC/$\Delta$CO
- Lowest near city.
- Begins to level off after ~1 day to $32 \pm 4$ (µg C/m$^3$)/ppmv.
- WSOC produced from compounds co-emitted with CO.
- Urban emissions rapidly converted to secondary products?
AMS Oxygenated and Hydrocarbon OC versus WSOC

AMS
- m/z 44 - oxygenated OA, accumulation mode
- m/z 57 - hydrocarbon OA, ultrafine mode

WSOC = 0.8 (OOA)
Secondary?

(OOA = oxygenated organic aerosol µgC/m³)

Tokyo Japan

Y. Kondo et al, GRL, submitted, 2005
Other Studies: WSOC and SOA from EC Tracer Method

SOC = OC - [OC/EC]_{pri} EC

WSOC = 0.75 SOC: \( r^2 = 0.79 \)

WSOC appears to be mainly from SOA formation

Tokyo Japan, 2004

Y. Miyazaki et al, submitted, 2005
Atlanta Fly-Over: WSOC-CO

- Wide-spread elevated CO and WSOC in boundary layer
- WSOC-CO $R^2 = 0.83$
- WSOC doesn’t track in fresher CO plumes (point C)

$\Delta WSOC/\Delta CO \sim 33 \pm 5 \, (\mu g \, C/m^3)/ppmv$, similar to NYC (32 $\pm$ 4)
**Sampling Sites For WSOC Group Speciation**

- **Georgia Institute of Technology (GIT)**
  - Roof top of ES&T Building

- **Yorkville, GA**
  - ~80 km west of GIT
  - (during period of poor air quality)

- Next to I-75/85
  - ~400 m from GIT and
  - ~1 m from highway

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Hi-Volume Samplers: B. Yan and M. Zheng,
Georgia Institute of Technology
Paired Experiments

GIT vs. Highway

From: http://maps.google.com/

GIT vs. Yorkville

400 m

80 km
EC = Primary: Greater near expressway
OC = Primary + Secondary: Somewhat higher near expressway
WSOC = Not Primary, Secondary ?: Little difference between sites

Uncertainty is 5%, based on side by side comparisons
Three Main Chemical Components of WSOC

Includes expected biogenic SOA products

A. Hydrophilic aliphatic acids, e.g., C < 5 acids
B. Hydrophilic neutrals, e.g. saccharides and C< 5 carbonyls
C. Recovered hydrophobic acids, e.g. aromatic acids or compounds with similar properties.
Three Main Components of WSOC Measured at Various Sites In Summer 2004 & 2005

Fractions are correlated: $R^2 > 0.79$

A vs B

$\omega = 0.24 \pm 0.09$
$S = 1.4 \pm 0.1$
$R^2 = 0.87$

A vs C

$\omega = 0.01 \pm 0.1$
$S = 2.3 \pm 0.2$
$R^2 = 0.79$

B vs C

$\omega = -0.1 \pm 0.1$
$S = 1.5 \pm 0.1$
$R^2 = 0.81$

Major fractions of WSOC are linked to same source?
# WSOC Chemistry vs A.Q.

<table>
<thead>
<tr>
<th>Means</th>
<th>Atl. 2004</th>
<th>Atl. 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily Peak $O_3$, ppbv</td>
<td>61</td>
<td>100</td>
</tr>
<tr>
<td>PM2.5, μg/m$^3$</td>
<td>17</td>
<td>36</td>
</tr>
<tr>
<td>EC, μgC/m$^3$</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>OC, μgC/m$^3$</td>
<td>6.4</td>
<td>11</td>
</tr>
<tr>
<td>A+B+C, μgC/m$^3$</td>
<td>1.7</td>
<td>4.9</td>
</tr>
<tr>
<td>D, μgC/m$^3$</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**GIT 2005:** WSOC/OC 64%

**D** $\text{WSOC}_{\text{xru}}$

- 8%

**C** $\text{WSOC}_{\text{xrr} \_\text{a}}$

- 15%

**B** $\text{WSOC}_{\text{xrr} \_\text{n}}$

- 6%

**A** $\text{WSOC}_{\text{xp} \_\text{a}}$

- 36%

**GIT 2004:** WSOC/OC 50%

**D** $\text{WSOC}_{\text{xru}}$

- 18%

**C** $\text{WSOC}_{\text{xrr} \_\text{u}}$

- 15%

**B** $\text{WSOC}_{\text{xrr} \_\text{n}}$

- 4%

**A** $\text{WSOC}_{\text{xp} \_\text{a}}$

- 28%

**Means**

- $\text{EC, } \mu g/m^3$
- $\text{OC, } \mu g/m^3$
- $\text{A+B+C, } \mu g/m^3$
- $\text{D, } \mu g/m^3$
Summary: Based on a limited number of samples

- In summer urban Atlanta and its surrounding areas, WSOC has a regional characteristic and the source appears to be largely SOA formation.
  - Spatially uniform compared to primary particles (EC)
  - $\Delta$WSOC/$\Delta$CO NYC plume evolution suggest secondary.
  - Comparisons with AMS & SOA by EC-tracer in Tokyo.

- No clear evidence for strong biogenic SOA signal, instead points to precursors from mobile sources
  - Supported by:
    - High WSOC-CO correlations on large spatial scale
    - Similar $\Delta$WSOC/$\Delta$CO in Atlanta and NYC
    - Known biogenic SOA products small fraction of WSOC, remains constant during poorest AQ
    - Three major components of SOA linked to common source and highest under poorest AQ.
Implication that mobile source emissions play a large role in the formation of WSOC and hence SOA in summer-time metropolitan Atlanta.

No known (to me) chemical mechanism to explain observations.
Mass Balance on Measured VOCs and OC (POM) from NEAQS 2002

From: J.A. de Gouw et al., JGR, 2005

- SOA: little evidence for biogenic, not explained by aromatic VOCs
- SOA from anthropogenic VOCs not well understood
What about C$^{14}$

Houston: Lemire et al, JGR, 2002

- Higher OC/EC $\rightarrow$ higher % modern C
  - Suggests that most SOA modern C

**Future Work?**
Radio-C analysis on Atlanta WSOC and isolated fractions.
Acid Catalyzed reactions?

[Graph showing NH4/SO4 levels with values 1.5 ± 0.3, 2.1 ± 0.2, and 1.4 ± 0.5]