Evidence for Secondary Organic Aerosol Formation Involving Liquid-Phase Partitioning to Haze Particles in Summertime Atlanta

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Approach: Measure Gases and Particle Water-Soluble Organic Carbon

VOC

Oxidant (OH, O₃, NO₃)

Partitioning

SVOCs

Particle

WSOCᵣ

WSOCᵣ

SOA is oxygenated and water-soluble

Lose chemical specificity but gain comprehensiveness

• measure **Partitioning** to investigate WSOCᵣ formation mechanisms
Study Overview

• Measurements at Georgia Tech (Atlanta) from May 11 – Sept. 20, 2007 of:
  – WSOC\(_p\), WSOC\(_g\), OC, EC, NO\(_x\), O\(_3\), met data...

• Determine WSOC partitioning:

\[
F_p = \frac{\text{WSOC}_p}{\text{WSOC}_p + \text{WSOC}_g}
\]

Investigated \(F_p\) as a function of

RH, Organic Aerosol Mass, T, NO\(_x\),
Atlanta 2007 May-Sept. 
WSOCₚ and WSOC₉g 
Measurements

WSOC₉g: Mist Chamber-TOC 
(H > 10³ M/atm)

WSOCₚ: PILS-TOC

Sampling: one 5-min sample every 10 minutes (N = 10,988)
**WSOC_p = Most SOA in Atlanta**

WSOC_p is secondary*, but what fraction of SOA in Atlanta is water soluble?

* (Weber et al., JGR, 2007; Sullivan et al., JGR, 2006)

**WSOC_p**: photochemical

**WIOC_p** has strong primary signature (minor insoluble SOA?)

**WSOC_p + WIOC_p = OC**

**WSOC_p** is significant fraction of SOA in Atlanta summer
$F_p$ vs. Relative Humidity

A statistical analysis

Stats within each bin:

- 90th %
- 75th %
- Median
- 25th %
- 10th %

Avg. N per bin = 1374
$F_p$ and Particle Liquid Water

$F_p$ linked to PM$_{2.5}$ liquid water at RH > 65%?
Enhancement in $WSOC_p$ with Relative Humidity

<table>
<thead>
<tr>
<th>Bin-midpoint RH</th>
<th>Total $WSOC$ (µg C m$^{-3}$)</th>
<th>$WSOC_p$ enhancement (µg C m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75%</td>
<td>13.4</td>
<td>0.3</td>
</tr>
<tr>
<td>85%</td>
<td>10.3</td>
<td>0.6</td>
</tr>
<tr>
<td>92%</td>
<td>7.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Mean study $WSOC_p = 3.3$ µg C m$^{-3}$

~ 30% increase in $WSOC_p$ at 95% RH

Much scatter: other factors also important
More than Dissolution: Heterogeneous Reactions?

**Example: Formic Acid:**

- Obs. $[\text{HCOOH}]_g = 5 \, \mu\text{g/m}^3$
- Henry's Law Const. $\sim 5000 \, \text{M/atm}$
- $\Delta LWC_{\text{max}} \sim 35 \, \mu\text{g/m}^3$
- $\Delta \text{WSOC}_p \sim 10^{-5} \, \mu\text{gC/m}^3$
- Observed $\Delta \text{WSOC}_p \sim 1 \, \mu\text{gC/m}^3$
$F_p$ vs. OC: Adsorptive Partitioning to OC

**Yield:**

$$Y = \frac{M_o}{\Delta \text{ROG}}$$

(Odum et al., *Science*, 1997)
$F_p$ vs. OC: Adsorptive Partitioning to OC

Ambient results show no $F_p$-OC relationship (even at RH<50%)

But most SOA is water soluble so,

…what about partitioning to WSOCP?
$F_p$ vs. WSOC$_p$: Partitioning to WSOC$_p$

A strong $F_p$-WSOC$_p$ relationship is observed for $\text{WSOC}_p < \sim 4 \, \mu\text{g C m}^{-3}$

A compositional effect of $M_o$ on partitioning species?

Somewhat similar to results of Odum et al. [1996, 1997]

Is it real: $F_p \sim \text{WSOC}_p$?
$F_p$ vs. RH and WSOC$_p$

- Importance of WSOC$_p$ across entire RH range
- Heterogeneous chemical reactions important in SOA formation?
Summary of Atlanta SOA Formation

Results from various studies

1. Role of liquid water and heterogeneous reactions (Hennigan et al. - this work)
   - Similar to Volkamer et al. glyoxal results

2. $\text{WSOC}_p ^{14}C$: 70-80% modern carbon (Weber et al. JGR 2007)

3. $\text{WSOC}_p$ correlated with isoprene SOA tracers (Ding et al. ES&T 2008)

Major SOA Formation Route?

$$\text{Isoprene} + \text{OH} \rightarrow \begin{array}{c} \text{Low MW Compounds} \\ (\text{dicarbonyls}) \end{array} \xrightarrow{\text{H}_2\text{O}_L/\text{Heterog}} \text{SOA}$$

Carter & Atkinson, 1996

anthropogenic component?