Fine Particle Composition Measured During ICARTT _ An Overview Of Inorganic Ions And Water Soluble Organic Carbon

Rick Peltier
Amy Sullivan
Chris Hennigan
Rodney Weber
Charles A. Brock
Joost de Gouw
John Holloway

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Support: NOAA
Roadmap

A. Measurement overview
   Statistics, altitude profile, charge balance

B. Case Study 1: Aerosol source variability

C. Case Study 2: Urban aerosols that are subjected to power plant influence.

D. Summary
PILS Overview

**IC:** 90-second time integrated sample every 2.45 minutes.

**Inorganic Ion Species:** Sulfate, Nitrate, Chloride, Ammonium, Sodium, Calcium, Magnesium, Potassium

**LOD:** 20-500 ng m\(^{-3}\), depending on species.

**Uncertainty:** 20% (40% below 2x LOD)

**TOC:** 3-sec. time integrated sample averaged to 1 minute.

**Water Soluble Organic Carbon (WSOC)**

**TOC = TC-TIC**

**LOD:** 0.1-1.0 ug Carbon m\(^{-3}\) (depending on averaging time)

**Uncertainty:** 10%.
Observed Plume Types

- Relatively pure biomass
  - High WSOC and Acetonitrile concs.
  - Well-correlated WSOC & Acetonitrile
  - Little sulfate
- Mixed Biomass/Regional (Flt 040722)
  - High WSOC, acetonitrile, sulfate.
- Urban/Regional
  - High sulfate, lower WSOC (~<4 µgC m⁻³)
Observation Overview

- Sulfate, WSOC, Ammonium often observed. Occasional nitrate (usually biomass).
- Sulfate well correlated with volume in urban/regional and mixed plumes, while WSOC correlated with volume in all plumes (strongest in biomass).
- Significant variability in aerosol concentrations.

<table>
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<tr>
<th>LOD</th>
<th>Mean</th>
<th>Median</th>
<th>Std Dev</th>
<th>Min</th>
<th>Max</th>
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<td>0.01</td>
<td>0.12</td>
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<tr>
<td>Sulfate</td>
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<td>Nitrate</td>
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<td>Potassium</td>
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<td>12.21</td>
<td>10.1</td>
<td>13.56</td>
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</tbody>
</table>

\(^1\) In µg m\(^{-3}\) for ions, µg Carbon m\(^{-3}\) for WSOC, and µm\(^3\) cm\(^{-3}\) for fine volume
Altitude Profiles

- $\text{SO}_4^{\text{2-}}$, $\text{NH}_4^+$, WSOC higher at lower altitudes.
- Significant increases in $\text{NH}_4^+$, $\text{NO}_3^-$, WSOC during biomass – distinct layers.
- Little altitude dependence for nitrate.
Additional Analysis of Altitude Profile

- Species/fine volume median of 500m bins.
- Little change in fraction for sulfate and biomass-derived WSOC.
- Increase in WSOC/fine volume fraction with altitude.
Charge Balance Along Altitude

- Measured aerosol ionic components generally in charge balance (especially at high alt)

- Many events where net charge is negative – driven by sulfate, and most frequently at low alt. (i.e. excess sulfate not balanced by ammonium)

- Transient events of positive net charge during biomass events – suggest unmeasured organic acid as anion pair (to $\text{NH}_4^+$?).
Case Study 1: Flight 040809
Nighttime flight, Penn. v.s. East-coast
Case Study 2: Flight 040815
Plumes over Atlanta, GA.

SO\textsubscript{2} and SO\textsubscript{4}\textsuperscript{2-} spikes from local power plants

WSOC-CO: \( R^2 = 0.77 \)
Case Study 2: Flight 040815
Plumes over Atlanta, GA.

Little WSOC enhancement in Power Plant Plumes
Summary (1/2)

- WSOC highest in biomass plumes, sulfate highest in urban/regional outflow.
  - Correlated: sulfate = regional, mixed; WSOC = all (but strongest in biomass)
- WSOC and sulfate highly variable (in both concentration and spatial distribution).
  Highest concentrations at lower altitude.
- Non-biomass WSOC fraction of fine volume increases with altitude; sulfate did not – why?
  - Difference in $\text{SO}_4^{2-}$/WSOC formation w/ alt.
  - Difference in $\text{SO}_4^{2-}$/WSOC scavenging w/ alt.
- $\text{NH}_4^+/$SO$_4^{2-}$ (molar) typ. 2; in power generation regions typ. 1.
Summary (2/2)

- **Case Study 1: example of aerosol source variability.**
  - Higher [sulfate/fine volume] in power generation regions, higher [WSOC/fine volume] in urban outflow
    - has implications on $O_3$ chemistry, Brown et al., Science, submitted.

- **Case Study 2: urban $SO_4^{2-}$ and WSOC w/ local power plant plumes.**
  - Sulfate composed of background ($\text{NH}_4^+/\text{SO}_4^{2-} \sim 2$) that is enhanced ($\sim x2$) by distinct high-concentration sulfate plumes ($\text{NH}_4^+/\text{SO}_4^{2-} \sim 1$)
  - WSOC correlated with CO, little enhancement in fresh PP plumes.