Sources and acidity of sulfate-nitrate-ammonium aerosol in Arctic spring

Jenny A. Fisher
Harvard University

D. J. Jacob, J. E. Dibb, R. Bahreini, A. Middlebrook, Q. Wang, J. Mao

IPY Oslo Science Conference
8 June 2010

Acknowledgments:
NASA Tropospheric Chemistry Program, Norwegian Research Council, International Arctic Science Committee
Motivation

- **Sulfate** is a dominant component of winter/spring **Arctic Haze** and has direct and indirect impacts on climate.

- **Acidic sulfate** aerosol can be neutralized by ammonium, influencing both atmospheric chemistry and climate.

- Arctic surface data show ammonium has been decreasing more quickly than sulfate, leading to **increasingly acidic aerosol**.

- The **sources** of inorganic aerosol to the Arctic, and those responsible for the increasing acidity, are **highly uncertain**.
Goal: Understand the sources and acidity of aerosol in the Arctic

Approach: Integrated analysis of sulfate-nitrate-ammonium aerosols from:
1. **ARCTAS (NASA) and ARCPAC (NOAA)** aircraft campaigns during April 2008, based in Fairbanks, AK
2. **Long-term monitoring sites** at Barrow, Denali, Trapper Creek, Tuxedni (Alaska) and Alert (Nunavut)

3. **GEOS-Chem** – Chemical Transport Model (CTM) coupled oxidant-aerosol simulation driven by GEOS-5 meteorology run at 2°x2.5° horizontal resolution (v8-02-03)

- **SO₂ emissions**: -EDGAR anthropogenic with regional overwrites (map) -FLAMBE biomass burning -AEROCOM volcanism
- **NH₃ emissions**: -Bouwman et al., 1997 anthropogenic & natural -FLAMBE biomass burning
Wet deposition data test GEOS-Chem simulation over source continents

April 2008

SULFATE

AMMONIUM

NADP

EMEP

EANET

April 2008
A diversity of sources contribute to SNA aerosol in the North American Arctic in spring

**SULFATE**

![Bar chart for sulfate distribution by altitude and source.

**AMMONIUM**

![Bar chart for ammonium distribution by altitude and source.

- Aerosols are more abundant and more neutralized in the free troposphere than in the boundary layer.
- E. Asia and Europe are major sources of sulfate and ammonium at all altitudes.
- Below 2 km, E. Asian, European, and N. American sources have comparable influences on sulfate.
- Biomass burning is an important ammonium source in the free troposphere.

Other sources:
- Biomass burning
- DMS oxidation
- Volcanic emission

Fossil fuel regions:
- Arctic
- North America
- Europe
- North Asia
- East Asia

(jafisher@fas.harvard.edu)
Spring SNA aerosol ranged from very acidic to fully neutralized.

Aircraft Observations:
- Aerosol is **very acidic**, sulfate is primarily as $\text{H}_2\text{SO}_4$
- Sulfate is primarily as $(\text{NH}_4)\text{HSO}_4$
- Aerosol is **fully neutralized**, sulfate as $(\text{NH}_4)_2\text{SO}_4$
GEOS-Chem simulates range of observed acidity

**OBSERVATIONS**

- Scatter plot showing the relationship between $\text{SO}_4^{2-}$ and $\text{NH}_4^+$ concentration.
- Dotted lines indicate slopes of 6, 2, and 1.
- Data points are scattered across the plot.

**GEOS-CHEM MODEL**

- Similar scatter plot for the model.
- The model data points are clustered more tightly around the dotted lines.

---

Jenny A. Fisher  
(jafisher@fas.harvard.edu)  
IPY Oslo Science Conference
Different aerosol source regions show different neutralization signatures in the Arctic

- GEOS-Chem simulation of ARCTAS data shows the most neutralized aerosol originates from Europe and East Asia
- North American aerosol is significantly more acidic
- NH$_3$ dry deposition may play a role
Different aerosol source regions show different neutralization signatures in the Arctic

- GEOS-Chem simulation of ARCTAS data shows the most neutralized aerosol originates from Europe and East Asia.
- North American aerosol is significantly more acidic.
- NH₃ dry deposition may play a role.

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>Emission Ratio NH₃/(2 SO₂)</th>
<th>Deposition Ratio NH₄/(2 SO₄)</th>
<th>Aerosol Ratio NH₄/(2 SO₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. Asia</td>
<td>2.0</td>
<td>1.1 (0.46)</td>
<td>1.02</td>
</tr>
<tr>
<td>Europe</td>
<td>2.6</td>
<td>2.9 (1.8)</td>
<td>0.85</td>
</tr>
<tr>
<td>N. America</td>
<td>0.53</td>
<td>0.42 (0.93)</td>
<td>0.59</td>
</tr>
<tr>
<td>N. Asia</td>
<td>0.42</td>
<td>—</td>
<td>0.36</td>
</tr>
<tr>
<td>Arctic</td>
<td>0.47</td>
<td>—</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Surface data provide seasonal perspective

**SULFATE**

- Barrow (71.3°N, 156.6°W)

**AMMONIUM**

- Barrow (71.3°N, 156.6°W)

- Sulfate is higher at Barrow than at Denali in winter but not in spring, suggesting a seasonal transition in transport.
- GEOS-Chem underestimates winter sulfate and ammonium at Barrow despite good simulation of mid-Alaskan sites (e.g., Denali).
- Possible explanations:
  - Missing SO$_2$ oxidation pathway?
  - Underestimated sources?
Possible solution: increased winter SO$_2$ oxidation

- **SULFATE**
  - Barrow (71.3°N, 156.6°W)
  - **New oxidation**
  - **Original**

- **AMMONIUM**
  - Barrow (71.3°N, 156.6°W)

- **SULFATE**
  - Denali (63.7°N, 149.0°W)

- Added metal-catalyzed SO$_2$ oxidation by O$_2$ to GEOS-Chem (Alexander et al., 2009)

- New simulation shows improved agreement at Barrow, but agreement at inland sites worsens
Underestimate of N. Asian/Russian emissions may explain Barrow sulfate underestimate

**SULFATE**

- Fossil fuel emissions from N. Asia / S. Russia are only important at Barrow in winter; increasing these emissions may improve model-data agreement at Barrow without worsening agreement elsewhere.

- DMS oxidation is an important sulfate source at all sites, especially in spring.

---

Other Non-eruptive volcanism

DMS oxidation

Biomass burning

---

Arctic fossil fuel

North Asian fossil fuel

North American fossil fuel

European fossil fuel

East Asian fossil fuel

---

Jenny A. Fisher (jafisher@fas.harvard.edu)

IPY Oslo Science Conference
Aerosol acidity shows a strong vertical gradient, decreasing with altitude.

Mean April neutralized fraction from GEOS-Chem

![Map showing acidity distribution with color scale from very acidic aerosol to fully neutralized aerosol.](image)

\[
\frac{[\text{NH}_4^+]}{2[\text{SO}_4^{2-}]+[\text{NO}_3^-]}
\]

Very acidic aerosol \rightarrow Acidity \rightarrow Fully neutralized aerosol
Conclusions

• Arctic aerosol ranged from very acidic to fully neutralized in April 2008. The mean observed neutralized fractions were 0.75 (ARCTAS) and 0.90 (ARCPAC).

• A diversity of sources contribute to the spring SNA aerosol burden in the North American Arctic, with the biggest contributions from East Asia and Europe.

• East Asian and European sources provide the most fully neutralized aerosol to the Arctic.

• Despite having a higher NH$_3$/SO$_2$ precursor emission ratio and a higher NH$_4$/SO$_4$ wet deposition ratio, European-sourced aerosol is more acidic than East Asian aerosol when it reaches the North American Arctic.

• Surface data from the high Arctic (Barrow) show higher winter sulfate burdens than sites in inland Alaska, perhaps due to more influence at these sites from North Asian and Russian industrial sources.

• GEOS-Chem simulations show a strong vertical gradient in aerosol acidity, with more acidic aerosol at the surface aerosol than in the free troposphere.

Acknowledgments:
NASA Tropospheric Chemistry Program, Norwegian Research Council, International Arctic Science Committee