Bulk characterization of organosulfates in continental fine aerosol

Gelencsér, A., Kiss, G., Lukács, H., Hoffer, A.

Department of Earth and Environmental Sciences, University of Pannonia, Veszprém, Hungary

Schmitt-Kopplin, P. & Gebefügi, I.

Institut für Ökologische Chemie, Helmholtz Zentrum München, German Research Center for Environmental Health, Neuherberg, Germany

Dabek-Zlotorzynska, E.

Analysis and Air Quality Division, Environmental Technology Centre, Environment Canada, Ottawa, Canada
Sulfate esters (organosulfates) are important components of SOA—chamber studies

First observations:

• Acidic seeds significantly enhance SOA yield in smog chambers (Jang, Science 2002)

Smog-chamber studies

α-pinene (Czoschke, AE 2003; Gao, EST 2004; Iinuma AE 2004; Kleindienst, EST 2006; Jang, EST, 2006)

β-pinene (Iinuma EST, 2007; Northcross AE, 2007)

Isoprene (Czoschke AE 2003; Edney AE 2005; Surratt JPC, 2006; Surratt EST, 2007)

Limonene (Iinuma AE 2007; Northcross AE, 2007)

Pinonaldehyde (Liggio GRL, 2006)

Glyoxal (Kroll AE, 2005; Liggio JGR 2005)
Sulfate esters (organosulfates) are important components of SOA—field studies

Sulfate esters have been identified

In urban and rural aerosol by

- **LC-ESI-MS** (Gao JGR 2006; Surratt EST, 2007; Iinuma EST, 2007, Gómez-González, JMS 2008)
- **FTIR** (Blando EST 1998; Gilardoni JGR, 2007)

In water-soluble HULIS by

- **ESI-ITMS and ESI-TOF** (Romero and Oehme, JAC 2005)
Suggested mechanisms of sulfate esters formation

In the presence of acidic seed aerosols
   - Reactive uptake of semi-volatile BVOC photooxidation products
     - Hydroxy compounds: esterification with sulfuric acid
     - Carbonyl compounds: esterification after gem-diol formation
   - Direct uptake of BVOC (Liggio GRL, 2005)

In the absence of seed aerosols
   - Photooxidation of BVOC (α-pinene or isoprene) and SO₂ (Surratt EST, 2007)

High NOₓ strongly suppresses organosulfate formation (organic acid formation vs. esterification)
Open questions

1) Could organosulfate formation be a quantitatively important SOA formation mechanism in ambient aerosol?

2) In which particle size fraction do organosulfates occur?

3) How is sulfur distributed between organic compounds?

4) Which formation mechanism could be operative in the atmosphere?
Sampling and analysis methods

- 48-h aerosol samples were collected with 8-stage Berner impactor at K-puszta (rural site) in summer 2006
- Samples were extracted in water and analyzed for
  - total sulfur by XRFS
  - sulfate and methanesulfonate by IC
- Organic S = Total S – sulfate – methanesulfonate
- Uncertainties were minimized and carefully evaluated
- TC mass concentrations were also measured by thermal analysis
Size-distributions of total S and S_{sulfate+MSA}
## Mass concentrations of major sulfur species in water extract of PM2.5 aerosols

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{total}}$ (µgSm$^{-3}$)</th>
<th>$S_{\text{sulfate}}$ (µgSm$^{-3}$)</th>
<th>$S_{\text{org}}$ (µgSm$^{-3}$)</th>
<th>$S_{\text{org}}/S_{\text{sulfate}}$</th>
<th>%</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>29-31 May 2006</td>
<td>0.57</td>
<td>0.50</td>
<td>0.06</td>
<td>13</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>04-06 June 2006</td>
<td>0.70</td>
<td>0.60</td>
<td>0.09</td>
<td>14</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>06-08 June 2006</td>
<td>0.70</td>
<td>0.63</td>
<td>0.05</td>
<td>9</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>14-16 June 2006</td>
<td>0.38</td>
<td>0.35</td>
<td>0.02</td>
<td>6</td>
<td>129</td>
<td></td>
</tr>
</tbody>
</table>
Estimated mass contribution of water-soluble organosulfates to WSOC

Can only be estimated with a high level of uncertainty: mass-weighted average C-to-S molar ratio would be needed

C:S ratio 2:1 in sulfate ester of glyoxal
10:1 in sulfate esters of monoterpene derivatives
15:1 in sulfate esters of sesquiterpenes derivatives

16–57% of WSOC (SOA) are bound in organosulfates
Analysis of organosulfates in water-soluble sub-fraction of rural PM2.5 aerosols

- PM2.5 aerosol samples were collected on quartz filters at rural sites of K-puszta (Hungary) and St. Anicet and Canterbury (Canada) in summer 2004 and 2005.
- Samples were extracted in water.
- Extracts were isolated on a C18 column, eluted with methanol and brought to dryness.
- Samples were analyzed with an ultra high resolution Bruker (Bremen, Germany) APEX 12 Qe Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) coupled to an APOLLO II microelectrospray source.
- Mass range m/z 100-2000, Resolution >> 100,000.
- Peak assignment with software using theoretical isotope scoring.
**Peak number statistics by elemental composition in water-soluble sub-fraction of rural PM2.5 aerosols**

<table>
<thead>
<tr>
<th>Elemental formula</th>
<th>Occurrence %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHO</td>
<td>67–75</td>
</tr>
<tr>
<td>CHOS</td>
<td>17–23</td>
</tr>
<tr>
<td>CHON</td>
<td>4–6</td>
</tr>
<tr>
<td>CHONS</td>
<td>4–5</td>
</tr>
</tbody>
</table>

Based on 770–1000 assigned peaks of four PM2.5 samples each.

Number of compounds can be substantially larger since a single elemental formula may belong to several compounds.
Van Krevelen diagram of assigned peaks

**Typical BSOA region**

$$\text{CHO}_{\text{precursors}} = \text{CHOS} - \text{SO}_3 (80)$$
Mass resolved van Krevelen in H/C of assigned peaks

Typical BSOA region
Conceptual model of organosulfate formation in the atmosphere

- Photooxidation: BVOC → SVOC$_g$
- Partitioning/reactive uptake
- Condensation: H$_2$SO$_4$(g) → SO$_2$
- Esterification on particle surface

No acidic aerosols are needed.
TEM-EELS studies on individual particles from K-puszta

ammonium sulfate particles

S-containing organic residue remains after irradiation
Conclusions

1) Organosulfates seem to be quite significant SOA components at least in summer rural aerosols;
2) Total sulfur in organosulfates may not be negligible even related to sulfate S;
3) They tend to be overwhelmingly in (on) accumulation (condensation) mode particles;
4) There are several hundreds of S-containing organic peaks even in a subfraction of WSOC;
5) These compounds span a wide range of MW and O/C-H/C ratios;
6) Likely formation mechanism is reactive uptake of BSOA powered by heterogeneous reactions with gaseous sulfuric acid.
Thanks for your attention!