Sources and Radiative Properties of Organosulfates in the Atmosphere

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Sources and Radiative Properties of Organosulfates in the Atmosphere

Central research hypotheses:
- Anthropogenic emissions impact biogenic SOA formation
- Organosulfates are climate forcing agents

Synthesis
Hygroscopic growth
Method development
Chemical analysis of PM$_{2.5}$
Source apportionment

Approach
Synthesis of Organosulfate Standards

1) Reaction of alcohol with pyridine sulfur trioxide complex

   (Hoff, et al., JACS, 2001)

2) Cation exchange

   Potassium salts formed white needles upon recrystallization

   Structure and purity confirmed by $^{13}$C NMR, $^1$H NMR, high-resolution MS, elemental analysis

(Hettiyyadura, et al., AMT, 2015; Estillore et al. ES&T, in press)
Organosulfate Standards

Glycolic acid sulfate (45%)

\[
\text{HO-COO-OSO}_3^-
\]

Hydroxyacetone sulfate (35%)

\[
\text{CH}_3\text{C(OH)-OSO}_3^-\cdot\text{K}^+
\]

Acetoin sulfate (65%)

\[
\text{CH}_3\text{O-C(OH)-OSO}_3^-\cdot\text{K}^+
\]

Butenediol sulfate (67%)

\[
\text{HO-CH}_2\text{CH(OH)-OSO}_3^-\cdot\text{K}^+
\]

Oxirane sulfate (97%)

\[
\text{HO-CH}_2\text{CH(OH)-OSO}_3^-\cdot\text{K}^+
\]

Benzyl sulfate (75%)

\[
\text{C}_6\text{H}_5\text{CH(OH)-OSO}_3^-\cdot\text{K}^+
\]

2-Methyltetrol sulfate

\[
\text{HO-C(OH)-OSO}_3^-\cdot\text{K}^+
\]

Lactic acid sulfate

\[
\text{CH}_3\text{C(OH)-OSO}_3^-\cdot\text{K}^+
\]

Commercially available as sodium salts:
- Methyl sulfate
- Ethyl sulfate
- Propyl sulfate
“Water uptake and hygroscopic growth of organosulfate aerosol”
Armando Estillore, Anusha Hettiyadura, Zhen Qin, Erin Leckrone, Becky Wombacher, Tim Humphry, Elizabeth Stone, Vicki Grassian
Available online as a just accepted article in Environmental Science & Technology (10.1021/acs.est.5b05014)
# Characterization of climate-relevant properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Measurement technique</th>
<th>Summary of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light absorption</td>
<td>UV-vis spectrophotometry</td>
<td>No absorption</td>
</tr>
<tr>
<td>Hygroscopicity</td>
<td>Hygroscopicity-tandem differential mobility analyzer</td>
<td>Continuous water uptake</td>
</tr>
</tbody>
</table>

## Model Compounds

<table>
<thead>
<tr>
<th>Model Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium methyl sulfate</td>
<td>CH$_3$SO$_4$Na</td>
</tr>
<tr>
<td>Sodium ethyl sulfate</td>
<td>C$_2$H$_5$SO$_4$Na</td>
</tr>
<tr>
<td>Sodium propyl sulfate</td>
<td>C$_3$H$_7$SO$_4$Na</td>
</tr>
<tr>
<td>Potassium 2-butenediol sulfate</td>
<td>C$_4$H$_7$SO$_5$K</td>
</tr>
<tr>
<td>Potassium 4-hydroxy-2,3-epoxybutane sulfate</td>
<td>C$_4$H$_7$SO$_6$K</td>
</tr>
<tr>
<td>Potassium glycolic acid sulfate</td>
<td>C$_2$H$_3$SO$_6$K</td>
</tr>
<tr>
<td>Potassium hydroxyacetone sulfate</td>
<td>C$_3$H$_5$SO$_5$K</td>
</tr>
<tr>
<td>Sodium benzyl sulfate</td>
<td>C$_7$H$_7$SO$_4$Na</td>
</tr>
</tbody>
</table>
Ammonium sulfate has distinct phase transitions. The hydration curve for ammonium sulfate shows:

Deliquescence RH $79.9 \pm 0.10\%$
Efflorescence RH $36.7 \pm 1.8\%$

(Estillore, et al. *ES&T, in press*)
Organosulfates show continuous and reversible uptake of water

Hydration curve for organosulfates

No distinct transitions; continuous growth upon hydration

Absorption of water at low RH

(Estillore, et al. ES&T, in press)
Organosulfates show continuous and reversible uptake of water. A hydration curve for additional organosulfates is shown, with growth factor vs. relative humidity. The curve illustrates the continuous and reversible uptake of water by organosulfates. The figure includes chemical structures of sodium methyl sulfate, sodium ethyl sulfate, potassium 2-butenediol sulfate, and potassium 4-hydroxy-2,3-epoxybutane sulfate. (Estillore, et al. ES&T, in press)
## Growth factors of 100 nm particles at 85% RH

<table>
<thead>
<tr>
<th>Organosulfate</th>
<th>Molecular weight</th>
<th>Growth factor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium methyl sulfate</td>
<td>111</td>
<td>1.50</td>
<td>Estillore, et al. <em>in press</em></td>
</tr>
<tr>
<td>Sodium ethyl sulfate</td>
<td>125</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>Potassium 2-butenediol sulfate</td>
<td>167</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
<td>Potassium 4-hydroxy-2,3-epoxybutane sulfate</td>
<td>183</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>Potassium glycolic acid sulfate</td>
<td>155</td>
<td>1.29</td>
<td></td>
</tr>
<tr>
<td>Potassium hydroxyacetone sulfate</td>
<td>153</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>Limonene-derived organosulfates (OS)</td>
<td>250</td>
<td>1.03</td>
<td><em>Hansen et al. ACPD, 2015</em></td>
</tr>
<tr>
<td>Limonene OS 10% w/w ammonium sulfate</td>
<td>250</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>Limonene OS &gt; 20% w/w ammonium sulfate</td>
<td>250</td>
<td>~ 1.5</td>
<td></td>
</tr>
</tbody>
</table>

*Low molecular weight, alkyl organosulfates have the greatest growth factors*
Hygroscopic growth of methyl sulfate and NaCl

Hydration curve for sodium chloride

Deliquescence RH 75.0 ± 0.50 %
Efflorescence RH 44.0 ± 1.0%

Hydration curve for methyl sulfate/NaCl (1:1 wt%)

Deliquescence RH 69.6 ± 1.0 %
Efflorescence RH 36.0 ± 0.5%

(Estillore, et al. ES&T, in press)
Conclusions from Hygroscopic Growth Studies

• While ammonium sulfate shows distinct deliquescence and efflorescence points upon hydration and dehydration, organosulfates show continuous water uptake.
  → Organosulfates are hygroscopic even at low relative humidity
  → Thus, they are expected to extend the range of environmental conditions that water is taken up onto aerosol particles

• When mixed with organosulfates, the deliquescence and efflorescence RH of sodium chloride were shifted to lower values
  → Organosulfates modify the hygroscopic properties of inorganic salts

(Estillore, et al. *ES&T, in press*)
Develop and validate a method for organosulfate speciation:

1) ESI-MS/MS optimization
2) LC separation development using HILIC
3) Assess sample preparation protocols
4) Apply to ambient aerosol
ESI Fragmentation of Organosulfates

Methyl sulfate
\[ \text{O} \quad 96 \quad \text{O} \quad 80/81 \quad \text{SO}_3^- \]

Ethyl sulfate
\[ \text{O} \quad 97 \quad \text{O} \quad 80 \quad \text{SO}_3^- \]

Glycolic acid sulfate
\[ \text{HO} \quad \text{O} \quad 97 \quad \text{O} \quad 75 \quad \text{SO}_3^- \]

Benzyl sulfate
\[ \text{O} \quad 96 \quad \text{O} \quad 81 \quad \text{SO}_3^- \]

Hydroxyacetone sulfate
\[ \text{O} \quad 97 \quad \text{O} \quad 80/81 \quad \text{SO}_3^- \]

(Hettiyyadura, et al. AMT 2015)
Multiple Reaction Monitoring (MRM)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Precursor ion and m/z</th>
<th>Product ion and m/z</th>
<th>Cone voltage (V)</th>
<th>Collision energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl sulfate</td>
<td>CH$_3$SO$_4^-$ 111</td>
<td>SO$_3^-$ 80</td>
<td>36</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_4^-$ 96</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Ethyl sulfate</td>
<td>C$_2$H$_5$SO$_4^-$ 125</td>
<td>HSO$_4^-$ 97</td>
<td>26</td>
<td>12</td>
</tr>
<tr>
<td>Benzyl sulfate</td>
<td>C$_7$H$_7$SO$_4^-$ 187</td>
<td>HSO$_3^-$ 81</td>
<td>42</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO$_4^-$ 96</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Hydroxyacetone sulfate</td>
<td>C$_3$H$_5$SO$_5^-$ 153</td>
<td>SO$_3^-$ 80</td>
<td>32</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HSO$_4^-$ 97</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Glycolic acid sulfate</td>
<td>C$_2$H$_3$SO$_6^-$ 155</td>
<td>C$_2$H$_3$O$_3^-$ 75</td>
<td>26</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HSO$_4^-$ 97</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Lactic acid sulfate</td>
<td>C$_3$H$_5$SO$_6^-$ 169</td>
<td>HSO$_4^-$ 97</td>
<td>28</td>
<td>16</td>
</tr>
</tbody>
</table>

(Hettiyadura, et al. AMT 2015)
Separation of Organosulfates

Objectives:
1) Selective retention of oxygenated organosulfates
2) Separation from the sample matrix

Retention of organosulfates on a reversed-phase (C18) column:

- Inorganic sulfate
- Highly oxygenated organosulfates
- Precursor to m/z 97 (HSO$_4^-$)
- Aromatic and monoterpene organosulfates are better resolved
Hydrophilic interaction liquid chromatography (HILIC)

**Stationary phase:**
Ethylene Bridged Hybrid (BEH) amide column (Waters)
*Retains extremely polar compounds (including sugars) and involves ion exchange*

**Mobile phase:**
Acetonitrile (ACN) and water
10 mM ammonium acetate
pH 9

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>H$_2$O</th>
<th>ACN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

(Hettiyadura, et al. AMT 2015)
HILIC Separation Development

A) Standard Solution

- methyl sulfate
- ethyl sulfate
- benzyl sulfate
- hydroxyacetone sulfate
- glycolic acid sulfate
- lactic acid sulfate

Response (a.u.)
- 0.0
- 4.0e+5
- 8.0e+5
- 1.2e+6
- 1.6e+6

Retention time (min.)

(Hettiyadura, et al. AMT 2015)
HILIC separation of PM$_{2.5}$ from Centreville, AL

A) Standard Solution

- methyl sulfate
- ethyl sulfate
- benzyl sulfate
- hydroxyacetone sulfate
- glycolic acid sulfate
- lactic acid sulfate

B) Centreville, AL - Summer 2013

Response of GAS and LAS (a.u.)®

Response (a.u.)

Retention time (min.) (Hettiyadura, et al. AMT 2015)
## UPLC-MS/MS Method Performance

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min.)</th>
<th>Linear range (µg L⁻¹)</th>
<th>R²</th>
<th>LOD (µg L⁻¹)</th>
<th>LOQ (µg L⁻¹)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl sulfate</td>
<td>0.88 ± 0.03</td>
<td>25.0-500.0</td>
<td>0.998</td>
<td>2.6</td>
<td>8.6</td>
<td>2.9</td>
</tr>
<tr>
<td>ethyl sulfate</td>
<td>0.78 ± 0.03</td>
<td>25.0-500.0</td>
<td>0.998</td>
<td>3.4</td>
<td>11.2</td>
<td>2.5</td>
</tr>
<tr>
<td>benzyl sulfate</td>
<td>0.58 ± 0.02</td>
<td>25.0-300.0</td>
<td>0.995</td>
<td>3.9</td>
<td>13.2</td>
<td>3.0</td>
</tr>
<tr>
<td>hydroxyacetone sulfate</td>
<td>0.66 ± 0.02</td>
<td>25.0-300.0</td>
<td>0.996</td>
<td>2.6</td>
<td>8.7</td>
<td>3.0</td>
</tr>
<tr>
<td>glycolic acid sulfate</td>
<td>7.84 ± 0.01</td>
<td>25.0-300.0</td>
<td>0.998</td>
<td>1.9</td>
<td>6.3</td>
<td>15.6</td>
</tr>
<tr>
<td>lactic acid sulfate</td>
<td>7.57 ± 0.02</td>
<td>25.0-300.0</td>
<td>0.995</td>
<td>3.9</td>
<td>13.0</td>
<td>5.9</td>
</tr>
</tbody>
</table>

(Hettiyyadura, et al. AMT 2015)
Sample preparation: to shake or sonicate?

a) Extraction by sonication
- methyl sulfate
- ethyl sulfate
- benzyl sulfate
- hydroxyacetone sulfate
- lactic acid sulfate
- glycolic acid sulfate

b) Extraction by shaking
- methyl sulfate
- ethyl sulfate
- benzyl sulfate
- hydroxyacetone sulfate
- lactic acid sulfate
- glycolic acid sulfate

(Spike recovery (%))

(Hettiyadura, et al. AMT 2015)
Southern Oxidant and Aerosol Study

- Centreville, AL (CTR) Ground Site
- June 1 – July 15, 2013
- Daytime (08:00-19:00) and nighttime (20:00-07:00)
- Chemical measurements
  - Elemental and organic carbon
  - Organic species by GCMS
  - Organosulfates by LCMS
- Source apportionment of PM$_{2.5}$ and organic carbon
Methyltetrol sulfates (m/z 215)

Low-NOx isoprene oxidation products:

\[
\begin{align*}
\beta-\text{IEPOX} & \quad \gamma_4-\text{IEPOX} \\
\text{HO} & \quad \text{HO} \\
\text{HO} & \quad \text{OH}
\end{align*}
\]

(Paulot et al., Science, 2009)

IEPOX-sulfates form by acid catalyzed ring opening of IEPOX with sulfate

(Surratt et al., PNAS, 2010)

HILIC resolves 6 IEPOX-sulfate isomers

Regioselectivity: \(3^\circ > 1^\circ > 2^\circ\)

Chiral centers

(Hettiyadura, et al., AMT, 2015)
Other biogenic organosulfates ($m/z$ 213)

High resolution extracted ion chromatogram

- Forms in chamber experiments of isoprene (Surratt et al. *JPCA*, 2008) and potentially other VOC (Gómez-Gónzalez et al. 2008; Shalamzari et al. *ES&T*, 2014)
- Short retention times suggest keto- and hydroxy- groups, not carboxylic acids
- Isomers positively correlate ($r_s > 0.75; p < 0.05$)

\[
C_5H_9O_7S^- 
\]

![Chemical structure](image)
Other biogenic organosulfates (m/z 211)

High resolution extracted ion chromatogram

- Forms in chamber experiments of isoprene (Surratt et al. JPCA, 2008)
- Similarly, short retention times suggest keto- and hydroxy-groups, not carboxylic acids
- Isomers positively correlate ($r_s > 0.9; p < 0.05$)
# Molecular marker source apportionment

<table>
<thead>
<tr>
<th>Aerosol Source</th>
<th>Markers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary- biogenic</td>
<td>Derivatives of isoprene, monoterpenes, including organosulfates</td>
</tr>
<tr>
<td>Secondary- anthropogenic</td>
<td>Aromatic acids</td>
</tr>
<tr>
<td>Secondary – inorganic</td>
<td>Ammonium sulfate</td>
</tr>
<tr>
<td>Primary biogenic (detritus)</td>
<td>Linear $n$-alkanes (odd C preference)</td>
</tr>
<tr>
<td></td>
<td>Linear $n$-alkanoic acids (even C preference)</td>
</tr>
<tr>
<td>Diesel engines</td>
<td>Hopanes, steranes, elemental carbon</td>
</tr>
<tr>
<td>Gasoline vehicles</td>
<td>Hopanes, steranes, polycyclic aromatic hydrocarbons (PAH)</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>Levoglucosan, plant sterols</td>
</tr>
</tbody>
</table>
Biomass burning

Chemical Signatures: Anhydrosugars

(Simoneit, et al., 1999)

(photo by Joost de Gouw)
Biomass Burning at Centreville

Levoglucosan concentration (ng m$^{-3}$)
Chemical mass balance source apportionment

EPA CMB v. 8.2

\[ c_i = \sum_{i=1}^{p} a_{ij} s_j \]

- \( c_i \) = ambient concentration of species \( i \)
- \( a_{ij} \) = fractional concentration of species \( i \) at source \( j \)
- \( s_j \) = mass contribution of source \( j \)

Key assumptions:
1) Conservation of mass, i.e. tracers do not react or interact
2) Source compositions are independent of one another
3) Sources have been identified and are characterized
Conclusions

• HILIC chromatography provides improved retention and resolution of carboxy- and hydroxy-substituted organosulfates
  • Diagnostic tool for carboxy-organosulfates
  • Complementary to reversed-phase separations
  • May aid in understanding isoprene SOA product distributions
• Organosulfates in Centerville are largely biogenic, showing consistent signatures from isoprene
  • Correlation analysis implies an important role for sulfate
  • pH is consistently low enough to support their formation
• Preliminary source apportionment indicates a very small role for primary sources relative to secondary in Centreville.
Acknowledgements

University of Iowa
Anusha Priyadarshani Silva Hettiyyadura, Shuvashish Kundu, Sean Staudt, Zach Baker, Thilina Jayarathne, Vicki Grassian, Armando Estillore, Zhen Qin, Vic Parcell, Lynn Teesch

Wisconsin State Laboratory of Hygiene
Brandon Shelton, Steve Geis, Jeff DeMinter

Truman State University
Tim Humphry, Emily Geddes, Erin Lekrone, Becky Wombacher, Katherine Richards

UNC
Jason Surratt, Avram Gold, Zenfa Zheng

University of Wisconsin-Madison
Frank Keutsch, Sean Staudt

SOAS Organizers
Ann Marie Carlton, Jose Jimenez, Allen Goldstein, Joost deGouw, Lindsay Yee (filter captain)

This research is funded by U.S. EPA - Science To Achieve Results (STAR) Program
Grant # 83540101