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***Supplementary Material***

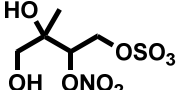
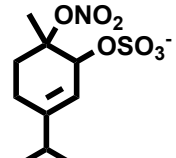
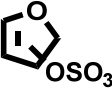

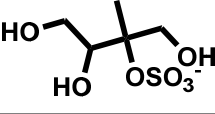
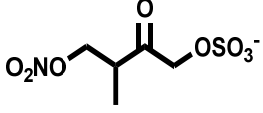
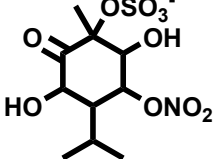
**Organosulfates in the Midwestern United States: abundance, composition, and stability**

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**Table S1.** Organosulfates identified in Iowa City, IA from the precursor to  $m/z$  96 scan. Summarized for each compound is the calculated monoisotopic mass, formula determined by TOF-MS, proposed structure, VOC precursor(s) with reference to prior studies, HILIC retention time for major peaks,  $m/z$  error (mDa), and percent contribution to the precursor ion signal.

Calculated Mass [M-H] <sup>-</sup>	Formula	Structure	VOC Precursor(s)	T <sub>R</sub> (min.)	Error (mDa)	Contribution to precursor ion signal (%)
151.0065	C <sub>4</sub> H <sub>7</sub> SO <sub>4</sub> <sup>-</sup>	Unknown	Diesel <sup>A</sup>	0.65	1.4	5.1
260.0076	C <sub>5</sub> H <sub>10</sub> NSO <sub>9</sub> <sup>-</sup>	<sup>B</sup> 	Isoprene <sup>B</sup>	0.91	1.1	4.9
294.0647	C <sub>10</sub> H <sub>16</sub> NSO <sub>7</sub> <sup>-</sup>	<sup>B</sup> 	$\alpha$ -pinene, terpinolene, & $\alpha$ -terpinene <sup>B</sup> $\beta$ -pinene <sup>B,C</sup>	0.58	0.8	4.3
164.9858	C <sub>4</sub> H <sub>5</sub> SO <sub>5</sub> <sup>-</sup>	<sup>D</sup> 	Cyclohexene <sup>E</sup>	0.55	1.2	3.1
110.9759	CH <sub>3</sub> SO <sub>4</sub> <sup>-</sup> Methyl Sulfate		Numerous Sources	0.96	0.7	2.8
215.0225	C <sub>5</sub> H <sub>11</sub> SO <sub>7</sub> <sup>-</sup> 2-methyltetrol sulfate	<sup>B</sup> 	Isoprene <sup>B</sup>	1.40 1.72 2.76 3.44	-0.6 0.7 -0.6 0.5	1.8
241.9971	C <sub>5</sub> H <sub>8</sub> NSO <sub>8</sub> <sup>-</sup>	<sup>F</sup> 	Unknown	0.57	1.5	1.5
136.9909	C <sub>3</sub> H <sub>5</sub> SO <sub>4</sub> <sup>-</sup>	Unknown	Biodiesel & diesel <sup>A</sup>	0.66	1.0	1.4
342.0495	C <sub>10</sub> H <sub>11</sub> NSO <sub>10</sub> <sup>-</sup>	<sup>B</sup> 	$\alpha$ -pinene & $\alpha$ -terpinene <sup>B</sup> $\beta$ -pinene <sup>B,C</sup>	0.51	0.6	1.2

<sup>A</sup>Blair et al. (2017); <sup>B</sup>Surratt et al. (2008); <sup>C</sup>Inuma et al. (2007); <sup>D</sup>Hettiyadura et al. (2017); <sup>E</sup>Liu et al. (2017); <sup>F</sup>Hettiyadura et al. (2018)

**Table S2.** Additional organosulfates quantified or semi-quantified in Iowa City, IA and their respective contribution to OC.

<b>Organosulfate</b>	<b>Concentration (ng m<sup>-3</sup>)</b>	<b>% OC</b>
Methyl sulfate ( <i>m/z</i> 111) <sup>A</sup>	0.7 ± 0.2	0.01
Ethyl sulfate ( <i>m/z</i> 125) <sup>A</sup>	0.10 ± 0.02	0.001
Dodecyl Sulfate ( <i>m/z</i> 265) <sup>B</sup>	1.4 ± 0.3	0.04
C <sub>6</sub> H <sub>9</sub> SO <sub>6</sub> <sup>-</sup> ( <i>m/z</i> 209) <sup>B</sup>	8.3 ± 0.2	0.16
C <sub>7</sub> H <sub>11</sub> SO <sub>7</sub> <sup>-</sup> ( <i>m/z</i> 239) <sup>B</sup>	1.8 ± 0.3	0.04
C <sub>7</sub> H <sub>11</sub> SO <sub>6</sub> <sup>-</sup> ( <i>m/z</i> 223) <sup>B</sup>	1.8 ± 0.28	0.04
C <sub>8</sub> H <sub>13</sub> SO <sub>6</sub> <sup>-</sup> ( <i>m/z</i> 237) <sup>B</sup>	2.1 ± 0.2	0.05
C <sub>10</sub> H <sub>15</sub> SO <sub>7</sub> <sup>-</sup> ( <i>m/z</i> 279) <sup>B</sup>	0.7 ± 0.1	0.02
Hydroxyethyl sulfate ( <i>m/z</i> 141) <sup>B</sup>	2.9 ± 0.2	0.03

<sup>A</sup>Quantified using commercial standards; <sup>B</sup>Quantified using hydroxyacetone sulfate as a surrogate standard.

**Table S3.** Comparisons of means for each analysis time relative to concentration determined on Day 2. Two-sample t-test conducted (n=6) where  $\alpha = 0.05$  such that a P-value >  $\alpha$  indicates the difference between the means is not statistically significant.

<b>Storage Time</b>	<b>Methyl sulfate <i>P</i>-value</b>	<b>Ethyl sulfate <i>P</i>-value</b>	<b>Hydroxyacetone sulfate <i>P</i>-value</b>	<b>Glycolic acid sulfate <i>P</i>-value</b>
Day 8 <sup>A</sup>	0.20	0.96	0.12	0.08
Day 29	0.29	0.42	0.90	0.09
Day 83	0.22	0.42	0.78	0.06
Day 180	0.24	0.13	0.23	0.62
Day 251 <sup>A</sup>	0.09	0.77	0.06	0.95
Day 364	0.11	0.17	0.38	0.01

<sup>A</sup>n=5

## References

- Blair, S. L., Macmillan, A. C., Drozd, G. T., Goldstein, A. H., Chu, R. K., Paša-Tolić, L., Shaw, J. B., Tolić, N., Lin, P., Laskin, J., Laskin, A., Nizkorodov, S. A. (2017). Molecular Characterization of Organosulfur Compounds in Biodiesel and Diesel Fuel Secondary Organic Aerosol. *Environmental Science & Technology*, 51, 119-127. doi:10.1021/acs.est.6b03304
- Hettiyadura, A. P. S., Al-Naiema, I. M., Hughes, D. D., Fang, T. Stone, E. A. (2018). Organosulfates in Atlanta, Georgia: Anthropogenic influences on biogenic secondary organic aerosol formation. *Atmospheric Chemistry and Physics Discussion*, 2018, 1-27. doi:10.5194/acp-2018-834
- Hettiyadura, A. P. S., Jayarathne, T., Baumann, K., Goldstein, A. H., De Gouw, J. A., Koss, A., Keutsch, F. N., Skog, K. Stone, E. A. (2017). Qualitative and quantitative analysis of atmospheric organosulfates in Centreville, Alabama. *Atmospheric Chemistry and Physics*, 17, 1343-1359. doi:10.5194/acp-17-1343-2017
- Iinuma, Y., Müller, C., Böge, O., Gnauk, T. Herrmann, H. (2007). The formation of organic sulfate esters in the limonene ozonolysis secondary organic aerosol (SOA) under acidic conditions. *Atmospheric Environment*, 41, 5571-5583. doi:10.1016/j.atmosenv.2007.03.007
- Liu, S., Jia, L., Xu, Y., Tsona, N. T., Ge, S. Du, L. (2017). Photooxidation of cyclohexene in the presence of SO<sub>2</sub>: SOA yield and chemical composition. *Atmospheric Chemistry and Physics*, 17, 13329-13343. doi:10.5194/acp-17-13329-2017
- Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C. Seinfeld, J. H. (2008). Organosulfate Formation in Biogenic Secondary Organic Aerosol. *The Journal of Physical Chemistry*, 112, 8345-8378. doi:10.1021/jp802310p