



Supplement of

Qualitative and quantitative analysis of atmospheric organosulfates in Centreville, Alabama

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A. Acid hydrolysis of 2-methyltetrol sulfates

An aliquot (100 μL) of $\text{PM}_{2.5}$ sample (collected on 21 June nighttime during SOAS 2013) that was prepared according to the method described in Sect. 2.4 was transferred to an LC vial and evaporated to dryness under ultra-pure N_2 gas at 50 $^\circ\text{C}$. Then it was reconstituted in ultra-pure water (1.0 mL) and split into three equal aliquots: two for acid hydrolysis (at 4 M and 1M HNO_3) and one control. All samples were incubated at room temperature in the dark. After a reaction period of 48 h (for the sample acid hydrolyzed at 4 M HNO_3) and 58 h (for the sample acid hydrolyzed at 1 M HNO_3) acid hydrolyzed samples were neutralized with NH_4OH . Then all samples were evaporated to dryness under ultra-pure N_2 gas at 50 $^\circ\text{C}$ and reconstituted in acetonitrile and ultra-pure water (560 μL ; 60:40 for acid hydrolyzed samples and 95: 5 for control). Those samples were then analyzed using HILIC-TQD method described in Sect. 2.5.3. with an amended version of the multiple reaction monitoring (MRM) method that included the transition of m/z 215 to bisulfate ion (m/z 97) with a cone voltage and the collision energy of 40 V and 22 eV, respectively.

Figure S1: A schematic diagram of the experimental set-up used to assess positive filter sampling artifacts; front quartz fiber filter (Q_F), bare back-up quartz fiber filter (Q_B) and sulfuric acid impregnated back-up quartz fiber filter ($Q_B\text{-H}_2\text{SO}_4$). Q_F of both samplers collect $\text{PM}_{2.5}$. Q_B in sampler A collects adsorbed gases. $Q_B\text{-H}_2\text{SO}_4$ in sampler B collects adsorbed gases as well as those that form by reaction with sulfuric acid.

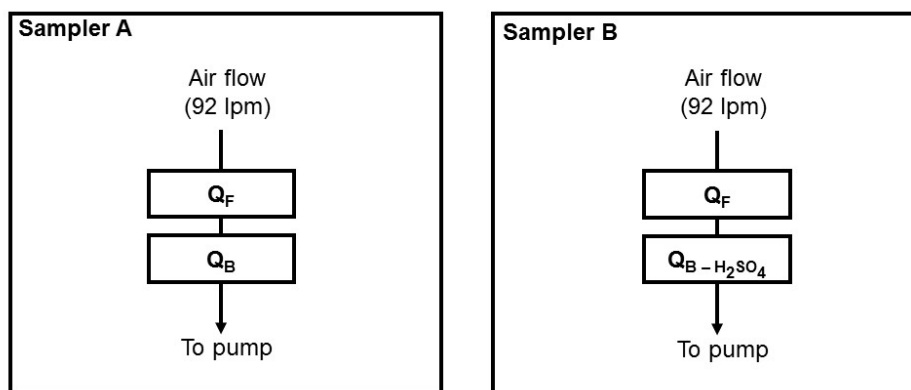


Figure S2: The mass spectrum of precursors of m/z 97 (HSO_4^-) for the nighttime sample collected on 10 July 2013 using HILIC-TQD. Major m/z are labeled; black labeled peaks are among the ten highest signals in both the 10 July daytime and nighttime samples; red labeled peaks are among the ten highest signals in the 10 July nighttime sample, but not the daytime sample; blue labeled peaks were among the ten highest signals in the 10 July 2013 daytime sample, but not the nighttime sample.

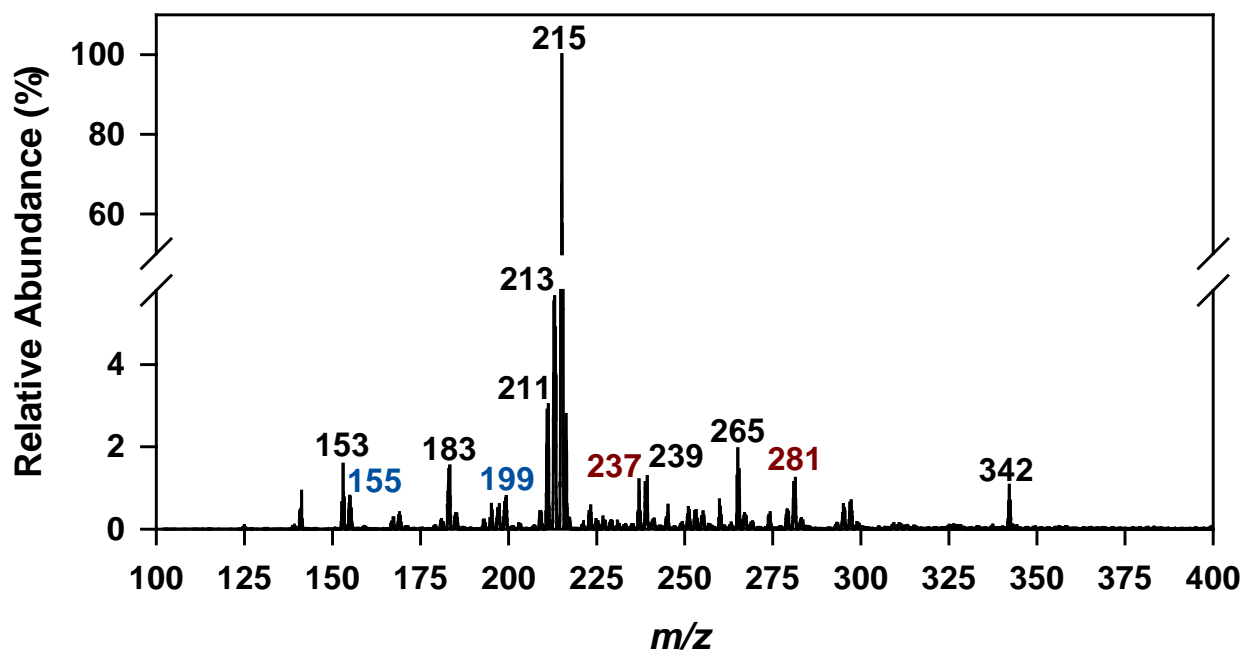


Figure S3: The mass spectra of precursors of m/z 97 (HSO_4^-) for $\text{PM}_{2.5}$ samples collected during daytime (D) and nighttime (N) periods from 07 - 09 and 11 July 2013 by HILIC-TQD. Major m/z are labeled; black labeled peaks are among the ten highest signals in the given sample and the 10 July daytime sample (Fig. 2); red labeled peaks are among the ten highest signals in the given sample, but not the 10 July daytime sample; blue labeled peaks were among the ten highest signals in the 10 July 2013 daytime sample, but not the given sample; gray labeled peaks were among the ten highest signals in the given sample, but were neither present in other samples nor confirmed by TOF-MS.

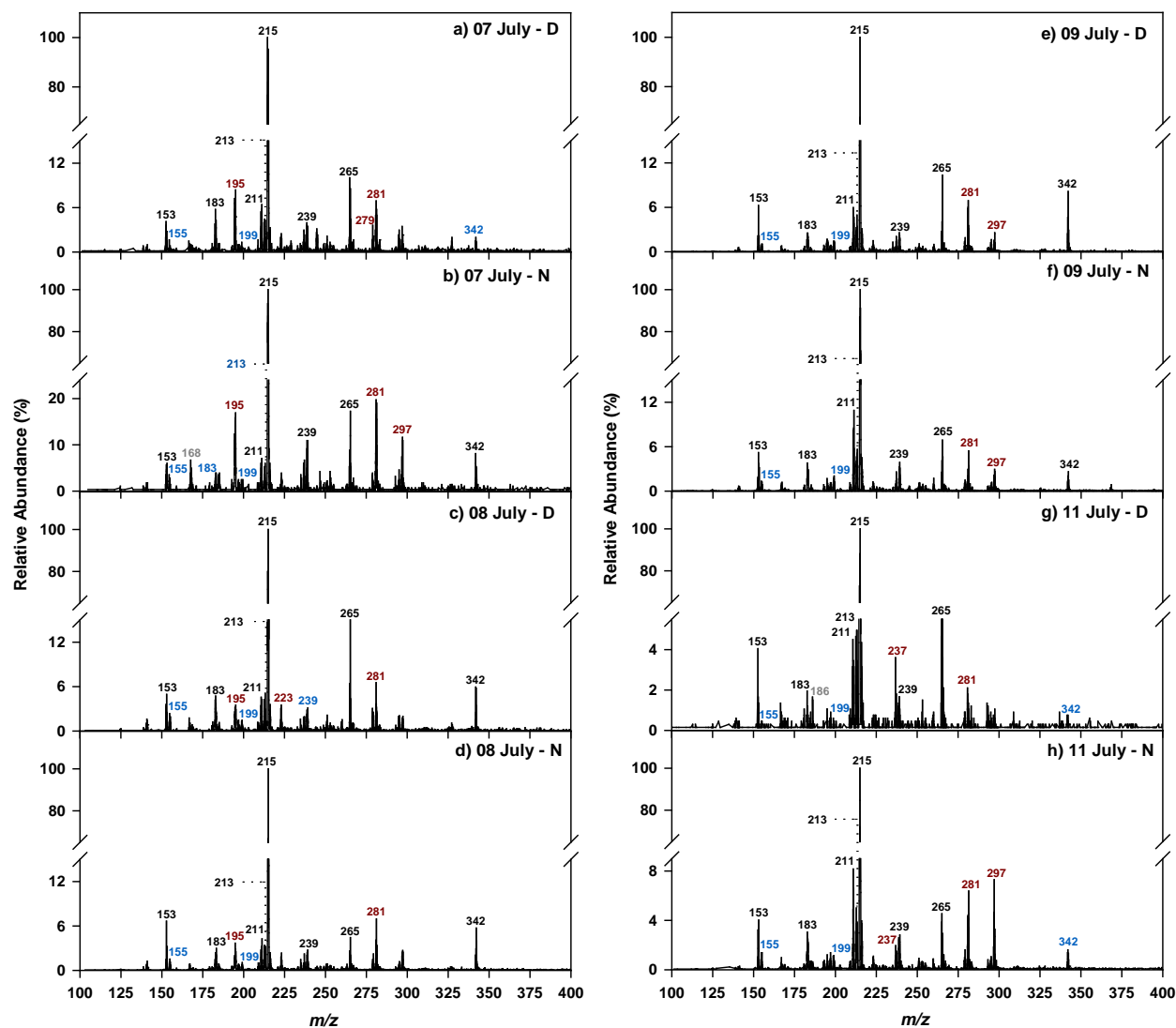


Figure S4: The mass spectrum of precursors of m/z 96 ($\text{SO}_4^{\cdot-}$) for the daytime and nighttime sample collected on 10 July 2013 using HILIC-TQD.

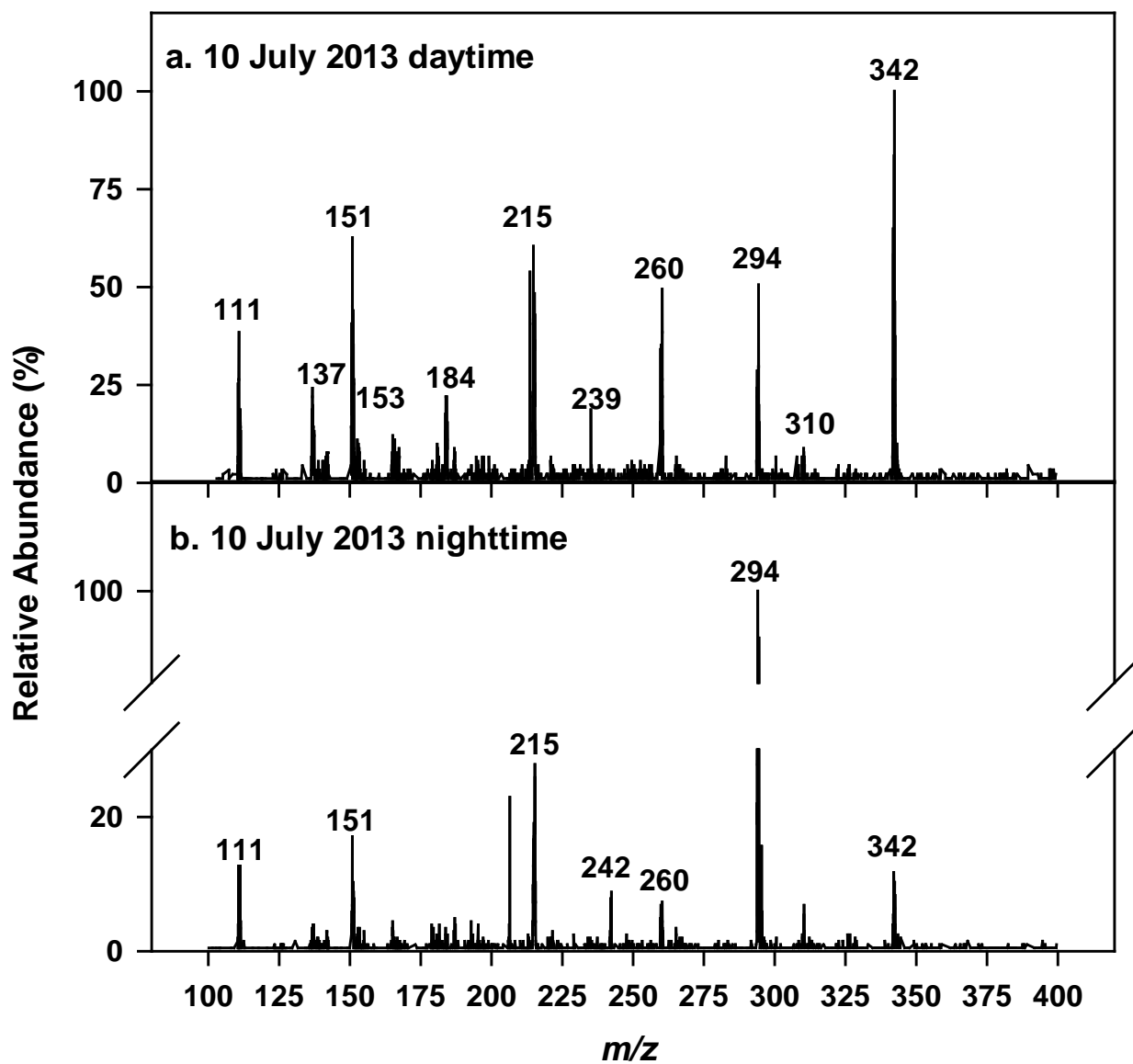


Figure S5: MS² spectrum of m/z 183 (t_R 0.91 min) obtained from HILIC-Q-TOF at 10 eV collision energy.

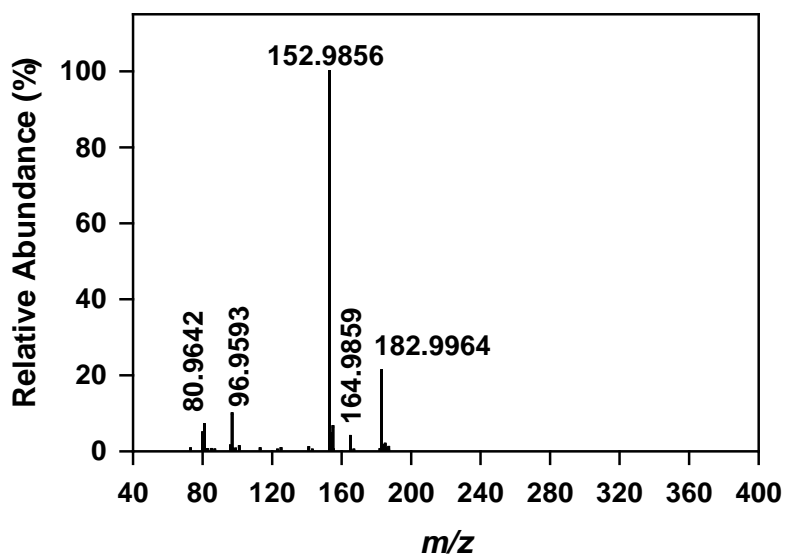


Figure S6: Extracted chromatograms of m/z 199 obtained from precursors of m/z 97 (HSO_4^-) by HILIC-TQD indicating the $\text{C}_5\text{H}_{11}\text{SO}_6^-$ eluting early (t_R 0.99 and 1.80) and $\text{C}_4\text{H}_7\text{SO}_7^-$ eluting later (t_R 8.29 min.) in 10 July 2013 daytime sample. The MS² of the peak eluting at 8.29 min. (Figure S7) corresponds to 2-methylglyceric acid sulfate.

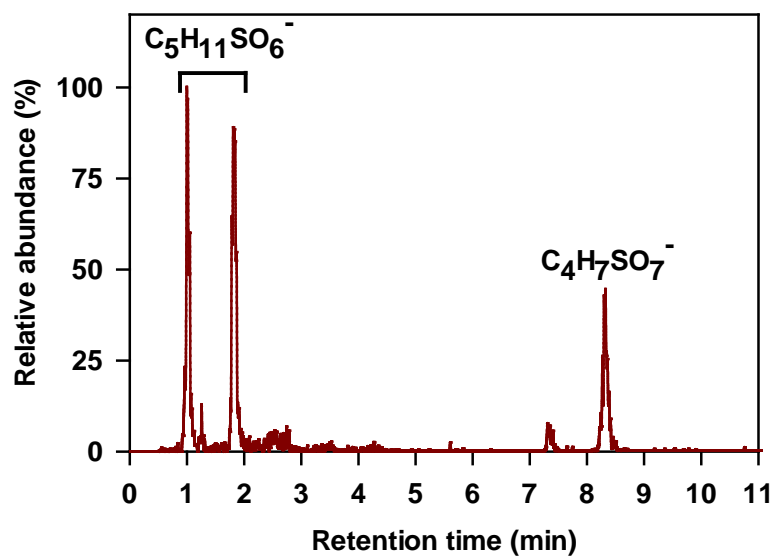


Figure S7: MS² spectrum of m/z 199 (t_R 8.30, $C_4H_7SO_7^-$) obtained from HILIC-Q-TOF at 10 eV collision energy.

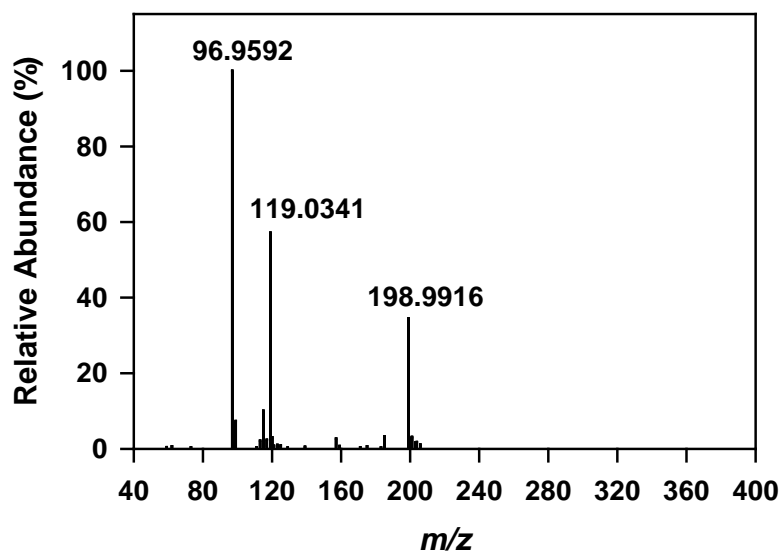


Figure S8: Extracted chromatograms of m/z 155 obtained from precursors of m/z 97 (HSO_4^-) by HILIC-TQD for the 10 July 2013 daytime sample, indicating the two isomers of $C_2H_3SO_6^-$ (t_R 0.55 min and 7.82 min, with the latter being confirmed as glycolic acid sulfate [GAS]) and $C_3H_7SO_5^-$ (t_R 1.19 min).

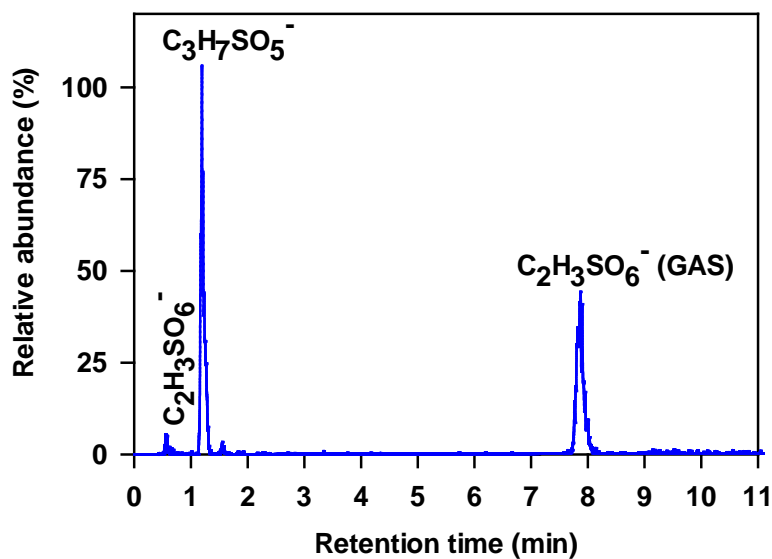


Figure S9: MRM transition of m/z 215 \rightarrow 97 (smoothed 2×1) in a $PM_{2.5}$ sample collected from Centreville, AL on 21 June 2013 during nighttime by HILIC-TQD. Peaks 1 and 2 were the most readily hydrolyzed and were assigned as tertiary. Peaks 3 and 4 were the next-most labile and were assigned as secondary organosulfates. Peaks 5 and 6 were the most stable, and were assigned as primary organosulfates.

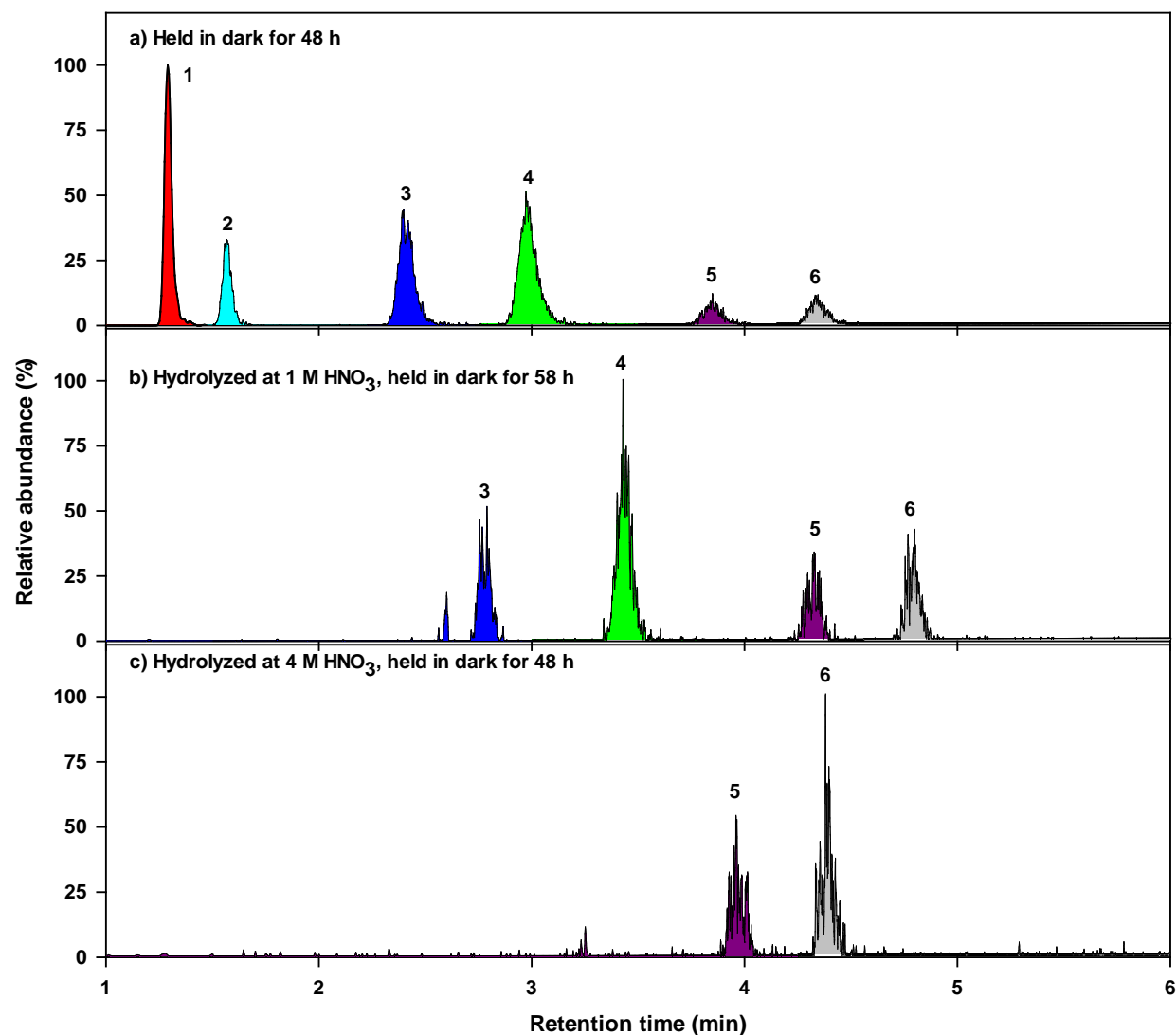


Table S1: HR-MS characterization of organosulfates that fragmented to m/z 96 ($\text{SO}_4^{\bullet-}$) in the $\text{PM}_{2.5}$ samples collected on 10 July 2013 daytime (8:00 – 19:00) and nighttime (20:00 – 7:00) in Centreville, AL. Listed are organosulfates with percent contributions to total m/z 96 signal greater than or equal to 1.0 % in total.

Molecular formula [M-H] ⁻	Double bond equivalence(s)	Monoisotopic mass [M-H] ⁻	Error in observed mass (mDa)	Contribution to total m/z 96 signal					
				Daytime			Nighttime		
				t_{R} , HILIC-TQD (min)	By peak (%)	Total	t_{R} , HILIC-TQD (min)	By peak (%)	Total (%)
$\text{C}_5\text{H}_{11}\text{O}_7\text{S}^-$	0.5	215.0225	-0.6	1.33	3.0	9.5	1.31	0.7	9.9
			0.5	1.64	1.5		1.65	0.3	
			-0.3	2.86	1.8		2.83	3.7	
			-1.7	3.65	3.3		3.63	5.2	
$\text{C}_{10}\text{H}_{16}\text{NO}_{10}\text{S}^-$	3.5	342.0495	0.5	0.48	7.5	9.4	0.49	2.6	3.2
			1.4	0.55	1.9		0.57	0.5	
$\text{C}_4\text{H}_7\text{O}_4\text{S}^-$	1.5	151.0065	-1.1	0.56	8.1	8.1	0.55	3.5	3.5
$\text{C}_5\text{H}_{10}\text{NO}_9\text{S}^-$	1.5	260.0076	1.3	0.83	5.4	5.4	0.86	1.5	1.5
$\text{C}_{10}\text{H}_{16}\text{NO}_7\text{S}^-$	3.5	294.0647	1.4	0.49	0.6	4.4	0.48	2.3	24.5
			3	0.54	3.8		0.54	22.2	
$\text{CH}_3\text{O}_4\text{S}^-$	0.5	110.9752 ^a	-1.1	0.86	4.0	4.0	0.85	2.0	2.0
$\text{C}_4\text{H}_7\text{O}_6\text{S}^-$	1.5	182.9963	-0.2	0.67	0.1	2.9			
			1.9	0.75	0.2				
			0.3	0.79	0.9				
			2.6	0.85	1.3				
			-0.8	0.9	0.4				
			-1.1	1.02	0.1				
$\text{C}_3\text{H}_5\text{O}_4\text{S}^-$	1.5	136.9909	-1.6	0.59	2.8	2.8			
$\text{C}_3\text{H}_5\text{O}_5\text{S}^-$	1.5	152.9858 ^b	-1.1	0.65	1.1	1.1			
$\text{C}_{10}\text{H}_{16}\text{NO}_8\text{S}^-$	3.5	310.0597	3.7	0.55	0.6	1.0			
			5.7	0.65	0.3				
			-6.4	0.71	0.1				
$\text{C}_5\text{H}_8\text{NO}_8\text{S}^-$	2.5	241.9971	0.4				0.52	1.3	1.3

^astructure was confirmed using a commercial standard of methyl sulfate

^bstructure was confirmed using a synthesized authentic standard of hydroxyacetone sulfate

Table S2: Other organosulfates that were detected among the ten greatest intensity signals in precursors of m/z 97 (HSO_4^-) for $\text{PM}_{2.5}$ samples collected from 07-11 July 2013 during SOAS by HILIC-TQD and their HR-MS characterization using HILIC-ToF.

Molecular formula [M-H] ⁻	Double bond equivalence(s)	Monoisotopic mass	Error in observed mass (mDa)	t_R , HILIC-TOF (min)
$\text{C}_5\text{H}_7\text{SO}_6^-$ ^a	2.5	194.9963	0.5	0.57
			1.5	0.74
			-0.9	0.51
$\text{C}_7\text{H}_{11}\text{SO}_6^-$ ^b	2.5	223.0276	-0.8	0.65
			1.0	0.80
			-0.6	1.02
			-0.8	1.16
$\text{C}_7\text{H}_9\text{SO}_7^-$ ^a	3.5	237.0069	1.1	0.65
$\text{C}_{10}\text{H}_{15}\text{SO}_7^-$ ^b	3.5	279.0538	-3.7	0.54
			0.8	0.80
$\text{C}_{10}\text{H}_{17}\text{SO}_7^-$ ^b	2.5	281.0695	-4.3	0.59
			-8.8	0.80
$\text{C}_{10}\text{H}_{17}\text{SO}_8^-$ ^b	2.5	297.0644	-1.7	0.74
			-3.6	1.08
			0.1	1.85

^aVOC precursors are unknown, although these m/z have been previously identified in rain water (Altieri et al., 2009) and cloud water (Boone et al., 2015)

^bMonoterpenes have been identified as VOC precursors to these m/z (Surratt et al., 2008)

References

- Altieri, K. E., Turpin, B. J., and Seitzinger, S. P.: Oligomers, organosulfates, and nitrooxy organosulfates in rainwater identified by ultra-high resolution electrospray ionization FT-ICR mass spectrometry, *Atmos. Chem. Phys.*, 9, 2533-2542, 10.5194/acp-9-2533-2009, 2009.
- Boone, E. J., Laskin, A., Laskin, J., Wirth, C., Shepson, P. B., Stirr, B. H., and Pratt, K. A.: Aqueous Processing of Atmospheric Organic Particles in Cloud Water Collected via Aircraft Sampling, *Environ. Sci. Technol.*, 49, 8523-8530, 10.1021/acs.est.5b01639, 2015.
- Surratt, J. D., Gomez-Gonzalez, 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., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A*, 112, 8345-8378, 10.1021/jp802310p, 2008.