A. Acid hydrolysis of 2-methyltetrol sulfates

An aliquot (100 µL) of $PM_{2.5}$ 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 a very light stream of ultra-pure N_2 gas at 50 °C. Then it was reconstituted in ultra-pure water (100 %, 1.0 mL). Three equal aliquots (120 µL) of the aqueous sample, two for acid hydrolysis and one as a control, were transferred into three LC vials, separately. HNO_3 (14.89 M), 81.0 µL (4 M acid hydrolyzed sample) and 20.0 µL (1 M acid hydrolyzed sample) were added to two aliquots of the sample separately, with the final volume adjusted to 300 µL using ultra-pure water (100 %). Only ultra-pure water (180 µL) was added to the control and held for 48 h. All samples were incubated at room temperature in 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 (5.13 M). Then all samples were evaporated to dryness under a very light stream of ultra-pure N_2 gas at 50 °C and reconstituted in acetonitrile and ultra-pure water (acid hydrolyzed samples; 60: 40, 560 µL, control; 95: 5, 560 µL). Those samples were then analyzed using HILIC-TQD method described in Sect. 2.5.2. 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 ($Q_{B-H_2SO_4}$). Q_F of both samplers collect $PM_{2.5}$. Q_B in sampler A collects adsorbed gases. $Q_{B-H_2SO_4}$ in sampler B collects any gases by adsorption and reaction with sulfuric acid.

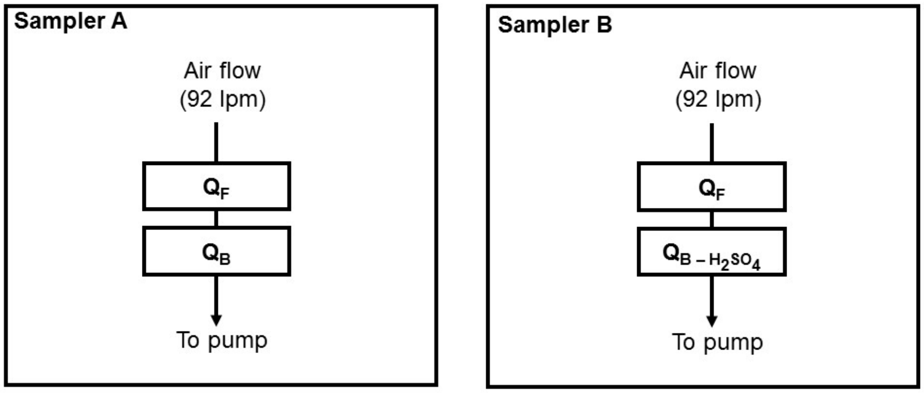

Figure S2: MRM transition of *m/z* 215 → 97 (smoothed 2 ×1) in a $PM_{2.5}$ sample collected from Centreville, AL on 21 June 2013 during nighttime determined by HILIC-TQD. Peaks 1 and 2 were the most readily hydrolyzed and were assigned as tertiary. Peaks 3 and 4 were the next-most labile and were assigned as secondary organosulfates. Peaks 5 and 6 were the most stable, and were assigned as primary organosulfates.

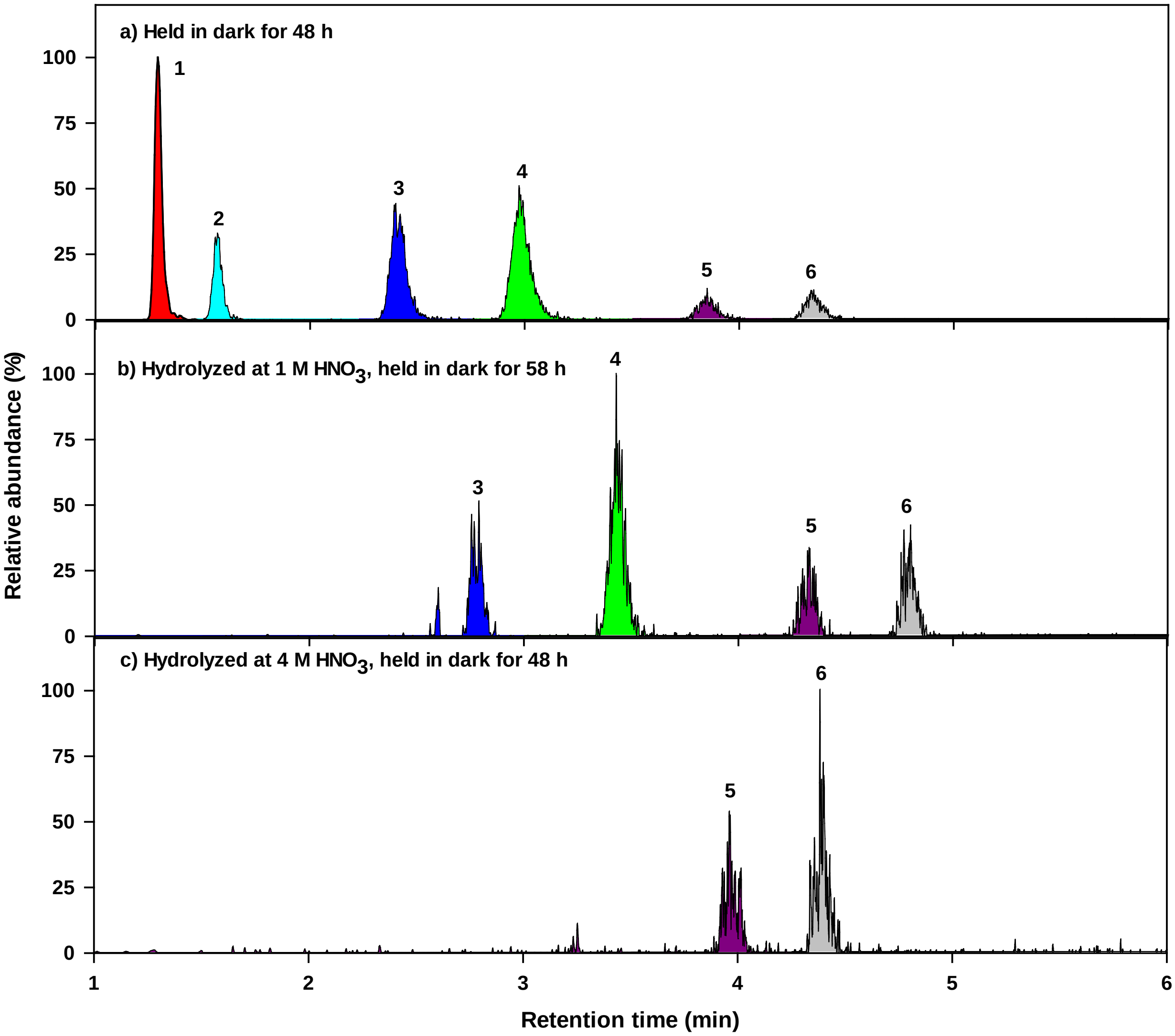

Figure S3: MS^2 spectrum of *m/z* 183 (t_R 0.91 min) obtained from HILIC-Q-TOF at 10 eV collision energy.

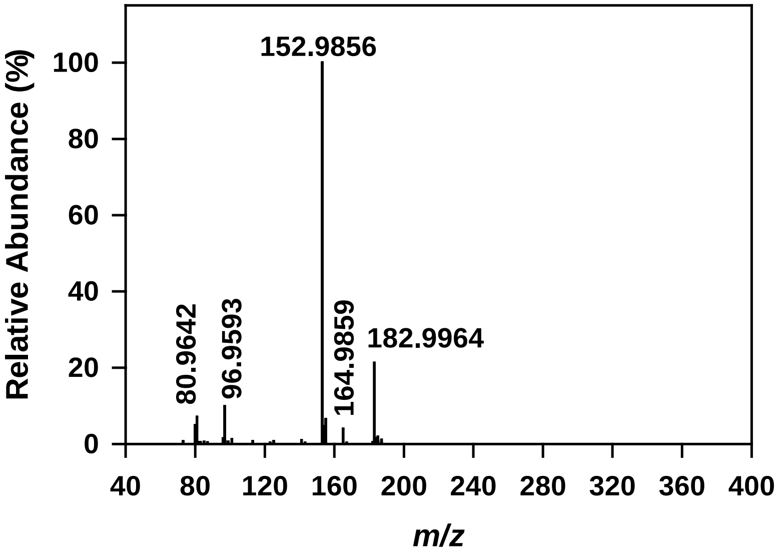

Figure S4: Extracted chromatograms of *m/z* 199 obtained from precursor ion scan to bisulfate anion by HILIC-TQD indicating the $C_5H_{11}SO_6^-$ eluting early (t_R 0.99 and 1.80) and $C_4H_7SO_7^-$ eluting later (t_R 8.29 min.) in 10 July 2013 daytime sample. The latter likely corresponds to 2-methylglyceric acid sulfate.

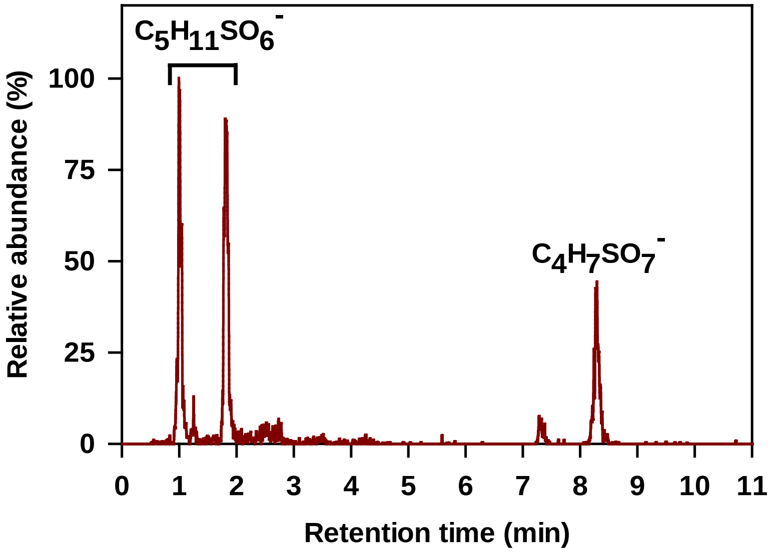

Figure S5: MS^2 spectrum of *m/z* 199 (t_R 8.30, $C_4H_7SO_7^-$) obtained from HILIC-Q-TOF at 10 eV collision energy.

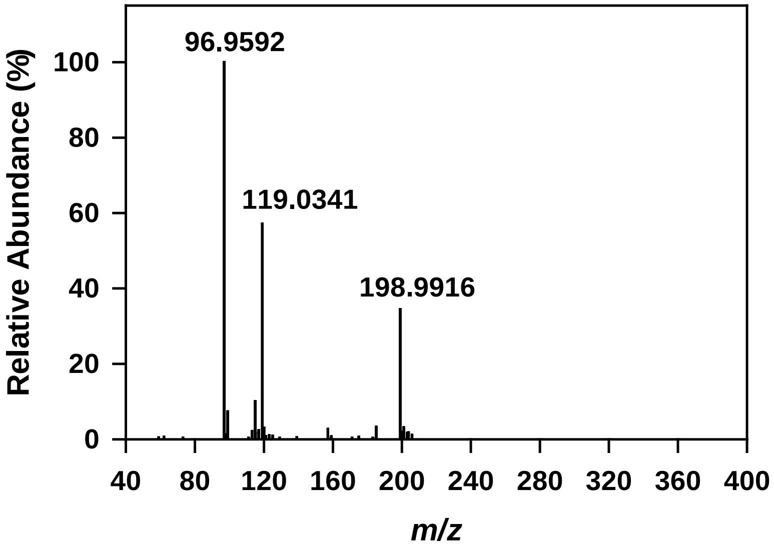

Figure S6: Extracted chromatograms of *m/z* 155 obtained from precursor ion scan to bisulfate anion by HILIC-TQD for the 10 July 2013 daytime sample. Two isomers of $C_2H_3SO_6^-$ (t_R 0.55 min and 7.82 min, with the latter being confirmed as glycolic acid sulfate [GAS]) and $C_3H_7SO_5^-$ and (t_R 1.19 min).

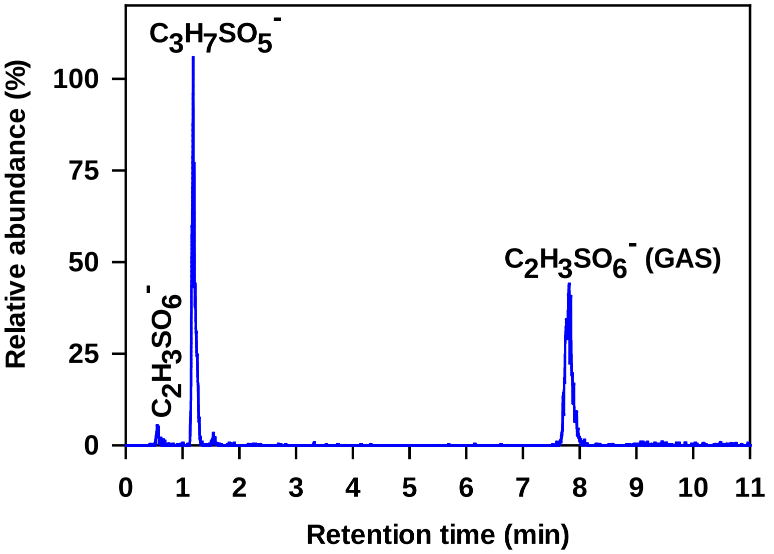

Figure S7: The integrated precursor to *m/z* 97 (HSO_4^-) mass spectrum for the nighttime sample collected on 10 July 2013 using HILIC-TQD. Major *m/z* are labeled; black labeled peaks are among the ten highest signals in both the 10 July daytime and nighttime samples; red labeled peaks are among the 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.

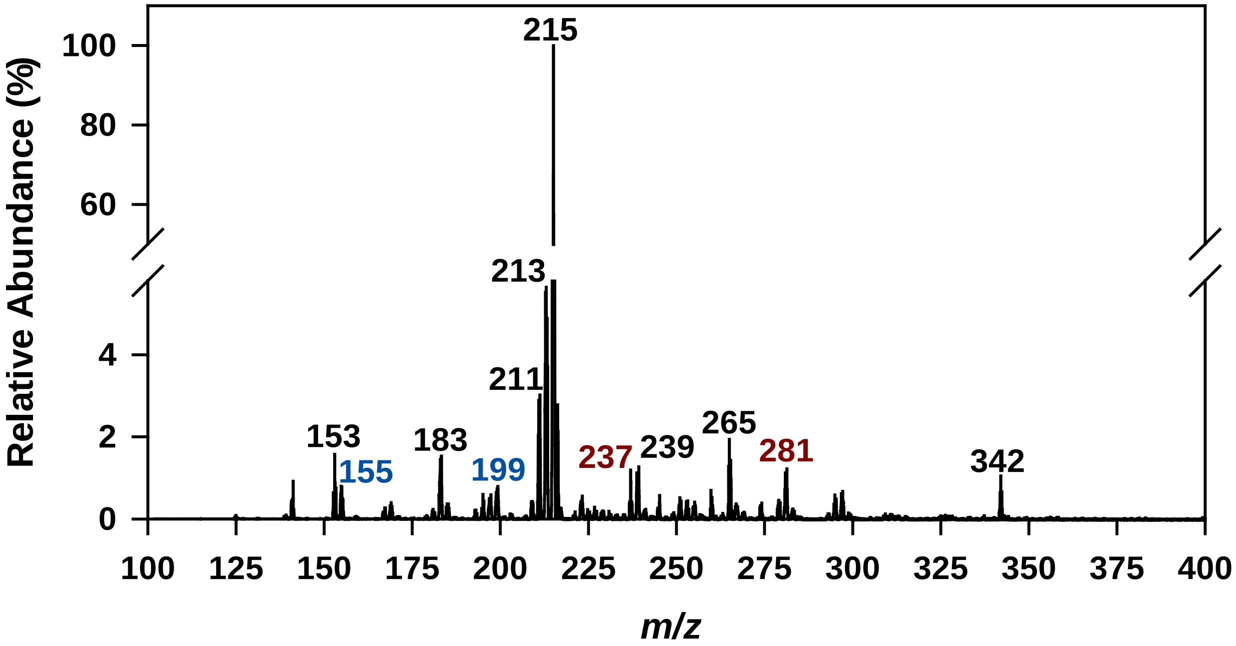

Figure S8: Organosulfate precursors to the bisulfate anion (*m/z* 97, HSO_4^-) for $PM_{2.5}$ samples collected during daytime (D) and nighttime (N) periods from 07-09 and 11 July 2013, integrated from HILIC-TQD. Major *m/z* are labeled; black labeled peaks are among the ten highest signals in the given sample and the 10 July daytime sample (section 3.3); 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.

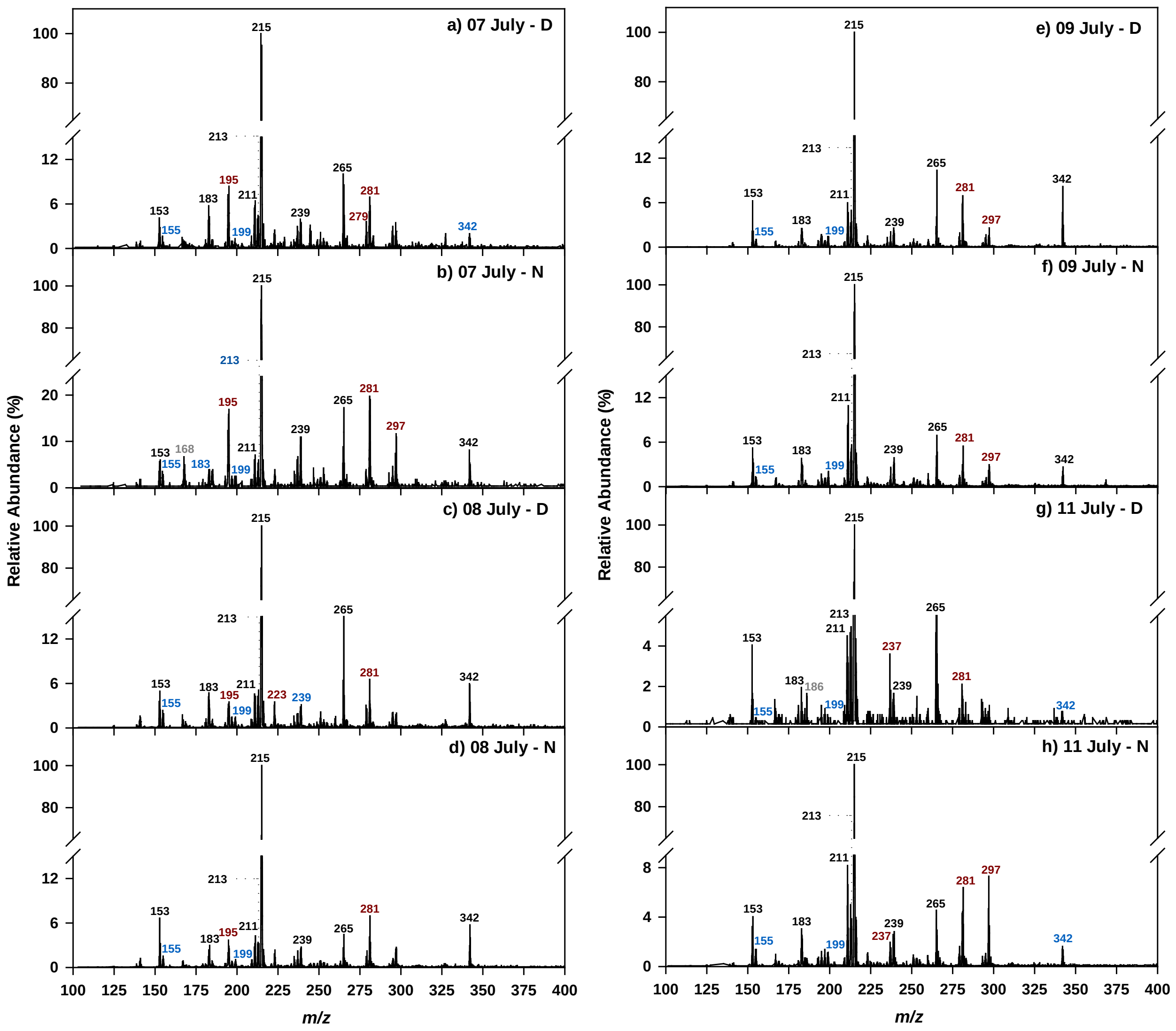

Table S1: HR-MS characterization of other organosulfates that were detected among the ten highest signals in precursor ion scan to the bisulfate anion (*m/z* 97, HSO_4^-) for $PM_{2.5}$ samples collected from 07-11 July 2013 during SOAS analyzed by HILIC-TQD and HILIC-ToF.

Molecular formula [M-H]$^-$	**Double bond equivalence(s)**	**Monoisotopic mass**	**Error in observed mass (mDa)**	**t_R, HILIC-TOF (min)**
$C_5H_7SO_6^-$ [a]	2.5	194.9963	0.5 1.5	0.57 0.74
$C_7H_{11}SO_6^-$ [b]	2.5	223.0276	-0.9 -0.8 1.0 -0.6 -0.8	0.51 0.65 0.80 1.02 1.16
$C_7H_9SO_7^-$ [a]	3.5	237.0069	1.1	0.65
$C_{10}H_{15}SO_7^-$ [b]	3.5	279.0538	-3.7 0.8	0.54 0.80
$C_{10}H_{17}SO_7^-$ [b]	2.5	281.0695	-4.3 -8.8	0.59 0.80
$C_{10}H_{17}SO_8^-$ [b]	2.5	297.0644	-1.7 -3.6 0.1	0.74 1.08 1.85

[a] VOC precursors are unknown. Previously identified in rain water (Altieri et al., 2009) and cloud water (Boone et al., 2015)

[b] Monoterpene is identified as the VOC precursor (Surratt et al., 2008)

References

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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.