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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Qualitative and Quantitative Analysis of Atmospheric Organosulfates in Centreville, Alabama" *by* Anusha P. S. Hettiyadura et al.

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Anonymous Referee # 1, Summary and Recommendation: "This manuscript summarizes quantitative and semi-quantitative data obtained for organosulfates chemically characterized from PM2.5 samples collected from the main ground site (Centreville, AL) during the 2013 Southern Oxidant and Aerosol Study (SOAS). This study had 3 major goals: (1) to quantify select organosulfates that had authentic standards available using HILIC interfaced to ESI-triple quadrupole mass spectrometry; (2) assess for potential positive filter sampling artifacts of organosulfates; and (3) identify other major organosulfates that should be targets for future quantification once authentic standards are available. Analytically, this paper is very solid. The authors make a serious effort

in understanding potential positive artifacts of organosulfates and find that they have fairly small artifacts. This is good to have these results in the literature. This paper will certainly be of interest to the broader readership of ACP since organosulfates are good indicator compounds of mulitphase chemical reactions! However, there are some weaknesses that need to be improved upon before full publication in ACP."

Response to Anonymous Referee # 1 Summary and Recommendations: We thank the referee for their thoughtful and valuable insights. We agree with their summary of the scope of this work. We have revised this paper addressing each of the weaknesses and specific comments, point by point as indicated below.

Anonymous Referee # 1 Weakness 1: "In some parts of the manuscript the writing is unclear or not explicit enough. I will point these out in my specific comments below."

Response to Anonymous referee # 1 Weakness 1: We have provided responses and revisions to the referee's suggestions on writing in specific comments 1 – 13.

Anonymous Referee # 1 Weakness 2: "If your goal was to identify the major organosulfates at CTR during the 2013 SOAS study, I'm curious as to why only 4 days of sampling were considered? Why weren't the periods of intensive sampling included? From what I understand from this campaign (Budisulistiorini et al., 2015, ACP), chemical forecasts were made when biogenic VOCs and anthropogenic pollutants (sulfate) would be high. I believe the period chosen falls outside of these periods. Further, wouldn't analyzing most of the days for organosulfates also provide stronger statistics?"

Response to Referee # 1 Weakness 2: This comment has brought about two major changes to the manuscript. First, we provide a more detailed description of the subset of samples studied for sampling artifacts and how these days relate to average conditions during SOAS. We also note that the subset of samples (07 – 11 July, 2013) overlaps with the 4th intensive sampling period during SOAS (9-14 July). Second, we have expanded the range of quantitative data presented to include 13 June – 13 July as described in response to the next comment.

Section 2.2 has been revised to read: “The positive filter sampling artifacts associated with the three most abundant organosulfates quantified in Sect. 3.1 (glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate, respectively) were assessed from 07 – 11 July, 2013. This time period followed several days with rain, thus had slightly lower average PM2.5 (5.24 ± 1.68 μg m-3), OC (2.00 ± 0.67 μg m-3), sulfate (1.26 ± 0.66 μg m-3) and organosulfate concentrations relative to the average PM2.5 (7.52 ± 3.41 μg m-3), OC (3.07 ± 1.35 μg m-3), sulfate (1.78 ± 0.81 μg m-3) and organosulfate concentrations measured during SOAS in Centreville (Fig. 1 and Table 1). Within the studied subset of days, the 09 July daytime and nighttime, and 10 July daytime concentrations (Fig. 1) were similar to the average conditions observed during SOAS, and are considered to be most representative of the average conditions at Centreville during SOAS.”

This text has been added to section 3.3, page 9 at line 8: “This analysis was applied to samples collected from 07 – 11 July, 2013, with a focus on the 10 July daytime sample with levels of PM2.5 (7.01 ± 0.80 μg m-3), OC (2.63 ± 0.21 μg m-3), sulfate (1.06 ± 0.17 μg m-3) and organosulfates (Fig. 1) near to the study average (Sect. 3.2 and Table 1).”

Anonymous Referee # 1 Weakness 3: “In section 3.1 of the results and discussion, why wasn’t more work done to investigate the potential sources (VOCs and/or their oxidation products as well as reactions) of these quantified organosulfates, especially since CTR had a wealth of gas and aerosol phase data? Since you focus on the quantification of these 4 organosulfates, it seems to me it would be interesting to at least examine potential correlations with other data sets to test previously proposed mechanisms for these products. That would add some more "beef" to the scientific discussion of these organosulfates.”

Response to Referee # 1 Weakness 3: As suggested, we have extended the data presented from 7 – 11, July 2013 to 13 June – 13 July, 2013; with this larger dataset, we provide a more in-depth correlation analysis with VOC precursors and other PM constituents measured in Centreville, during SOAS 2013. Accordingly, we have revised our objectives to include correlations and a paragraph was added to section at 3.2 discussing the correlation results. Also, note that by adding more measurements required minor updates to numerical values in Tables 1 and 3 (where the latter was previously Table 2).

The text that has been added to page 7, section 3.2, line 23: “Correlations of hydroxyacetone sulfate, lactic acid sulfate and glycolic acid sulfate with co-located gas and aerosol measurements were used to gain insights to their potential precursors and conditions conducive to their formation (Table 2). Strong inter-correlations were observed for these organosulfates suggesting that they have common precursors and/or formation pathways. All three species had higher correlations with formaldehyde, MACR and glyoxal relative to isoprene, ISOPOOH and IEPOX that are low NOx oxidation products of isoprene (Bates et al., 2016; Krechmer et al., 2015)), as well as MVK and isoprene nitrates (ISOPN) that are high NOx oxidation product (Xiong et al., 2015)). While MVK, MACR, glyoxal and formaldehyde may be either biogenic or anthropogenic in origin, they primarily form from isoprene oxidation in SE US during summer (Xiong et al., 2015; Kaiser et al., 2015). Previous studies have shown that MVK, MACR, glyoxal and formaldehyde form in higher yields when isoprene was oxidized under high NOx (Kaiser et al., 2015; Liu et al., 2013). Of MVK and MACR, MACR is the major SOA precursor form from isoprene oxidation under high NOx conditions (Surratt et al., 2006; Kroll et al., 2006; Surratt et al., 2010). Thus the higher correlations with formaldehyde, MACR and glyoxal relative to other VOC precursors suggest that these organosulfates are enhanced by high NOx conditions.

All three species had moderate to strong correlations with sulfate, but not with liquid water content or acidity, suggesting that neither aerosol water nor aerosol acidity limit organosulfate formation. Similar correlations were reported at Centreville for isoprene derived SOA, and were attributed to variation of sulfate compared to consistently high aerosol acidity and high relative humidity observed during SOAS 2013 (Xu et al., 2015). Further, these correlations are consistent across other SOAS ground sites (Rattanavaraha et al., 2016; Budisulistiorini et al., 2015) indicating that the association of organosulfates with sulfate is a regional characteristic. The correlations of organosulfates derived from isoprene and sulfate in the SE US, suggests that sulfate is a key factor that influences biogenic SOA formation."

Anonymous Referee # 1 Weakness 4, Page 7, Section 3.1: "Have the authors considered adding into their discussion of the mass contribution of organosulfates quantified previously using authentic standards to the total OC/PM mass the data from Rattanavaraha et al. (2016, ACP, Table 5). That paper included the average MAE- and IEPOX-derived OSs quantified using the authentic standards for the CTR site. I think you can use these numbers to provide further insights into the potential overall mass contribution of these organosulfates (with yours here) to the total OC/PM2.5 mass. That seems like an important thing to do here. Once you add these in, how much closer do you get to the mass fractions of organosulfates reported by Tolocka and Turpin (2012, ES&T)?"

Response to Referee # 1 Weakness 4: As suggested by the reviewer, we have expanded our discussion to include the total mass contribution of organosulfates quantified in Centreville using authentic standards and the mass closure achieved when combining our results with those of Rattanavaraha et al. (2016).

Page 7, section 3.1, lines 18 – 22 originally read: "The total contribution of the organosulfates quantified using authentic standards accounted for less than 0.5 % of PM2.5 and less than 0.3 % of OC (Table 1). Meanwhile, organosulfates are estimated to contribute 1-2 % of PM2.5 and 5-10 % OC in Eastern US (Shakya and Peltier, 2015). Therefore, the organosulfates quantified against authentic standards account for a minority of the total organosulfates, while other organosulfates likely comprise the majority of this class of compounds in Centreville, AL (as discussed in Sect. 3.3)."

This text has been revised to read: "The total contribution of the organosulfates quantified using authentic standards was less than 0.3 % of OC (Table 1). Meanwhile, the estimated upper bound contribution of organosulfates to organic matter (OM) is 5.0 – 9.3 % in the SE US (Tolocka and Turpin, 2012). Assuming OM/OC of 1.8 (Tolocka and Turpin, 2012), the calculated contribution of the organosulfates quantified in this study comprise 0.7 % of OM. Measurements of 2-methyltetrol sulfates reported by Ratanvahara et al. (2016) for Centreville had a mean concentration of 207.1 ng m-3 and were estimated to account for 3.7% while 2-methylglyceric acid sulfate had a mean concentration of 10.2 ng m-3 and accounted for 0.2% of OM, y considering the average OC concentration of 3.07 ug m-3 and an OM/OC ratio of 1.8. Together, the organosulfates quantified against authentic standards in Centreville accounts for 4.7 % of OM. Additional species that contribute significantly to MS2 organosulfate signals are qualitatively and semi-quantitatively examined in Sect. 3.3.

Anonymous Referee # 1 Weakness 5: "For your qualitative discussion of other major organosulfates present at CTR, what about OSs that do not fragment to the m/z 97 ion in MS2? Prior work has shown that other important organosulfates, especially from monoterpenes (like m/z 294), may produce only the m/z 96 product ion (Surratt et al., 2008, JPCA) in MS2 spectra. I would at least acknowledge that you may be missing some important organosulfates since you focus your analyses only on those that produce the m/z 97 product ion in MS2 analyses."

Response to Referee # 1 Weakness 5: We thank the referee for pointing this out. We have analyzed the organosulfates that fragmented to m/z 96, but initially did not include these results because of the low signal (2 % of the precursors of m/z 97). However, this comment suggests that the community would be interested in our findings from our studies of precursors to m/z 96 and thus we have added them to the revised manuscript.

Results from MS2 scans of precursors are shown in Figure S4 and Table S2. In addition, these results have been discussed in added to section 3.3. In particular, the following text has been added: "In addition, a nitro-oxy organosulfate, C5H10NSO9-

(260.0076; Fig. S4) contributed up to 5.4 % of the m/z 96 precursor ion signal (Table S1) and is also associated with isoprene (Surratt et al., 2008; Gómez-González et al., 2008)."

"Monoterpene-derived nitro-oxy organosulfates were particularly responsive to precursors of m/z 96; C10H16NSO10- Âň (342.0495), C10H16NSO8- (310.0597 (Ma et al., 2014; Surratt et al., 2008)) and C10H16NSO7- (294.0647) (Table S1 and Fig. S4). The nitro-oxy organosulfate C10H16NSO7- (294.0647) accounted for 25 % of the total m/z 96 signal in PM2.5 sample collected during nighttime on 10 July 2013 (Table S1). This semi-quantitative result is consistent with prior field studies reported m/z 294 as the most abundant nitro-oxy organosulfate in SE US, particularly during night time (Gao et al., 2006; Surratt et al., 2008).

Other major organosulfate signals identified from m/z 96, were C4H7SO4- (151.0065), C3H5SO4- (136.9909) and C5H8NO8S- (241.9971), were not previously reported in the atmosphere (Table S2). Based on the molecular formula and double bond equivalence (Table S1), m/z 151 is suggested as a methylallyl sulfate, m/z 137 may be allyl sulfate and m/z 242 may be a nitro-oxy organosulfate with a carbonyl group. However, the precursors to these organosulfates are unknown."

Anonymous Referee # 1 Specific Comments:

Referee # 1 Specific Comment 1) Abstract, Page 1, Lines 18-19: "You should probably emphasize that this organosulfate is derived from multiphase chemistry of IEPOX (Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T)."

Response to Referee # 1 Specific Comment 1: While we agree with the reviewer, we do not think the abstract is the appropriate place to convey results from prior studies. Instead, this information has been integrated into the introduction and discussion of 2-methyltetrol sulfate results.

Referee # 1 Specific Comment 2) Introduction, Page 2, Lines 2-5: "Should you be more specific and emphasize that PM2.5 has these adverse effects on human health and climate as well as contains most of the SOA?"

Response to Referee # 1 Specific Comment 2: We agree with the reviewer and have revised the text accordingly.

The Introduction, Page 2, Lines 2-5 originally read: "Atmospheric particulate matter (PM) adversely affects human health and climate (Anderson et al., 2011; Kim et al., 2015; Rosenfeld et al., 2014; Levy et al., 2013). A significant fraction of PM is comprised of secondary organic aerosols (SOA) (Zhang et al., 2011) that form from reactions of volatile organic compounds (VOC) yielding semi-volatile products that partition to the aerosol phase."

This text has been revised to read: "Atmospheric fine particulate matter (PM2.5; particles $\leq$2.5 μm in aerodynamic diameter) adversely affects human health (Valavanidis et al., 2008; Anderson et al., 2011; Kim et al., 2015) and influences the Earth's climate via direct and indirect radiative forcing (Novakov and Penner, 1993; Haywood and Boucher, 2000). A significant fraction of PM2.5 organic matter is secondary in origin (Zhang et al., 2011), and forms by atmospheric oxidation reactions of volatile organic compounds (VOC) and partitioning of reaction products to the aerosol phase (Hallquist et al., 2009)."

Referee # 1 Specific Comment 3) Introduction, Page 2, Line 4: "I would insert "atmospheric oxidation" before "reactions""

Response to Referee # 1 Specific Comment 3: Introduction, Page 2, Lines 4: We have revised this sentence as indicated in the response to specific comment 2 (last sentence).

Referee # 1 Specific Comment 4) Introduction, Page 2, Lines 5-6: "You should rephrase this sentence to be more correct. Maybe something like: "Organosulfates, which are produced from acid-catalyzed particle-phase reactions of gaseous oxidation products, such as epoxides (Lin et al., 2012, ES&T) and hydroperoxides (Mutzel et al., 2015, ES&T), contribute to SOA."

Response to Referee # 1 Specific Comment 4: The introduction, Page 2, Lines 5-6 originally read: "Among SOA products are organosulfates, which are produced in the presence of sulfate aerosol and are particularly enhanced under acidic conditions (Surratt et al., 2007b; Surratt et al., 2010; Surratt et al., 2008; Surratt et al., 2007a)."

The text has been revised to read: "Among secondary organic aerosols (SOA) are organosulfates, which are mainly produced from acid-catalyzed particle-phase reactions of gaseous oxidation products such as epoxides (Lin et al., 2012) and hydroperoxides (Mutzel et al., 2015) with sulfate (Surratt et al., 2007b; Surratt et al., 2010; Surratt et al., 2008; Surratt et al., 2007a; Liao et al., 2015)."

Referee # 1 Specific Comment 5) Introduction, Page 2, Line 13: "Now you switch to PM2.5. You should define this since this is its first use."

Response to referee # 1 Specific Comment 5: We have implemented this suggestion and the revised text is provided in response to Referee # 1 Specific Comment 2.

Referee # 1 Specific Comment 6) Introduction, Page 2, Line 25: "The beginning of this sentence should be reworded, possibly to "The most abundant organosulfates to be previously quantified include.....""

Response to referee # 1 Specific Comment 6: We have revised this sentence as suggested.

Referee # 1 Specific Comment 7) Introduction, Page 2, Line 32: "change "instead" to "used"".

Response to referee # 1 Specific Comment 7: We have revised this sentence as suggested.

Referee # 1 Specific Comment 8) Introduction, Page 2, Line 32: "Define the acronym

"(-) ESI" for the first time here."

Response to Referee # 1 Specific Comment 8: Introduction, Page 2, Line 32: We have defined '(-) ESI', as indicated in the response to specific comment 7.

Referee # 1 Specific Comment 9) Introduction, Page 3, Line 9: "change ", however" to "; however, ""

Response to Referee # 1 Specific Comment 9: As suggested, we have changed the comma to a semicolon.

Referee # 1 Specific Comment 10) Introduction, Page 3, Lines 18-19: "Not sure how relevant this sentence is to the discussion here. I believe the Ehn et al. (2010, ACP) study could measure extremely low vapor pressure products in the gas phase (there still of course is an equilibrium between the gas and aerosol phase) such as the glycolic acid sulfate due to the high sensitivity of their CIMS instrument."

Response to Referee # 1 Specific Comment 10: We agree with the referee that detection of gaseous glycolic acid sulfate in Ehn et al., 2010 emphasize the high sensitivity of their detection method (APi-ToF) to extremely low concentrations of glycolic acid sulfate in the gas phase that is in equilibrium with aerosol phase. Consequently, we have removed this sentence from the text.

Referee # 1 Specific Comment 11) Introduction, Page 3, Line 27: "Change "epoxides" to "epoxydiols""

Response to Referee # 1 Specific Comment 11: We have revised this sentence as suggested.

Referee # 1 Specific Comment 12) Section 2.2: "In this section, I would be clear on which samples were analyzed. You should also be clear on why on these samples were extracted and analyzed for this study."

Response to referee # 1 specific comment 12: As suggested by the reviewer, we have indicated which samples were analyzed for quantification of organosulfates and for the sampling artifacts study in section 2.2. The reason for why these samples were analyzed to identify major organosulfates in Centreville is given in response to weakness 2.

Referee # 1 Specific Comment 13) Page 7, Line 12: “Is this an average glycolic acid sulfate concentration from this BHM study or the upper limit? Please clarify.”

Response to referee #1 specific comment 13: Section 3.1, Page 7, Line 12 originally read: “At the nearby Birmingham, AL which is an industrial and residential site even higher glycolic acid sulfate concentrations (75.2 ng m-3) were reported from 01 June – 15 July, 2013 during SOAS (Rattanavaraha et al., 2016) with a mean concentration of 26.2 ng m-3.”

This text is revised to read: “At the nearby Birmingham, AL site during SOAS, similar organosulfate concentrations were reported: glycolic acid sulfate averaged 26.2 ng m-3 and had a maximum value of 75.2 ng m-3. . .”

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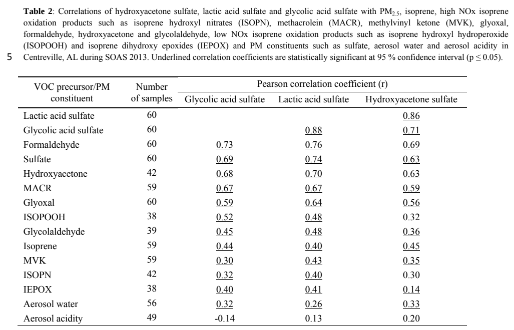

Table 2: Correlations of hydroxyacetone sulfate, lactic acid sulfate and glycolic acid sulfate with $PM_{2.5}$, isoprene, high NOx isoprene oxidation products such as isoprene hydroxyl nitrates (ISOPN), methacrolein (MACR), methylvinyl ketone (MVK), glyoxal, formaldehyde, hydroxyacetone and glycolaldehyde, low NOx isoprene oxidation products such as isoprene hydroxyl hydroperoxide (ISOPOOH) and isoprene dihydroxy epoxides (IEPOX) and PM constituents such as sulfate, aerosol water and aerosol acidity in Centreville, AL during SOAS 2013. Underlined correlation coefficients are statistically significant at 95 % confidence interval ($p \leq 0.05$).

VOC precursor/PM constituent	Number of samples	Pearson correlation coefficient (r)		
		Glycolic acid sulfate	Lactic acid sulfate	Hydroxyacetone sulfate
Lactic acid sulfate	60			0.86
Glycolic acid sulfate	60		0.88	0.71
Formaldehyde	60	0.73	0.76	0.69
Sulfate	60	0.69	0.74	0.63
Hydroxyacetone	42	0.68	0.70	0.63
MACR	59	0.67	0.67	0.59
Glyoxal	60	0.59	0.64	0.56
ISOPOOH	38	0.52	0.48	0.32
Glycolaldehyde	39	0.45	0.48	0.36
Isoprene	59	0.44	0.40	0.45
MVK	59	0.30	0.43	0.35
ISOPN	42	0.32	0.40	0.30
IEPOX	38	0.40	0.41	0.14
Aerosol water	56	0.32	0.26	0.33
Aerosol acidity	49	-0.14	0.13	0.20

Fig. 1.

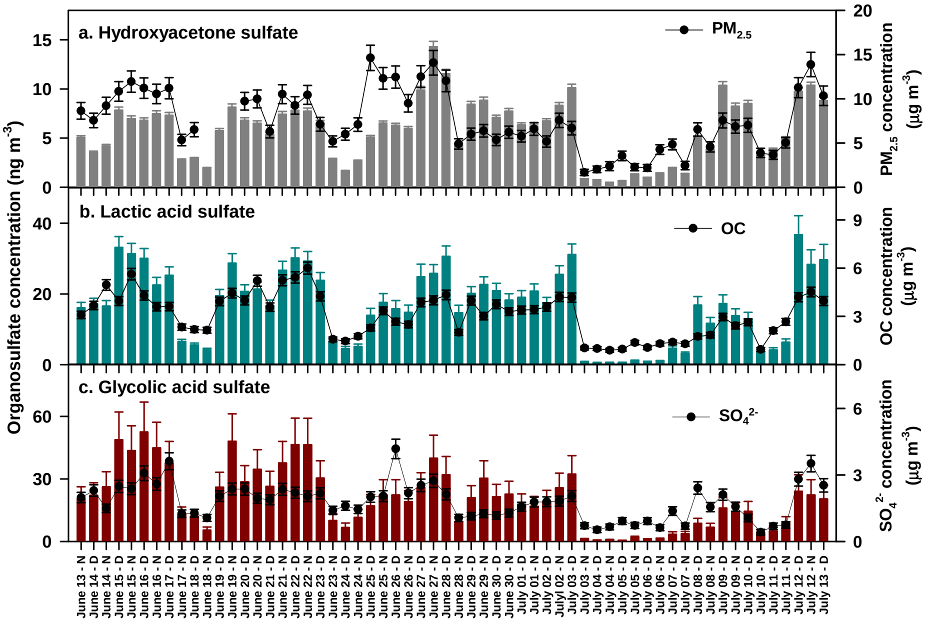

Fig. 2.

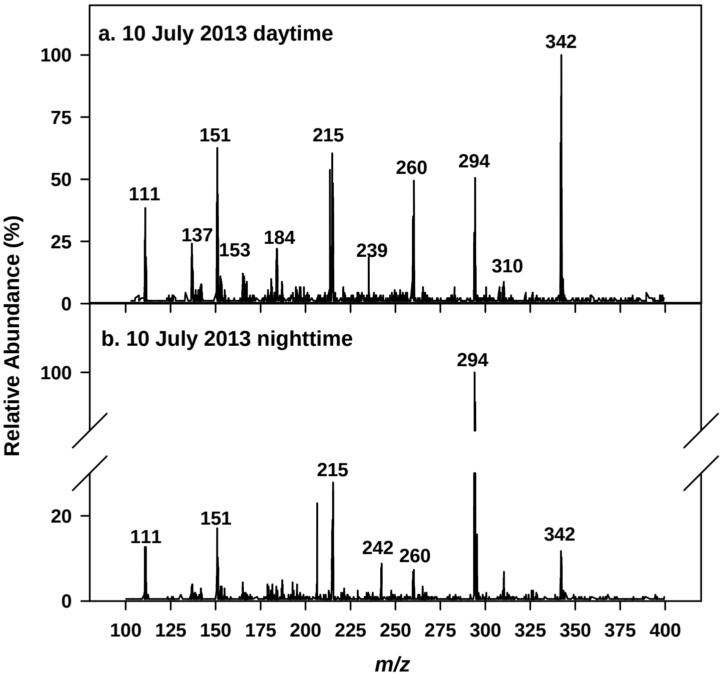

Fig. 3.

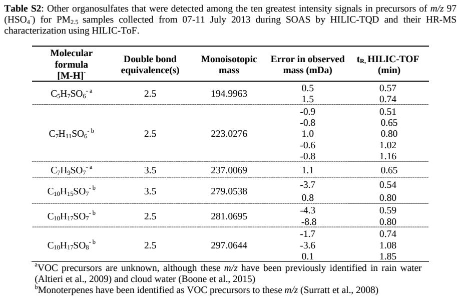

Table S2: Other organosulfates that were detected among the ten greatest intensity signals in precursors of *m/z* 97 (HSO_4^-) for $PM_{2.5}$ samples collected from 07-11 July 2013 during SOAS by HILIC-TQD and their HR-MS characterization using HILIC-ToF.

Molecular formula [M-H]⁻	Double bond equivalence(s)	Monoisotopic mass	Error in observed mass (mDa)	$t_{R,}$ HILIC-TOF (min)
$C_5H_7SO_6^{-\,a}$	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, although these *m/z* have been previously identified in rain water (Altieri et al., 2009) and cloud water (Boone et al., 2015)

[b] Monoterpenes have been identified as VOC precursors to these *m/z* (Surratt et al., 2008)

Fig. 4.