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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 # 2 Summary and Recommendations: "The manuscript by Hettiyadura et al. presents measured organosulphate (OS) concentrations in aerosol from the South East US from a four-day period during the SOAS campaign in the summer of 2013 at Centreville, Alabama. OS are an important contributor not necessarily due to their contribution to PM mass, but because they are the result of multi-phase processes and anthropogenic influence. The stated goals of the study are (i) quantification of OS (for which authentic standards are available) in PM2.5, (ii) assessment of filter sampling artefacts, and (iii) identifying major OS in Centreville. The analytical work is very thorough using state-of-the-art methods and the finding on the filter artefacts will

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be important for future work on OS. Similarly, the progress toward identifying/ruling out isomers/functional groups is an important contribution. The main concerns I have that should be addressed before publication is considered are clearer statements on the broader impact/significance beyond the analytical approach/work."

Response to the Referee # 2 Summary and Recommendations: We thank the referee for their review and suggestions. We have revised this paper carefully considering the referee's major comments, minor comments, technical comments and other comments. Our responses and revisions for each of the referee comment is provided point by point below.

Anonymous referee # 2 Major Comment 1: "In order for the measurements to have significance beyond the very nice analytical method and artefact description and not simply be an anecdotal note of specific OS, it is critical to describe to what degree the very limited 4 day period was representative. As there was a plethora of measurements obtained at the Centreville site this should be easy. For example, where temperature, photochemical conditions, NOx conditions, amount of PM typical and, even more importantly, how variable were these conditions and is there any correlation with the observed OS variability shown in figure 1 (see point 2). Such a description of putting the measurements within the broader context of the SOAS campaign would help readers evaluate the broader significance of the observations described here."

Response to referee # 2 Major Comment 1: We agree with the referee that it is important to show how representative this subset of days to the larger SOAS.

The text at page 7, section 3.2, line 4 – 5 originally 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."

This text 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, 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)."

We have also extended the time series of organosulfate quantified to include 13 June – 13 July 2013 as shown in our new figure 1 and present correlation analysis in Table 2. The text that has been added to page 8, section 3.2: "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 # 2 Major Comment 2: "It is stated that the work is complementary to that of Riva et al. 2016. However, it would be helpful if the similarities and differences with both the work/findings by Riva et al. 2016 and Rattanavaraha et al. 2016 would be stated more explicitly. For example, which OS were not observed by the two mentioned studies and how are the results similar and different? In fact, the time series in the Riva et al. 2016 (figure 4 of that manuscript) has a much longer dataset and it shows dramatic variability for organosulfate concentrations, which directly relates to point 1. In fact, a strong recommendation would be to collaborate with the Surratt group and use their much more extensive set of filter samples for the work described here."

Response to referee # 2 Major Comment 2: As suggested by the reviewer, we have discussed the relationship of our work to Riva et al. (2016) and Rattanavahara (2016) both quantitatively (as described in response to referee # 1 weakness 4) and qualitatively.

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."

The text has been added at the end of section 3.3: "The semi-quantitative results of organosulfates are both consistent and complementary to Riva et al. (2016) during SOAS. Five of the thirteen organosulfates quantified by Riva et al. (2016) in Centreville were among the ten major organosulfate signals observed herein; these included isoprene photo-oxidation products C5H11SO7- (215.0225), C5H9SO7- (213.0069), C3H5SO5- (152.9858) and isoprene ozonolysis products C4H7SO6- (182.9963) and

C5H11SO6- (199.0276). Other organosulfates, with m/z 181, 201, 227, 249, 267 and 315 were reported to have lower relative abundance (Riva et al., 2016) and were not among the ten major organosulfates in this study. Meanwhile, the organosulfate with m/z 197 (C5H9SO6-) was reported to be relatively high in Centreville (Riva et al., 2016), but was not identified as a major organosulfate in our study, likely due to differences in semi-quantitation methods. Together, these data demonstrate that organosulfates in Centreville are primarily derived from isoprene. In addition, our semi-quantiative analysis demonstrates relatively strong organosulfate signals from monoterpenes and to a lesser extent anthropogenic sources at Centreville."

Anonymous referee # 2 Major Comment 3: "It is stated that the work provides new insights for the major OS species in the SE US. Again, it would be helpful to explicitly state what the new insights are. For example, which of the major OS had not been identified before, and if they had been identified it would be useful to describe what additional new insight is gained for each of the major species. Clearly, such new insights exist, e.g., resulting from the analytical approach such as ruling out carboxylic acid functional groups for some OS. Ending the manuscript by stating that there are new insights but not mentioning what they are could then be improved. In summary, it would be helpful to make it easier for readers to identify clearly the novelty of the work/findings and the significance. To this end it may make sense to reorganize findings, e.g, (i) first show the 10 major OS, (ii) highlight the work to identify functional groups and isomers, which is a very nice and important contribution, and (iii) then discuss insights/recommendations. I think this may make it easier to recognize the significance, as the interesting new findings would not be interspersed within the "long" list of ten major OS. My second recommendation is to collaborate with the Surratt group using their extensive filter sample range, if possible."

Response to anonymous referee # 2 Major Comment 3: We thank the referee for the helpful guidance provided to improve this section. We have reorganized the discussion of major organosulfates at section 3.3 as suggested, and summarized the new insights gain through semi-quantitative analysis at the end of the conclusion section as indicated below.

The text at section 3.3, page 10 line 5 - page 13 line 24 have been revised to read: The strongest organosulfate signals were associated with isoprene and its oxidation products. The dominant organosulfate signal was $C_5H_{11}SO_7^-$ (215.0225; Fig. 3a) that corresponded to 2-methyltetrol sulfates that predominantly form by the acid catalyzed nucleophilic addition of sulfate to IEPOX (Surratt et al., 2010). This species accounted for 42-62% of the bisulfate anion signal across the samples analyzed semi-quantitatively. Other major organosulfate signals that were consistently observed ($\geq$90% of the 10 samples) included m/z 153, 183, 211, and 213 that have been associated with isoprene. The species with formula $C_5H_9SO_7^-$ (213.0069; Fig. 3b) has been observed to form from isoprene photo-oxidation in the presence of acidic sulfate under low NOx pathways (Surratt et al., 2008) and ozonolysis (Riva et al., 2016). Structurally, $C_5H_9SO_7^-$ is closely related to 2-methyltetrol sulfate, with one increasing unit of unsaturation. The short retention time (< 3 min) indicates the absence of carboxyl group and has been proposed to result from the oxidation of a primary hydroxyl group in a 2-methyltetrol sulfate followed by subsequent ring closing (Hettiyadura et al. 2015), although this has not been confirmed. Likewise, $C_5H_7SO_7^-$ (210.9912; Fig 3c) is related to 2-methyltetrol sulfate by two units of unsaturation and has been suggested to form by further oxidation of 2-methyltetrol sulfate and inter-molecular ring closing (Hettiyadura et al., 2015). An organosulfate with this formula has been observed in an isoprene chamber experiment, but may have other VOC precursors (Surratt et al., 2008). The species $C_4H_7SO_6^-$ (182.9963) has multiple constitutional isomers (Fig. 3e) with the dominant peak eluting at 0.91 minutes. The MS/MS spectrum (Fig. S3) included signals (by chemical formula, observed mass, and error in mDa) at HSO_3^-. (80.9642, -0.4), HSO_4^- (96.9593, -0.3), $C_3H_5SO_5^-$ (152.9856, -0.2) and $C_4H_5SO_5^-$ (164.9859, 0.1) corresponding to hydroxybutan-3-one-2-sulfate (Shalamzari et al., 2013) that is derived from isoprene oxidation products MVK and MACR (Schindelka et al., 2013; Riva et al., 2016). Also among the strongest signals are $C_5H_{11}SO_6^-$ (199.0276;

Fig. 3h) an isoprene ozonolysis product (Riva et al., 2016) that can also form from MBO in the presence of oxidants and sulfate under low NOx conditions (Zhang et al., 2012a) and C4H7O4- (119.0341, -0.3) whose mass spectrum matched that of 2-methylglyceric acid sulfate (Fig S5). An isoprene-derived nitro-oxy organosulfate, C5H10NSO9- (260.0076) contributed up to 5.4 % and 1.0 % of the m/z 96 precursor ion signal and is also associated with isoprene (Surratt et al., 2008; Gómez-González et al., 2008), In addition, C3H5SO5- (152.9858) and C3H7SO5- (155.0014; Fig. 3j) were among the strongest organosulfate signals, with the dominant isomers corresponding to hydroxyacetone sulfate and glycolic acid sulfate (discussed in Sect. 3.1). The importance of these isoprene-derived organosulfates is also supported by their high abundance reported previously during SOAS 2013 at Look Rock, TN (Budisulistiorini et al., 2015), Birmingham, AL and Centreville (Rattanavaraha et al., 2016; Riva et al., 2016) during SOAS 2013. Together, these data demonstrate that isoprene chemistry dominates the formation of organosulfates in Centreville. Organosulfates with formulas C7H11SO7- (239.0225; Fig. 3d) and C10H16NSO10- Âň (342.0495; Fig. 3f) were also among the strongest signals and have been associated with monoterpene SOA formed in the presence of acidic sulfate (Surratt et al., 2008). Other monoterpene derived organosulfates identified from bisulfate ion signal include C10H17SO7- (281.0695; observed in 90 % of the samples analyzed) C10H17SO8- (297.0644), C7H11SO6- (223.0276) and C10H15SO7- (279.0538) (Table S2 and Fig. S2 and S3). Monoterpene-derived nitro-oxy organosulfates were particularly responsive to precursors of m/z 96; C10H16NSO10- Âň(342.0495), C10H16NSO8- (310.0597) 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),

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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.

The organosulfate with the formula C12H25SO4- (265.1474; Fig. 3i) is consistent with dodecyl sulfate (a.k.a. lauryl sulfate), the most common surfactant use in manufacture of cleaning and hygiene products. A single peak with a very short retention time is consistent with a largely aliphatic structure. Anionic surfactants including dodecyl sulfate have been observed in aerosol generated from waste water (Radke, 2005) and in coastal sea spray aerosol (Cochran et al., 2016). While sea spray was observed to impact the Centreville site on some days during SOAS (Allen et al., 2015), it was not a major source on the dates discussed herein, pointing towards waste water as a possible origin.

Together, the ten highest organosulfate signals in each sample analyzed (Fig. 2, S2 and S3) contributed 58-78 % of the total bisulfate ion signal, with the tenth greatest intensity signal accounting for 0.25 to 1.12 % of the total bisulfate ion signal. From the remaining organosulfate signal, we estimate a minimum of ∼20-200 other minor organosulfates are present in Centreville, AL. In summary, a few highly abundant organosulfate species (e.g. 2-methyltetrol sulfates) dominate the bisulfate ion signal, while a relatively large number of minor organosulfate species are present in Centreville during the summer.

A new section was added at section 3.4 to highlight the new information on isomers of 2-methyltetrol sulfates. “3.4 Tentative identification of 2-methyltetrol sulfate isomers HILIC chromatography resolved six, baseline resolved peaks of 2-methyltetrol sulfates (C5H11SO7-; Fig. 3a) with retention times consistent with those reported by Hettiyadura et al. (2015). Based on the structures of β- and δ-IEPOX (Paulot et al., 2009), it is possible that the resulting 2-methyltetrol sulfate include the sulfate moiety at primary, secondary or tertiary positions. The position of the sulfate group in 2-methyltetrol sulfates were tentatively identified by their relative acid hydrolysis rates as primary (most stable), secondary (intermediate stability), or tertiary (least stable; as discussed in the SI and shown in Fig. S9). These assignments are based upon their enthalpy of hydrolysis and neutral hydrolysis lifetime reported by Darer et al. (2011) and Hu et al. (2011). Accordingly, the first two 2-methyltetrol sulfate peaks to elute were assigned as diastereomers of the tertiary conformation, the middle two peaks as diastereomers of the secondary conformation, and the last two peaks as diastereomers of primary 2-methyltetrol sulfate (Fig. 3a and Fig. S9). The relative contribution of these peaks to the bisulfate anion signal in order of elution were 23.9 %, 10.5 %, 23.4 %, 41.0 %, 0.8 %, and 0.4 % (Table 4). With a negative bias in peak area for late-eluting peaks, these percentages are expected to underestimate the contribution from primary organosulfates. With this knowledge, we expect that 2-methyltetrol sulfates have appreciable contributions from primary, secondary, and tertiary organosulfates. Confirmation of the configuration and their absolute quantitation would be made possible through synthesized standards."

In the conclusion, we have enumerated the specific insights gained from qualitative analysis: "The precursors of bisulfate ion and sulfate radical insight for the major organosulfate species in SE US that should be targets for future organosulfate standard development: i) 2-Methyltetrol sulfates in Centreville have a sizable contribution from primary, secondary and tertiary isomers. Because of their different atmospheric lifetimes (e.g., towards hydrolysis (Darer et al., 2011; Hu et al., 2011)), the relative amounts of these isomers may provide insights to the ageing and fate of anthropogenically influenced isoprene-derived SOA. To facilitate this, future studies should focus on synthesizing standards and quantifying each of these isomers. ii) The isoprene related organosulfates, C5H9SO7- (213.0069) and C5H7SO7- (210.9912) contributed ~ 4 % each of the total bisulfate ion signal (Table 4), which suggest that they are relatively abundant in Centreville and prime targets for standard development. Further, the lower retention times of these two organosulfates on BEH-amide column during HILIC separation reflects an absence of carboxylic acid groups and point towards to the structures proposed by Hettiyadura et al. (2015). iii) Multiple isomers of many organosulfates are observed with HILIC chromatography that co-elute under reversed-phase LC conditions. HILIC-MS/MS provides a basis for assessing the relative abundance of isomers and indicate that 1-hydroxybutane-3-one-2-sulfate is the dominant isomer of C4H7SO6- (182.9963) in Centreville, AL. Likewise, C10H16NSO10- (342.0495) and C7H11SO7- (239.0225) are expected to be among abundant monoterpene derived organosulfates in Centreville, AL. Similar to Riva et al. (2016), C5H11SO6- (199.0276) is relatively abundant in Centreville, but further experiments are need to identify its origin. Because of their relatively strong MS2 signals, these species are also strong candidates for standard development and/or quantification in ambient aerosol. Future efforts at standard development should focus on organosulfates that are expected to have high abundance, frequently detected in ambient aerosol, and/or have high specificity to VOC precursors."

Minor comments:

Referee #2 Minor Comment 1) p.1 line 5: "from biogenic volatile: : :" As written it implies that only BVOCs form OS?"

Response to minor comment 1: We have deleted the word "biogenic" from this sentence to avoid misunderstanding.

Referee #2 Minor Comment 2) p.1 Line 13-14: "their VOC precursors" is a little vague, as isoprene is one of the VOC precursors for OS, but I don't think the authors are implying that isoprene reacts on the filters to form SO. It would be useful to clarify."

Response to referee #2 minor comment 2: p.1 Line 13-4: We agree with the referee. We have replaced 'their VOC precursors' with 'gas phase precursors of organosulfates'.

Referee #2 Minor Comment 3) p.1 line 19: "Most of the ten: : :" Please be specific. How many?"

Response to Referee #2 Minor Comment 3: The text at page 1, line 19 originally read: “Most of the ten most prevalent organosulfate were associated with biogenic VOC precursors (i.e. isoprene, monoterpenes, and 2-methyl-3-buten-2-ol [MBO]).”

This text has been revised to read: “Nine of the ten strongest organosulfate signals were associated with biogenic VOC precursors (i.e. isoprene, monoterpenes, and 2-methyl-3-buten-2-ol [MBO]).”

Referee # 2 Minor Comment 4) p.2 line 2: “PM adversely affects : : : climate” This is a matter of debate. Some would say that PM positively affects climate due to counter-acting greenhouse gas radiative effects. I would consider rephrasing.”

Response to referee # 2 minor comment 4: We agree with the referee. We have rephrased this sentence in the response to referee # 1 specific comment 2 as given below.

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).”

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).”

Referee # 2 Minor Comment 5) p.2 line 6-7: “The authors could also consider the work of Liao et al. 2015 as it discusses acid effects. Currently, only ground based studies are cited.”

Response to referee # 2 minor comment 5: We have added this citation with the additional revisions made to this text in referee # 1 response to specific comment 4.

The text at page 2, line 5-7 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 # 2 Minor Comment 6) p.2 line 12: "I think it would be more specific to state that OS may be useful markers for one type of anthropogenic influence on SOA formation from biogenic VOCs, as there surely must be aspects of anthropogenic influence that the sulphate does not represent."

Response to referee # 2 minor comment 6: We agree with the referee, we will indicate this in the text as given below.

The text at page 2, line 12 originally read: "Thus, organosulfates may be useful markers of anthropogenically influenced biogenic SOA."

This text has been revised to read: "Thus, organosulfates may be useful markers for sulfate-influenced biogenic SOA."

Referee # 2 Minor Comment 7) p.3 line 28: "My understanding is that it is not clear whether the organosulfate is from methacrylic acid epoxide (MAE)or from hydroxymethyl-methyl-alpha-lactone (HMML), see Rattanavaraha et al. 2016?"

Response to referee # 2 minor comment 7: We thank the referee for pointing this out; this text has been revised as follows:

This text has been revised to read: "2-Methylglyceric acid sulfate forms from either methacrylic acid epoxide (Lin et al., 2013) or hydroxymethyl-methyl-α-lactone (isoprene oxidation products), similarly to 2-methyltetrol sulfates, in the presence of sulfate under high NOx conditions (Nguyen et al., 2015)."

Referee # 2 Minor Comment 8) p. 3 line 31-32: "I think follow-up studies (Gallowy et al. 2011 and Liao et al. 2015) showed that glycolic acid sulphate was unlikely to result from (photochemical formation) from glyoxal and that the mechanism/source was unknown? Similarly, the formation of lactic acid sulphate from methylglyoxal seems mechanistically challenging."

Response to Referee #2 Minor Comment 8: The text at page 3, line 31-32 originally read: "Formation of glycolic acid sulfate has been observed from reactive uptake of glyoxal to neutral or acidic sulfate aerosol upon irradiation (Galloway et al., 2009)."

This text has been revised to read: "Glycolic acid sulfate forms more efficiently from glycolic acid relative to glyoxal in the presence of acidic sulfate (Liao et al., 2015), while both precursors have biogenic and anthropogenic origins (Liao et al., 2015; Fu et al., 2008)."

The text at page 3, line 32 – 33 have been removed: "Lactic acid sulfate is also suggested to form from similar pathways from methylglyoxal (Shalamzari et al., 2013)."

Referee # 2 Minor Comment 9) p. 4 line 25: "Please state the total organic carbon content as resistivity does not address the content of uncharged organic compounds."

Response to Referee #2 Minor Comment 9: The text at page 4, line 24-25 originally read: "Ultra-pure water was prepared on site (Thermo, Barnsted EasyPure-II; > 18.2 MΩ cm resistivity)."

This text has been revised to read: "Ultra-pure water was prepared on site (Thermo, Barnsted EasyPure-II; 18.2 MΩ cm resistivity, OC < 40 μg/L)."

Referee # 2 Minor Comment 10) p. 5 line 7: "front QFF. Although it is fairly clear, defining better what the front QFF is would be useful (actual sample QFF?)"

Response to referee # 2 minor comment 10: We have indicated that the front QFF is the filter that collect PM2.5 during sampling in the original manuscript as given below.

The text at page 5, line 5-7 read: “Positive filter sampling artifacts associated with lactic acid sulfate, glycolic acid sulfate, and hydroxyacetone sulfate from 07-11 July 2013 were assessed using filter samples collected on bare back-up QFF (QB) and sulfuric acid impregnated back-up QFF (QB-H2SO4; H2SO4 - 8.65 μg cm-2) collected in series behind front QFF (QF) that collected PM2.5 (Fig. S1).”

Referee # 2 Minor Comment 11) p. 6 line 29-30: “If the mass range was 400 Da, why consider up to 500 carbon atoms, corresponding to 6000 Da?”

Response to referee # 2 minor comment 11: p. 6 line 29-30: We agree with the referee that it is not necessary to use 500 carbons as the maximum mass range is 400 Da. These are the default settings used in the formula calculation software. In the future we will narrow down the range. However, it does not affect our results.

Referee # 2 Minor Comment 12) p.7 line 18-20: “Please put these results in context with the ones previously mentioned by Tolocka and Turpin 2012).”

Response to referee # 2 minor comment 12: The requested revision is provided in response to major comment 2.

Referee # 2 Minor Comment 13) p.8 line 24-27: “I don’t understand how the second sentence follows from the first: (i) there is some OS formation on the acidified filters, (ii) SOA is acidic enough and has high enough sulphate that these are not limiting factors. Are the authors implying that the gas-phase is already depleted of precursors or what is then limiting?”

Response to referee # 2 minor comment 13: We thank the referee for pointing this out. Sulfate is the limiting factor in organosulfate formation, whereas other factors such as biogenic VOC precursors, aerosol acidity and aerosol water are consistently high in Centreville during SOAS, which is also consistent with the correlation results shown in response to major comment 1. The text at page 8, line 24 – 27 has been revised to read: “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.”

Referee # 2 Minor Comment 14) p. 9 line 3: “Does “negative sampling artefact” imply destruction of the OS in question? It would be helpful to clarify and explain.”

Response to referee # 2 minor comment 14: We thank the referee for pointing this out and have clarified that negative sampling artifacts may “result from degradation during sampling, sample preparation, or analysis”

Referee # 2 Minor Comment 15) p.9 line 23-24: “Does this mean that not all condensed-phase is evaporated when using water with little acetonitrile, i.e., that liquid water remains or just a few H2O molecules on the OS and are such signals seen? Could it be that the water takes some of the charge and that or in some other way suppresses/reduces the ionization efficiency of the OS? Please explain this effect better.”

Response to referee # 2 minor comment 15: p.9 line 23-24: Experimentally we have seen decrease of MS signal response with increase of aqueouscomponent of the eluent, and vice versa. This is expected due to the low vapor pressure of water, relative to organic solvent such as acetonitrile, which suppress desolvation of ions in the ionization source. This will reduce the ions generate within the ESI source, thus result in lower signal. Organosulfates readily deprotonate in the ESI source (soft ionization technique). If assume that the water take some of the charge thus positively charged (abstracting H+), yet they will be removed by the large negative potential applied in the ESI source, thus may not have an influence on deprotonated organosulfate ions.

The text at section 3.3, page 9, line 23 – 24 originally read: “Acetonitrile has a higher vapor pressure than water and more readily desolvates in the mass spectrometer, leading to higher signals.”

This text has been revised to read: “Acetonitrile has a higher vapor pressure than water and more readily desolvates in the ionization source. When increases the water content of the eluent, the signal of later-eluting ions is lower. Consequently, organosulfates retained longer on the BEH-amide column during HILIC gradient separation, such as organosulfates containing carboxyl and multiple hydroxyl groups are expected to be under-represented in this semi-quantitative analysis. These results emphasize the importance of using authentic standards to calibrate the instrument, particularly when using gradient elution.”

Referee # 2 Minor Comment 16) p.11 line 20: “Given the very high vapour pressure of MVK and MACR is it reasonable to assume that they are present in any significant concentration in PM in the first place to be able to oligomerize?”

Response to referee # 2 minor comment 16: We agree that this is unlikely and have removed this sentence from the text.

Anonymous Referee # 2 Technical Comments: “There are some grammatical errors, e.g., noun-verb agreement, and the manuscript could benefit from some proof reading.”

Response to Anonymous Reference # 2 Technical Comments: We have addressed the technical comments point by point as indicated below.

Technical Comment 1) p.2 line 13:“SOA accounts for a significant : : : and suggested: : :”"

The text at page 2, line 13 originally read: “SOA accounts for a significant fraction of organic PM2.5 in SE US (Lee et al., 2010) and suggested to derive primarily from isoprene (Ying et al., 2015).”

This text has been revised to read: “SOA accounts for a significant fraction of organic PM2.5 in SE US (Lee et al., 2010) and is expected to derive primarily from isoprene (Ying et al., 2015).”

Referee # 2 Technical Comment 2) p.2 Line 25: “Among them are most abundant organosulfate has been : : :”

Response to referee # 2 technical comment 2: We have corrected this sentence in response to referee # 1 specific comment 6 as indicated below.

Introduction, Page 2, Line 24 - 31 originally read: “Among them are most abundant organosulfate has been 2-methyltetrol sulfate, followed by 2-methylglyceric acid sulfate, glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate during SOAS 2013 in Birmingham, AL (Rattanavaraha et al., 2016), Look Rock, TN (Budisulistiorini et al., 2015; Riva et al., 2016) and Centreville, AL (Hettiyadura et al., 2015; Riva et al., 2016).”

The text has been revised to read: “The most abundant organosulfates to be previously quantified, during SOAS 2013, using authentic standards include 2-methyltetrol sulfate (Budisulistiorini et al., 2015; Rattanavaraha et al., 2016), 2-methylglyceric acid sulfate (Budisulistiorini et al., 2015; Rattanavaraha et al., 2016), glycolic acid sulfate (Liao et al., 2015; Hettiyadura et al., 2015; Rattanavaraha et al., 2016), lactic acid sulfate (Hettiyadura et al., 2015) and hydroxyacetone sulfate (Budisulistiorini et al., 2015; Hettiyadura et al., 2015).”

Referee # 2 Technical Comment 3) p.2 Line 31-32: “In the absence of authentic standards, surrogate standards are commonly instead, but can”

Response to Referee #2 Technical Comment 3: Introduction, Page 2, Line 32 originally read: “In the absence of authentic standards, surrogate standards are commonly instead, but can lead to significant and often uncharacterized biases that result from differences in (-) ESI ionization efficiencies (Staudt et al., 2014).”

The text has been revised to read: "In the absence of authentic standards, surrogate standards are commonly used, but can lead to significant and often uncharacterized biases that result from differences in negative electrospray ionization ((-) ESI) efficiencies (Staudt et al., 2014)."

Referee # 2 Technical Comment 4) p.3 line 9: "have been discussed", "are discussed" is perhaps more suitable"

Response to Referee #2 Technical Comment 4: Introduction, Page 3, Line 9 originally read: "Thus MS2 of precursors to bisulfate ion can be used for semi-quantification of organosulfates in the absence of authentic standards (Stone et al., 2009), however there are some limitations which have been discussed in Sect. 3.3."

The text has been revised to read: "Thus MS2 of precursors to bisulfate ion (which scan all the precursors of a common product ion) can be used for semi-quantification of organosulfates in the absence of authentic standards (Stone et al., 2009); limitations of this approach are discussed in Sect. 3.3."

Referee # 2 Technical Comment 5) p.8 line 20 14-15: "the potential : : : were assessed"

Response to Referee #2 Technical Comment 5: The text at p.8 line 13-14 originally read: "The potential for glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate to form on QFF by acid catalyzed heterogeneous reactions were assessed..."

This text is revised to read: "The potential for glycolic acid sulfate, lactic acid sulfate and hydroxyacetone sulfate to form on QFF by acid catalyzed heterogeneous reactions was assessed...."

Referee # 2 Technical Comment 6) p.11 line 19-21: "forms" instead of "form"

Response to referee # 2 technical comment 6: p.11 line 19-21: This sentence has been removed in response to minor comment 16.

Referee # 2 Technical Comment 7) p. 14 line 9: "of" instead of "to"?"

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Response to Referee #2 Technical Comment 7: The text at page 14, line 9 originally read: “The precursor ion scan to the bisulfate anion fragment (m/z 97) was used semi-quantitatively to assess major organosulfate species in ambient aerosol in the SE US.”

This text will be revised to read: “The precursor ion scan of the bisulfate anion (m/z 97) and sulfate ion radical (m/z 96) were used semi-quantitatively to assess major organosulfate species in ambient aerosol in the Centreville, AL.”

Anonymous Referee Other Comments: “There are some places where it is not quite clear what is meant,”

Response to Anonymous Reference # 2 Other Comments: We have addressed these comments point by point below.

Referee # 2 Other Comment 1) p.2 line 16-17: “Stating that high sulphate etc. make the atmosphere subject to anthropogenic influence sounds a little odd to me. Do they actually not directly represent the anthropogenic influence?”

Response to referee # 2 other comment 1: We thank the referee for pointing this out. We have revised this sentence as indicated below.

Introduction, Page 2, Line 13-21 originally read: “Together, high sulfate, isoprene, and aerosol acidity make the atmosphere in the SE US subject to anthropogenic influences on biogenic SOA formation (Weber et al., 2007; Goldstein et al., 2009; Watson et al., 2015).”

This text has been revised to read: “Together, high isoprene, sulfate and aerosol acidity make the SE US prime for the formation of sulfate-influenced biogenic SOA, including organosulfates.”

Referee # 2 Other Comment 2) p.8 line 9-11: “The very minor influence of : : : may be promoted : : :” I am not sure what promoting a minor influence means, and the “and possibly temperature” also seems a little out of place.”

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Response to Referee #2 Other Comment 2: The text at section 3.2, page 8, line 9 - 12 have been removed: “The very minor influence of gas-phase glycolic acid sulfate and lactic acid sulfate in Centreville may be promoted by the higher organosulfate concentrations in the SE US, as well as the higher acidity (Guo et al., 2015) that can promote partitioning of acidic species like organosulfates to the gas-phase, and possibly temperature.”

Referee # 2 Other Comment 3) p. 3 line 8: “MS2 has not been defined, I think. Some explanation of this method would be useful for readers to understand the following statements.”

Response to Anonymous Referee # 2 other comment 3: We have provided a brief explanation to MS2 of precursor ions in the response to technical comment 4.

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Discussion paper

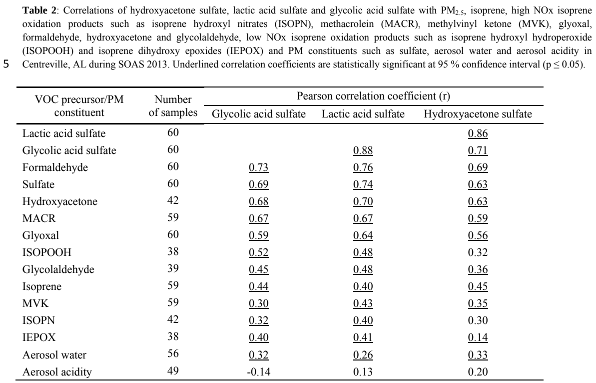
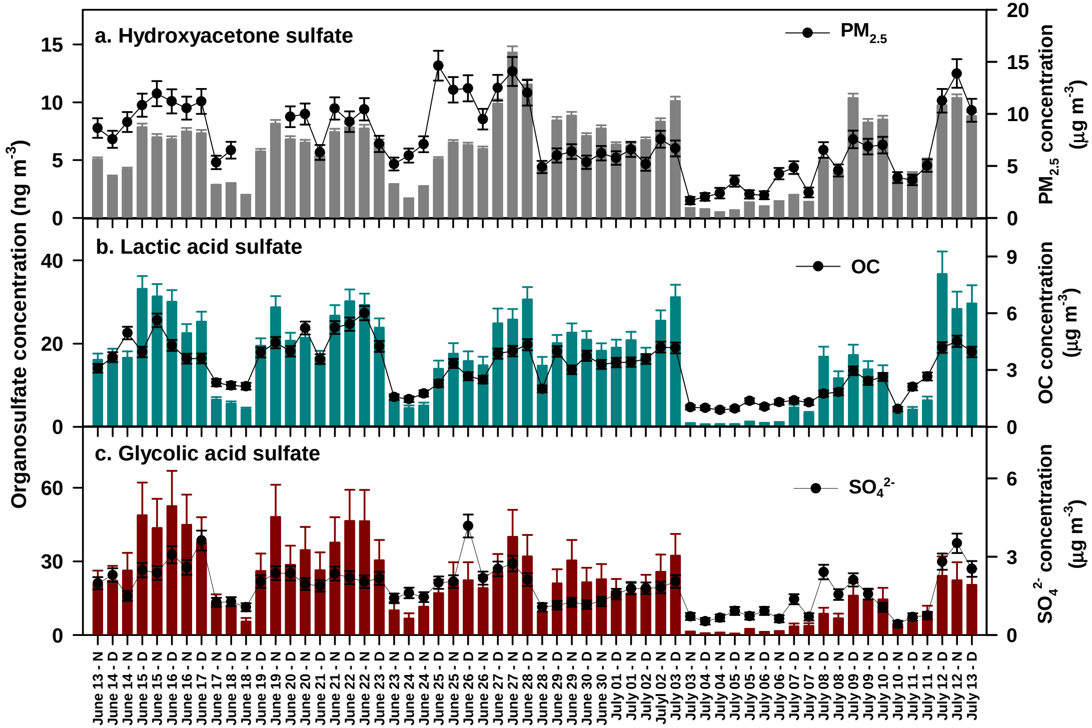


Table 2: Correlations of hydroxyacetone sulfate, lactic acid sulfate and glycolic acid sulfate with $PM_{2.5}$, isoprene, high NOx isoprene oxidation products such as isoprene hydroxyl nitrates (ISOPN), methacrolein (MACR), methylvinyl ketone (MVK), glyoxal, formaldehyde, hydroxyacetone and glycolaldehyde, 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.


a. Hydroxyacetone sulfate
PM$_{2.5}$
b. Lactic acid sulfate
OC
c. Glycolic acid sulfate
SO$_4^{2-}$
Organosulfate concentration (ng m^{-3})
PM$_{2.5}$ concentration (µg m^{-3})
OC concentration (µg m^{-3})
SO$_4^{2-}$ concentration (µg m^{-3})
0
5
10
15
20
0
20
40
0
30
60
0
5
10
15
20
0
3
6
9
0
3
6
June 13 - N
June 14 - D
June 14 - N
June 15 - D
June 15 - N
June 16 - D
June 16 - N
June 17 - D
June 17 - N
June 18 - D
June 18 - N
June 19 - D
June 19 - N
June 20 - D
June 20 - N
June 21 - D
June 21 - N
June 22 - D
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June 28 - D
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June 29 - D
June 29 - N
June 30 - D
June 30 - N
July 01 - D
July 01 - N
July 02 - D
Julyl 02 - N
July 03 - D
July 03 - N
July 04 - D
July 04 - N
July 05 - D
July 05 - N
July 06 - D
July 06 - N
July 07 - D
July 07 - N
July 08 - D
July 08 - N
July 09 - D
July 09 - N
July 10 - D
July 10 - N
July 11 - D
July 11 - N
July 12 - D
July 12 - N
July 13 - D

Fig. 2.